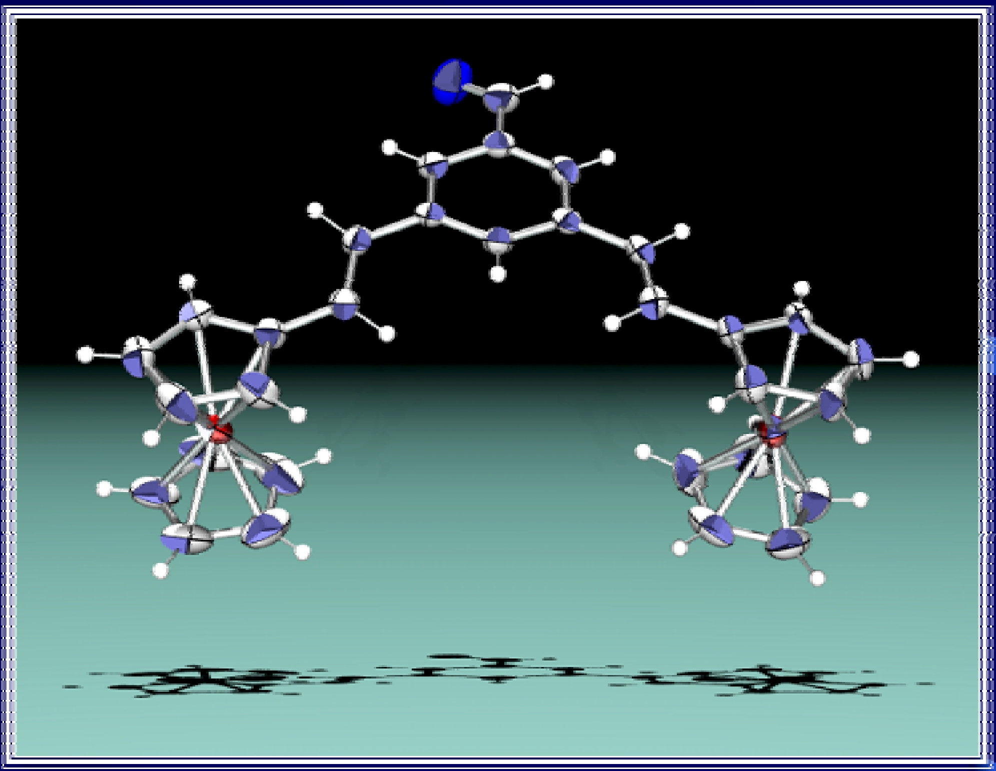
Tesis Doctoral: Jose A. Mata

Abril
2002

Escola Superior de Tecnología i Ciències Experimentals.
Departament de Química Inorgànica i Orgànica.

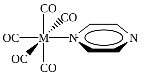


# *Estudio de las Propiedades Electrónicas y Ópticas de Ferrocenos Funcionalizados con Sistemas Conjugados.*

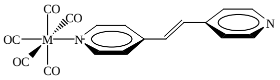
**Tesis Doctoral:**

Jose A. Mata Martínez
Castelló, Abril 2002

## *Capítulo III*



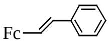
M = Cr, ***1***
M = W, ***2***

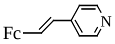


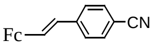
M = Cr, ***3***
M = W, ***4***

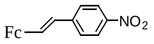
## *Capítulo IV*

### 2.1 Precursores.



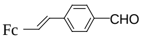




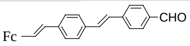


### 2.2 Aumento de la cadena conjugada.

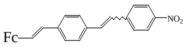
Fc-CHO **1**

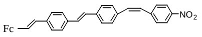


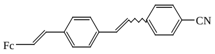
**2**-(E)



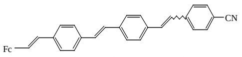
**3**-(E,E)



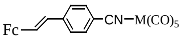




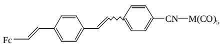
**5**-(E,Z); **5**-(E,E)



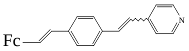
**6**-(E,E,Z); **6**-(E,E,E)

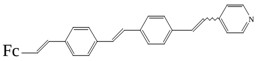


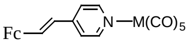
M = Cr, W



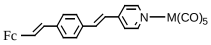
M = Cr, W





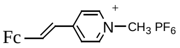


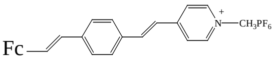
M = Cr, Mo, W

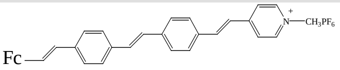


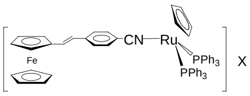
M = Cr, Mo, W

### 2.3 Modificaciones en el fragmento aceptor.

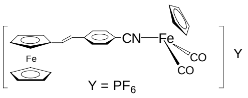






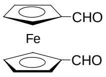


$X = BF_4$
$X = PF_6$

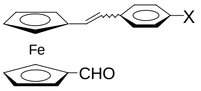


$Y = PF_6$

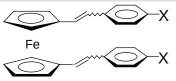
### 3. Ferrocenos 1,1'-Bisustituidos.



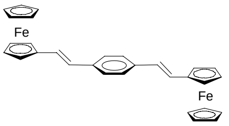
**1**



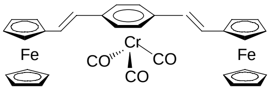
X = $NO_2$, **2**-(E), **2**-(Z)
X = CN, **3**-(E), **3**-(Z)



X = $NO_2$, **4**-(E,E), **4**-(E,Z), **4**-(Z,Z)
X = CN, **5**-(E,E), **5**-(E,Z), **5**-(Z,Z)

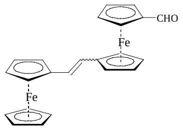


**6**

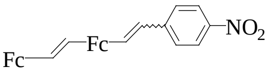


**7**

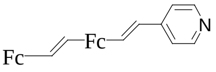
## *Capítulo V*



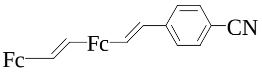
**1**-(E), **1**-(Z)



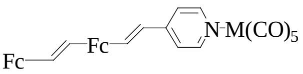
**2**-(E,E), **2**-(E,Z)



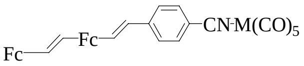
**3**



**4**

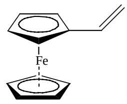


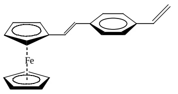
M = **3**-Cr, **3**-Mo, **3**-W

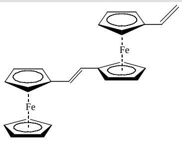


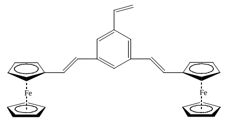
M = **4**-Cr, **4**-W

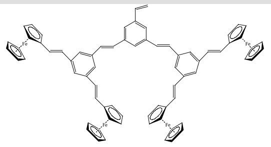
## 2.1 Síntesis de los precursores y dendrones utilizados.


1

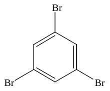

2

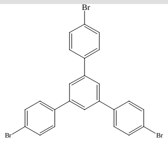

3

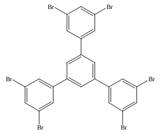

4

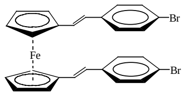

5

## 2.2 Cores.

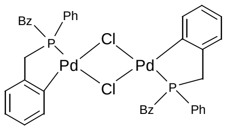

8

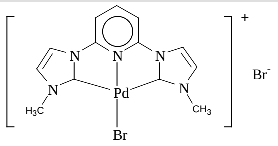

9


10

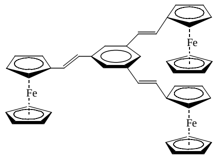

11

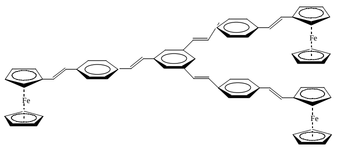
## 2.3 Catalizadores.

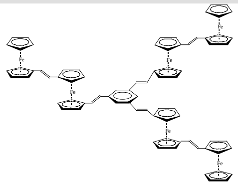


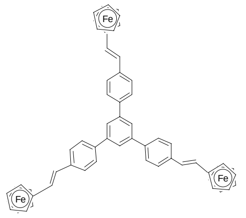


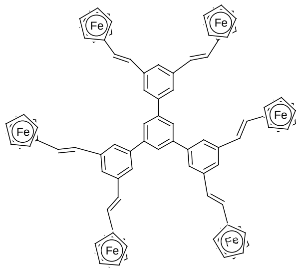
## 2.4 Dendrímeros.

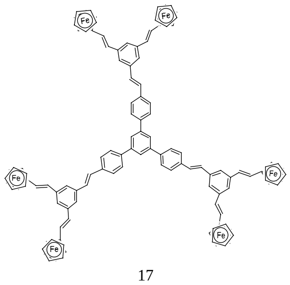

12

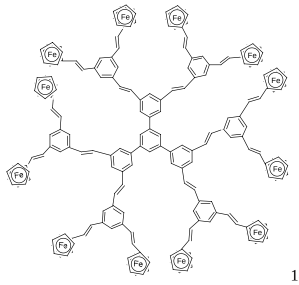

13

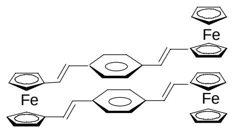

14

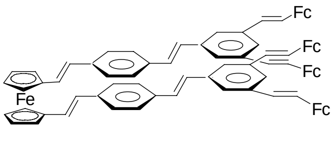

15


16


17


18


19


20

UNIVERSITAT JAUME I

*Departament de Química Inorgànica i Orgànica.*

*Química Inorgànica.*

# *Estudio de las Propiedades Electrónicas y Ópticas de Ferrocenos Funcionalizados con Sistemas Conjugados.*

Tesis Doctoral.
Jose A. Mata Martínez

Directores.
Dra. Rosa M. Llusar Barelles
Dr. Eduardo V. Peris Fajarnés

Castelló de la Plana, 29 d'Abril de 2002

**ROSA M. LLUSAR BARELLES, PROFESORA TITULAR DEL ÁREA DE QUÍMICA FÍSICA Y EDUARDO V. PERIS FAJARNÉS, PROFESOR TITULAR DEL ÁREA DE QUÍMICA INORGÁNICA DE LA UNIVERSITAT JAUME I DE CASTELLÓN,**

CERTIFICAN: Que Jose Antonio Mata Martínez, Licenciado en Ciencias Químicas por la Universidad de Valencia, ha realizado bajo su dirección, en las áreas de Química Física y Química Inorgánica de la Universitat Jaume I, el trabajo titulado "*Estudio de las Propiedades Electrónicas y Ópticas de Ferrocenos Funcionalizados con Sistemas Conjugados.*" y que constituye su memoria de tesis doctoral para optar al grado de Doctor en Ciencias Químicas.

Y para que conste a los efectos oportunos firmamos el presente certificado en Castellón a 21 de Marzo de 2002.

| | |
|---|---|
| Dra. Rosa M. Llusar Barelles | Dr. Eduardo V. Peris Fajarnés |
| Prof. Titular de Química Física | Prof. Titular de Química Inorgánica |

Departament de Química Inorgànica i Orgànica
Telf. 964728215 / Fax 964728214
Campus Riu Sec s/n
12071 Castelló

# Agraïments.

M’agradaria fer arribar el meu agraïment a totes aquelles persones que han fet posible, d’un mode o d’un altre la realització d’aquest treball:

Per començar, als meus directors Rosa i Edu per la confiança dipositada en mi i per tot el que he aprés d’ells. Així mateix vull agrair-li a Santi els seus savis consells, que tant m’han ajudat. A Marta i Cristian, pel bon ambient de treball del que he disfrutat, i les xarrades de les que tant hem disfrutat, almenys jo…

A Maca i E+, les dues companyes que comencen ara la seva llabor investigadora, per a que descobreisquen la passió per la recerca, i a tots aquells que han estat relacionats amb la realització d’aquest treball Arantxa, Juan i Javi.

Als meus veïns de laboratori, amb els que he compartit i furtat tantes coses. Puri, la tutora de la meua formació docent, Eloisa, Héctor, Bea, Nahúm i Raquel.

Al grup de química orgànica dirigit per Miguel Carda, sempre tant atents a l’hora d’ajudar-me a sol.lucionar problemes relacionats amb la síntesi orgànica. Floren, Santiago, Juan, Eva i Raúl.

Als físics òptics que m’han ajudat a comprendre un poc més les unitats i les equacions Enrique, Mercedes, Jose i molt especialment a Gladys.

A la gent dels dinars, algún que altre ‘cafenet’ i més activitats extrauniversitaries… Silvia (gràcies per les dites), Vicent, Mari (està bé Maria), Eva, Mercé, Mónica, Gema i Ángela.

Als biòlegs Pilar, Mitxel, Victor i Mª Carmen…pel seu ajud especialment al començament de la meva vida investigadora… Als hidrogeòlegs, per tota l’ajuda rebuda Juanito (vaja cor) i Pablete. A tota la gent de crista i mine, per a que deixen de patrocinar-ho tot i comencen ja a pagar-se alguna coseta Eva, Carlos, David, Juanjo, Mercedes, Jacinta, Miguel i Ana, i com no al del vint-i-vuit, Juandi… Una menció especial a tots aquells que han passat per aquesta casa per a realitzar algún treball, Pau (que cabró!), Germán, Juanjo,…

A tots eixos companys que he fet ací a la universitat i amb els que tant he disfrutat el Moli, Begonya, Sixte, Bea, Juan Felipe, Juanito, Mónica, Sergi, Elena, Mª Jesus, Araceli, els psicobiòlegs (Carlos, Marta, Mercè, Carles) i com no a Mamencita i Miguel.

Un dels primers viatges que vaig fer hem va portar fins a Xile per a realitzar una estada de dos mesos… a partir d’ací va començar una molt bona relació amb el grup dels professors David Carrillo i Carola Manzur, que avui en dia encara es mantè i esperem que continue. Moltes gràcies per tots els consells, discussions i fer que una part del meu cor estiga ara capgirada. Tambè vull agraïr l'ajuda prestada per Mauricio (moltes gràcies per el dibuix de la portada), Lorena, Walter i com no a l'espanyo-xilena Anita.

L'altra banda sudamericana es troba un poc més al nord, en Colombia, així que, moltes gràcies per els bons moments passats i per eixe mode d'afrontar la vida a Dora Hoyos.

Al Prof. Robert Crabtree i als seu grup per els bons moments passats durante la meva estada a la seva Universitat. Martin, Stephan, John, Anes, Jen, Xing Wei i Karin. I com no a un bon amic Americà d'Idaho ('good potatoes') Adrien Lavoie.

A aquella gent amb la que he tingut l'oportunitat de treballar i col.laborar Helena T., Montse G., Daniel S., Inge A., Andre P., Humphrey M., Pascual, Merche, Larry F. i Milagros.

Tambè vull agraïr molt energicament a tots aquells becaris que, perdent part del seu temps, estan aconseguint que milloren les coses per al personal en formació tant a nivell estatal, regional com inclús ací a l'UJI.

A la gent que desde fora m'ha ajudat a seguir amb el meu treball, els meus amics, Isma, Calp, Belín, Maika, Mª Carmen, Txussa, Cárol, Oscar, Ximo, Lorena, Galo, Sabino, Gloria, Ángel, Ana i la resta de la penya 'Estem, o no?'. Seraaaaaaà posible!!! Tambè a la nova adquisició de la penya, Climent, amb el que tantes coses hem passat junts.

A les dues persones (ara ja tres) que sempre estàn ahí per a tot, i que formen part d'eixe as sota la màniga que es reserva per a les ocasions, a Yasmi, Salo i Júlia.

Així mateix, vull fer arribar el meu agraïment a la Conselleria de Cultura Educació i Ciència per la concessió d'una beca FPI que m'ha permés realitzar aquest treball, així com viatjar a l'estranger per a complimentar la meva formació i l'assitència a congresos.

A la meua familia.

Molt especialment, als meus pares.

# Prólogo.

Hace cincuenta años se descubrió de forma casual un nuevo compuesto con una estructura y unas propiedades sorprendentes. Este compuesto denominado ferroceno, por su analogía con el benceno, condujo al desarrollo de la química organometálica moderna.

Hoy en día, el ferroceno es una molécula muy conocida en todos los ámbitos de la química y son muchos los investigadores que de una forma directa o indirecta trabajan en el desarrollo de derivados de ferroceno. Los cerca de cuatrocientos artículos internacionales, publicados anualmente, relacionados con el ferroceno avalan su utilización. La revista científica '*Journal of Organometallic Chemistry*' ha dedicado recientemente un volumen especial (Vol. 638-639 Diciembre de 2001) en el que únicamente aparecen artículos relacionados con el ferroceno y sus derivados, a consecuencia del cincuenta aniversario de su descubrimimento. Nosotros hemos contribuido a la edición de este volumen con la publicación de un artículo sobre de dendrímeros funcionalizados con ferroceno.

Esta memoria doctoral esta compuesta por una recopilación de los artículos que hemos publicado en el transcurso de la realización de esta tesis doctoral. A lo largo de este trabajo se tratan diferentes tipos de aplicaciones en los que se han utilizado derivados de ferroceno. En base a estas aplicaciones hemos considerado oportuno dividir esta memoria doctoral en diferentes capítulos. En cada uno de ellos hemos estudiado diferentes tipos de propiedades, tanto generales como específicas. El primer capítulo es una introducción general a la química del ferroceno, pasando por la historia y centrándonos sobre todo en las propiedades y aplicaciones. El resto de capítulos constan de una breve introducción, en la que se presentan los fundamentos de las propiedades tratadas seguida de una descripción general de los procedimientos de síntesis, recalcando sobre todo las ventajas e inconvenientes con los que nos hemos ido encontrando. A continuación analizamos y discutimos los resultados obtenidos y presentamos un listado de las referencias bibliográficas más generales. Al final de cada capítulo hemos adjuntado los artículos publicados relacionados con el tema tratado.

La numeración de los compuestos se ha realizado siguiendo, en los casos que ha sido posible, la numeración utilizada en los artículos, y para facilitar su comprensión se ha añadido una hoja maestra en la que se identifican todos los compuestos a los que se hace referencia.

La parte experimental y la descripción de los equipos utilizados se encuentra detallada en los artículos adjuntos al final de cada capítulo. El material suplementario se encuentra disponible en soporte informático en el CD, así como la versión electrónica de la presente memoria de tesis doctoral.

# Resumen.

La importancia del ferroceno y sus derivados en el campo de la química, se debe a sus propiedades, estabilidad y un gran número de aplicaciones. Es bien conocida la estructura tipo sandwich de este compuesto y sus propiedades electroquímicas, pero además, entre el gran número de aplicaciones en las que se utiliza el ferroceno hay que destacar campos como la catálisis homogénea, sales de transferencia de carga, óptica no lineal, polímeros y cristales líquidos.

El trabajo desarrollado durante esta tesis doctoral ha consistido en el estudio de las propiedades ópticas y electrónicas de nuevos ferrocenos funcionalizados con sistemas conjugados. Desde este punto de vista, la primera parte de la tesis doctoral se basa en el desarrollo de vías de síntesis que nos permitan acceder a los sistemas deseados. Los procedimientos de síntesis desarrollados han sido fundamentalmente la formación de enlaces carbono-carbono a través de la metodología de *Wittig* o de *Heck*.

En el estudio de las propiedades ópticas nos hemos centrado en las propiedades ópticas no lineales. Para que un compuesto posea este tipo de propiedades debe poseer una serie de características, como son, la presencia de un centro dador y aceptor de densidad electrónica unidos a través de un sistema conjugado, un momento dipolar distinto de cero, etc.; características que hemos tenido en cuenta a la hora de diseñar nuestros compuestos. La finalidad de nuestro trabajo es racionalizar cuáles son los factores que contribuyen de un modo significativo a este tipo de propiedades. De este modo, hemos estudiado los efectos de aumento de la cadena conjugada, la influencia del aceptor de densidad electrónica, el contraión, etc., en la respuesta óptica no lineal.

La síntesis de compuestos biferrocénicos nos ha permitido abordar el estudio de la interacción metal-metal en este tipo de sistemas. Son muchos los trabajos que abordan la interacción entre metales en metalocenos, no obstante, todavía hoy en día es difícil averiguar cuáles son los factores que conducen a elevadas interacciones. En nuestro caso, hemos observado como nuestros compuestos presentan un fuerte acoplamiento entre los metales, y los valores encontrados difieren mucho de los descritos en la bibliografía para sistemas similares.

Ya por último, hemos abordado la síntesis de dendrímeros funcionalizados con ferroceno. La obtención de metalodendrímeros es un campo de gran difusión en los últimos años. Nuestra contribución consiste en el estudio de las propiedades de dendrímeros hiperconjugados funcionalizados con ferrocenos, tanto en el core como en la periferia. Una de las características más importantes de estos dendrímeros, es que simulan el comportamiento redox de ciertas proteínas.

# Abreviaturas.

| | |
|---|---|
| ca. | *Circa* (aproximadamente) |
| *CIP* | *Cahn-Ingold-Prelog* |
| *Cp* | Ciclopentadienilo |
| *Cp** | Pentametilciclociclopentadienilo |
| *DFWM* | *Degenerate Four-Wave Mixing* |
| *DMA* | N,N-Dimetilacetamida |
| *DMF* | N,N-Dimetilformamida |
| *Dmit* | Ligando 4,5-dimercapto-1,3-ditiol-2-tiona |
| *dppf* | 1,1'-bis(difenilfosfina)ferroceno |
| *EFISH* | *Electric Field Second Harmonic Generation* |
| *e.s.u.* | *Electrostatic units* |
| et al. | *Et alii* ( y otros autores) |
| *Et* | Grupo etilo |
| $Et_2O$ | Dietil eter |
| *Fc* | Ferroceno |
| *Fc** | Decametilferroceno |
| GOD | Enzima Glucosa Oxidasa |
| *HEW* | *Horner-Emmons-Wadsword* |
| *HRS* | *Hyper-Rayleigh Scattering* |
| *IR* | Infrarojo |
| *PPFA* | (*R*)-N,N-dimetil-1-[(S)-2-(difenilfosfina)ferrocenil)]etelamina |
| *Pn* | Pentaleno, $C_{10}H_6$ |
| *RMN* | Resonancia Magnética Nuclear |
| *SHG* | *Second Harmonic Generation* |
| *TCML* | Transferencia de carga metal ligando |
| *TCNE* | Tetracianoetileno |
| *TCNQ* | 7,7,8,8-tetracianoquinodimetano |
| *THF* | Tetrahidrofurano |
| *THG* | *Third Harmonic Generation* |
| *TMEDA* | N,N,N’N’-tetrametiletilendiamina |
| *TTF* | Tetratiofulvaleno |
| *UV/Vis* | Ultravioleta Visible |

# Índice.

IV-5.1 J. A. Mata, E. Peris, Rosa Llusar, S. Uriel, S. Houbrechts, A. Persoons. “New Advances in the Search of organometallic NLO Chromophores.” *J. Organomet. Chem. 562*, (***1998***), 197.

IV-5.2 J. A. Mata, E. Falomir, R. Llusar, E. Peris. “Preparation, properties and coordination of new conjugated ferrocenyl-based ligands with an end-capped nitrile.” *J. Organomet. Chem. 616* (***2000***) *80.*

IV-5.3 J. A. Mata, S. Uriel, R. Llusar, E. Peris. “Preparation, properties and crystal structure of new conjugated oligomers with a pendant ferrocenyl and an end-capped pyridine.” *Organometallics 19* (***2000***) *3797.*

IV-5.4 J. A. Mata, E. Peris, I. Asselberghs, R. V. Boxel, A. Persoons. “Large second order NLO properties of new conjugated oligomers with a pendant ferrocenyl and an end-capped pyridine.” *New Journal of Chemistry 25 (**2001**) 1043.*

IV-5.5 J. A. Mata, E. Peris, I. Asselberghs, R. V. Boxel, A. Persoons.” Syntheses characterization and second order nonlinear optical behavior of new ferrocenyl-based oligomers with a pendant nitro group.” *New Journal of Chemistry 25 (**2001**) 299.*

IV-5.6 J. A. Mata, E. Peris, S. Uriel, R. Llusar, I. Asselberghs, A. Persoons. “Preparation, properties of new ferrocenyl heterobimetallic complexes and solvent dependent NLO responses.” *Polyhedron. 20 (**2001**) 2083.*

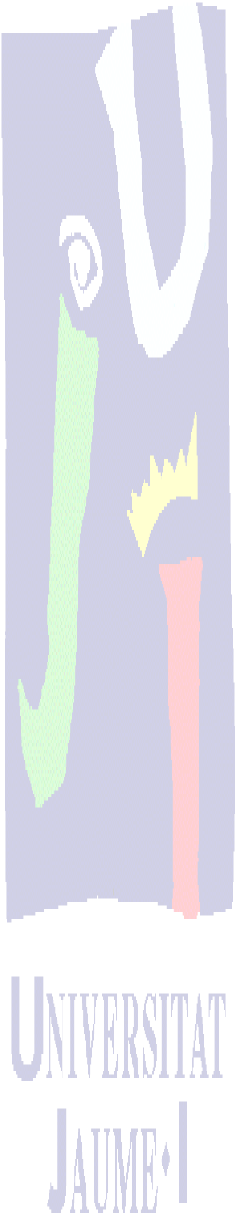
IV-5.7 J. A. Mata, E. Peris, M. P. Cifuentes, M. G. Humphrey, M. Samoc, B. Luther-Davies. “Syntheses, structures and nonlinear optical properties of ferrocenyl complexes with arylethenyl substituents.” *Eur. J. of Inorganic Chem.8 (**2001**) 2113.*

VI-5.1 A. Peruga, J. A. Mata, D. Sainz**,** E. Peris. “Facile synthesis of bidimensional ferrocenyl-based branched oligomers by Palladium catalyzed coupling reactions.” *J. Organomet. Chem. 637-639 (**2001**) 191*.

VI-5.2 J. Palomero, J. A. Mata, F. González, E. Peris. “Facile Synthesis of First Generation Ferrocene Dendrimers by a Convergent Approach Using Ditopic Conjugated Dendrons.” *New J. Of Chem.* (Aceptado ***2001***).

VI-5.3 J. A. Mata, J. Palomero, E. Peris. “Pd-Mediated synthesis of linked conjugated tri- and penta-ferrocenyl complexes.” *J. Organomet. Chem* Enviado (***2002***).

VI-5.4 E. Peris, J. Loch, J. A. Mata, R.H. Crabtree. “A Pd Complex of a Tridentate Pincer CNC Bis-carbene Ligand as a Robust Homogenous Heck Catalyst.” *Chem. Comm. 2 (**2001**) 201*.



# Capítulo I

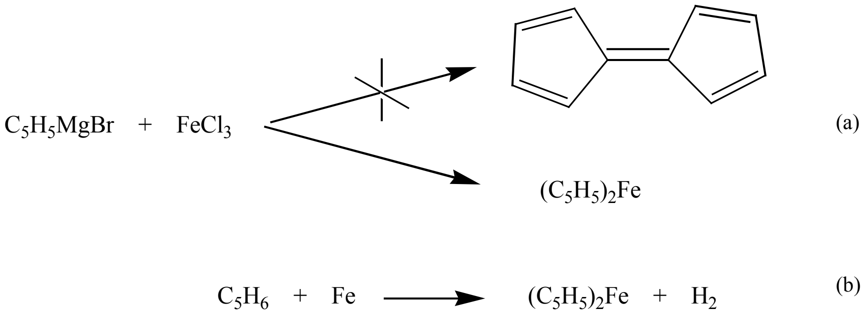
## INTRODUCCIÓN

*La casualidad favorece a las mentes entrenadas.*

William Thomson(1824-1907) Matemático y Físico.

# 1. HISTORIA DEL FERROCENO

El descubrimiento del compuesto diciclopentadienilhierro a principios de los años cincuenta, marcó el inicio de una revolución en el campo de la química organometálica. Dos grupos de investigación independientes sintetizan el mismo producto por casualidad mientras están trabajando en otros campos de la química. El primero de ellos (*Kealey* y *Pauson*, Diciembre de 1951),[1] tratando de obtener fulvaleno a partir del bromuro de ciclopentadienilmagnesio y de tricloruro de hierro, obtuvieron unos cristales de color naranja cuyo análisis elemental consistía en $C_{10}H_{10}Fe$, como se muestra en el esquema 1.1. Al mismo tiempo, (*Miller* et al. Enero 1952)[2] trabajando en la síntesis de aminas obtienen el mismo compuesto por reacción directa de ciclopentadieno con hierro, en presencia de oxidos de aluminio, potasio o molibdeno a 300 ºC. Ambos grupos coincidían en que el producto obtenido era estable al aire, sublimable, con un punto de fusión de 173 ºC, muy soluble en disolventes orgánicos e insoluble en agua.



***Esquema 1.1***
*Procedimientos que condujeron a la obtención del ferroceno de forma casual, a) Kealey y Pauson y b) Miller et al.*

Las primera estructura propuesta para este compuesto consistía en dos anillos de ciclopentadienilo planos unidos a un átomo central de hierro destacando el carácter covalente, como se representa en la figura 1.1 Esta química pronto despertó el interés de muchos grupos de investigación, de modo que la estructura de este compuesto no tardó en resolverse. En primer lugar había algunos hechos que no podían ser explicados considerando dos enlaces sigma en el compuesto $C_{10}H_{10}Fe$, por ejemplo las propiedades térmicas y químicas. Además el enlace sigma entre el fragmento metálico y el orgánico debería ser relativamente inestable y la volatilidad observada no podía ser consecuencia de una interacción iónica.

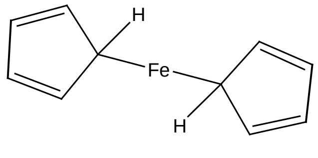


***Figura 1.1***
*Primera estructura propuesta para el ferroceno.*

En la Universidad de *Harvard*, *Wilkinson*, *Woodward* et al. utilizaron métodos químicos, físicos y espectroscópicos para determinar la estructura correcta del diciclopenta-dienilhierro,[3] mientras que independientemente *Fischer* y *Pfab* utilizaban cristalografía de rayos-X sobre monocristal.[4] *Wilkinson* advirtió que los diez átomos de carbono debían contribuir del mismo modo al enlace con el hierro y en base a ello formula una estructura con dos anillos ciclopendadienilo paralelos y el átomo de hierro en el centro de ambos como si fuera un "sandwich". De este modo, el enlace parecía muy fuerte debido al solapamiento entre los orbitales *d* del metal, y los electrones π de los orbitales *p* del ciclopentadienilo. Para corraborar su hipótesis, se realizaron medidas de infrarojo, ultravioleta, susceptibilidad magnética y medidas del momento dipolar, llegando a la conclusión de que existía un único tipo de enlace C-H, que el compuesto era diamagnético, sin electrones desapareados, y que el momento dipolar efectivo era cero. Esta información indicaba que la estructura tipo sandwich debería ser correcta. Unos meses más tarde los estudios cristalográficos de *Fischer* corraboraron inequívocamente la estructura propuesta. Aunque este tipo de enlace había sido propuesto con anterioridad, no había ninguna prueba de su existencia hasta entonces. El descubrimiento y reconocimiento de este nuevo tipo de enlace entre fragmentos orgánicos insaturados y metales, marcó un hito en la química organometálica.

Hoy en día resulta difícil de comprender el impacto que tuvo la revolucionaria estructura del ferroceno. A continuación se describen las primeras impresiones de *J. D. Dunitz*, químico contemporáneo famoso por sus estudios estructurales y también por los trabajos sobre la estructura del ferroceno. [5]

> One afternoon, I opened the Library copy of JACS [in Cambridge, England] and come across R. B. Woodward's proposal that the molecule consists of two parallel cyclopentadienyl rings with the iron atom sandwiched between them. I was skeptical. Nothing like this had never been seen before. On my way out of the Library I met Leslie [Orgel] and asked if he had seen this astonishing proposal. He was as skeptical as I was. When we found that the compound was relatively easy to prepare in crystalline form, I decided to determine its crystal structure and so demonstrate the incorrectness of the proposed molecular structure. Within a few weeks, it became clear to us that Woodward's proposal was correct after all. There was no doubt about it.

Muy pronto se extendió la química de los compuestos tipo sandwich a otros metales de transición como por ejemplo cobalto y niquel, poniendo de manifiesto que este tipo de enlace no era único para el hierro. *Woodward* descubrió que los ciclopendadienilos eran de una naturaleza lo suficientemente aromática como para dar reacciones de substituciones de *Friedel-Crafts*. Esta y otras muchas mas similitudes entre los anillos Cp y el benceno, condujo a uno de sus estudiantes postdoctorales, *Mark Whiting*, a darle el nombre de *'ferroceno'*, extendiéndose luego esta nomenclatura a todos los metales que formaban este tipo de compuestos como *metalocenos.*

Por el trabajo realizado en la química de los compuestos tipo sandwich y su contribución al desarrollo de la química organometálica, *Wilkinson* y *Fischer*, compartieron el premio Nobel de química en 1973.

## 2. SÍNTESIS DE FERROCENO

Las vías por las que se puede preparar el ferroceno son numerosas, y las más habituales son las que se muestran esquema 2.1. Cabe destacar que es un compuesto relativamente barato, que se fabrica comercialmente, fácil de aislar en forma cristalina mediante recristalización, muy soluble en disolventes orgánicos, insoluble en agua y estable al aire.

i) A partir de una fuente de $Cp^-$ $\quad 2NaCp + FeCl_2 \rightarrow Cp_2Fe$

ii) A partir de Ciclopentadieno $\quad 2C_5H_6 + FeCl_2 + 2Et_2NH \rightarrow Cp_2Fe + 2[Et_2NH_2]\ Cl$

iii) A partir de hierro metálico $\quad Fe + 2C_5H_6 \xrightarrow{500°C} Cp_2Fe + H_2$

***Esquema 2.1***
*Procedimientos de síntesis de ferroceno.*

## 3. PROPIEDADES DEL FERROCENO

### 3.1 Propiedades electroquímicas.

El ferroceno se puede oxidar fácilmente para dar ferricinio [catión diciclopentadienil-hierro(III)] de color verde-azul en disoluciones diluidas o rojo-sangre en disoluciones concentradas. En la figura 3.1 se esquematiza este proceso. La oxidación del ferroceno se puede conseguir de muchos modos: electroquímicamente, fotoquímicamente o por agentes oxidantes como pueden ser $HNO_3$, $FeCl_3$, $I_2$, $Ag^+$ y *N-Bromosuccinamida*. La solubilidad del ferricinio depende del contraión utilizado siendo en cualquier caso mucho más insoluble que el ferroceno.

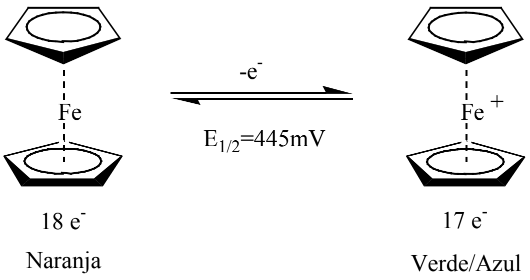


**Figura 3.1**
*Proceso redox en el ferroceno.*

El voltagrama del ferroceno muestra una única onda de oxidación en el barrido directo acompañada de la correspondiente onda de reducción en el barrido inverso, como se muestra en la figura 3.2. La simetría de la onda obtenida, la independencia de los valores del potencial formal respecto de la velocidad de barrido y los valores de la relación $i_{pa}/i_{pc}$ cercanos a la unidad, confirman la existencia de un proceso redox reversible. Sin embargo, la separación entre picos $\Delta E$ es mayor que el valor ideal de 60 mV característico de un proceso redox monoelectrónico completamente reversible. Este hecho puede atribuirse a diferentes factores: la compensación incompleta de la resistencia de la disolución, la presencia del potencial de unión líquida y un proceso de transferencia electrónico ligeramente lento.

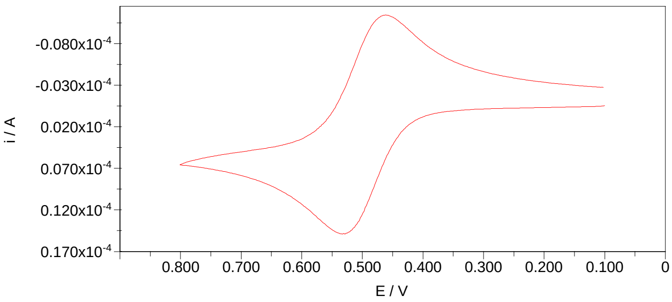


**Figura 3.2**
*Voltagrama de ferroceno en $CH_2Cl_2$/ $TBAPF_6$.*

Las sales de ferricinio son muy utilizadas como agentes oxidantes suaves de un electrón y el par redox ferroceno/ferricinio se utiliza como un estándar secundario en muchos estudios electroquímicos. Esta actividad redox ha desencadenado en la incorporación de ferroceno en muchos sistemas para que actuae como interruptor o receptor molecular. En algunos sistemas los vínculos selectivos pueden afectar el potencial redox del ferroceno ofreciendo así la posibilidad de su aplicación en el campo de los sensores químicos y la electrónica molecular.

## 3.2 Propiedades estructurales.

Los primeros estudios cristalográficos del ferroceno indicaban que a temperatura ambiente este cristaliza en el sistema monoclínico adoptando una conformación alternada y con una simetría molecular $D_{5d}$.[4] Estudios posteriores han demostrado que esta estructura no es correcta y que el ferroceno presenta polimorfismo. A una temperatura inferior a 164 *K* el ferroceno cristaliza en el sistema triclínico con una conformación pseudo-eclipsada, desviada $\delta = 9^{\circ}$. En la figura 3.3 se define el ángulo $\delta$ y las distancias más características. Por debajo de 110 *K* la cristalización del ferroceno es ortorrómbica con una conformación totalmente eclipsada y simetría molecular $D_{5h.}$ [5]

Estudios teóricos demuestran que la forma eclipsada del ferroceno es ligeramente más estable (2.78 *KJ/mol*) que la forma alternada. Estos cálculos han sido corroborados de forma experimental obteniendo unas energías para la barrera rotacional de 3.8 *KJ/mol*. La diferencia de energía tan pequeña entre ambos isómeros justifica la existencia de ambos confórmeros.

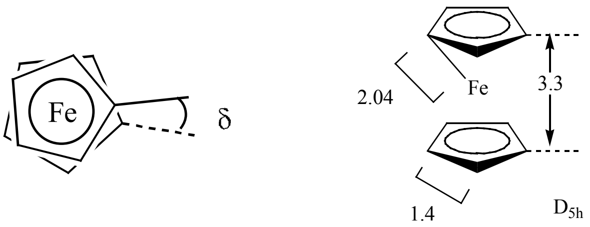


***Figura 3.3***
*Estructura pseudo-eclipsada y eclipsada del ferroceno.*

## 3.3 Quiralidad del ferroceno.

Estudios de reactividad con ferroceno ponen de manifiesto que su comportamiento es en muchos aspectos similar al de los sistemas aromáticos. Sin embargo la estereoquímica del ferroceno es muy diferente. En concreto los derivados del ferroceno con al menos dos sustituyentes diferentes en el mismo anillo no son superponibles con su imagen especular, es decir, son quirales. El primer compuesto que se sintetizó de este tipo fue el ácido 3,1'-dimetil-ferrocenocarboxílico en 1962.[6]

Hoy en día existe aún cierta controversia a la hora de asignar la nomenclatura de los enantiomeros en los metalocenos, si bien son dos los procedimientos más empleados. En primer lugar el trabajo desarrollado por *K. Schlögl* sugiere que este tipo de isomería es un ejemplo de quiralidad plana.[7] Los índices quirales se pueden asignar del siguiente modo. El observador tiene que colocar la molécula de modo que el anillo *Cp* sustituido este mas cercano a este. Luego los sustituyentes se ordenan siguiendo las reglas de prioridad de *Cahn-Ingold-Prelog* (*CIP*) y finalmente si la rotación se produce en el sentido de las agujas del reloj se dice que es *R* y si es al contrario *S*, como se ilustra en la figura 3.4.

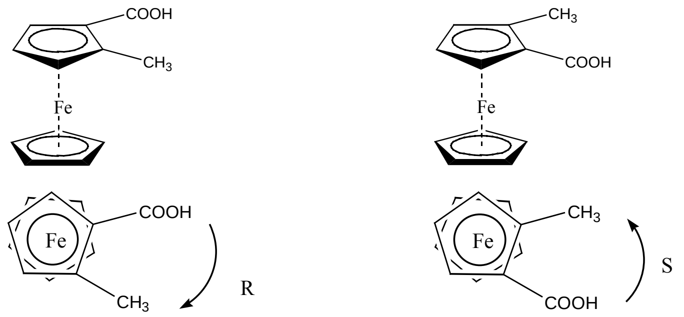


***Figura 3.4***
*Enantiomeros del ácido 2-metil-ferrocenocarboxilico.*

Otro modo utilizado en la nomenclatura de estos sistemas se debe a *Cahn-Ingold-Prelog* en su tratado básico sobre estereoquímica del 1966.[8] La sugerencia de estos autores es reducir la quiralidad plana del ferroceno a una quiralidad central, considerando enlaces simples entre los átomos de carbono del anillo y el hierro. De este modo puede observarse que cada uno de los carbonos sustituidos de los anillos de *Cp* forma un tetraedro distorsionado. El carbono que se utiliza para describir la quiralidad es aquel que esta enlazado al grupo de mayor prioridad como se muestra en la figura 3.5.

***Figura 3.5***
*Nomenclatura según el modelo propuesto por CIP.*

Hay que destacar que dependiendo del sistema utilizado llegaremos a soluciones opuestas. En muchos de los trabajos sobre ferrocenos quirales se utiliza la quiralidad plana, pero no es una nomenclatura general, de modo que para evitar confusiones es conveniente hacer referencia al sistema de nomenclatura utilizado, haciendo uso de subíndices ($S_p$ o $R_p$).

# 4. REACTIVIDAD

## 4.1 Química Orgánica del ferroceno.

Una de las características fundamentales del ferroceno es que se comporta como un sistema aromático, debido a la aromaticidad proporcionada por los anillos ciclopentadienilo. De este modo la química orgánica del ferroceno se basa y se puede predecir en términos de la aromaticidad de los anillos ciclopentadienilo. Es importante resaltar que la estabilidad del ferroceno bajo condiciones de reacción violentas hace muy extensa su utilización. En el esquema 4.1 se muestran algunas de las reacciones orgánicas más significativas del ferroceno.

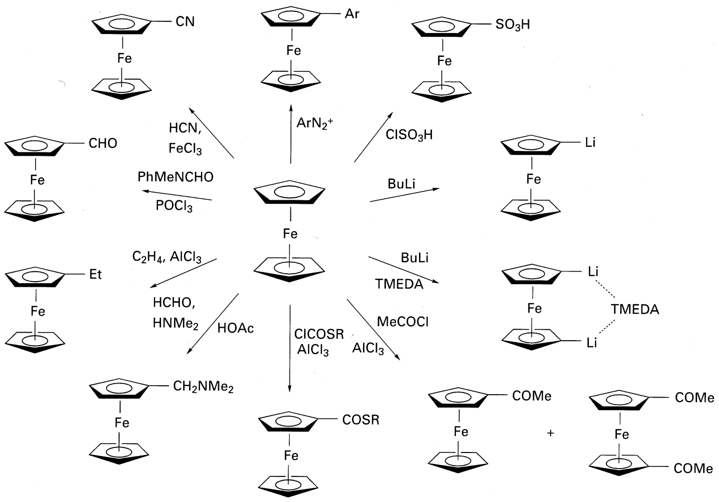
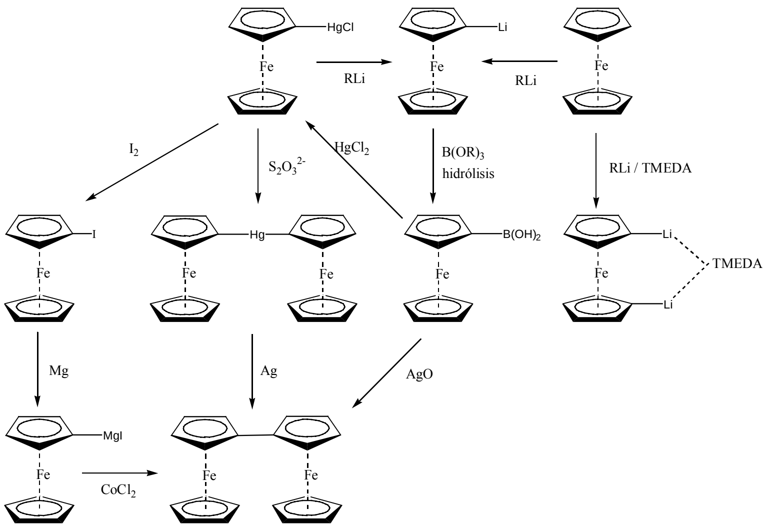


*Figura 4.1*
*Reacciones orgánicas más significativas del ferroceno.*

## 4.2 Metalación.

Este tipo de reacciones son muy importantes en la química del ferroceno porque son los intermedios para la formación de una gran variedad de derivados. Los metales alcalinos en general son buenos candidatos para producir la metalación del ferroceno, entre ellos hay que destacar los derivados alquílicos de litio. Otros metales también utilizados son por ejemplo el sodio, mercurio y boro, como se describe en el esquema 4.5.

Las monometalaciónes utilizando RLi son muy sencillas aunque los protones del anillo ciclopentadienilo no son muy ácidos. El principal inconveniente es la formación de productos 1,1'-bisustituidos. Si el producto deseado es 1,1'-bisustituidos exclusivamente, se puede emplear TMEDA (N,N,N',N'-tetrametiletilendiamina), que forma un complejo con el litio lo que conduce a la formación del producto bisustituido.



***Esquema 4.5***
*Metalación y derivados del ferroceno.*

Experimentalmente se ha observado que los sustituyentes alquilicos reducen la acidez del resto de protones de los ciclopentadienilos. Por ello, cuando se metala un ferroceno monoalquilado la sustitución se produce en las posiciones homo-3,4 o en el anillo *Cp* que no está sustituido (hetero). Las posiciones adyacentes al sustituyente alquílico son las menos reactivas. Sin embargo si el sustituyente posee un par de electrones no enlazante, la sustitución se produce predominantemente en la posición 2 (*orto*). En la figura 4.1 se describen las posibles orientaciones en la metalación. Este hecho se atribuye a una interacción intramolecular entre el átomo de litio y el par de electrones solitario, produciendo de este modo lo que se denomina un mecanismo orientativo.

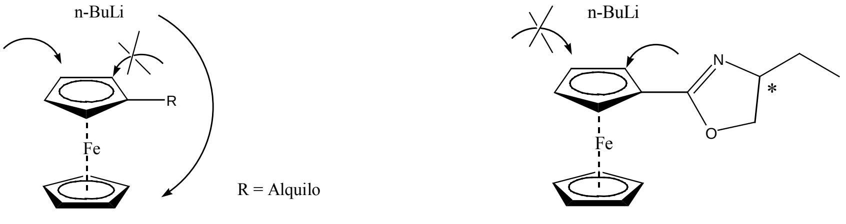


***Figura 4.1***
*Efecto orientativo de los sustituyentes.*

# 5. APLICACIONES

Sin duda alguna la importancia del ferroceno y sus derivados reside en la gran cantidad de aplicaciones que poseen. La estabilidad, sus propiedades físicas y químicas le otorgan unas características especiales que hacen muy factible su utilización en muchas áreas de la química. A continuación se describen algunas de las aplicaciones más importantes del ferroceno, como por ejemplo su utilización en el campo de la medicina, catálisis y síntesis asimétrica. El estudio de las propiedades de óptica no lineal, la interacción entre metales y su utilización en el campo de los dendrímeros se aborda en capítulos posteriores.

## 5.1 Sales de transferencia de carga: Materiales conductores y magnéticos.

El fenómeno de la electricidad y del magnetismo ha cautivado la imaginación y la fascinación de la humanidad desde su descubrimiento, hasta el punto que es casi imposible concebir la sociedad moderna sin considerar los efectos que se derivan de estos fenómenos. El descubrimiento, en la década de los ochenta, de materiales moleculares con propiedades tradicionalmente relacionadas con los metales, tales como superconductividad[9] y magnetismo,[10] ha estimulado el interés científico en esta área de conocimiento. Los materiales moleculares suelen ser, en general, ligeros, solubles, trasparentes y poseen propiedades ópticas.

La base molecular de un compuesto de transferencia de carga (*TC*) consiste en un dador y un aceptor de densidad electrónica, capaces de formar cationes y aniones radicales estables, y en estado sólido estos compuestos deben presentar el apilamiento adecuado para que pueda producirse la conducción eléctrica. El estudio de este campo se transformó en 1973 con el descubrimiento de la elevada conductividad eléctrica y el comportamiento metálico del compuesto monodimensional de *TC* formado por el dador tetratiofulvaleno (*TTF*) y el aceptor 7,7,8,8-tetracianoquinodimetano (*TCNQ*). Los complejos de *TC* necesitan cumplir ciertos requisitos para presentar un cierto apilamiento en estado sólido. i) las moléculas tienen que ser planas o estar compuestas de fragmentos que lo sean, ii) deben de formar radicales estables en disolución en los que la diferencia de energía entre el *HOMO* y el *LUMO* sea relativamente pequeña y iii) las moléculas deben poseer sistemas conjugados y deben ser capaces de aproximarse unas a otras más cerca que la suma de la distancia de los radios de *Van der Waals*, aumentando de este modo el solapamiento intermolecular. El ferroceno es una molécula cilíndrica compacta con dos anillos planos paralelos. Además, el ferroceno es fácilmente oxidable para dar sales estables de ferricinio, y su capacidad dadora puede ser modificada con el número y la naturaleza de los sustituyentes.

El ferroceno forma complejos de *TC* débiles, sin embargo el decametilferroceno forma complejos mucho más interesantes. La introducción de los metilos produce que el compuesto sea más fácil de oxidar y más resistente a reacciones de sustitución. En 1979 se descubrió que el compuesto $[Cp^{*}Fe^{III}]^{\cdot +}$ $[TCNQ]^{\cdot -}$ poseía un elevado momento ferromagnético y una estructura lineal. A partir de aquí son muchos los estudios que se han realizado para evaluar características estéricas/electrónicas necesarias para estabilizar el ferromagnetismo.

A parte de estas sales de *TC* son muchos los compuestos derivados de ferroceno que se han estudiado, con aceptores organicos (como el *TCNQ* y *TCNE*) e incluso con inorgánicos $[Pt\{C_2S_2(CN)_2\}_2]$ y $[Au(dmit)_2]$.[11] En la figura 5.1 se muestra el empaquetamiento de una de estas sales de transferencia de carga.

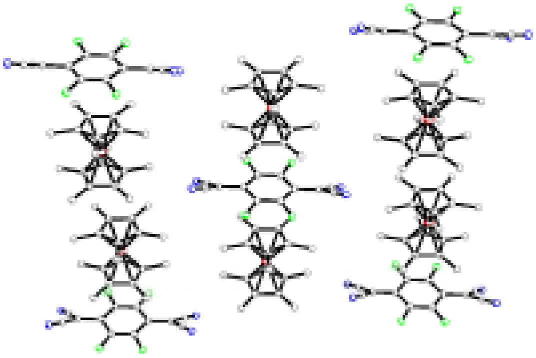


***Figura 5.1***

*Empaquetamiento del compuesto de transferencia de carga formada por $TCNQF_4$ con Fc*. Muestra un apilamiento dimérico del tipo DAAD.*

El ferroceno y sus derivados son buenos candidatos para la formación de sales de *TC* y ofrecen la posibilidad de nuevas vías en el desarrollo de la química organometálica en estado sólido. El estudio sistemático de las propiedades magnéticas del decametilferroceno por *Miller-Epstein* ha desencadenado en el descubrimiento de materiales moleculares ferromagnéticos y ha generado nuevas perspectivas en los mecanismos de acoplamientos magnéticos.[12] Tales resultados han demostrado que compuestos monodimensionales (como la mayoria de las sales de *TC*) pueden comportarse como tridimensionales si los componentes moleculares están dispuestos de forma adecuada. A pesar de esto, el diseño de materiales ferromagnéticos orgánicos/organometállicos, con unas propiedades físicas y estructurales determinadas continúa siendo un reto en investigación y desarrollo, así como la preparación de materiales organometálicos con propiedades superconductoras.

## 5.2 Polímeros con ferroceno.

Dentro del campo de los materiales poliméricos están adquiriendo gran importancia los polímeros que contienen metales en su estructura, debido a las propiedades que presentan en comparación con los polímeros orgánicos tradicionales. Como muestra de estas propiedades cabe destacar la conductividad eléctrica (posible superconductividad), el comportamiento magnético, el aumento de la estabilidad térmica, propiedades ignífugas y las características ópticas como los efectos de óptica no lineal (*ONL*). En particular, la estabilidad y el comportamiento redox del ferroceno y sus derivados han producido su incorporación en muchas estructuras poliméricas.

La síntesis de estos polímeros se ha realizado fundamentalmente a través de dos metodologías: *i)* a partir de la funcionalización de los polímeros orgánicos tradicionales, de modo que sea fácil la introducción del fragmento metálico. *ii)* a partir de los introducción de fragmentos polimerizables en los derivados metálicos.

Uno de los primeros ejemplos utilizado en este campo fue el vinilferroceno para dar poli(vinilferroceno), cuya estructura se muestra en la figura 5.2. El fragmento organometálico ejerce unos efectos electrónicos y estéricos poco usuales durante la polimerización, debido a un gran número de estados de oxidación accesibles y al propio efecto estérico del ferroceno.[13] El ferroceno es un compuesto que presenta propiedades ignífugas importantes, de ahí que se haya utilizado para la obtención de materiales poliméricos ignífugos. Otros compuestos poliméricos, aquellos que poseen las unidades de ferroceno bastante próximas, pueden presentar una gran deslocalización de la carga debido a la formación de compuestos de valencia mixta después de la oxidación de un electrón.

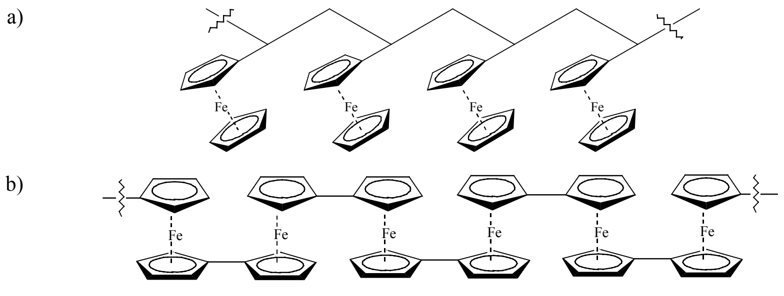


***Figura 5.2***
*Polimeros con ferroceno. a) Secuencia del poli(vinilferroceno) y b) poli(ferrocenilenos).*

Existen muchos otros tipos de polímeros derivados de ferroceno, como pueden ser los polímeros quirales, los unidos cara a cara, los polímeros tridimensionales y los dendrímeros. Estos últimos se diferencian de los anteriores principalmente en la estructura que poseen, y su estudio se aborda en el capítulo VI.

## 5.3 Derivados de Ferroceno en Medicina.

### 5.3.1 Biosensores.

Uno de los biosensores más importantes es el correspondiente a la glucosa. No solo por su utilización en procesos biotecnológicos como el control de procesos de fermentación, sino también en el campo de la medicina. Se utiliza por ejemplo para medir la glucosa en sangre en el diagnóstico del estado de la diabetes y de la hiperglucemia. La oxidación de la glucosa por la enzima glucosa oxidasa (*GOD*) para dar gluconato es sensible y específica, y de este modo, apropiada para la determinación de la glucosa con sensores. El resultado de la reacción bioquímica entre la enzima y la glucosa puede ser evaluado a través del oxígeno consumido o del peróxido de hidrogeno formado. Sin embargo la medida electroquímica directa del producto oxidado esta impedida debido a que el enzima no reacciona con las superficies del electrodo directamente y también allí puede ser disuelto el oxígeno de las muestras. Así pues, se puede utilizar un mediador redox para facilitar la oxidación de la glucosa en condiciones catalíticas. Por oxidación de la forma reducida de la *GOD* puede saberse la cantidad de glucosa transformada en gluconato. El par ferroceno/ferricinio puede actuar como mediador permitiendo la determinación electroquímica de la glusosa a través de unos ciclos electroquímicos encadenados, como se muestra en la figura 5.3.

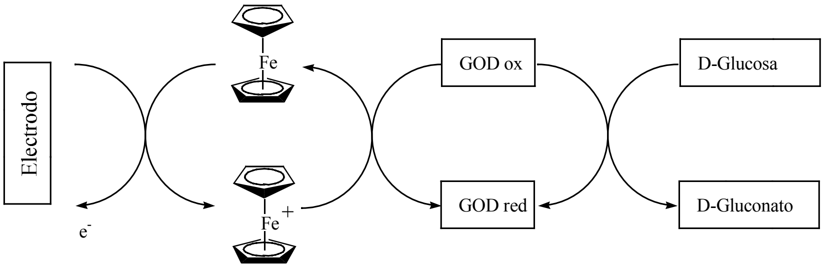


***Figura 5.3***
*Utilización del ferroceno como mediador en la determinación de la glucosa.*

### 5.3.2 Agentes antitumorales.

En 1965 *B. Rosenberg* et al. mientras estudiaban la rapidez del crecimiento bacteriano en presencia de campos eléctricos observaron que se producía el crecimiento de las bacterias pero no su reproducción o división. Después de buscar la posibles causas de este fenómeno como la variación del *pH*, cambios de temperatura y demás, llegaron a la conclusión de que se debía a la utilización de los electrodos de platino. El platino metálico es poco reactivo, pero son los productos de la oxidación [$PtCl_2(NH_3)_2$ y $PtCl_4(NH_3)_2$] los que producían el comportamiento anormal de las bacterias. Además, solo los isómeros *cis* son activos. Esta actividad biológica de los compuestos de platino era totalmente inesperada. Debido a que los compuestos impedían la división celular, se probaron para ver si tenían actividad antitumoral, y el compuesto *cis-diaminodicloroplatino(II)* resulto ser especialmente eficaz. Este compuesto es muy conocido en el tratamiento contra el cáncer y se conoce con el nombre de *cisplatino*. El principal inconveniente de este compuesto es que presenta algunos efectos colaterales, hoy en día los estudios para tratar el cáncer se centran en la búsqueda de compuestos altamente eficaces y que sean menos tóxicos.

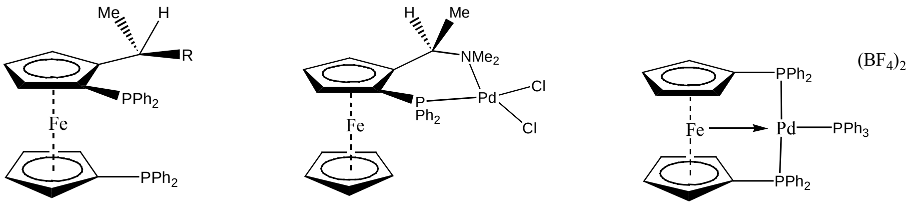
Algunos derivados del ferroceno han mostrado poseer propiedades antitumorales muy buenas, como por ejemplo el ferricinio. Las sales derivadas de ferricinio solubles en agua son agentes eficaces en el tratamiento del tumor *Ehrlich Ascites*, llegando a unos niveles de curación de entre el 70 y el 100%. Otros tumores inhibidos por el ferricinio son el melanoma *B16*, *carcinoma colon 38* y el *carcinoma de pulmón de Lewis*. La principal ventaja en la utilización de estos derivados es que son mucho menos tóxicos que los derivados de platino.

## 5.4 Catálisis asimétrica con ligandos ferrocenilo.

Existen una gran variedad de catalizadores derivados de metales de transición que tienen muchas aplicaciones, sobretodo en química orgánica. Entre ellos cabe destacar la utilización de ligandos de ferroceno quirales. Estos compuestos han demostrado ser muy eficaces en reacciones asimétricas como por ejemplo en la síntesis de péptidos estereoselectiva, y en transaminaciones y condensaciones asimétricas.

Uno de los derivados del ferroceno más ampliamente utilizado en catálisis son las ferrocenilfosfinas quirales. Su importancia reside en la en un conjunto de características que difícilmente puede encontrarse en otros ligandos fosfina quirales: i) fácil introducción de grupos funcionales en la posición del ferrocenilmetilo; ii) poseen la quiralidad impuesta por el ferroceno; iii) modos sintéticos de preparación relativamente sencillos; iv) la coloración naranja del ferroceno permite que la purificación por columna sea muy sencilla.

La versatilidad de coordinación de las ferrocenilfosfinas permite controlar la influencia de los factores estéricos y electrónicos del ligando en la estereoselectividad del catalizador. En la figura 5.4 se muestra la estructura más común de los ligandos quirales ferrocenilfosfina y dos modos diferentes de coordinación.



*R = OMe, NMe$_2$, ...* *PdCl$_2$[(R)-(S)-PPFA]* *[Pd(dppf-P,P')(PPh$_3$)][BF$_4$]$_2$*

***Figura 5.4***
*Ligandos quirales ferrocenilfosfina y diferentes modos de coordinación.*

Existen otras familias de ligandos quirales derivados de ferroceno como pueden ser los alcoholes, aminoalcoholes y calcogenuros. Estos ligandos conducen a la obtención de catalizadores similares a los de ferrocenilfosfinas, pero su estudio esta muchos menos desarrollado.

## 6. REFERENCIAS

(1) Kealy, T. J.; Pauson, P. L. *Nature* **1951**, *168*, 1039.

(2) Miller, S. A.; Tebboth, J. A.; Tremaine, J. F. *J. Chem. Soc.* **1952**, 632.

(3) Wilkinson, G.; Rosenblum, M.; Whiting, M. C.; Woodward, R. B. *J. Am. Chem. Soc.* **1952**, *74*, 2125.

(4) Fischer, E. O.; Pfab, W. *Zeitschrift Fur Naturforschung Section B-a J. Chem. Sci.* **1952**, *7*, 377.

(5) Dunitz, J. D. In *Organic Chemistry: Its language and its stsate of the art.* **1993**, p 9-23.

(6) Westman, L.; Rinehart, K. L. *Acta Chem. Scan.* **1962**, *16*, 1199.

(7) Egger, H.; Schlogl, K. *J. Organomet. Chem.* **1964**, *2*, 398.

(8) Cahn, R. S.; Ingold, C.; Prelog, V. *Angew. Chem. Inter.Ed.* **1966**, *5*, 385.

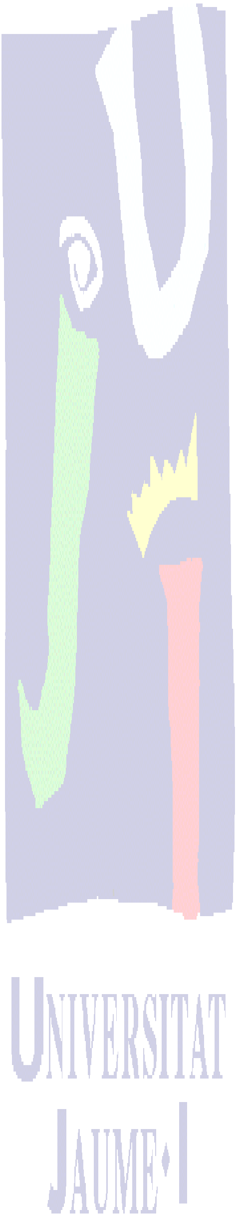
(9) Williams, J. M.; Ferrato, J. R.; Thorn, R. J.; Carlson, K. D.; Geiser, U.; Wang, H. H.; Kini, A. M.; Whanbo, M.-H. *Organic Superconductors. Synthesis, Structure, Properties, and Theory*; Prentice Hall: Englewood Cliffs, New Jersey, **1992**.

(10) Gatteschi, D.; Kahn, O.; Miller, J. S.; Palacio, F. *Magnetic molecular materials.* Kluwer, Dordrecht, **1991**; Vol. 198.

(11) Togni, A.; Hayashi, T. *Ferrocenes*; VCH Verlagsgesellschaft mbH: Weinheim, Germany, **1995**.

(12) Dixon, D. A.; Calabrese, J. C.; Miller, J. S. *J. Phys. Chem.* **1989**, *93*, 2284.

(13) Arimoto, F. S.; Haven, A. C. *J. Am. Chem. Soc.* **1955**, *77*, 6295.



# Capítulo II

## OBJETIVOS

*Tanto si piensas que puedes como que no puedes,*
*estás en lo cierto.*
Henry Ford

# OBJETIVOS

El estudio de materiales moleculares, es un campo multidisciplinar que trata sobre la preparación de sistemas, basados en moléculas, que presentan unas propiedades físicas determinadas. La finalidad del trabajo presentado en esta tesis doctoral consiste en el desarrollo de vías de síntesis racionales de nuevos compuestos moleculares derivados de ferroceno con aplicaciones de interés tecnológico en los campos de la electrónica y la óptica.

Con esta finalidad los objetivos concretos que nos hemos planteado son:

***1.-*** Obtención de derivados de ferroceno homo y heterometálicos con aplicaciones en el campo de la óptica no lineal.

***2.-*** Estudio sistemático de la influencia de los componentes del cromóforo en las propiedades ópticas: aumento de la cadena conjugada, utilización de diferentes aceptores de densidad electrónica y efecto del contraión.

***3.-*** Síntesis y caracterización de biferrocenos; estudio de las propiedades electrónicas derivadas de la interacción metal-metal.

***4.-*** Desarrollo de procesos de síntesis que nos permitan obtener metalodendrímeros funcionalizados con sistemas hiperconjugados de ferroceno.

***5.-*** Estudio de la relación entre la estructura electrónica y molecular de los sistemas obtenidos con las propiedades físicas y químicas. Evaluación de las posibles aplicaciones de interés tecnológico.

# Capítulo III

## TRANSFERENCIA ELECTRÓNICA EN SISTEMAS VINIL-ARENO

> *La educación científica de los jóvenes es al menos tan importante,*
> *quizá incluso más, que la propia investigación.*
> Paul Erdos (1913-1996)

# 1. INTRODUCCIÓN

## 1.1 Introducción.

Todos los compuestos descritos en la presente memoria, son derivados de ferroceno, unidos a una cadena conjugada que termina en un grupo aceptor. La comunicación electrónica que se establece entre el dador (ferroceno) y el aceptor, va a determinar en gran medida las propiedades físicas y químicas del sistema molecular en estudio. A partir del estudio de las propiedades de los compuestos obtenidos, hemos intentado establecer relaciones estructura-propiedades, fundamentalmente con vistas a obtener compuestos con elevada respuesta óptica no lineal (*ONL*).

Si lo que pretendemos es que en un compuesto que contiene un fragmento electrón-dador, y otro aceptor, se establezca comunicación electrónica entre ambos extremos, debemos escoger con gran cuidado el puente de unión entre ellos. El puente debe ser conjugado, de manera que se facilite la deslocalización electrónica a lo largo de la molécula. La gran mayoría de los compuestos que se describen en la presente memoria, contienen puentes del tipo vinil-areno, escogidos debido a su carácter conjugado, ya que muchos de los compuestos descritos hasta el momento con este tipo de puentes, presentan elevadas respuestas *ONL*.

Con objeto de analizar la intensidad de la comunicación electrónica[1] en este tipo de puentes, decidimos aprovechar la altísima dependencia de la energía de las bandas de los carbonilos metálicos (en espectros de *IR*), al modificarse el carácter electrónico del metal y con esto la retrodonación sobre el ligando *CO*. De hecho, el análisis de las señales de los ligandos *CO* suele ser elegido en sistemas de análisis espectroscópico,[2] debido a que aparecen en una región en la que no suele haber otras absorciones, y porque las bandas son bastante estrechas. A partir de esta idea básica, elaboramos las bases de la investigación publicada en el artículo 'IR Spectroscopic Study of Hydrogen Bonding Using a Metal Carbonyl Probe', que se adjunta al final del presente capítulo. La numeración utilizada en este capítulo se basa en la del trabajo citado anteriormente.

El objetivo de este estudio es detectar si la adición de dadores de hidrógeno a los carbonilos descritos, puede provocar un cambio en la frecuencia de resonancia de las bandas de los *CO* en *IR*. Una interacción de tipo '*enlace de hidrógeno*' sobre el par de electrones del nitrógeno no coordinado, debería disminuir la densidad electrónica del metal si es que el ligando facilita la comunicación electrónica entre el metal y dicho átomo de nitrógeno. Esta disminución de densidad de carga sobre el metal, provoca una disminución de la retrodonación sobre el orbital $\pi^*$ del carbonilo, que a su vez aumentará su frecuencia de resonancia en *IR*. En general, los enlaces de hidrógeno son interacciones débiles (2 - 12 *Kcal/mol*) entre grupos dadores de hidrógeno (*H-A*) y pares solitarios de electrones de heteroátomos ($:X$). Hoy en día el interés no sólo se centra en averiguar si existe o no enlace de hidrógeno, sino también en evaluar la naturaleza y la magnitud de esta interacción.[3]

### 1.2 Carbonilos metálicos.

Los carbonilos metálicos de los metales de transición forman una de las mayores familias dentro de la química organometálica. Son materiales de partida bastante comunes para la síntesis de nuevos compuestos organometálicos de bajo estado de oxidación. La sustitución de los ligandos carbonilo es bastante sencilla y confieren una estabilidad adicional frente a la oxidación y descomposición térmica.

El enlace que forma el ligando carbonilo con el metal se puede desglosar en tres componentes. La donación sigma del ligando carbonilo al metal, la donación $\pi$ del ligando al metal y también una componente de retrodonación del metal al ligando $\pi^*$.

El número y los modos activos en *IR* de los carbonilos metálicos depende de la simetría local del fragmento $M(CO)_n$. De este modo, tenemos que los compuestos tratados en este trabajo presentan una simetría pseudo-$C_{4v}$ al que corresponden dos modos de vibración $A_1$, un $B_2$ y un E.[4] En la figura 1.1 se muestra la asignación de estos modos de vibración para el compuesto $(CO)_5CrL$ ($L$ = (*E*)-1,2-di-4-piridileteno) (**3**).

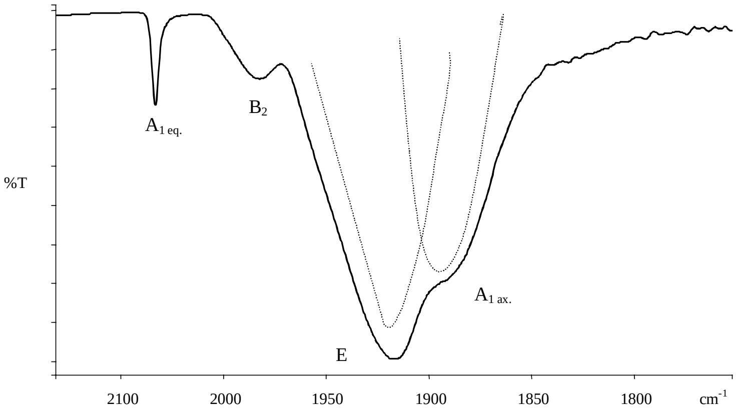
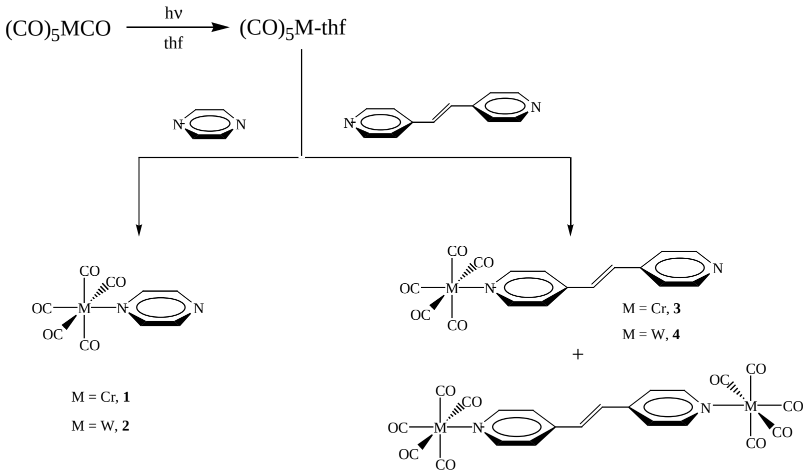


***Figura 1.1***
*Asignación de los modos de vibración para el compuesto **3**.*

# 2. SÍNTESIS Y CARACTERIZACIÓN

## 2.1 Síntesis de los aceptores de hidrógeno.

Los compuestos de fórmula general $(CO)_5ML$ (*M* = *Cr* o *W*; L = pirazina o (*E*)-1,2-di-4-piridiletene) se han obtenido por vía fotoquímica a partir del hexacarbonilo correspondiente y la posterior coordinación del ligando nitrogenado, como se muestra en el esquema 2.1 y en el apartado 2.3 del capitulo IV. El principal inconveniente de este proceso reside en la formación del producto dimetálico $\{(CO)_5M\}_2L$ en el caso de *L* = (*E*)-1,2-di-4-piridileteno.[5] Este problema se solucionó utilizando un ligero exceso de ligando nitrogenado, y por separación en columna de alúmina.



***Esquema 2.1***
*Procedimiento de síntesis de los aceptores de hidrógeno.*

## 2.2 Preparación de los aductos dador-aceptor de hidrógeno.

Para favorecer la asociación entre el dador y el complejo metálico es necesario impedir la autoasociación del dador de hidrógeno. Por ello hemos utilizado aminas aromáticas en donde el par solitario del nitrógeno está desactivado por resonancia, y fenoles en donde la autoasociación está impedida estéricamente. Los dadores de hidrógeno utilizados fueron difenilamina, imidazol, 4-nitrodifenilamina, pirazol, carbazol, indol, 2,4,6-trimetilfenol y 3,6-dibromocarbazol. Los dadores de hidrógeno deben ser lo suficientemente ácidos para participar en la formación del enlace de hidrógeno, pero no lo demasiado como para inducir la transferencia completa del protón.

Para detectar la formación del enlace de hidrógeno es necesario trabajar a elevadas concentraciones, ya que la entropía ($\Delta S^o$) varía en el intervalo desde -5 a -20 $J\,K^{-1}\,mol^{-1}$. Los mejores resultados los hemos obtenido al evaporar disoluciones de dador - aceptor en diclorometano sobre una pastilla prensada de *NaCl*, formando una película amorfa de los aductos. El modo de trabajo consistía en preparar una serie de disoluciones con diferentes proporciónes de dador (*H-A*) y aceptor organometálico (*M*) en el intervalo de *M* : *H-A* 1/0.25 hasta 1/20, dejar evaporar en la pastilla de *NaCl* y medir el espectro de *IR*.

## 3. RESULTADOS Y DISCUSIÓN. ANÁLISIS POR *IR*.

Nuestro objetivo inicial era investigar si la adición de dadores de hidrógeno a los compuestos **1**, **2**, **3** y **4**, producía un cambio en la frecuencia de vibración de los grupos carbonilo, y analizar la naturaleza y la magnitud de este efecto. En concreto, la formación del enlace de hidrógeno, con el par de electrones solitario del nitrógeno, produce un descenso de la densidad electrónica del metal vía un efecto inductivo que se trasmite a través del sistema conjugado, produciendo un aumento de la frecuencia de vibración de los carbonilos.

En el caso de los derivados de pirazina (compuestos **1** y **2**) no se observa ningún tipo de variación significativa en la frecuencia de vibración de los carbonilos, lo que sugiere que no se forma ningún tipo de enlace de hidrógeno. Nosotros interpretamos este resultado cómo una consecuencia de la desactivación del par solitario del nitrógeno debido al efecto atrayente de densidad electrónica producido por el fragmento $M(CO)_5$.

En los compuestos **3** y **4** sí que se observa un aumento en la frecuencia de resonancia de los carbonilos. Este desplazamiento es más importante para los modos de vibración *E* y $A_{1ax}$ (vibración del *CO* trans a la bispiridina), pero insignificante para los modos $B_2$ y $A_{1eq}$ (modo de vibración simétrico de los carbonilos ecuatoriales). En la figura 3.1 se muestra la variación de la frecuencia de los carbonilos para el caso del compuesto **4** utilizando diferentes cantidades de difenilamina.

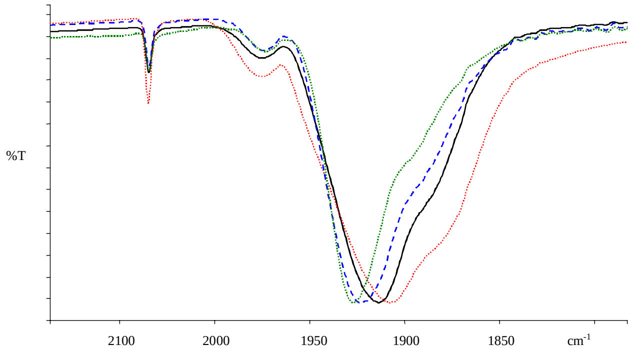


**Figura 3.1**

*Variación de la frecuencia de vibración de los carbonilos del compuesto **4** con diferentes cantidades de difenilamina. Al aumentar la proporción de difenilamina, se observa un aumento de la frecuencia de resonancia de los carbonilos, en especial las bandas correspondientes a los modos de vibración E y $A_{1ax}$.*

A medida que incrementamos la concentración de dador de hidrógeno, aumenta la frecuencia de vibración de los modos E y $A_{1ax}$, hasta llegar a un valor máximo, como se muestra en la figura 3.2. El máximo incremento en la frecuencia de los carbonilos es de 20 $cm^{-1}$, que se produce cuando utilizamos difenilamina.

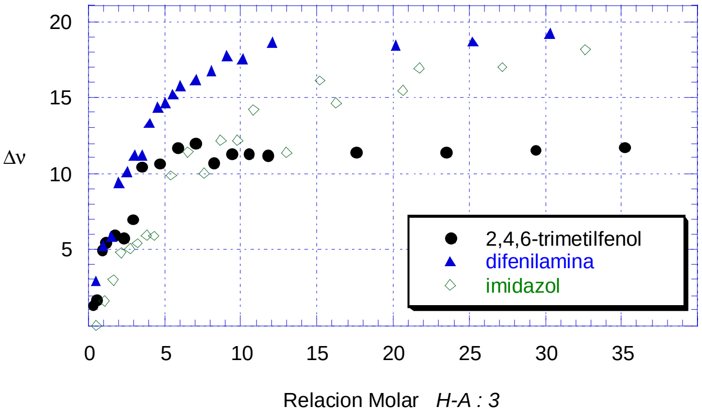


**Figura 3.2**

*Variación de la frecuencia de vibración de los carbonilos a medida que aumenta la concentración del dador de hidrógeno.*

Los resultados obtenidos también podrían ser interpretados considerando la formación del enlace de hidrógeno directamente sobre el metal.[6] Sin embargo, esta posibilidad queda descartada porque los derivados de pirazina **1** y **2** no presentan ningún tipo de variación. Otra posibilidad que podría presentarse es la formación del enlace de hidrógeno sobre los carbonilos, pero el efecto que tendría sobre la frecuencia de vibración de estos sería el contrario, es decir, al añadir los dadores de hidrógeno disminuiría la frecuencia de vibración de los carbonilos.

Para evaluar la magnitud del enlace de hidrógeno hemos realizado una estimación de las constantes de enlace suponiendo que se forman aductos 1:1 dador-aceptor.[7] A partir de las representaciones gráficas de *Lineweaver-Burk*[8] de la variación de frecuencia de carbonilo de los compuestos **3** y **4** frente a diferentes proporciones de dador de hidrógeno, hemos obtenido las constantes de enlace. En la figura 3.3 se muestra este tipo de representaciones para el caso concreto del compuesto **4** con diferentes dadores de hidrógeno. En la tabla 1 del trabajo III-6.1 se muestran las constantes de enlace y las energías libres calculadas, observando que las interacciones de hidrógeno son más fuertes en el caso del compuesto **4**, seguramente debido a una mayor basicidad del *W*, y en consecuencia un mayor retrodonación, en comparación con el *Cr*.

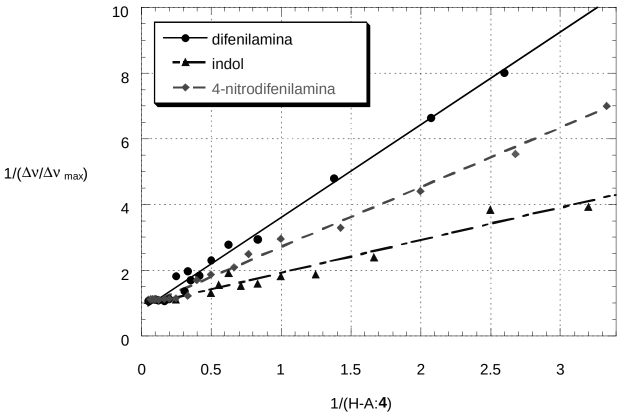


***Figura 3.3***

*Representaciones de Lineweaver-Burk para el compuesto **4**, para diferentes dadores de hidrógeno.*

Con la finalidad de confirmar los resultados experimentales obtenidos, se realizaron estudios teóricos de los aductos **3** y **4** con difenilamina. La principal característica[9] de estos estudios es que muestran la presencia de un mínimo local en la superficie de energía potencial correspondiente a una distancia de enlace de hidrogeno *A-H···N* de 2.01 *Å* y 2.07 *Å* para los aductos **3** y **4** respectivamente, que es más pequeña que la suma de los radios de *Van der Waals*.

## 4. CONCLUSIONES

Mediante el uso de un carbonilo metálico, al que podemos denominar '*sonda*', podemos detectar y evaluar la formación de interacciones débiles por enlace de hidrógeno, basándonos en la espectroscopia *IR*. La variación de la frecuencia de vibración de los grupos carbonilos nos permite cuantificar la magnitud del enlace formado. El enlace de hidrógeno se produce con el par solitario de electrones del ligando dipiridileteno y no directamente sobre el metal o los grupos carbonilos, observándose un aumento de la frecuencia de vibración de los grupos carbonilos debido a un efecto inductivo. La conclusión más importante que se deriva de este trabajo es que interacciones débiles, como son los enlaces de hidrógeno, producen una comunicación electrónica a larga distancia que se trasmite a través del sistema conjugado.

## 5. REFERENCIAS

(1) Launay, J. P. *Chem. Soc. Rev.* **2001**, *30*, 386.

(2) Shubina, E. S.; Belkova, N. V.; Krylov, A. N.; Vorontsov, E. V.; Epstein, L. M.; Gusev, D. G.; Niedermann, M.; Berke, H. *J. Am. Chem. Soc.* **1996**, *118*, 1105.

(3) Huyskens, P. L.; Luck, W. A.; Zeegers-Huyskens, T. *Intermolecular Forces; An Introduction to Modern Methods and Results*; Springer-Verlag: Berlin, **1991**.

(4) Bratterman, P. S. *Metal Carbonyl Spectra*; Academic Press: New York, **1975**.

(5) Kaim, W. *Angew. Chem. Int. Ed. Engl.* **1983**, *22*, 171.

(6) Shubina, E. A.; Belkova, N. V.; Krylov, A. N.; Vorontsov, E. V.; Epstein, L. M.; Gusev, D. g.; Niedermann, M.; Berke, H. *J. Am. Chem. Soc.* **1996**, *118*, 1105.

(7) Connors, K. A. *Binding Constants: The measurement of molecular complex stabilities.*; Wiley: New York, **1985**.

(8) Lineweaver, H.; Burk, D. *J. Am. Chem. Soc.* **1934**, *56*, 658.

(9) Etter, M. C. *Acc. Chem. Res.* **1990**, *23*, 120.

DALTON
FULL PAPER

# IR Spectroscopic study of hydrogen bonding using a metal carbonyl probe

**Eduardo Peris,***[a] **Jose A. Mata**[a] **and Vicent Moliner**[b]

[a] *Departament de Química Inorgànica i Orgànica, Universitat Jaume I, Ctra. Borriol s/n, 12080 Castellón, Spain. E-mail: eperis@qio.uji.es*
[b] *Departament de Ciències Experimentals, Universitat Jaume I, Ctra. Borriol s/n, 12080 Castellón, Spain*

***Received 19th July 1999, Accepted 13th September 1999***

The interaction of different hydrogen bond donors with [M(CO)$_5$L] [L = (*E*)-1,2-di-4-pyridylethene, M = Cr or W] was studied by means of IR spectroscopy. A clear shift to higher wavenumbers of the E and A$_1$ carbonyl vibration modes upon addition of the hydrogen bond donors is observed. The binding isotherms allowed calculation of both the equilibrium constants and free energies of formation of the adducts. These parameters depend on the nature of the carbonyl compound used, the p$K_a$ of the hydrogen bond donor and the steric hindrance of its A–H bond.

During the last five decades a large number of investigations have been carried out on hydrogen bonding.[1] Much experimental data obtained from the application of different methods with a variety of hydrogen bonded systems have been published, and theoretical advances on the study of hydrogen bonding have approached a high level of development.

Typically, hydrogen bonds are weak interactions (2–12 kcal mol$^{-1}$) between proton donor groups and lone pairs of heteroatoms. Although this interaction has been mainly studied in organic and biological systems, many examples of inorganic and organometallic compounds have recently been published opening a great field of research and potential applications in molecular recognition and catalysis.

Most often the question in a potential hydrogen-bonding interaction is not 'does hydrogen bonding occur?', but 'to what extent, or with what energy, does hydrogen bonding occur?' It is usually easy to decide whether some interaction has occurred (A–H stretching frequency, proton magnetic resonance, *etc.*), but there are only a few examples in which simple methods to evaluate the energy have been reported.[2] In particular, one of the most widely used methods is based in the shift of the A–H frequency in the IR spectrum[2] although these methods have led to controversy regarding the validity and generality of such an approach.

The great structural diversity of organometallic compounds has led to a large number of hydrogen-bonded patterns being discovered in solution and in the solid state.[3] Recently, Crabtree and co-workers[4] found a new type of hydrogen bonding (or dihydrogen bond) of the type M–H···H–A, where M is a transition metal. The characterization of this intriguing type of interaction was carried out by means of IR and NMR spectroscopy, and the energies were found from both theoretical and experimental data. Shubina, Epstein and co-workers[5] have also found this kind of interaction in metal hydrides and have elegantly shown that the *ν*(CO) shift to higher wavenumbers of the carbonyl coligands is an indirect indication of the existence of hydrogen bonding to the hydride or the metal. In fact, an exhaustive study of the Cambridge Crystallographic data base by Braga *et al.*[6] has shown that H···H interactions have been known for more than thirty years, although the observations remained unexplained. Metal carbonyls such as [Cr(η$^6$-C$_6$H$_5$-CO$_2$H)(CO)$_3$] have also recently been used as 'IR-active organometallic pH probes', due to the shift of the CO band to lower wavenumbers upon increasing the pH of the solution, which favours deprotonation of the π bonded ligand.[7] In fact, detection of such (CO) modes offers substantial benefits when employed in spectroscopic sensing measurements, mainly because the bands are narrow relative to the overall spectral width (small shifts can be determined precisely) and because they occur in a region of the spectrum that is generally free from other absorptions.

With these ideas in mind, we decided to use metal carbonyl compounds as hydrogen bonding probes for various proton donors. Specifically, we have used tungsten and chromium pentacarbonyls with pyrazine- and bipyridine-like ligands, in order to allow hydrogen bonding by the proton donor to the lone pair of the unco-ordinated nitrogen atom of the ligand. In this paper we report the shift of the *ν*(CO) bands of pentacarbonyl(*E*)-1,2-di-4-pyridylethene)metal (metal = Cr or W) with several typical hydrogen-bonding donors such as indole, diphenylamine and 2,4,6-trimethylphenol, and its dependence on the hydrogen-bonding donor type and concentration.

## Results and discussion

### Syntheses of compounds

The compounds [M(CO)$_5$L] [L = pyrazine or (*E*)-1,2-di-4-pyridylethene; M = Cr or W] were obtained from photochemical reaction of the hexacarbonyl complex in THF to generate [M(CO)$_5$(THF)], and subsequent addition of the corresponding ligand in excess to avoid generation of the thermodynamically more favourable dinuclear compounds.[8] The IR spectra of the compounds so obtained are virtually identical, indicating the presence of a metal pentacarbonyl moiety, the bands being readily assigned to the two A$_1$, B$_2$ and E modes for the pseudo $C_{4v}$ metal centre (see Fig. 1 for compounds **3** and **4**), by comparison with other monosubstituted metal carbonyl derivatives.[9] The $^1$H NMR spectra confirm the η$^1$ co-ordination of the N-donor ligands, and $^{13}$C NMR clearly shows the two carbonyl inequivalent sites of the pentacarbonyl fragments, so confirming the proposed geometry of the compounds.

Syntheses of the pyridyl compounds **3** (M = Cr) and **4** (M = W) also afford [{M(CO)$_5$}$_2$L] [L = (*E*)-1,2-di-4-pyridylethene, M = Cr or W] as minor products; in these compounds the N-donor behaves as an ambidentate bridging ligand as confirmed by $^1$H and $^{13}$C NMR spectroscopy. The IR spectra are

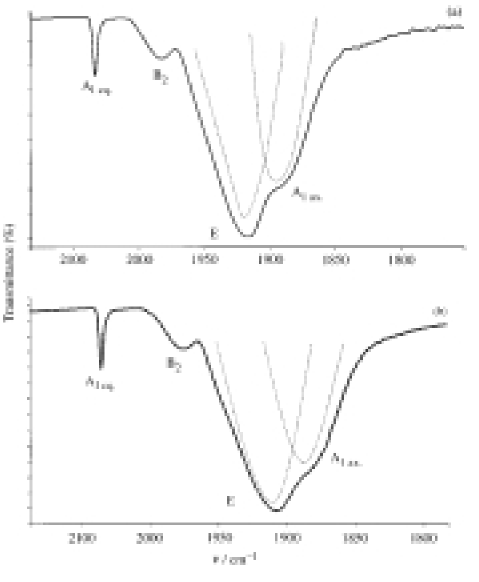


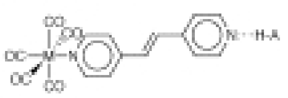
**Fig. 1** The IR spectra of compounds **3** (a) and **4** (b) with the assignment of the bands.

similar to those of the monometallic compounds, indicating a local $C_{4v}$ symmetry about the metal atoms.

### Addition of hydrogen-bonding donors

The initial objective was to investigate whether the addition of hydrogen-bonding donors to compounds **1**, **2**, **3** and **4** could be detected spectroscopically from changes in the wavenumber of the *ν*(CO) vibration modes. A hydrogen-bonding interaction with the electron pair of the unco-ordinated nitrogen atom would be expected to decrease the electron density of the metal carbonyl fragment *via* an inductive effect and so decrease the extent of electron back donation from the metal to the CO π* antibonding orbitals. In this way, hydrogen bonding should lead to an increase of the wavenumber of the *ν*(CO) vibration modes.

M = Cr, **1**, M = W, **2**



M = Cr, **3**, M = W, **4**

H-A: *N*-diphenylamine, 4-nitrophenyl(phenyl)amine, pyrazole, imidazole, 2,4,6-trimethylphenol, indole, carbazole and 3,6-dibromocarbazole

To favour association between the donor and the metal complex we sought to prevent self association of the hydrogen bond donor. We therefore selected aromatic amines where the nitrogen lone pair is deactivated by resonance, and phenols where self association is sterically inhibited. These hydrogen-bond donors were: diphenylamine, 4-nitrophenyl(phenyl)amine, pyrazole, imidazole, 2,4,6-trimethylphenol, indole, carbazole and 3,6-dibromocarbazole. Only in the case of 4-nitrophenyl(phenyl)amine some self association is to be expected owing to the accepting character of the nitro group. The hydrogen bond donors also need to be sufficiently acidic to participate in bonding, but not so acidic as to induce complete proton transfer. With respect to our compounds, we have found that this requires a p$K_a$ (DMSO) value in the range 17–25.

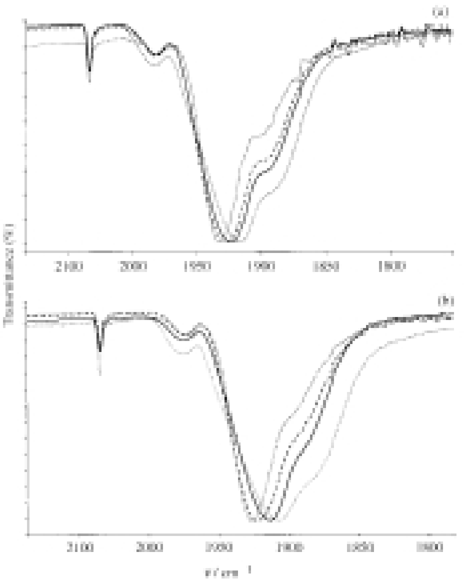


**Fig. 2** The FTIR spectra in the carbonyl region for the reaction of compounds **3** (a) and **4** (b) with different amounts of diphenylamine (A–H).

Since typical thermodynamic values for bimolecular associative intermolecular interactions are in the range $-\Delta S°$ 5–20 J K$^{-1}$ mol$^{-1}$,[10] we carried out our experiments at high concentration where the process becomes most readily detectable. The best results were achieved when the mixtures of the solutions of the hydrogen-bond donor and acceptor in $CH_2Cl_2$ were evaporated on a NaCl plate, to obtain an amorphous thin film of the adducts. The experiments were performed by adding small aliquots of a solution of the complex (**1**, **2**, **3** or **4**) to a range of solutions of the eight hydrogen-bonding donors employed, to give a final composition in the range of M : A–H 1 : 0.25 to 1 : 20.

Addition of the hydrogen-bond donors to pyrazine compounds **1** and **2** failed to show any significant changes in the wavenumber of the *ν*(CO) vibration modes, indicating that, apparently, no hydrogen bonding is occurring in these complexes. We interpret this result as a consequence of the inductive deactivation of the unco-ordinated lone pair of the pyrazine upon co-ordination to the highly electron withdrawing metal fragment, $M(CO)_5$.

With the more basic complexes $[M(CO)_5L]$ [L = (*E*)-1,2-di-4-pyridylethene; M = Cr **3** or W **4**] addition of the hydrogen-bond donors produced an increase of the wavenumber of the *ν*(CO) vibration modes. The shift is large for the E and $A_{1ax}$ (vibration of the CO *trans* to the pyridyl ligand) band, but insignificant for the $B_2$ and $A_{1eq}$ (symmetric vibration mode of the equatorial carbonyl groups) carbonyl bands, as shown in Fig. 2. As stated before, this shift is attributed to hydrogen bonding to the lone pair of the co-ordinated pyridyl ligand. The experiments were completely reproducible and the *ν*(CO) shifts were highly

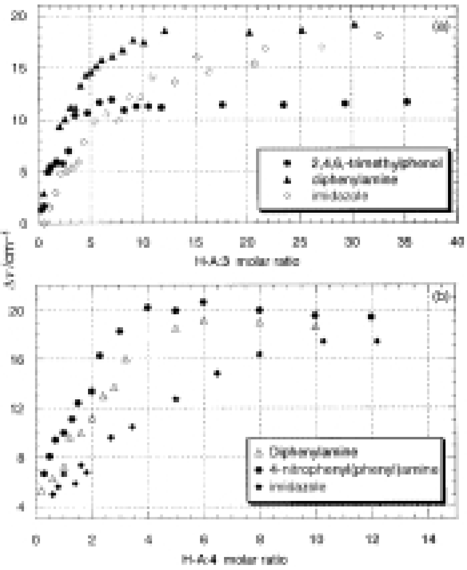


**Fig. 3** Plots of $\Delta\nu$ *vs.* A–H : M ratio for the reaction of compounds **3** (a) and **4** (b) for different hydrogen-bonding donors.

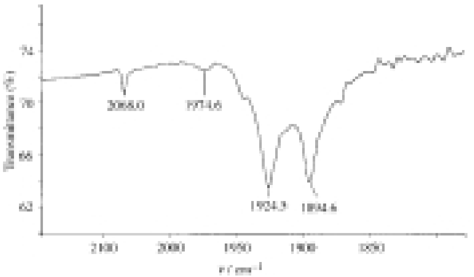


**Fig. 4** The IR spectrum of compound **4** with 3,6-dibromocarbazole at a A–H : M 1 : 10 molar ratio.

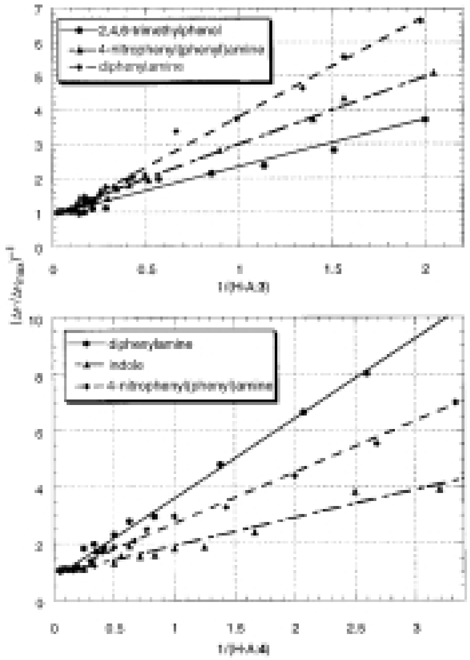


**Fig. 5** Lineweaver–Burk plots of compounds **3** (a) and **4** (b) for different hydrogen-bonding donors.

dependent on the nature of the H-bond donor and its concentration relative to compounds **3** or **4**. The band shows an isosbestic point at 1949 cm$^{-1}$ for **3** and 1944 cm$^{-1}$ for **4**, indicating that two species are present in the solutions, the relative concentrations of which change with A–H concentration. A stepwise increase in the donor concentration resulted in a gradual increase of the $\nu$(CO) wavenumber of the E and $A_{1ax}$ vibration modes, until a frequency asymptote is achieved, as shown in Fig. 3. The maximum $\Delta\nu$(CO) value was 20 cm$^{-1}$ for the two diphenylamine cases. Addition of an excess of a more powerful hydrogen-bond acceptor such as $OPPh_3$ to a mixture of **3** or **4** and the different donors resulted in a shift of $\nu$(CO) to their original frequency, indicating that the A–H···$OPPh_3$ interaction is now preferred over formation of the M–N–N···H–A bond. Hydrogen bonding to the carbonyl ligands can also be ruled out in this case, since no decrease of the $\nu$(CO) is observed at any concentration of the donors used. These results could also be interpreted in terms of hydrogen bonding to the metal[5] since this interaction should produce an increase of the $\nu$(CO) shift as seen. However, the fact that compounds **1**, **2** and $[\{M(CO)_5\}_2L]$ [L = (*E*)-1,2-di-4-pyridylethene, M = Cr or W] failed to show this effect rules out this possibility.

We were a little concerned by the fact that only the E and $A_{1ax}$ carbonyl vibration modes shifted upon hydrogen bond formation, while the $B_2$ and $A_{1eq}$ bands remained practically unchanged. In order to confirm this unexpected spectroscopic behaviour we tried to protonate **3** and **4** and then get the IR spectra. Unfortunately these two compounds decompose upon protonation with loss of the bipyridyl ligand. The reaction of **3** and **4** with trimethylaluminium leads to the formation of the adducts $[(OC)_5MNC_5H_4C_2H_2C_5H_4NAlMe_3]$ which were characterized by IR spectroscopy. The spectra show that the E and $A_{1ax}$ bands appear at a higher frequency than for **3** or **4** while the $A_{1eq}$ and $B_2$ carbonyl bands appear at the same frequency (**3**·$AlMe_3$: E, 1934; $B_2$, 1984; $A_{1eq}$, 2068. **4**·$AlMe_3$: E, 1930; $B_2$, 1975; $A_{1eq}$, 2070 cm$^{-1}$; the $A_{1ax}$ band appears as a hump of the E band, as for **3** and **4**).

The fact that a gradual shift of the E and $A_{1ax}$ bands is observed, instead of the appearence of a new band due to the newly formed hydrogen-bonded species, is not surprising since similar studies have been reported leading to the same results.[6] Besides, it is known that IR spectra are usually, but not invariably, in slow exchange,[11] and adduct formation, with its low activation barrier, is one of the most rapid reaction processes. Only the reactions of **3** and **4** with carbazole and 3,6-dibromocarbazole showed separated bands for the free and hydrogen-bonded carbonyl species as shown in Fig. 4.

A careful analysis of the binding isotherms shown in Fig. 3 allowed us to estimate the binding equilibrium constants assuming that 1 : 1 adducts are formed.[12] The Lineweaver–Burk[13] plots for the binding data of compounds **3** and **4** with the different hydrogen-bonding donors, from which the equilibrium constants are obtained, are shown in Fig. 5. Only for the carbazole and 3,6-dibromocarbazole cases, and for the reaction of **3** and indole, the separated bands for the free and hydrogen-bonded metal carbonyls made difficult the determination of the binding constants, since no binding isotherms

**Table 1** Binding constants and free energies (kcal mol$^{-1}$, relative to the reaction of **3** + diphenylamine) determined from the binding isotherms of reactions of compounds **3** and **4** with A–H

| A–H | p$K_a$$^a$ | $K_{(3+\text{A–H})}$$^b$ | $K_{(4+\text{A–H})}$$^b$ | $\Delta G_{(3+\text{A–H})}$$^c$ | $\Delta G_{(4+\text{A–H})}$$^c$ |
|---|---|---|---|---|---|
| Diphenylamine | 24.95 | 0.338 | 0.353 | 0.00 | −0.03 |
| 4-Nitrophenyl(phenyl)amine | 16.85 | 0.503 | 0.549 | −0.23 | −0.28 |
| Imidazole | 18.6 | 0.120 | 0.152 | 0.60 | 0.47 |
| 2,4,6-Trimethylphenol | 18.4 | 0.694 | 1.064 | −0.42 | −0.67 |
| Pyrazole | 19.8 | 0.079 | 0.120 | 0.849 | 0.60 |
| Indole | 20.95 | — | 1.101 | — | −0.64 |

[a] In DMSO, from ref. 14. [b] In mol$^{-1}$. [c] In kcal mol$^{-1}$, relative to the reaction of **3** + diphenylamine.

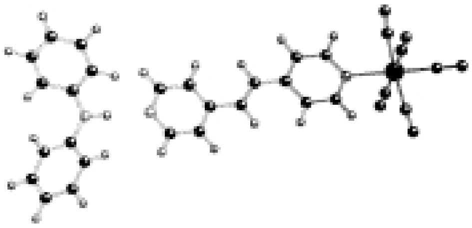


**Fig. 6** Optimized structure of the adduct of compound **3** with diphenylamine obtained by means of HF/3-21G.

could be obtained. Table 1 shows the binding constants for the adducts studied, and the free energies (relative to the reaction of **3** and diphenylamine) obtained. The free energies for the formation of the adducts **4** ··· H–A are slightly lower (more negative) than those for **3** ··· H–A. This result may indicate the higher basicity of the tungsten carbonyl compound, probably because of the higher back donation capability of the metal. Since we have estimated the relative free energy values for the hydrogen-bond formation at room temperature, we cannot evaluate the entropy of the process, which we believe must show important differences for the different hydrogen-bond donors. For this reason, the binding constants do not show a clear trend when we compare them with the p$K_a$ of the hydrogen-bond donors used. However, when we compare the binding constants and relative free energies of donors with similar steric size (which we believe must show a similar value of the formation entropy), we observe that those with lower p$K_a$ show higher formation constants and hence lower formation free energies (this is the case for diphenylamine and 4-nitrophenyl(phenyl)-amine, and imidazole and pyrazole).

### Theoretical data on the structure and energy of the 3 ··· H–A and 4 ··· H–A hydrogen bonds

The theoretical studies of adducts of complexes **3** and **4** with diphenylamine revealed the existence of local minima on the potential energy surfaces corresponding to the structure presented in Fig. 6. The hydrogen-bond distances for the two adducts are 2.01 and 2.07 Å for **3** and **4** respectively, smaller than the sum of the van der Waals radii of H and N and close to those for other A–H ··· N hydrogen bonds. The N–H ··· N angles obtained for the two characterized compounds are in the range between 171 to 177° close to 180° for similar to classical hydrogen bonds and previous theoretical examples. The M–C and C–O distances of the hydrogen-bonded adducts did not show any significant differences compared to those of the free compounds **3** and **4**.

The calculated energies by which the adducts of compounds **3** and **4** with diphenylamine are stabilized relative to the separated molecules are 8.61 and 7.76 kcal mol$^{-1}$ respectively, both being in the range of classical hydrogen bond energies.[1] It is important to point out that we expected a higher energy for the tungsten complex **4**, while we theoretically determined that **3** is the one that shows the higher energy. We believe that this difference between theoretical and experimental data is mainly due to the different theoretical methods used to optimize the structures of the adducts of **3** (HF/3-21G) and **4** with diphenylamine (B3LYP/LanL2DZ).

## Conclusion

By using a metal carbonyl ‘sensor’ we have detected the hydrogen-bonding capability of several weak acids, based on FTIR spectroscopy of the carbonyl region. The hydrogen bond occurs to the non-bonding lone pair of the dipyridylethene ligand of compounds **3** and **4**, promoting an increase of the $\nu$(CO) shift due to an inductive effect. Plots of the binding isotherms allowed us to determine the binding constants of the hydrogen-bonded adducts formed. The binding constants depend on the p$K_a$ of the hydrogen bond donor used, the nature of the carbonyl compound and on the steric hindrance of its A–H bond. The geometry, energy and electron redistribution were theoretically analysed for two model complexes including the Cr and W atoms.

## Experimental

### General

All synthetic reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques. Solvents for synthesis were dried and degassed by standard methods before use. Chromatographic work was performed on silica gel 60 Å or alumina columns.

Proton and carbon NMR spectra were recorded on a Varian 300 MHz spectrometer, using $CDCl_3$ or $CD_2Cl_2$ as solvent, IR spectra on a Perkin-Elmer System 2000 FT-IR using NaCl plates.

### Syntheses of compounds 1–4

The compound [Cr(CO)$_6$] or [W(CO)$_6$] (176 mg, 0.8 mmol) was dissolved in THF (20 ml) and the resulting suspension irradiated for 30 min to yield the yellow solvate [M(CO)$_5$-(THF)]. Pyrazine (for **1** and **2**) or (*E*)-1,2-di-4-pyridylethene (for **3** and **4**) was then added (1 mmol) and the reaction mixture stirred for 20 min. The solution was filtered and the solvent removed under reduced pressure. Purification by column chromatography on alumina with $CH_2Cl_2$–hexane (1 : 1) afforded pure compounds **1** (yield: 51%) or **3** (yield 41%) (M = Cr) and **2** (yield 62%) and **4** (yield 57%) (M = W). The syntheses of **3** and **4** yielded the dimetallic compound [{M(CO)$_5$}$_2$L] [L = (*E*)-1,2-di-4-pyridylethene] as a minor product (*ca.* 20%).

**Pentacarbonyl(pyrazine)chromium 1.** $^1$H NMR: $\delta$ 8.63 (s, 2 H, $C_5H_4N_2$) and 8.32 (s, 2 H, $C_5H_4N_2$). $^{13}$C NMR: $\delta$ 217.1 (4 C, *cis* CO), 210.9 (1 C, *trans* CO), 152.9 (2 C, pyrazine) and 146.7 (2 C, pyrazine). IR (cm$^{-1}$): 2062.2w, 1992.6w and 1920.1s. Calc. for $C_9H_4CrN_2O_5$: C, 37.92; H, 1.48; N, 10.69. Found: C, 38.26; H, 1.85; N, 10.71%.

**Pentacarbonyl(pyrazine)tungsten 2.** $^{1}$H NMR: $\delta$ 8.54 (s, 2 H, $C_5H_4N_2$) and 8.43 (s, 2 H, $C_5H_4N_2$). $^{13}$C NMR: $\delta$ 211.1 (4 C, *cis* CO), 208.9 (1 C, *trans* CO), 149.9 (2 C, pyrazine) and 145.7 (2 C, pyrazine). IR (cm$^{-1}$): 2062.3w, 1997.2w and 1926.8s. Calc. for $C_9H_4N_2O_5W$: C, 26.76; H, 1.00; N, 6.93. Found: C, 27.05; H, 1.05; N, 6.71%.

**Pentacarbonyl[(*E*)-1,2-di-4-pyridylethene] chromium 3**. $^{1}$H NMR: $\delta$ 8.66 (d, 2 H, $^{3}J_{H-H} = 5.4$, $C_5H_4N$), 8.57 (d, 2 H, $^{3}J_{H-H} = 6.2$, $C_5H_4N$), 7.40 (d, 2 H, $^{3}J_{H-H} = 5.4$, $C_5H_4N$), 7.30 (d, 2 H, $^{3}J_{H-H} = 6.0$, $C_5H_4N$), 7.25 (d, 1 H, $^{3}J_{H-H} = 16.2$, CH=CH) and 7.16 (d, 1 H, $^{3}J_{H-H} = 16.2$ Hz, CH=CH). $^{13}$C NMR: $\delta$ 221.4 (1 C, *trans* CO), 215.0 (4 C, *cis* CO), 156.3 (2 C, $C_5H_4N$), 151.2 (2 C, $C_5H_4N$), 145.4 (1 C, $C_5H_4N$), 143.2 (1 C, $C_5H_4N$), 133.4 (2 C, $C_5H_4N$), 129.1 (1 C, $C_5H_4N$), 122.6 (1 C, CH=CH) and 121.9 (1 C, CH=CH). IR (cm$^{-1}$): 2067.0w, 1982.8w and 1914.4s. Calc. for $C_{17}H_{10}CrN_2O_5$: C, 54.56; H, 2.69; N, 7.48. Found: C, 55.05; H, 2.90; N, 7.45%.

**Pentacarbonyl[(*E*)-1,2-di-4-pyridylethene]tungsten 4.** $^{1}$H NMR: $\delta$ 8.80 (d, 2 H, $^{3}J_{H-H} = 6.3$, $C_5H_4N$), 8.68 (d, 2 H, $^{3}J_{H-H} = 5.1$, $C_5H_4N$), 7.42 (d, 2 H, $^{3}J_{H-H} = 5.7$, $C_5H_4N$), 7.35 (d, 2 H, $^{3}J_{H-H} = 6.3$, $C_5H_4N$), 7.30 (d, 1 H, $^{3}J_{H-H} = 16.2$, CH=CH) and 7.18 (d, 1 H, $^{3}J_{H-H} = 16.2$ Hz, CH=CH). $^{13}$C NMR: $\delta$ 202.8 (1 C, *trans* CO), 199.2 (4 C, *cis* CO), 156.8 (2 C, $C_5H_4N$), 151.2 (2 C, $C_5H_4N$), 145.4 (1 C, $C_5H_4N$), 143.0 (1 C, $C_5H_4N$), 133.8 (2 C, $C_5H_4N$), 129.0 (1 C, $C_5H_4N$), 123.3 (1 C, CH=CH) and 121.9 (1 C, CH=CH). IR (cm$^{-1}$): 2070.6w, 1978.6w and 1900.4s. Calc. for $C_{17}H_{10}N_2O_5W$: C, 40.34; H, 1.99; N, 5.54. Found: C, 40.58; H, 2.02; N, 5.78%.

**μ-(*E*)-1,2-Di-4-pyridylethene-bis(pentacarbonylchromium).** $^{1}$H NMR: $\delta$ 8.69 (s, 4 H, $C_5H_4N$), 7.38 (s, 4 H, $C_5H_4N$) and 7.25 (s, 2 H, CH=CH). $^{13}$C NMR: $\delta$ 221.4 (2 C, *trans* CO), 215.0 (8 C, *cis* CO), 156.5 (4 C, $C_5H_4N$), 144.6 (2 C, $C_5H_4N$) and 131.3 (4 C, $C_5H_4N$) and 122.7 (2 C, CH=CH). IR (cm$^{-1}$): 2068.2w, 1980.6w and 1915.4s. Calc. for $C_{11}H_5CrNO_5$: C, 46.66; H, 1.78; N, 4.95. Found: C, 47.06; H, 1.92; N, 4.95%.

**μ-(*E*)-1,2-Di-4-pyridylethene-bis(pentacarbonyltungsten).** $^{1}$H NMR: $\delta$ 8.56 (d, 4 H, $^{3}J_{H-H} = 6.6$, $C_5H_4N$), 7.37 (d, 4 H, $^{3}J_{H-H} = 6.6$ Hz, $C_5H_4N$) and 7.25 (s, 2 H, CH=CH). $^{13}$C NMR: $\delta$ 202.7 (2 C, *trans* CO), 199.2 (8 C, *cis* CO), 157.0 (4 C, $C_5H_4N$), 144.4 (2 C, $C_5H_4N$), 131.5 (4 C, $C_5H_4N$) and 123.4 (2 C, CH=CH). IR (cm$^{-1}$): 2070.6w, 1974.7w and 1903.1s. Calc. for $C_{11}H_5NO_5W$: C, 31.84; H, 1.21; N, 3.38. Found: C, 31.97; H, 1.34; N, 3.45%.

### FTIR Measurements

Aliquots of a stock $CH_2Cl_2$ solution of the hydrogen-bond donors (A–H) were added to solutions of the complexes **1**, **2**, **3** and **4** in $CH_2Cl_2$ (typically 100 μL, 0.01 M). The donors were diphenylamine, 4-nitrodiphenylamine, pyrazole, imidazole, 2,4,6-trimethylphenol, indole, carbazole and 3,6-dibromocarbazole. The solutions so obtained had a M : A–H ratio in the range 1 : 0.25 to 1 : 10. The FTIR samples were prepared by evaporating the resulting $CH_2Cl_2$ solutions on a NaCl plate, to obtain an amorphous thin film of the adducts.

### Computational details

Calculations have been performed with the GAUSSIAN 94 package of programs.[15] *Ab initio* molecular orbital calculations were made at the Hartree-Fock (HF) level with a 3-21G basis set and with methods based on density functional theory (DFT) using the LanL2DZ basis set.[15] We used Becke's 3 parameter functional (B3)[16] which includes Slater exchange along with corrections involving the gradient of the electron density, and the correlation functional of Lee, Yang and Parr, which includes both local and non-local terms (LYP).[17,18] The parameters are those determined by Becke by fitting to the G1 molecule set.[16b,19]

The geometries of adducts of compounds **3** and **4** with diphenylamine have been completely optimized using HF and DFT methods, respectively, and characterized as minima in the potential energy surface by computing the matrix of second energy derivatives (Hessian matrix). The requested convergence on the density matrix was $10^{-9}$ atomic units and the threshold value of maximum displacement was 0.0018 Å and that of maximum force was 0.00045 hartree bohr$^{-1}$ using the Berny analytical gradient optimization routine.[20,21]

## Acknowledgements

We thank the Generalitat Valenciana for financial support of this work (GV-C-CN-09-071-96). We would also like to thank Professor Robert H. Crabtree for his valuable help and advice.

## References

1 D. Hadzi, *Hydrogen Bonding*, Pergamon, London, 1959; G. A. Jeffrey and W. Saenger, *Hydrogen Bonding in Biological Structures*, Springer, Berlin, 1991; P. Schuster, G. Zundel and C. Sandorfy, *The Hydrogen Bond*, North-Holland, Amsterdam, 1976; M. C. Etter, *Acc. Chem. Res.*, 1990, **23**, 120.

2 P. L. Huyskens, W. A. Luck and T. Zeegers-Huyskens, *Intermolecular Forces; An Introduction to Modern Methods and Results*, Springer, Berlin, 1991; A. V. Ioagansen, *Hydrogen Bond*, Nauka, Moscow, 1981; A. V. Iogansen, G. A. Kurkchi, V. M. Furman, V. P. Glazunov and S. E. Odinokov, *Prikl. Spektrosk.*, 1980, **33**, 460; R. M. Badger and S. H. Bauer, *J. Chem. Phys.*, 1937, **5**, 839.

3 D. Braga, F. Grepioni, E. Tedesco, K. Biradha and G. R. Desiraju, *Organometallics*, 1996, **15**, 2692; 1997, **16**, 1846; D. Braga and F. Grepioni, *Acc. Chem. Res.*, 1997, **30**, 81; D. Zhao, F. T. Ladipo, J. Bradock-Wilking, L. Brammer and P. Sherwood, *Organometallics*, 1996, **15**, 1441; S. G. Kazarian, P. A. Hamley and M. Poliakoff, *J. Am. Chem. Soc.*, 1993, **115**, 9069; *J. Chem. Soc.*, *Chem. Commun.*, 1992, 994; L. M. Epstein, A. N. Krylov, A. Z. Kreindlin, M. I. Rubinskaya and E. S. Shubina, *J. Mol. Struct.*, 1993, **301**, 1; L. M. Epstein, A. N. Krylov and E. S. Shubina, *J. Mol. Struct.*, 1994, **322**, 345.

4 E. Peris, J. C. Lee, J. R. Rambo, O. Eisenstein and R. H. Crabtree, *J. Am. Chem. Soc.*, 1995, **117**, 3485; B. P. Patel, J. Wessel, W. Yao, J. C. Lee, E. Peris, T. F. Koeztle, G. P. A. Yap, J. B. Fortin, J. S. Ricci, G. Sini, A. Albinati, O. Eisenstein, A. L. Rheingold and R. H. Crabtree, *New J. Chem.*, 1997, **21**, 413; E. Peris, J. C. Lee and R. H. Crabtree, *J. Chem. Soc.*, *Chem. Commun.*, 1994, 2573; E. Peris, J. Wessel, B. P. Patel and R. H. Crabtree, *J. Chem. Soc.*, *Chem. Commun.*, 1995, 2175; E. Peris and R. H. Crabtree, *J. Chem. Soc.*, *Chem. Commun.*, 1995, 2179; J. C. Lee, E. Peris, A. L. Rheingold and R. H. Crabtree, *J. Am. Chem. Soc.*, 1994, **116**, 11014; J. Wessel, J. C. Lee, E. Peris, T. F. Koeztle, G. P. A. Yap, J. B. Fortin, J. S. Ricci, A. Albinati, O. Eisenstein, A. L. Rheingold and R. H. Crabtree, *Angew. Chem.*, *Int. Ed. Engl.*, 1995, **34**, 2507.

5 E. A. Shubina, N. V. Belkova, A. N. Krylov, E. V. Vorontsov, L. M. Epstein, D. G. Gusev, M. Niedermann and H. Berke, *J. Am. Chem. Soc.*, 1996, **118**, 1105; L. M. Epstein, E. S. Shubina, E. V. Bakhmutova, L. N. Saitkulova, V. I. Bakhmutov, A. L. Chistiakov and I. V. Stankevich, *Inorg. Chem.*, 1998, **37**, 3013.

6 D. Braga, P. De Leonardis, F. Grepioni, E. Tedesco and M. J. Calhorda, *Inorg. Chem.*, 1998, **37**, 3337.

7 C. E. Anson, T. J. Baldwin, C. S. Creaser, M. A. Fey and R. Stephenson, *Organometallics*, 1996, **15**, 1451.

8 W. Kaim, *Angew. Chem.*, *Int. Ed. Engl.*, 1983, **22**, 171.

9 P. S. Bratterman, *Metal Carbonyl Spectra*, Academic Press, New York, 1975.

10 E. M. Arnett, L. Joris, E. Mitchell, T. S. S. R. Murty, T. M. Gorrie and R. Schleyer, *J. Am. Chem. Soc.*, 1970, **92**, 2365; H. H. Jaffe, *J. Am. Chem. Soc.*, 1957, **79**, 2373.

11 J. J. Turner, F. W. Grevels, S. M. Howdle, J. Jacke, M. T. Haward and W. E. Klotzbücher, *J. Am. Chem. Soc.*, 1991, **113**, 8347.

12 K. A. Connors, *Binding Constants: The measurement of molecular complex stabilities*, Wiley, New York, 1985.

13 H. Lineweaver and D. Burk, *J. Am. Chem. Soc.*, 1934, **56**, 658.

14 F. G. Bordwell, *Acc. Chem. Res.*, 1988, **21**, 456.

15 M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson,

J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez and J. A. Pople, GAUSSIAN 94, Revision B.1, Gaussian, Inc., Pittsburgh, PA, 1995.

16 A. D. Becke, (*a*) *Phys. Rev. A*, 1988, **38**, 3098; (*b*) *J. Chem. Phys.*, 1993, **98**, 5648.

17 C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785.

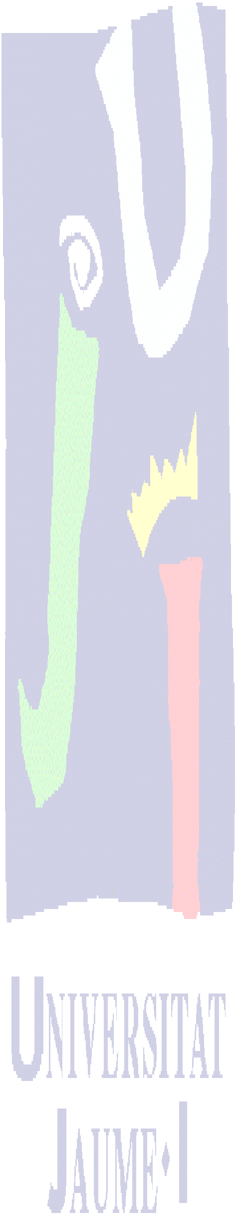
18 B. Miehlich, A. Savin, H. Stoll and H. Preuss, *Chem. Phys. Lett.*, 1989, **157**, 200.

19 J. A. Pople, M. Head-Gordon, D. J. Fox, K. Raghavachari and L. A. Curtis, *J. Chem. Phys.*, 1989, **90**, 5622; L. A. Curtis, C. Jones, G. W. Trucks, K. Raghavachari and J. A. Pople, *J. Chem. Phys.*, 1990, **93**, 2537.

20 H. B. Schlegel, *J. Comput. Chem.*, 1982, **3**, 214.

21 H. B. Schlegel, *J. Chem. Phys.*, 1982, **77**, 3676.

*Paper 9/05793E*



# Capítulo IV

## SISTEMAS CON UN FERROCENO. PROPIEDADES DE ONL

# 1. INTRODUCCIÓN

El descubrimiento en la década de los sesenta de fenómenos ópticos no lineales, tales como la generación del segundo armónico o duplicación de la frecuencia de la luz en un material, abre las puertas a un nuevo campo del conocimiento que actualmente conocemos como óptica no lineal (*ONL*).[1] La importancia de este descubrimiento radica en el estudio de las desviaciones del comportamiento lineal gobernado por las leyes de la física clásica y en las aplicaciones tecnológicas que se derivan. Entre otras aplicaciones, hay que destacar la fabricación de procesadores ópticos de señales, generadores de nuevas frecuencias láser e interruptores ópticos. La multidisciplinaridad es una característica intrínseca de este nuevo campo de estudio, ya que abarca áreas tan diferentes como la física, telecomunicaciones, informática y química, entre otras.[2]

La interacción de un campo electromagnético, normalmente un láser de elevada intensidad, con un material que posea una respuesta óptica no lineal, puede dar como resultado la generación de nuevos campos electromagnéticos. Este fenómeno se produce porque al pasar la luz a través del material, el campo electromagnético interacciona con las cargas inherentes de éste, pudiendo producir una alteración de la fase, frecuencia, amplitud y/o polarización de la radiación incidente.

En la actualidad existe una gran variedad de compuestos inorgánicos, orgánicos e incluso poliméricos que presentan actividad óptica no lineal. La existencia de propiedades ópticas no lineales fue observada por primera vez en cristales inorgánicos tales como el cuarzo, $LiNbO_3$, $KH_2PO_4$, y posteriormente en semiconductores inorgánicos tales como GaAs o InSb.[3] Algunos años más tarde, los compuestos orgánicos se presentan como una alternativa a los anteriores por su bajo coste, su respuesta no lineal más rápida y su mayor flexibilidad sintética. Entre los compuestos orgánicos utilizados en *ONL* de segundo orden hay que destacar aquellos formados por benceno o estilbeno, unidos a fragmentos dadores y aceptores de electrones. Por otra parte los sistemas poliméricos conjugados, como el poliacetileno, han sido utilizados con éxito en el estudio de la *ONL* de tercer orden. Durante los últimos años la utilización de compuestos organométalicos ha ampliado este área de conocimiento como consecuencia de la versatilidad intrínseca de estos sistemas: diversidad de metales, estados de oxidación accesibles, ligandos, geometrías, solubilidad, etc.

A continuación se describen los fundamentos básicos de la óptica no lineal, el modelo teórico y la interpretación de resultados. Finalizaremos este capítulo con un resumen sobre los antecedentes históricos del uso de materiales organometálicos en *ONL*, donde nos hemos centrado en los metalocenos y en los carbonilos metálicos por su relación con los compuestos objeto de estudio en este trabajo.

## 1.1 Conceptos básicos sobre óptica no lineal.

Al irradiar un material con una radiación electromagnética se produce una polarización, pero ¿qué hace que la densidad electrónica de un material pueda acoplarse y polarizarse con el campo electromagnético de una radiación? Para entender este proceso es necesario recurrir al nivel molecular y observar qué es lo que ocurre cuando una radiación se acopla o interacciona con los electrones de una molécula.

La radiación electromagnética posee un campo eléctrico, *E*, que interacciona con las cargas del material produciendo una fuerza (*qE*, donde *q* es la carga). Esta interacción origina un desplazamiento instantáneo, es decir una polarización, *p*, de la densidad electrónica de la molécula. El desplazamiento de esta densidad electrónica produce una separación de cargas que se traduce en un dipolo instantáneo con momento dipolar inducido $\mu$. Para campos pequeños el momento dipolar inducido es proporcional a la intensidad del campo:

$$polarización(p) = \mu = \alpha\ E \qquad \textit{(\textbf{1})}$$

donde la constante de proporcionalidad $\alpha$ se denomina *polarizabilidad lineal* de la molécula. Para un determinado valor del campo externo aplicado, cuanto mayor es la polarizabilidad, mayor es el momento dipolar inducido. Si la respuesta es instantánea, la polarización inducida tendrá la misma frecuencia y fase que el campo externo aplicado.

Los experimentos de *ONL* se realizan sobre materiales macroscópicos, no sobre moléculas aisladas. En estas condiciones definimos la polarización *P* como el momento dipolar por unidad de volumen, de modo que la ecuación *(**1**)* conduce a*:*

$$P = P_0 + \chi\ E \qquad \textit{(\textbf{2})}$$

donde $P_0$ es la polarización permanente de la muestra y $\chi$ es la susceptibilidad lineal que representa la polarizabilidad lineal de un conjunto de moléculas por unidad de volumen.

Cuando irradiamos una molécula con una radiación que posea un campo eléctrico muy intenso, p. e. un láser, la dependencia del momento dipolar inducido con el campo eléctrico deja de ser lineal. En este caso la polarización molecular no lineal puede expresarse tal y como muestra la ecuación *(**3**)*.

$$p = \alpha\ E + \beta\ E^2 + \gamma\ E^3 + \ldots \qquad \textit{(\textbf{3})}$$

donde el coeficiente $\beta$ representa la primera hiperpolarizabilidad molecular (polarizabilidad de segundo orden), $\gamma$ la segunda hiperpolarizabilidad molecular (polarizabilidad de tercer orden), y así sucesivamente. Con el aumento de la intensidad del campo aplicado, los efectos no lineales se hacen cada vez más importantes.

La polarización de un material macroscópico con respuesta no lineal se muestra en la ecuación ***(4)***, en donde $\chi^{(n)}$ es la susceptibilidad no lineal, de orden n.

$$P = P_0 + \chi^{(1)}\varepsilon_0 E + \chi^{(2)} E^2 + \chi^{(3)} E^3 + \ldots \qquad \textit{(4)}$$

En materiales sólidos, para que la hiperpolarizabilidad β sea distinta de cero, es necesario que el material cristalice en un grupo espacial no centrosimétrico. Este requisito puede explicarse teniendo en cuenta el hecho de que si aplicamos un campo $+E$ a una muestra, de acuerdo con la ecuación ***(3)***, el primer término no lineal inducirá una polarización $+\beta E^2$, mientras que si se aplica un campo $-E$ la polarización que se inducirá será también $+\beta E^2$, aunque esta debería ser $-\beta E^2$ como consecuencia de que el material es centrosimétrico. Esta contradicción sólo puede ser racionalizada sí $\beta = 0$ en grupos espaciales centrosimétricos.

Tal como hemos visto, un campo eléctrico oscilante puede inducir una polarización en una distribución electrónica, pero ¿cómo afecta esto a las propiedades observables de la óptica no lineal? El desplazamiento de la distribución electrónica de su posición de equilibrio (polarización) inducido por un campo eléctrico oscilante (láser) puede ser visto como un dipolo clásico oscilante que emite radiación a la frecuencia de oscilación de la radiación incidente. Para un material que tiene propiedades ópticas lineales la radiación emitida por el dipolo tiene la misma frecuencia que la radiación incidente, tal como se representa en la siguiente figura 1.1.

***Figura 1.1***

*Material que no presenta propiedades de ONL. El haz emitido por este material tiene la misma frecuencia que la radiación incidente.*

Para analizar el efecto que se produce cuando en lugar de un material lineal, utilizamos un material con propiedades ópticas no lineales, consideremos la expresión del campo eléctrico de una radiación en un plano según la ecuación ***(5)***:

$$E = E_0 \cos(\omega\ t) \qquad \textit{(5)}$$

donde $E_0$ es la amplitud y $\omega$ la frecuencia de la radiación incidente. Sustituyendo la expresión anterior en la ecuación ***(4)*** se obtiene:

$$P = P_0 + \chi^{(1)} E_0 \cos(\omega\ t) + \chi^{(2)} E_0^2 \cos^2(\omega\ t) + \chi^{(3)} E_0^3 \cos^3(\omega\ t) + \ldots \qquad \textit{(6)}$$

La ecuación ***(6)*** se simplifica haciendo uso de las propiedades trigonométricas de la función coseno, y los tres primeros términos de la ecuación anterior dan lugar a la ecuación ***(7)***:

$$P = \left\{ P_0 + \left(\frac{1}{2}\right) \chi^{(2)} E_0^2 \right\} + \chi^{(1)} E_0 \cos(\omega\ t) + \left(\frac{1}{2}\right) \chi^{(2)} E_0^2 \cos(2\omega\ t) + \qquad \textit{(7)}$$

Esta ecuación es una descomposición de todos los términos que intervienen en la polarización de un material. El primer término se denomina la polarización estática, y depende del campo aplicado pero no de la frecuencia de éste. El segundo término posee la misma frecuencia que la radiación incidente al igual que ocurría en el caso de materiales que se comportan de forma lineal. La característica más importante de la ecuación *(7)* se produce en el tercer término, que introduce una nueva frecuencia que se ha generado y que es el doble de la frecuencia de la radiación incidente, como se observa en la figura 1.2.

***Figura 1.2***
*Material con propiedades ONL de segundo orden. Se genera un haz de frecuencia el doble que la incidente.*

Así pues, tal como se esquematiza en la figura anterior, si un haz intenso de luz atraviesa un material con propiedades de óptica no lineal de segundo orden, se obtiene un haz de luz de la misma frecuencia que la de la radiación incidente y otro haz de luz con una frecuencia doble que la de la radiación original. El primero de estos efectos se conoce como *la rectificación óptica*, mientras que el segundo recibe el nombre de *generación del segundo armónico* (*SHG*). En este proceso tenemos una interacción de tres ondas, debido a que dos fotones con frecuencia $\omega$ se han combinado para generar un único fotón con frecuencia $2\omega$. Este mismo desarrollo puede realizarse para tercer orden o incluso términos superiores. Por analogía con este desarrollo el proceso de tercer orden implica la interacción de cuatro ondas y se produce la generación del tercer armónico (*THG*). Una vez definidas cuales son las características de un compuesto con propiedades de *ONL*, es importante resaltar que a estos materiales se les denomina *cromóforos*.

## 1.2 Modelo teórico.

El desarrollo de cromóforos orgánicos y organometálicos para la generación del segundo armónico y otros efectos ópticos no lineales relacionados, depende de la medida en que seamos capaces de determinar qué factores controlan la hiperpolarizabilidad $\beta$. Una comprensión de cómo la estructura molecular se relaciona con los valores de $\beta$ nos proporcionaría los principios generales para el diseño de cromóforos con las propiedades ópticas no lineales deseadas. Hasta la fecha, esta relación estructura-propiedades ópticas no lineales, ha estado basada en el modelo de los dos estados, introducido por Oudar en 1977 y que supone la existencia de un único estado excitado para la molécula.[4]

De acuerdo con este modelo la hiperpolarizabilidad, $\beta$, puede expresarse en función de la frecuencia máxima de la banda de absorción ($\omega_{máx}$), la frecuencia del campo aplicado ($\omega$), el momento dipolar de transición entre el estado fundamental y el estado excitado ($\mu_{ge}$), y la diferencia entre el momento dipolar del estado fundamental y el del estado excitado ($\Delta\mu$), mediante la ecuación *(**8**)*:

$$\beta_\omega = \frac{12\pi^2}{h^2}\frac{\omega_{max}^2}{\left(\omega_{max}^2 - 4\omega^2\right)\left(\omega_{max}^2 - \omega^2\right)}\mu_{ge}^2\Delta\mu \qquad \textbf{\textit{(8)}}$$

El valor de β calculado según la ecuación (***8***) depende de la frecuencia de la fuente utilizada. Con objeto de comparar los valores de hiperpolarizabilidad de diferentes sistemas se hace una extrapolación del valor de $\beta$ a frecuencia cero, obteniéndose un nuevo valor que es independiente de la frecuencia de la radiación incidente y se denomina $\beta_0$.[5] Las magnitudes $\beta(\omega)$ y $\beta o$ están relacionadas mediante la ecuación *(**9**)*:

$$\beta_0 = \beta(\omega)\frac{\left(\omega_{max}^2 - \omega^2\right)\left(\omega_{max}^2 - 4\omega^2\right)}{\omega_{max}^4} \qquad \textbf{\textit{(9)}}$$

Este modelo predice que los materiales que nos proporcionen respuestas ópticas no lineales elevadas deben cumplir los siguientes requisitos:

a) Transiciones de transferencia de carga poco energéticas. Esto es, que la diferencia de energía entre el *HOMO* y el *LUMO* no sea muy elevada. Esta característica puede observarse fácilmente de la espectroscopia *UV/Vis.*

b) El momento de transición dipolar ($\mu_{ge}$) entre el estado fundamental y el estado excitado tiene que ser elevado. Este está relacionado con la fuerza del oscilador, que puede ser calculada a través de la integral de la banda de transferencia de carga (o lo que es lo mismo, el coeficiente de extinción ($\varepsilon$) debe de ser elevado).

c) Debe existir una gran diferencia entre el momento dipolar del estado fundamental y del estado excitado ($\Delta\mu$).

Hay que resaltar que el modelo de los dos estados es el más sencillo que podemos emplear y por tanto de aplicación muy limitada, ya que solo se considera la presencia de un único estado excitado. Sin embargo, este modelo nos proporciona las pistas adecuadas para el diseño molecular de materiales con elevadas propiedades de *ONL*. En general, funciona bastante bien para los derivados orgánicos, pero en el momento que introducimos algún metal aumenta el número de estados excitados con una energía similar, por lo que su aplicación deja de ser efectiva.

Las transiciones electrónicas y, en consecuencia, las propiedades de óptica no lineal, pueden modularse introduciendo cambios en el diseño molecular de los compuestos. La frecuencia óptica, el momento de transición dipolar y $\Delta\mu$, están asociados a transiciones de carga intramoleculares en compuestos orgánicos y organometálicos, y son susceptibles de ser modificadas mediante cambios en los grupos dadores/aceptores, en la cadena conjugada, en el grado de aromaticidad y en la introducción de átomos metálicos en la estructura electrónica. Como consecuencia de la introducción de orbitales *d*, las transiciones electrónicas en los compuestos organometálicos tienen propiedades que no poseen los compuestos puramente orgánicos.

### 1.3 Comparación de resultados.

La comparación de resultados de *ONL*, obtenidos por diferentes técnicas experimentales, ha de realizarse con precaución. El problema más importante radica en los efectos de dispersión por fluorescencia, pero también podemos encontrarnos con la medida de diferentes componentes tensoriales, algunos procesos físicos que contribuyen a la no linearidad y diferencias de solubilidad.

Por lo tanto, para comparar resultados de óptica no lineal, hay que tener en cuenta la técnica empleada, la longitud de onda de la radiación utilizada y el disolvente en el que se han realizado las medidas. El papel que desempeña el disolvente es muy importante, ya que la interacción de este con el sustrato puede ser muy diferente, llegando incluso a formarse pares iónicos que conducen a un aumento de la respuesta *ONL*.

## 1.4 Fluorescencia.

Como hemos visto anteriormente la dispersión es uno de los principales problemas para evaluar las propiedades *ONL*. De este modo, consideramos que es conveniente revisar la naturaleza de este efecto.

Del modelo de los dos estados se deduce que cuanto menor es la diferencia de energía entre el estado fundamental y el estado excitado, mayor es la respuesta *ONL*. Sin embargo, en un experimento utilizando la técnica *HRS (Hyper-Raileigh Scattering)*, el estado excitado no va a poblarse por la absorción de dos fotones de frecuencia $\omega$ de modo que la emisión instantánea de un fotón de frecuencia $2\omega$ ($E_{2\omega}$) va a ser más probable cuanto más nos aproximemos a la energía del estado excitado ($E_{CT}$). El problema es que si las energía $E_{2\omega}$ y $E_{CT}$ se igualan, entonces se produce la absorción de los dos fotones, por lo que la relajación puede ocurrir a través de fluorescencia. Este hecho afecta considerablemente a la señal *HRS* y produce una sobreestimación de la intensidad medida a $\lambda/2$ debido a la *SHG*. En la figura 1.3 se esquematiza la naturaleza de este efecto.

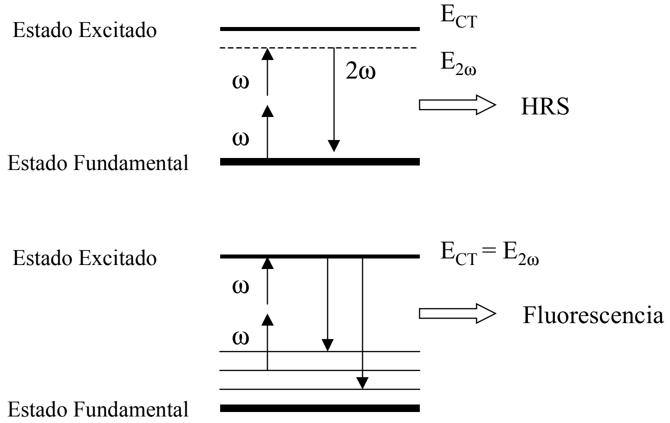


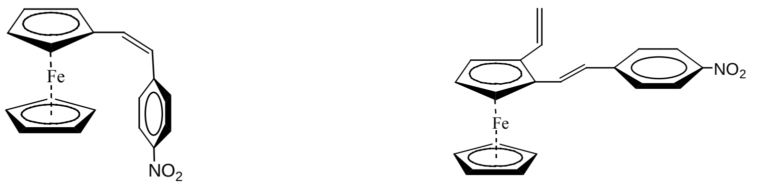
***Figura 1.3***
*Representación esquemática del origen de la señal HRS y de la fluorescencia.*

## 1.5 Antecedentes históricos.

La importancia de los compuestos organometálicos en el campo de la *ONL* se pone de manifiesto en 1987 cuando *Green* et al. observan la elevada respuesta que presenta el derivado de ferroceno *(Z)-2-(4-nitrofenil)etenilferroceno*, que se muestra en la figura 1.4a. [6] A mediados de los años ochenta son bastantes los grupos que estaban estudiando las propiedades *ONL* de derivados organometálicos, pero no es hasta la determinación de la *SHG* de este derivado de ferroceno cuando realmente se demuestra la aplicabilidad de estos compuestos. El estudio de las propiedades *ONL* del compuesto $\{(Z)\text{-}(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)(CH{=}CH)C_6H_4NO_2\}$ en estado sólido, muestra una eficacia de *SHG* 62 veces superior al de la urea. La facilidad de los procesos redox en los metalocenos, es una de las principales características que los convierten en buenos candidatos para procesos ópticos no lineales.

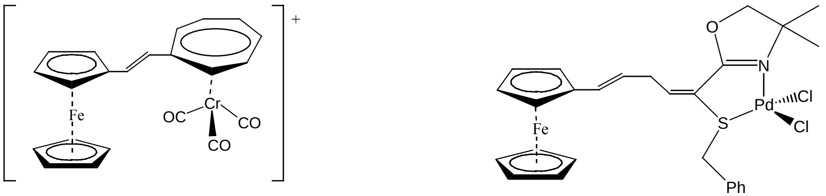
A partir de aquí fueron muchos los grupos que se interesaron por el desarrollo de nuevos cromóforos organometálicos. La mayoría de los estudios se realizaban en estado sólido, con el principal inconveniente de que el cromóforo debía cristalizar en un grupo espacial no centrosimétrico. Existen algunas estrategias para inducir a que el empaquetamiento sea no centrosimétrico, entre las cuales destacan la introducción de ligandos quirales y la introducción de fragmentos susceptibles de alinear los cromóforos, como pueden ser los enlaces de hidrógeno, o cualquier otro tipo de interacción. *Togni* y *Rihs* realizaron un estudio utilizando derivados de ferroceno en donde la quiralidad viene impuesta por el ferroceno, evitando, de este modo, el empaquetamiento centrosimétrico.[7] A pesar de todo, las respuestas ópticas no lineales resultaron ser bastante bajas debido a que el empaquetamiento producía una cancelación del momento dipolar total, debido a un disposición antiparalela de pares de moléculas. En la figura 1.4b se muestra un ejemplo de este tipo de cromóforos.

El desarrollo de las técnicas de medida de las propiedades *ONL* en disolución (*EFISH* y *HRS*) condujo al estudio de muchos otros derivados de ferroceno. Entre todos ellos los valores más elevados se han encontrado para ferrocenos unidos a sesquifulvalenos[8] y a derivados de paladio[9] como se muestra en la figura 1.4c y 1.4d.



a) $\beta =$ 62 veces urea

b) *SHG* $\approx 0$



c) $\beta = 320 \times 10^{-30}$ esu; $\beta_0 = 113 \times 10^{-30}$ esu

d) $\beta = 123 \times 10^{-30}$ esu; $\beta_0 = 19 \times 10^{-30}$ esu

***Figura 1.4***

*Diferentes tipos de ferrocenos utilizados en ONL. Estos compuestos presentan los valores más elevados de ONL de los descritos hasta la fecha.*

A pesar de que en la actualidad son muchos los ejemplos de compuestos organometálicos utilizados en *ONL*, existen pocos estudios sistemáticos. En uno de estos trabajos *Calabrese* et al. han estudiado el comportamiento de algunos metalocenos, en los que se han ido introduciendo ligeras modificaciones con la finalidad de observar cuáles son las variaciones producidas en las propiedades de *ONL*, como se observa en figura 1.5.[10]

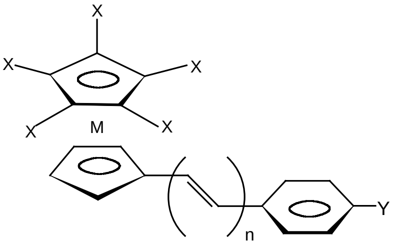


***Figura 1.5***

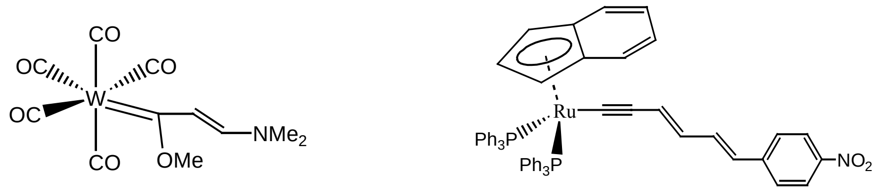
*M= Fe, Ru*
*X= $CH_3$, H*
*n= 1,2 (E y Z)*
*Y= $NO_2$, $COCH_3$, CN, CHO*

De este estudio se pueden obtener las siguientes conclusiones generales:

1) La substitución de los hidrógenos por metilos produce un aumento de las propiedades de *ONL*, debido a un aumento del poder dador del metaloceno, junto a un aumento del momento dipolar.
2) Los valores de $\beta$ en los ferrocenos son mayores que en los rutenocenos.
3) El aumento de la longitud de la cadena conjugada conlleva un aumento de la respuesta de *ONL*.
4) Los isómeros *trans (E)* tienen mayores valores de $\beta$, que los isómeros *cis (Z)*.

Además de los metalocenos, son muchos los compuestos organometálicos que se han utilizado en el campo de la óptica no lineal. Los carbonilos metálicos del grupo 6 han sido ampliamente estudiados a finales de los ochenta principalmente por *S. Marder* y *L. Cheng*.[11] Los valores obtenidos son en general relativamente bajos, excepto en el caso de los derivados con carbenos, como se muestra en la figura 1.6a.

Otro tipo de compuestos de gran interés en el campo de la *ONL* son los indenilos y acetiluros de rutenio, figura 1.6b. Estos compuestos presentan los mayores valores de $\beta$ encontrados para compuestos organometálicos.[12] El aumento de la cadena conjugada produce un aumento de la respuesta *ONL*. La introducción de fosfinas más básicas (como la trimetil fosfina) sorprendentemente no conduce a mejores resultados de *ONL*, y también se observa la influencia positiva de la introducción de carbonilos metálicos, como aceptores.[13]



a) $\beta = 34 \times 10^{-30}$ esu; $\beta_0 = 12 \times 10^{-30}$ esu

b) $\beta = 1320 \times 10^{-30}$ esu; $\beta_0 = 34 \times 10^{-30}$ esu

***Figura 1.6***

*a) Carbenos carbonílicos utilizados en ONL. b) Acetiluro de Ru. Presenta uno de los valores más altos de β encontrados hasta la fecha.*

## 1.6 Compuestos estudiados.

Los compuestos objeto de nuestro estudio han sido diseñados teniendo en cuenta las características generales de los cromóforos organometálicos que conducen a elevadas respuestas de *ONL (vide supra)*. De este modo, nuestros compuestos consisten en un dador de densidad electrónica conectado a un aceptor a través de un sistema conjugado como se muestra en la figura 1.7.

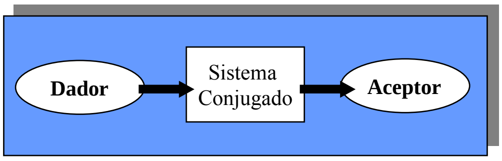


***Figura 1.7***

*Base molecular de los compuestos estudiados.*

Como dador de densidad electrónica hemos utilizado el ferroceno, debido a su estabilidad, comportamiento redox, versatilidad y los antecedentes históricos que avalan la utilización de este fragmento en el campo de la *ONL*. El sistema conjugado está formado por etilenos y fenilos alternados. Los más sencillos tienen solamente un grupo vinil-fenilo, y utilizando diferentes procedimientos de síntesis hemos obtenido sistemas que llegan a tener hasta tres grupos vinil-fenilo. Por último, los aceptores de densidad electrónica utilizados son de diferentes tipos. En principio hemos utilizado aceptores típicos orgánicos como son piridina, nitrilo y nitro. Tanto la piridina como el nitrilo nos permitieron realizar la coordinación de derivados carbonílicos del grupo 6 y fragmentos organometálicos catiónicos derivados de rutenio y hierro, figura 1.8.

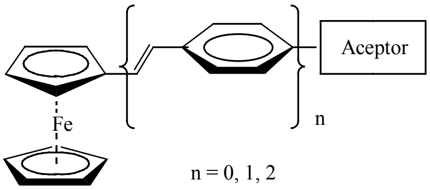


**Figura 1.8**
*Esquema general de los compuestos obtenidos.* Aceptor: $M(CO)_5$ ; M= Cr, Mo, W ;$[RuCp(PPh_3)_2]^+$ y $[FeCp(CO)_2]^+$

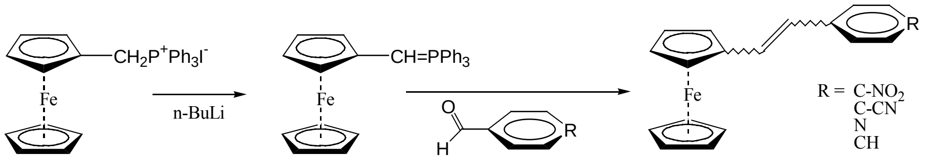
La utilización de esta metodología también nos ha conducido a la obtención de compuestos para el estudio de las propiedades ópticas no lineales de tercer orden. Estos compuestos tienen la misma base molecular que la de los compuestos descritos anteriormente, con la salvedad de que el ferroceno se encuentra sustituido en las posiciones 1,1'.

La introducción de todas estas variables nos ha permitido realizar un estudio en profundidad de los efectos que se producen en la respuesta óptica no lineal al modificar ligeramente la base molecular.

## 2. SÍNTESIS, CARACTERIZACIÓN Y PROPIEDADES *ONL* DE FERROCENOS MONOSUSTITUIDOS

### 2.1 Precursores.

El procedimiento general para la obtención de los derivados de ferroceno monosustituidos se basa en la formación de enlaces carbono-carbono conjugados mediante acoplamientos de *Wittig*. En este tipo de reacción se obtiene una olefina a partir de un grupo carbonilo y de una sal de fosfonio como se muestra en el esquema 2.1. La sencillez de esta metodología nos ha permitido obtener una gran variedad de compuestos en donde la cadena conjugada siempre es de tipo vinil-fenilo, y se modifica el aceptor conectado a uno de los extremos de ésta. Los fragmentos terminales utilizados han sido grupos aceptores de densidad electrónica como el nitro, nitrilo y piridina. En el artículo IV-5.1 se describen con detalle el procedimiento de síntesis de estos compuestos.



**Esquema 2.1**
*Procedimiento de Wittig utilizado en la síntesis de ferrocenos monosustituidos.*

El principal inconveniente de la reacción de *Wittig* reside en su baja estereoselectividad ya que se obtienen los dos isómeros geométricos *E* y *Z*. Este inconveniente se minimiza por el hecho de que la separación de ambos isómeros por columna cromatográfica es relativamente sencilla y además, también es posible la isomerización del isómero *Z* mediante la reacción con trazas de $I_2$ en reflujo de tolueno durante unos diez minutos. Es muy importante que el $I_2$ se encuentre en cantidades catalíticas para evitar la oxidación del ferroceno a ferricinio.

A lo largo de todo el trabajo desarrollado, nuestra atención se ha centrado en la obtención de isómeros *E*, ya que es ampliamente reconocido que el grado de conjugación en estos sistemas, es superior al presentado por los isómeros *Z*, lo que produce que la transferencia electrónica entre el dador y el aceptor sea más efectiva, conduciendo de este modo a la obtención de propiedades más interesantes.

La caracterización de los compuestos obtenidos se ha realizado fundamentalmente por *RMN* de $^1H$, ya que esta técnica nos sirve de diagnóstico eficaz a la hora de diferenciar entre los isómeros *E/Z*, ambos productos de la reacción de olefinación. Así, las señales correspondientes al isómero *E* aparecen a frecuencias más altas que las del isómero *Z*, y la separación entre las señales de los dos protones diferentes suele ser más grande (~0.25 *ppm*) en comparación a los 0.05 *ppm* de separación en los isomeros *Z*. Las constantes de acoplamiento de ambos isómeros son muy diferentes, ca. 16 *Hz*. en los isómeros *E* y ca. 12 *Hz*. en los isómeros *Z*, como se muestra en la figura 2.1. Otra característica que nos permite diferenciar entre los dos isómeros son las señales correspondientes a los protones del ferroceno. En general para los isómeros *Z* las señales aparecen más juntas y los protones correspondientes al anillo $C_5H_5$ aparecen a frecuencias más bajas.

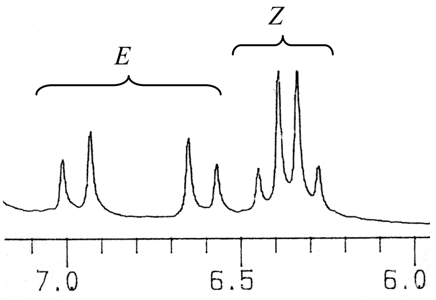


***Figura 2.1***

*Ampliación de la región correspondiente a los etilenos del espectro RMN de $^1H$ en el que se muestra la mezcla de isómeros E y Z del compuesto{( $\eta^5$-$C_5H_5$) Fe($\eta^5$-$C_5H_4$) (CH=CH)$C_6H_4N$}.*

El estudio de las propiedades redox de estos compuestos revela la existencia de una única onda de oxidación-reducción, asignada a la oxidación ferroceno/ferricinio. El proceso es reversible al igual que en el ferroceno, y aparece a unos valores de potencial formal similares, como se muestra en la figura 2.2. El hecho más significativo es que la introducción de fragmentos aceptores conduce a un desplazamiento hacía potenciales mayores (desplazamiento anódico) respecto al ferroceno, indicando que es más difícil conseguir la oxidación. Esto se debe a la existencia de una polarización de la carga hacia el aceptor, generándose una deficiencia de densidad electrónica en torno al átomo de hierro, lo que se traduce en una mayor dificultad para producir su oxidación. En el caso del fenilo se produce el efecto contrario. La onda se desplaza a potenciales más negativos (desplazamiento catódico), indicando que se produce una estabilización de la carga positiva a lo largo de la cadena conjugada.

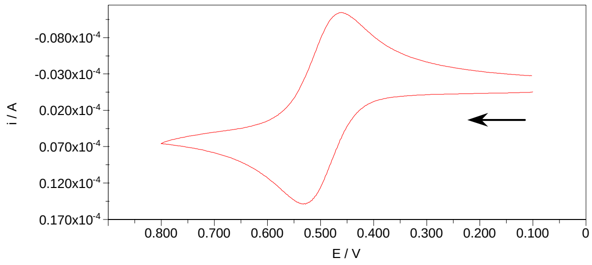


***Figura 2.2***

*Voltagrama del compuesto* $\{(E)\text{-}(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)(CH{=}CH)C_6H_4CN\}$ *realizado a 100mV/s.* $E_{1/2} = 480\ mV$.

Las propiedades electroquímicas nos permiten examinar las energías del *LUMO*. La introducción de un grupo aceptor de densidad electrónica nos conduce a un aumento del potencial de semionda comparándolo con el del ferroceno (445 *mV*). De este modo en la tabla 2.1 observamos que los compuestos con los aceptores *Py*, *-CN* y $-NO_2$ muestran potenciales mayores al del ferroceno, mientras que el compuesto vinil-fenilo muestra un potencial menor. Los potenciales de semionda nos proporcionan una indicación del grado de transferencia de densidad electrónica entre el dador y el aceptor, ya que a medida que el ferroceno ceda una mayor densidad electrónica, será más difícil oxidarlo.

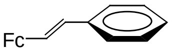
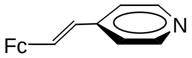
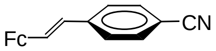
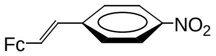
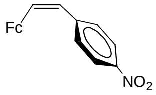
En la tabla 2.1 se muestran los valores más significativos de las propiedades ópticas y electroquímicas para una serie de compuestos ferrocenil-vinil-fenil con diferentes aceptores. La primera conclusión que se obtiene al analizar estos resultados, es que pequeños cambios en el cromóforo conducen a valores de $\beta$ muy diferentes.

Los espectros de *UV/Vis* muestran que la absorción de estos compuestos en la región en la que se produce la generación del segundo armónico (532 *nm*) es baja, por lo que es de esperar que no se produzca una sobreestimación de los parámetros de *ONL* debido a resonancia en la zona de generación del segundo armónico por fluorescencia, como se ha indicado en el apartado 1.4 de la introducción.

Los espectros de *UV/Vis* de los derivados neutros de ferroceno, muestran una banda muy intensa entre 310 – 390 *nm*, asociada a una transición $\pi - \pi^*$, tal y como se produce en otros compuestos derivados de ferroceno monosustituido descritos en la bibliografía.[14] La presencia de una banda mucho más débil en torno a 450 – 500 *nm* esta asociada a una transferencia de carga ML (metal-ligando), y es la que denominamos en la tabla 2.1 como $\lambda_{\text{máx.}}$ Esta banda es la que se utiliza en el cálculo de la hiperpolarizabilidad estática $\beta_o$. Si esta banda se encuentra en una zona cercana a la generación del segundo armónico (532 *nm*), entonces podemos encontrarnos con problemas de absorción y resultados erróneos en los valores de $\beta$.

***Tabla 2.1***

*Valores experimentales de $\beta$, $\beta_0$ y $E_{1/2}$. [a]En cloroformo. [b]En diclorometano. [c]Medido utilizando la técnica EFISH. [d]Medido utilizando SHG. Respecto a la urea.*

| Compuesto | $\lambda_{\text{max}}(nm)^a$ | $E_{1/2}(mV)^b$ | $\beta$ $10^{30}$ esu | $\beta_0$ $10^{30}$ esu |
|---|---|---|---|---|
|  | 330 | 440 | 72 | 15 |
|  | 468 | 500 | 21 | 4 |
|  | 473 | 480 | 203 | 34 |
|  | 511 | 500 | $31^c$ | --- |
|  | | | $62^d$ | --- |

El compuesto con el grupo nitrilo es el que presenta mayor respuesta óptica no lineal. Hay que destacar que las propiedades de *ONL* en estado sólido, de este compuesto, están descritas en la literatura utilizando la técnica *Kurtz Powder*. Este compuesto presenta un valor de actividad de generación del segundo armónico de 0.87 veces superior al de la urea.[15] Las razones que conducen a estos valores bajos en la respuesta *ONL* en estado sólido hay que analizarlas en base a la ordenación espacial de las moléculas en estado sólido. Nosotros conseguimos resolver la estructura cristalina de este compuesto, observando que la cristalización se produce en un grupo espacial no centrosimétrico. Esta es la condición necesaria que debe cumplirse para que un compuesto presente actividad *ONL*, sin embargo, aún así se produce la cancelación de los momentos dipolares debido a la presencia de un eje binario helicoidal, figura 2.3, lo que conlleva a que la generación del segundo armónico sea baja. En disolución esta cancelación no se produce, debido a que los cromóforos no se alinean del mismo modo que en estado sólido, y el valor de $\beta$ es de 203 x $10^{-30}$ *esu*.

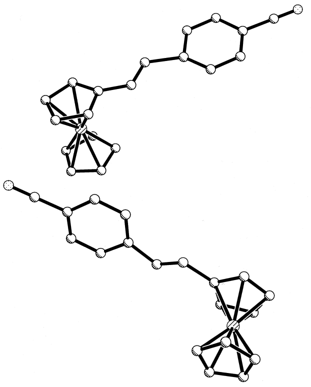


***Figura 2.3***

*Empaquetamiento del compuesto* $\{(E)\text{-}(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)(CH{=}CH)C_6H_4CN\}$*, en donde se produce la cancelación del momento dipolar, debido a la presencia de un eje binario helicoidal.*

Como hemos visto anteriormente en el apartado 1.5 del capítulo I, el compuesto *(Z)-2-(4-nitrofenil) etenilferroceno* es de gran importancia histórica porque fue el primer compuesto organometálico empleado en el campo de la *ONL* con resultados satisfactorios.[6] Este compuesto presenta una generación del segundo armónico (*SHG*) 62 veces superior al de la *urea*, mientras que el isómero *E* es completamente inactivo. En principio, la explicación que se dio a este hecho es que el compuesto *E*, cristaliza en un grupo espacial centrosimétrico, lo que se produce una cancelación de los momentos dipolares que tienen como consecuencia que el compuesto no presente propiedades ópticas no lineales. En nuestro grupo de investigación conseguimos la cristalización del compuesto *(E)-2-(4-nitrofenil)etenilferroceno*, corroborando la hipótesis de *M. Green* et al. De hecho, el isómero *E* cristaliza en el grupo centrosimétrico $P2_1/c$, y forma dímeros que adoptan una disposición cabeza-cola, produciéndose la cancelación de los dipolos moleculares entre cada dos moléculas, como se muestra en la figura 2.4.

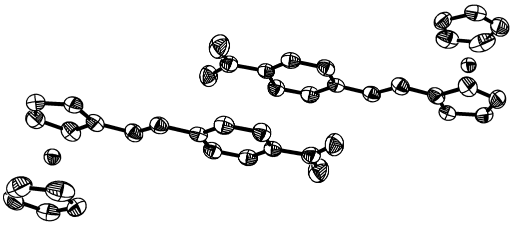


***Figura 2.4***

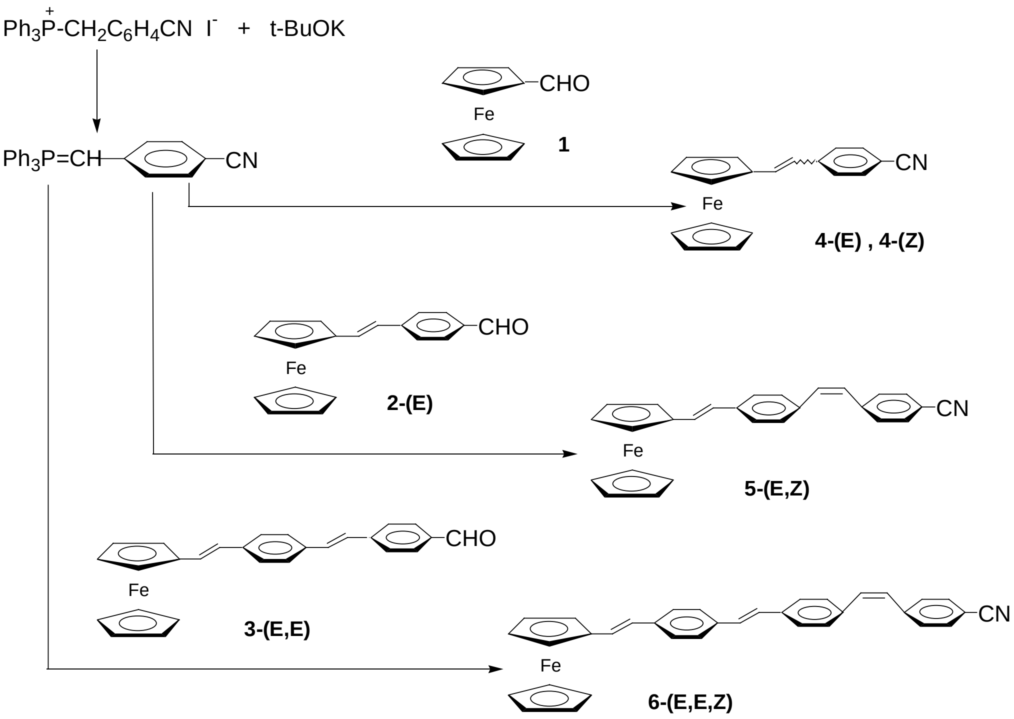
*Diagrama de empaquetamiento del compuesto (E)-2-(4-nitrofenil)etenil ferroceno, en donde se muestra la cancelación de los momentos dipolares moleculares entre cada dos moléculas.*

Un análisis más detallado de la descripción de la síntesis, caracterización y propiedades ópticas no lineales se encuentra descrito en los trabajos IV-5.1 y IV-5.5, recogidos al final del presente capítulo.

## 2.2 Aumento de la cadena conjugada.

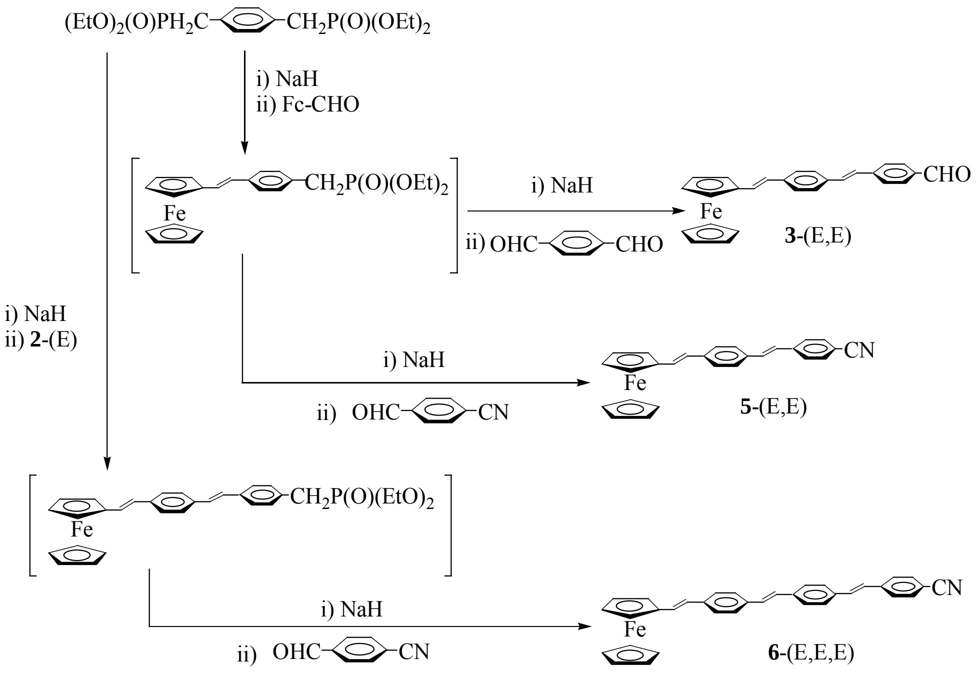
Con objeto de estudiar la influencia de la longitud de la cadena conjugada, entre el dador y el aceptor, en las propiedades opto-electrónicas, se sintetizaron compuestos análogos a los descritos en el apartado anterior con una mayor longitud en la cadena conjugada. Existen precedentes de estudios similares en derivados orgánicos en donde se pone de manifiesto la importancia del nexo de unión, y la influencia que tiene en la respuesta óptica no lineal. [16]

La síntesis de derivados de ferroceno con aumento de la cadena conjugada se abordó en primer lugar utilizando la metodología de *Wittig* como se resume en el esquema 2.2. El principal inconveniente con el que nos encontramos es que este procedimiento nos ha permitido obtener únicamente los isómeros *Z*.



***Esquema 2.2***
*Obtención de derivados hiperconjugados basados en la metodología de Wittig.*

Con la finalidad de obtener los isómeros *E* cambiamos la metodología de síntesis, utilizando el procedimiento de *Horner-Emmons-Wadsword* (*HEW*). Esta reacción es análoga a la de *Wittig*, con la única diferencia en que los sustratos de partida son diferentes ya que se utiliza un fosfonato en lugar de una sal de fosfonio. Este tipo de reacciones es estereospecífica en el isomero *E*, como se muestra en el esquema 2.3.



***Esquema 2.3***
*Obtención de derivados hiperconjugados basados en la metodología de HEW.*

El aumento de la longitud de la cadena conjugada aumenta la complejidad en la caracterización de los compuestos. Aunque la espectroscopia *RMN* de $^{1}H$ continúa siendo la técnica más habitual, en algunos casos la interpretación de los espectros ha resultado ser más complicada debido a la superposición de señales correspondientes a los diferentes etilenos. En la figura 2.5 se muestra el espectro de *RMN* de $^{1}H$ de un sistema con dos grupos vinil-fenilo, concretamente el correspondiente al compuesto $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)(CH{=}CH)(C_6H_4)(CH{=}CH)(C_6H_4)NO_2$ (E,Z).

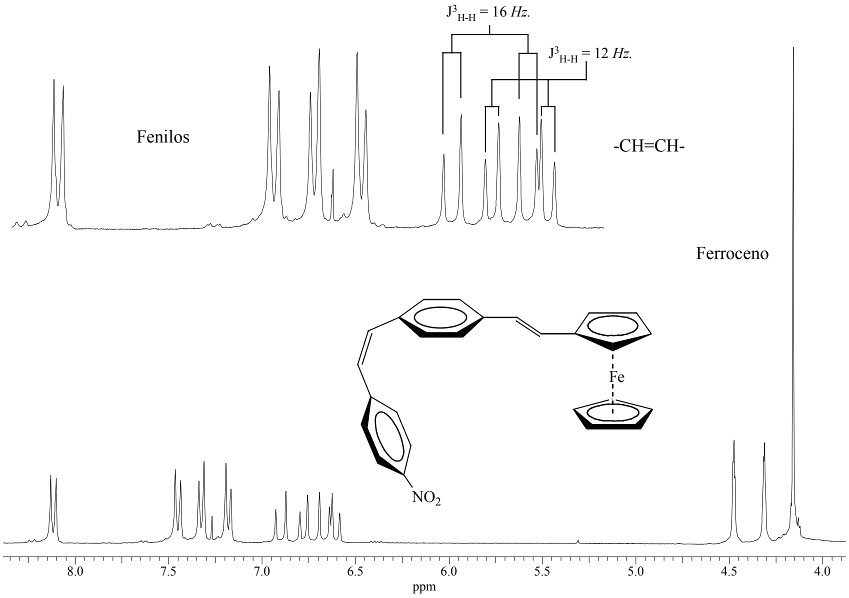


***Figura 2.5***

*Espectro RMN de $^1H$ del compuesto ($\eta^5$-$C_5H_5$)Fe($\eta^5$-$C_5H_4$)(CH=CH)($C_6H_4$) (CH=CH)($C_6H_4$)$NO_2$ (E,Z), con asignación de las señales y constantes de acoplamiento.*

Otra técnica que ha mostrado ser de gran utilidad para la caracterización de estos compuestos es la espectrometría de masas por ionización con electrospray (*ESMS*). Una de las ventajas de esta técnica es que permite analizar directamente los crudos de reacción. Además la distribución isotópica permite un alto grado de confianza a la hora de identificar un determinado compuesto. En la figura 2.6 se muestra el espectro experimental obtenido de un crudo de reacción y el simulado. Puede observarse como la concordancia entre ambos es muy buena.

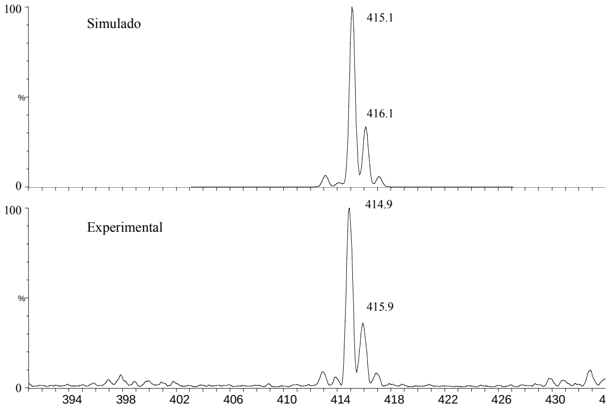


***Figura 2.6***

*Espectro de ESI-MS del compuesto Fc−=−Ph−=−Ph-CN (E,E).*

Las propiedades electroquímicas se han analizado mediante voltametría cíclica. Esta técnica muestra la presencia de un único proceso redox. Este proceso es reversible y esta asociado a la oxidación del $Fe^{2+}$ a $Fe^{3+}$, al igual que en el ferroceno. En la tabla 2.2 se resumen los valores del potencial de semionda para los compuestos en los que hemos ido aumentando la cadena conjugada. Esta técnica es importante porque nos proporciona una indicación de la naturaleza y las energías relativas del *HOMO* y *LUMO*. En nuestro caso hemos observado que al aumentar la longitud de la cadena conjugada se produce una disminución del potencial de semionda. Esta disminución del potencial es debida a la estabilización de la carga positiva a través de la cadena conjugada. En general, se observa que esta estabilización de la carga positiva es más efectiva en los derivados de ferroceno en donde todos los etilenos son *E*. En los casos en los que alguno de los dobles enlaces presenta configuración *Z*, la estabilización de la carga es menor, debido a la menor conjugación que ofrece el sistema, reflejándose este hecho en las propiedades redox por un aumento del potencial formal respecto al de los isómeros *E*. En la figura 2.7 se muestran los isómeros *E,E* y *E,Z* del compuestos *Fc−=−Ph−=−Py*. Lo más destacable de estas estructuras es que en el caso del isómero *E,E* la coplanaridad es mucho mayor que en el caso del isómero *E,Z*.

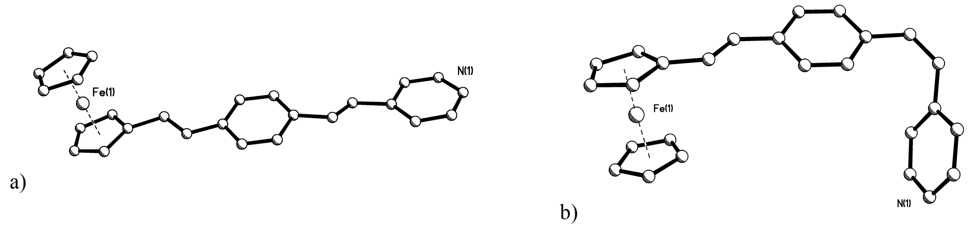


***Figura 2.7***
*Isómeros a) E,E y b) E,Z del compuesto Fc−=−Ph−=−Py. Se observa que la presencia de un etileno Z conduce a una disposición espacial no coplanar.*

Como hemos comentado en el aptartado 2.1 de este capítulo, los espectros de absorción electrónica de los derivados de ferroceno monosustituidos muestran, en general, tres bandas características. La más energética corresponde a una transición $\pi$-$\pi^*$, que además es la más intensa. Alrededor de los 500 *nm* aparece la banda correspondiente a una transferencia de carga metal-ligando (*TCML*). Por último, sólo en algunas ocasiones, es posible discernir una tercera banda de muy poca intensidad correspondiente a una transición *d-d*. Esta asignación está en concordancia con los estudios teóricos realizados por Barlow et al.[17] y con otros resultados experimentales,[18] aunque existe una cierta controversia a la hora de justificarla. En nuestros compuestos hemos observado que la banda $\pi$-$\pi^*$ es la que está fuertemente influenciada por la naturaleza del grupo aceptor y de la cadena conjugada. En el caso concreto de los derivados del grupo nitro, se observa que se produce un desplazamiento batocrómico a medida que aumentamos la cadena conjugada con estereoquímica *E*, indicando que se produce una disminución de la energía del orbital $\pi^*$. En el caso de la banda de *TCML* hemos observado una tendencia similar, aunque de menor magnitud que en el caso de la banda $\pi$-$\pi^*$, y con el inconveniente de que muchas veces se produce un solapamiento de las diferentes bandas dificultando la asignación. En el caso de las piridinas y nitrilos derivados de ferroceno se observa una tendencia análoga a la anterior.[19]

***Tabla 2.2***
*Resumen de las propiedades electroquímicas y valores de $\beta$.*

| *Compuesto* | | $\lambda$ *max (nm)* | $E_{1/2}$ *(mV)* | $\beta$ $10^{-30}$ *esu* |
|---|---|---|---|---|
| $Fc(-{=}-Ph)_2\text{-}CHO$ | *(E,E)* | --- | 450 | 125 |
| $Fc(-{=}-Ph\text{-})_2\text{-}CN$ | *(E,Z)* | --- | 445 | 110 |
| $Fc(-{=}-Ph\text{-})_2\text{-}CN$ | *(E,E)* | 370 | 440 | --- |
| $Fc(-{=}-Ph\text{-})_3\text{-}CN$ | *(E,E,Z)* | 380 | 420 | --- |
| $Fc(-{=}-Ph\text{-})_2\text{-}NO_2$ | *(E,Z)* | --- | 450 | 120 |
| $Fc(-{=}-Ph\text{-})_2\text{-}NO_2$ | *(E,E)* | 495 | 445 | 405 |
| $Fc(-{=}-Ph\text{-})_3\text{-}NO_2$ | *(E,E,Z)* | --- | 430 | 210 |
| $Fc-{=}-Ph-{=}-Py$ | *(E,Z)* | 445 | 435 | --- |
| $Fc-{=}-Ph-{=}-Py$ | *(E,E)* | 460 | 440 | 145 |
| $Fc(-{=}-Ph\text{-})_2-{=}-Py$ | *(E,E,Z)* | --- | 445 | --- |

El estudio de las propiedades *ONL* muestra que al incrementar la longitud de la cadena conjugada aumentan de forma considerable los valores de $\beta$. Este hecho es mucho más pronunciado en los isómeros con estereoquímica *E*. Comparando los diferentes grupos aceptores utilizados se observa que los valores de $\beta$ descienden de forma que $NO_2 > CN > Py > CHO$, tal y como era de esperar según la disminución del carácter aceptor de estos grupos. Por otro lado, aunque no hemos observado en ningún caso el límite de saturación descrito para sistemas en los que la longitud de la cadena conjugada es muy grande, sí que observamos que al ir aumentando la longitud de la cadena conjugada el $\Delta\beta$ es cada vez menor.

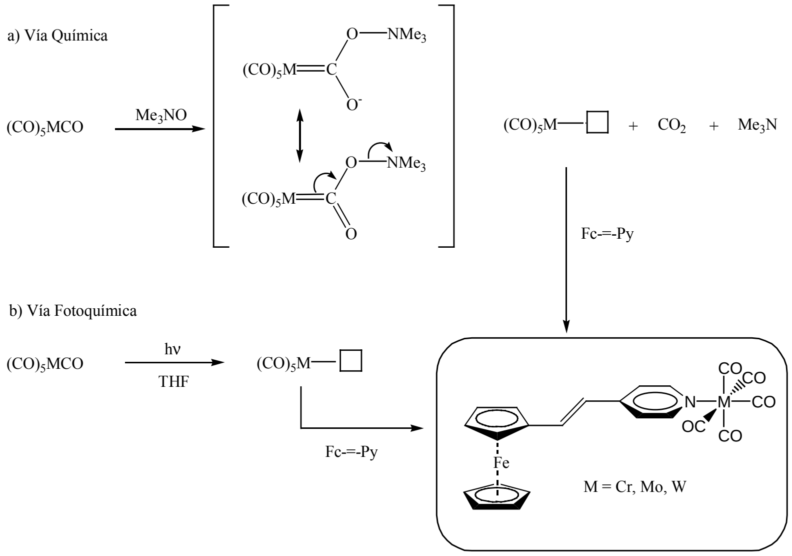
En los artículos IV-5.2, IV-5.4 y IV-5.5 se encuentran descritos los procedimientos de síntesis, la caracterización y una discusión más detallada de las propiedades ópticas y electrónicas.

## 2.3 Modificaciones en el fragmento aceptor.

Todos los compuestos derivados de ferroceno que hemos estudiado hasta el momento poseen grupos orgánicos aceptores de densidad electrónica. Los derivados con nitrilo y piridina se diseñaron con la finalidad de ser coordinados a centros metálicos. De este modo introducimos una nueva variable en el estudio de las propiedades ópticas no lineales de cromóforos derivados de ferroceno. A continuación se describe la obtención de los nuevos cromóforos cuya principal característica es la presencia de un grupo aceptor de densidad electrónica organometálico.

Como grupos aceptores de densidad electrónica hemos elegido los carbonilos metálicos del grupo 6. El carácter aceptor $\pi$ del grupo carbonilo les confiere la propiedad de actuar como buenos aceptores de densidad electrónica. Además, los compuestos heterobimetálicos resultantes son fáciles de caracterizar por espectroscopia infraroja y *RMN* de $^{13}C$.

Las dos vías generales para la coordinación de un fragmento $M(CO)_5$ son la vía química y la fotoquímica. En ambos procedimientos se genera primero la vacante de coordinación y luego se introduce el ligando dador de electrones. Nosotros empezamos utilizando la vía química para la generación de las vacantes de coordinación, pero después cambiamos a la vía fotoquímica por ser reacciones más limpias. En el esquema 2.4 se representan estos dos procedimientos de síntesis.



***Esquema 2.4***

*Mecanismos de reacción de coordinación de carbonilos metálicos a los derivados de ferroceno.*

En las reacciones de coordinación de carbonilos metálicos hemos observado que, de entre todos los disolventes utilizados, el mejor es el *THF*, debido a que se trata de un disolvente oxigeno dador capaz de estabilizar la vacante de coordinación generada. Los tiempos de reacción empleados en la generación de la vacante de coordinación del hexacarbonilo metálico suelen ser cortos (ca. 30 *min.*). La generación de la vacante de coordinación produce un cambio de la coloración de la disolución de incoloro a amarillo, mientras que si el tiempo de reacción es muy largo esta coloración pasa a ser verde-amarillento, indicando que se esta produciendo la descomposición del producto. Los compuestos heterobimetálicos obtenidos deben purificarse utilizando alúmina neutra o ligeramente básica, ya que la utilización de gel de silice produce la descoordinación del fragmento carbonílio. La estabilidad de estos productos en disolución depende mucho del disolvente empleado. En disolventes como acetonitrilo, por ejemplo, la descoordinación es muy rápida, mientras que en disolventes como el diclorometano son estables durante muchos días. En estado sólido los productos son estables durante largos periodos de tiempo.

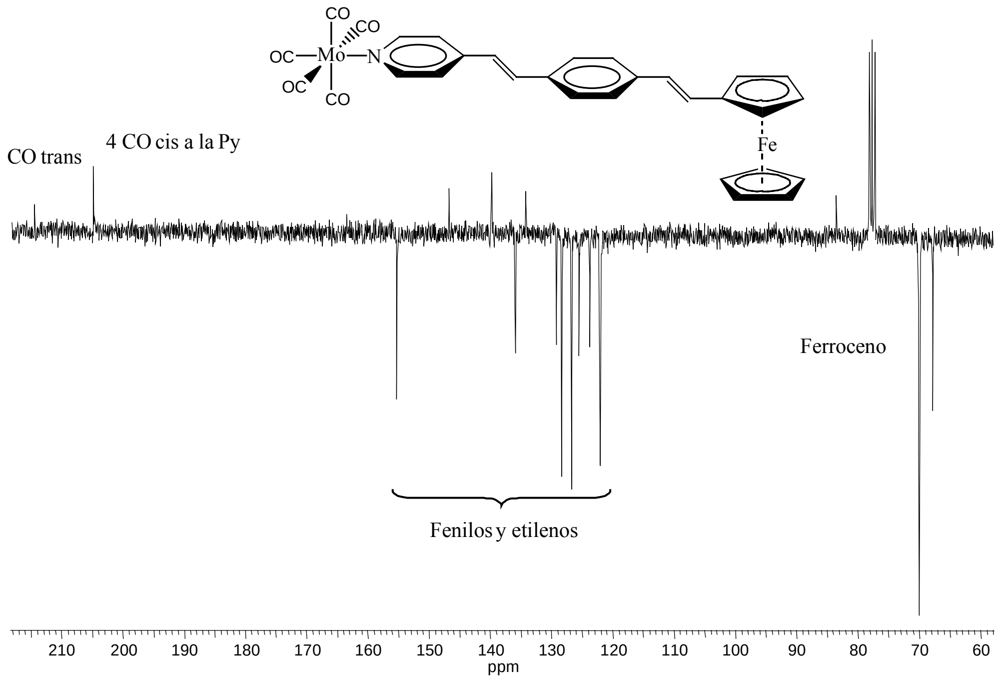


***Figura 2.8***

*Espectro de RMN de $^{13}C$-APT del compuesto Fc−=−Ph−=−Py-$Mo(CO)_5$ (E,E) en donde se observa la presencia de las bandas características de los carbonilos metálicos monosustituidos.*

Como hemos mencionado anteriormente, el *RMN* de $^{13}C$ y la espectroscopia *IR* son las técnicas más útiles, si bien, en el *RMN* de $^{1}H$ también se observa un desplazamiento sistemático a frecuencias más altas de los protones en $\beta$ respecto al metal del carbonilo metálico. En la figura 2.8 se muestra el espectro de $^{13}C$-*APT*, del que hay que destacar las señales en torno a 200 *ppm* correspondientes a los carbonilos axial y ecuatoriales. La espectroscopia *IR* muestra las bandas características (2 $A_1 + B_2 + E$) de los compuestos carbonilicos con simetría pseudo-$C_{4v}$. En general se observa que los derivados de wolframio poseen bandas de $\nu(CO)$ que aparecen a frecuencias más bajas, indicando que éste posee una mayor capacidad que el *Cr* o el *Mo* para reducir su densidad electrónica por retrodonación al *CO*.

Las propiedades electroquímicas de los derivados carbonílicos se caracterizan por la existencia de dos procesos redox, uno de ellos asociado al ferroceno (ca. 0.5 *V*) y el otro al fragmento $M(CO)_5$ (ca. 1.0 *V*). En todos los casos estudiados se observa que la onda asociada al *Cr* es reversible, mientras que las ondas del *Mo* y *W* son irreversibles, como se observa en la figura 2.9.

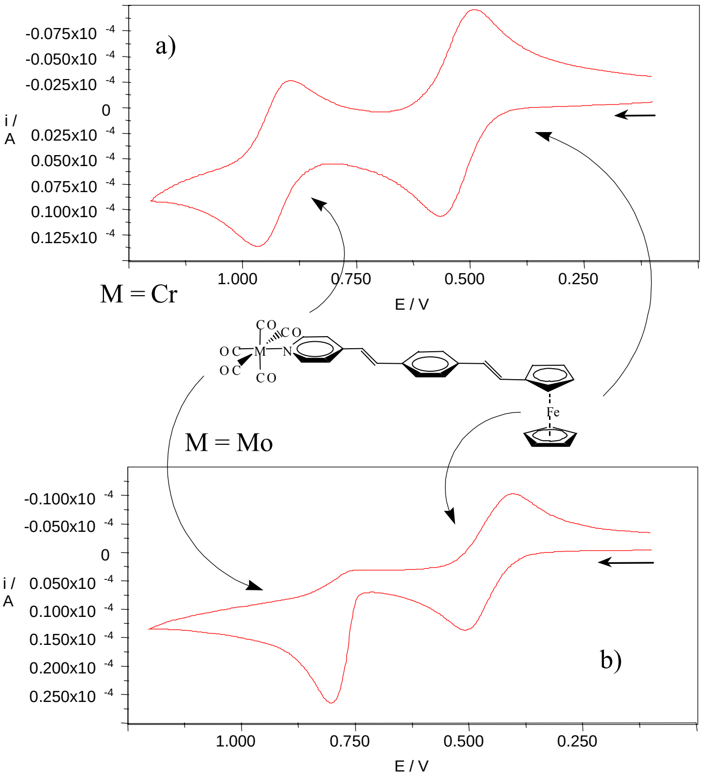


***Figura 2.9***

*Voltagramas de los compuestos a)* $\{(E)\text{-}(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)(CH{=}CH)PyCr(CO)_5\}$ *y b)* $\{(E,E)\text{-}(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)(CH{=}CH)(C_6H_4)(CH{=}CH)PyMo(CO)_5\}$

La tabla 2.3 resume los valores de los potenciales de semionda junto con las propiedades electrónicas y ópticas más relevantes. La onda asociada al ferroceno muestra un desplazamiento anódico para los derivados carbonilicos con un solo vinil-fenilo, tanto en los derivados de *-Py* como del *-CN*. Este desplazamiento a potenciales mayores se debe a que la introducción del fragmento carbonilico produce una transferencia electrónica en la dirección $Fc \rightarrow M(CO)_5$, que tiene como consecuencia que el sistema sea más difícil de oxidar que el compuesto homometálico. Sin embargo, para los derivados con cadenas conjugadas mayores, se observa que son más fáciles de oxidar que el ferroceno. Este hecho se debe al efecto combinado de la introducción del fragmento $M(CO)_5$ (aumenta el $E_{1/2}$), con el de la estabilización de la carga positiva a lo largo del sistema conjugado (disminuye el $E_{1/2}$); estos efectos son contrarios y, de acuerdo con los resultados experimentales observados, el efecto que predomina es la estabilización. En todos los casos se observa que los isómeros *E* conducen a variaciones mayores de los potenciales de semionda, indicando que la conjugación del sistema es mucho más efectiva para estos isómeros.

***Tabla 2.3***
*Propiedades ópticas y electroquímicas de los derivados carbonilicos.*

| Compuesto | | λ máx (nm) | $E_{1/2}$(mV) Fc | $E_{1/2}$(mV) $M(CO)_5$ | β $10^{-30}$ (esu) |
|---|---|---|---|---|---|
| $Fc{-}{=}{-}Py\text{-}Cr(CO)_5$ | (E) | 401 | 520 | 930 | 63 |
| $Fc{-}{=}{-}Py\text{-}Mo(CO)_5$ | (E) | 487 | 520 | 1110 | 95 |
| $Fc{-}{=}{-}Py\text{-}W(CO)_5$ | (E) | 491 | 530 | 1125 | 101 |
| $Fc{-}{=}{-}Ph\text{-}CN\text{-}Cr(CO)_5$ | (E) | 481 | 500 | 980 | 271 |
| $Fc{-}{=}{-}Ph\text{-}CN\text{-}W(CO)_5$ | (E) | 487 | 495 | 1150 | 375 |
| $Fc{-}{=}{-}Ph{-}{=}{-}Py\text{-}Cr(CO)_5$ | (E,E) | 462 | 440 | 906 | 369 |
| $Fc{-}{=}{-}Ph{-}{=}{-}Py\text{-}Mo(CO)_5$ | (E,E) | 476 | 450 | 1120 | 448 |
| $Fc{-}{=}{-}Ph{-}{=}{-}Py\text{-}W(CO)_5$ | (E,E) | 487 | 440 | 1125 | 535 |
| $Fc{-}{=}{-}Ph{-}{=}{-}Ph\text{-}CN\text{-}Cr(CO)_5$ | (E,Z) | 345 | 450 | 965 | --- |
| $Fc{-}{=}{-}Ph{-}{=}{-}Ph\text{-}CN\text{-}W(CO)_5$ | (E,Z) | 344 | 450 | 1160 | --- |
| $Fc{-}{=}{-}Ph{-}{=}{-}Ph\text{-}CN\text{-}Cr(CO)_5$ | (E,E) | 380 | 435 | 965 | --- |
| $Fc{-}{=}{-}Ph{-}{=}{-}Ph\text{-}CN\text{-}W(CO)_5$ | (E,E) | 394 | 435 | 965 | --- |

Todos los compuestos estudiados poseen valores de $\beta$ entre moderados-altos y altos para compuestos organometálicos y son de los más elevados observados entre los metalocenos descritos hasta la fecha. La introducción de los fragmentos carbonílicos a los derivados de *-Py* o *-CN* produce un aumento significativo de los valores de $\beta$. Este aumento es mucho mayor en el caso de los derivados de *-Py* en donde el valor de $\beta$ prácticamente se triplica. Las propiedades de *ONL* muestran que los derivados de *W* poseen valores de $\beta$ mayores que los de *Mo*, y estos a su vez mayores que los de *Cr*. Este hecho probablemente se debe al descenso de las electronegatividades de *Pauling* en el mismo sentido (*W* > *Mo* > *Cr*) y a una mayor capacidad de retrodonación de la densidad electrónica del *W* comparado con el *Mo* y el *Cr*, tal y como se observa en la disminución de la frecuencia de resonancia de las bandas de los carbonilos en *IR*.

Con el fin de estudiar la influencia de otros tipos de aceptores, hemos obtenido derivados de ferroceno en donde el grupo aceptor es un fragmento catiónico de naturaleza orgánica u organometálica. Uno de los procedimientos más sencillos para obtener este nuevo tipo de compuestos consiste en metilar las piridinas con yoduro de metilo. La utilización de yoduro de metilo también produce la isomerización de los etilenos *Z*, así pues, todos los derivados que se obtuvieron tienen estereoquímica *E* en todos los puentes etileno, como se muestra en la figura 2.10 para el compuesto con tres grupos vinil-fenilo. En este compuesto la distancia *Fe-N* a través del espacio es de 21.03 *Å* y a través de los enlaces de 27.13 *Å*. Se observa una clara pérdida de la coplanaridad entre los ciclopentadienos del ferroceno y los fenilos, seguramente debida a factores de empaquetamiento. Un comportamiento similar cabe esperar en disolución a juzgar por los espectros electrónicos y los resultados electroquímicos. En el artículo IV-5.3 se describe la metilación del resto de derivados de piridina y se discuten en detalle las estructuras cristalinas de los mismos.

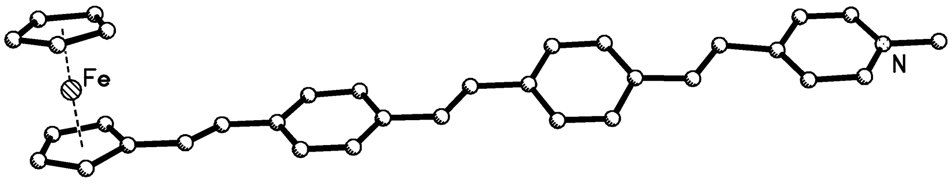
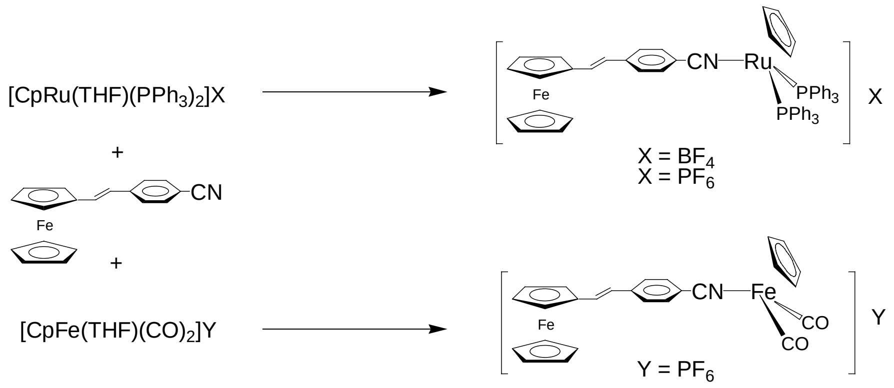


***Figura 2.10***

*Estructura cristalográfica del compuesto* $\{(E,E,E)\text{-}(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)(CH{=}CH)C_6H_4(CH{=}CH)C_6H_4(CH{=}CH)Py\text{-}CH_3\}^+ I^-$ *en donde se observa la isomerización del etileno más alejado del ferroceno debido a la utilización del* $CH_3I$ *para producir la metilación.*

La obtención de compuestos bimetálicos catiónicos se realizó por coordinación de fragmentos organometálicos catiónicos de *Ru(II)* y *Fe(II)* al derivado de nitrilo *(E)-Fc-(CH=CH)-Ph-CN,* como se muestra en el esquema 2.5.



**Esquema 2.5**
*Síntesis de derivados de ferroceno con aceptores catiónicos organometálicos.*

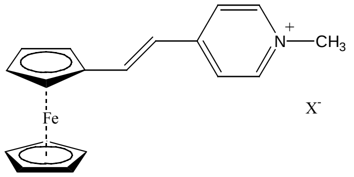
Las propiedades ópticas y electrónicas de estos derivados se resumen en la tabla 2.4. Los estudios de *ONL* de los derivados metilados de piridina muestran que los valores de $\beta$ son muy elevados y siguen la tendencia esperada al aumentar la longitud del sistema conjugado. En general no es muy aconsejable la utilización de $I^-$ como contraión en aquellos sistemas que se quieran utilizar en *ONL*, ya que se ha observado que la utilización de $I^-$ conduce a valores anormalmente altos en los valores de $\beta$.[20] En nuestro caso los valores de $\beta$ son elevados pero se encuentran en un intervalo lógico para los compuestos que hemos estudiado, así que no creemos que se produzca ningún incremento adicional por la presencia del $I^-$, como se muestra en la tabla 2.4. La introducción de grupos aceptores catiónicos conduce a mayores valores de $\beta$ que los derivados sin metilar. Los valores de $\beta$ obtenidos son similares a los obtenidos utilizando los carbonilos del grupo 6. En principio podríamos pensar que los grupos capaces de atraer más densidad electrónica, conducen a mayores respuestas de *ONL*, sin embargo, son muchos los factores que hay que considerar, y se ha observado experimentalmente que no necesariamente los mejores aceptores conducen a mayores respuestas *ONL*.[21]

**Tabla 2.4**
*Propiedades ópticas y electroquímicas de los derivadosde ferroceno con aceptores catiónicos. [a] Medidos en Acetona.*

| *Compuestos* | | $\lambda$ *máx (nm)* | $E_{1/2}$ *(mV)* | $\beta\ 10^{-30}$ *(esu)* |
|---|---|---|---|---|
| $[Fc{-}{=}{-}Py\text{-}CH_3]^+\ I^-$ | *(E)* | 553 | 595 | 40[a] |
| $[Fc{-}{=}{-}Ph{-}{=}{-}Py\text{-}CH_3]^+\ I^-$ | *(E,E)* | 503 | 385 | 197[a] |
| $[Fc{-}{=}{-}Ph{-}{=}{-}Ph{-}{=}{-}Py\text{-}CH_3]^+\ I^-$ | *(E,E,E)* | 462 | 355 | 458[a] |
| $[Fc{-}{=}{-}Ph\text{-}CN\text{-}Fe(\eta^5\text{-}C_5H_5)(CO)_2]^+\ PF_6^-$ | *(E)* | 474 | 515 | 171 |
| $[Fc{-}{=}{-}Ph\text{-}CN\text{-}Ru(\eta^5\text{-}C_5H_5)(PPh_3)_2]^+\ PF_6^-$ | *(E)* | 485 | 485 | 186 |
| $[Fc{-}{=}{-}Ph\text{-}CN\text{-}Ru(\eta^5\text{-}C_5H_5)(PPh_3)_2]^+\ BF_4^-$ | *(E)* | 484 | 495 | 325 |

La coordinación de fragmentos aceptores organometálicos produce una aumento considerable en los valores de $\beta$, comparables en magnitud a los obtenidos con los carbonilos metálicos. Estos compuestos muestran muy baja absorción en la zona del espectro *UV/Vis* en donde se produce la generación del segundo armónico, por lo que no hay problemas de aumento de las propiedades de *ONL* por resonancia. Desde el punto de vista electroquímico se observa un desplazamiento anódico de la onda asociada al ferroceno, indicando que se produce una transferencia de densidad electrónica del ferroceno al fragmento aceptor organometálico.

Un efecto muy importante a tener en cuenta en estos compuestos reside en la influencia del contraión. En la tabla 2.4 se observa como el intercambio de $PF_6^-$ por $BF_4^-$ duplica el valor de $\beta$. Marder et al. han estudiado la influencia del contraión en sales del tipo $\{(E)\text{-}(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)(CH{=}CH)Py\text{-}CH_3\}^+ X^-$ como se muestra en la figura 2.11, junto con un resumen de los resultados de *ONL*.[22] En este trabajo se observa que la generación del segundo armónico del derivado de $BF_4^-$ es mil veces superior a las del derivado con $PF_6^-$. Los autores atribuyen este hecho a factores de empaquetamiento, ya que las medidas se han realizado en estado sólido.



| $X^-$ | *SHG*[a] |
|---|---|
| I | 220 |
| Br | 165 |
| Cl | 0 |
| $BF_4$ | 50 |
| $NO_3$ | 120 |
| $B(C_6H_5)_4$ | 13 |
| $PF_6$ | 0.05 |
| $CF_3SO_3$ | 0 |
| $p\text{-}CH_3C_6H_4SO_3$ | 13 |

[a] Intensidad medida utilizando radiación fundamental a 1907 nm. GSH medido respecto a la urea.

***Figura 2.11***

*Valores de generación del segundo armónico (SHG) relativos a la urea en sales del tipo* $\{(E)\text{-}(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)(CH{=}CH)Py\text{-}CH_3\}^+ X^-$.

En nuestro caso, las medidas se han realizado en disolución por lo que deben descartarse los factores de empaquetamiento. Nosotros, atribuimos este valor de $\beta$ anormalmente alto a la menor simetría del anión $BF_4^-$ en comparación con el de $PF_6^-$, lo que puede contribuir a aumentar el valor de $\beta$. Para contrastar estas conclusiones se intentó medir los valores de $\beta$ de las sales sódicas de los aniónes $BF_4^-$ y $PF_6^-$, pero no se obtuvieron resultados satisfactorios debido a la baja solubilidad de estas sales en cloroformo. Otra explicación de este fenómeno, podría ser la formación de pares iónicos en disolución, aunque mediante la espectroscopia *UV/Vis* no se observa ninguna variación en $\lambda_{máx}$. Este hecho es consistente con la ausencia de pares iónicos o con la formación de algunos pares iónicos que no modifican la estructura electrónica del cromóforo. De modo análogo, *Humphrey* et al. han observado un comportamiento similar para series de arildizaovinilidenos.[23] Estos resultados experimentales inducen a pensar que los efectos ópticos no lineales del anión y del catión son independientes.

Una descripción más detallada del efecto del contraión en las propiedades de *ONL* se describe en el artículo IV-5.6, que se encuentra al final de este capítulo.

### 2.4 Conclusiones.

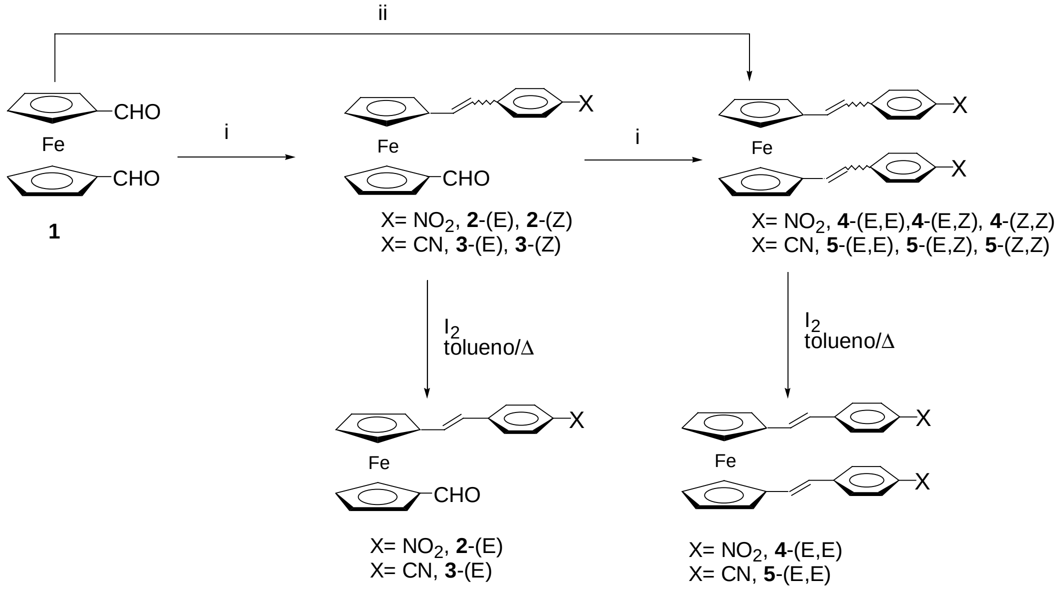
Los estudios electroquímicos y espectroscópicos constituyen, en general, un buen diagnóstico del comportamiento *ONL* que cabría esperar en series de compuestos. En este sentido, hemos observado que en series en las que se mantiene el mismo aceptor y el mismo dador de densidad electrónica, el aumento de la cadena conjugada produce un desplazamiento batocrómico de la banda $\pi$-$\pi^*$, una reducción del potencial de semionda y un aumento de la respuesta óptica no lineal de segundo orden. Estos resultados confirman que los derivados de ferroceno siguen el mismo comportamiento cualitativo que los cromóforos orgánicos. Sin embargo, nuestros intentos para realizar predicciones cuantitativas o correlaciones entre propiedades físicas y valores de *ONL* no han sido tan satisfactorios como en el caso de los compuestos orgánicos, probablemente debido a un aumento en el número de estados excitados implicados que contribuyen a la hiperpolarizabilidad, limitando el campo de aplicación del modelo de los dos estados.

## 3. FERROCENOS 1,1'-BISUSTITUIDOS Y PROPIEDADES DE *ONL* DE TERCER ORDEN

El procedimiento general para abordar el estudio de los derivados de ferroceno 1,1'-bisustituidos consiste en funcionalizar el ferroceno en ambos anillos. Con esta finalidad partimos de ferroceno-1,1'-biscarboxaldehído, porque es un compuesto fácilmente accesible, muy utilizado como precursor en muchas síntesis de ferrocenos, y que nos permite utilizar la misma metodología que hemos empleado para los ferrocenos monosustituidos.[24] La nomenclatura utilizada en este apartado es la misma que se ha utilizado en el trabajo IV-5.7.

### 3.1 Síntesis y caracterización.

El procedimiento de síntesis se basa, al igual que en el caso de los derivados monosustituidos, en la metodología de *Wittig*. Mediante la utilización de ferroceno-1,1'-biscarboxaldehído y las diferentes sales de fosfonio funcionalizadas con los grupos nitro y nitrilo, se obtienen los compuestos descritos en el esquema 3.1.



***Esquema 3.1***

*Procedimiento de síntesis de ferrocenos bisustituidos.(i) 1.5 equivalentes de la sal de fosfonio correspondiente y 1.5 equiv. de KOtBu (ii) 3 equivalentes de la sal de fosfonio y correspondiente y 3 equiv. de KOtBu.*

La utilización de cantidades estequiométricas o excesos de sal de fosfonio, nos ha permitido la obtención de derivados en donde se ha producido uno o dos acoplamientos *C-C*. La separación de los diferentes isómeros se ha realizado mediante columna de gradientes en gel de sílice, utilizando mezclas de hexano, diclorometano y acetona. En los experimentos realizados hemos observado que los productos mayoritarios siempre son los isómeros *E*. Del mismo modo que en el caso de los ferrocenos monosustituidos, también es posible la isomerización de los derivados *Z* mediante la utilización de trazas de $I_2$ y calentando a reflujo en tolueno.

La técnica de caracterización básica para este tipo de compuestos ha sido la espectroscopia de *RMN* de $^1H$. La principal diferencia de los espectros *RMN* de $^1H$ respecto a los ferrocenos monosustituidos, se produce en la región de los protones correspondientes al ferroceno (4.0 – 5.0 *ppm*). En el caso de los compuestos 1,1'-bisustituidos se observan las dos señales de intensidad 1:1 cuando los sustituyentes son iguales y 4 señales 1:1:1:1 cuando los sustituyentes son diferentes, como se muestra en la figura 3.1 en la región en torno a 4.5 *ppm*, para el compuestos **2**-(*E*).

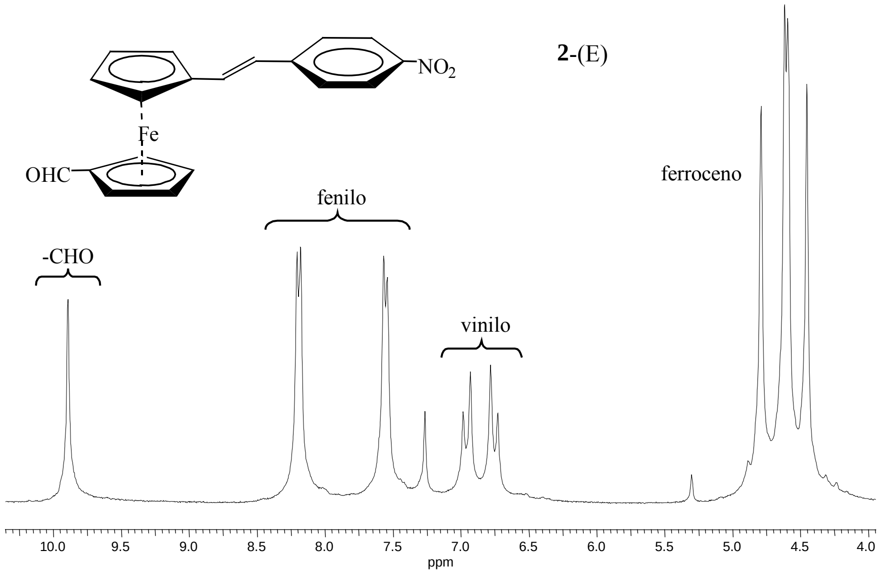
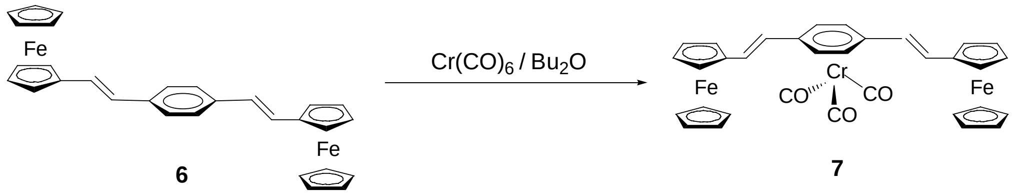


***Figura 3.1***
*Espectro RMN de $^1H$ en $CDCl_3$ del compuesto (E)-OHC-Fc-=-Ph-$NO_2$,* ***2****-(E).*

Además de los ferrocenos 1,1'-bisustituidos, también han sido objeto de estudio en este capítulo los compuestos de formula general *p-(E,E)-[Fc-CH=CH-]$_2$-Ph*, como se muestra en el esquema 3.2. Estos compuestos se estudian en este capítulo por sus propiedades *ONL* de tercer orden. La obtención del compuesto **7** se realizó mediante la coordinación del fragmento -*Cr(CO)$_3$* que se obtiene en dibutil eter a partir del hexacarbonilo de cromo y el compuesto **6**. La síntesis del compuesto **7** se encuentra descrita en la bibliografía mediante la utilización de otro procedimiento de síntesis.[25]



***Esquema 3.2***
*Síntesis del compuesto* ***7*** *por coordinación del fragmento* $-Cr(CO)_3$.

## 3.2 Propiedades electroquímicas y electrónicas.

Las propiedades electroquímicas obtenidas mediante voltametría cíclica muestran una onda reversible característica del proceso ferroceno/ferricinio. En la tabla 3.1 se resumen las propiedades electroquímicas y las bandas *UV/Vis*. En todos los casos se observa que el valor del potencial de semionda es mayor que el del ferroceno, indicando que se produce una transferencia de carga desde el ferroceno hacia el aceptor ($-NO_2$ o $-CN$). Si comparamos estos valores con los de los ferrocenos monosustituidos se observa que se produce un desplazamiento importante hacia potenciales más anódicos (ca. 100 *mV*), debido al efecto conjunto de ambos sustituyentes. Al igual que en el caso de los ferrocenos monosustituidos se observa que los derivados con el grupo nitro presentan un mayor potencial de semionda que los derivados de nitrilo, indicando su mayor poder aceptor. Es importante resaltar que cuanto mayor es el número de etilenos *E* (e. g. *E,E* > *E,Z* > *Z,Z*) el potencial de semionda es menor [$E_{1/2}$ para **4**-(*E,E*) < **4**-(*E,Z*) < **4**-(*Z,Z*) y **5**-(*E,E*) < **5**-(*E,Z*) < **5**-(*Z,Z*)]. Estas observaciones están en concordancia con la mayor estabilización de la carga positiva a través del sistema conjugado cuando la conjugación es más efectiva.

Los compuestos **6** y **7** muestran una única onda de oxidación-reducción, asociada a un proceso bielectrónico correspondiente a ambos ferrocenos al mismo tiempo. ($[Fc\text{-}Fc] \rightarrow [Fc\text{-}Fc]^{2+}$). Estos compuestos no muestran ningún tipo de interacción efectiva metal-metal. Sin embargo, el potencial de semionda de este proceso bielectrónico es muy sensible a cambios en el puente que une a los dos centros activos. En concreto en el compuesto **7** se produce un desplazamiento anódico del potencial de semionda de los ferrocenos de ca. 100 *mV* por la coordinación del fragmento $-Cr(CO)_3$.[25] De hecho, cabría esperar que la naturaleza aceptora de este fragmento condujera a un aumento del potencial de semionda de los ferrocenos en lugar de una disminución. Esta disminución del potencial de semionda, también ha sido descrito por *Müller* et al. para éste y otros compuestos similares, atribuyendo este efecto al carácter anfótero del fragmento tricarbonilo de cromo.[26]

***Tabla 3.1***

*Bandas UV/Vis medidas en varios disolventes, y valores del potencial de semionda obtenidos utilizando voltametría cíclica. Ferroceno $E_{1/2}$ = 445(105) mV.*

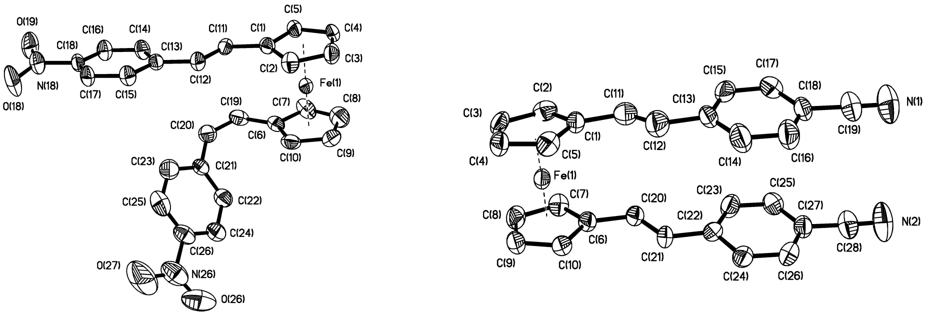
| | $\lambda_{máx}$ (nm) | | | | | | $E_{1/2}(\Delta E_p)$/mV |
|---|---|---|---|---|---|---|---|
| | $CHCl_3$ | | MeOH | | THF | | |
| Comp. | MLCT | π-π* | MLCT | π-π* | MLCT | π-π* | |
| 2-(E) | --- | 309 | --- | 356 | --- | 358 | 755(75) |
| 2-(Z) | --- | 308 | --- | 325 | --- | 329 | 790(170) |
| 3-(E) | --- | 327 | --- | 329 | --- | 329 | 775(125) |
| 4-(E,E) | 494 | 358 | 497 | 358 | 495 | 355 | 545(90) |
| 4-(E,Z) | 493 | 350 | 487 | 353 | 488 | 352 | 555(75) |
| 4-(Z,Z) | 481 | 335 | --- | 337 | 481 | 343 | 585(155) |
| 5-(E,E) | --- | 342 | --- | 340 | 492 | 340 | 500(100) |
| 5-(E,Z) | 473 | 334 | 473 | 333 | 469 | 335 | 545(115) |
| 5-(Z,Z) | --- | 318 | --- | 312 | --- | 319 | 565(80) |
| 6 | | | | | | | 455 |
| 7 | | | | | | | 351 |

Las bandas *UV/Vis* de los derivados de ferroceno 1,1'-bisustituidos muestran la presencia de dos bandas intensas entre 300 y 500 *nm*, al igual que ocurre en los derivados monosustituidos. La banda más energética (300 – 360 *nm*) corresponde a una transición *π-π** del ligando y la menos energética a una transición de *TCML* (400 – 500 *nm*). En torno a 500 *nm* es posible observar en algunos casos una transición *d-d* como un hombro de la banda de *TCML*. La banda de *TCML* esta influenciada por el sustituyente lateral, produciéndose un desplazamiento hipsocrómico al aumentar el número de etilenos *E* del compuesto. La banda *π-π** muestra una dependencia similar respecto a los sustituyentes. Esto es debido a que los isómeros *E* conllevan una mayor conjugación del sistema que los *Z*, produciéndose una estabilización energética del orbital *π**. Se observa un desplazamiento solvatocrómico moderado en los disolventes empleados, de lo que se deduce que la variación del momento dipolar entre el estado fundamental y el estado excitado no es muy elevada.[27]

### 3.3 Resultados cristalográficos.

La estructura de estos sistemas ha sido determinada por difracción de rayos-X sobre monocristal, y nos a proporcionado información relevante respecto a la influencia y comportamiento del sistema *π*-conjugado, estereoquímica, influencias del aceptor y los empaquetamientos que se producen.

La mayoría de los cristales se ha obtenido por evaporación lenta de mezclas de diclorometano/hexano. Las distancias *Fe-C* caen dentro del intervalo esperado para los ferrocenos, siendo esta distancia ligeramente mayor para el caso *Fe-C*(sustituido). Los ángulos correspondientes a los puentes etileno son más grandes de lo que cabría esperar, (ca. 130º) pero lo mismo ocurre en un gran número de compuestos similares.[28] La coplanaridad del sistema conjugado con los anillos *Cp* del ferroceno es una característica que hemos observado en todos los derivados de ferroceno obtenidos con esteroquímica *E*, como se observa en la figura 3.2, para los compuestos **4**-(*E,Z*) y **5**-(*E,E*).

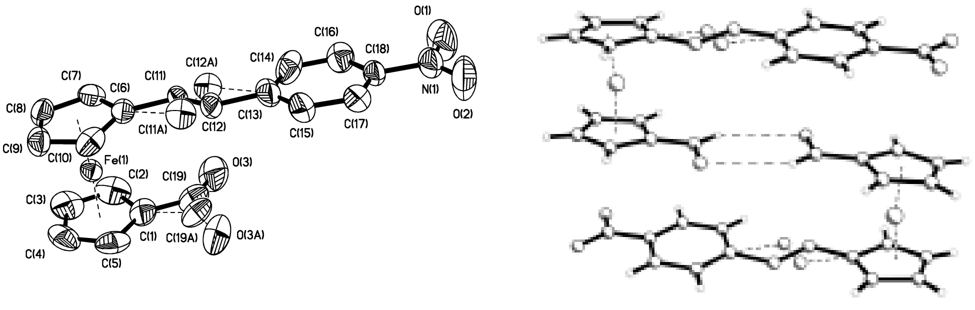


(a) **4**-(*E,Z*) (b) **5**-(*E,E*)

***Figura 3.2***
*En la figura se muestra la diferencia de coplanaridad entre los isómeros Z y los E.*

En la figura 3.2b se observa la coplanaridad del sistema conjugado, así como un apilamiento π a aprox. 3.8 *Å*. Podríamos pensar que este tipo de interacción es el que conduce a la obtención del rotámero *syn*, de máxima repulsión estérica. ($\delta \sim 0$, como se indica en el apartado 3.2 del capítulo I. No obstante, hemos observado que incluso en aquellos casos en los que no existe ningún tipo de interacción, también cristalizan los rotámeros *syn*, como es el caso del compuesto **4**-(*E,Z*), figura 3.2a. La diferencia de energía entre las formas *syn* y *anti* no es muy elevada, y podemos encontrar derivados 1,1'-bisustituidos análogos que poseen una configuración *anti*. Por ejemplo, el compuesto análogo al **5**-(*E,E*) pero con -*Py* en lugar de -*Ph-CN,* cristaliza en la forma *anti*. La cocristalización de este compuesto con diferentes alcoholes conduce a la formación de macroestructuras en donde la configuración del ferroceno es *syn*.[29] Este hecho pone de manifiesto como interacciones débiles cómo son los puentes de hidrógeno, conducen a la formación de estructuras *syn* o *anti*, debido a que la diferencia de energía entre ambos confórmeros no es muy elevada.

El compuesto **2**-(*E*), representado en la figura 3.3a, cristaliza en el grupo espacial $P2_1/n$. Se observa desorden en las posiciones del etileno puente y del aldehído, al igual que ocurre en muchos otros compuestos similares. La cristalización conlleva a la formación de dímeros unidos a través de enlaces de hidrógeno del grupo aldehído. Este tipo de enlace de hidrógeno $C\text{-}H\cdots O$ es bastante habitual en compuestos organometálicos, sobretodo cuando el carbono $C\text{-}H$ es $sp^2$.[30] La distancia de enlace O-H es de aprox. 2.7 Å, como se muestra en la figura 3.3b.



(a) (b)

***Figura 3.3***
*Diagrama ORTEP y enlace de hidrógeno del compuesto* $\{\mathbf{2}\text{-(E)-OHC-(}\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_4)(CH{=}CH)\ C_6H_4NO_2\}$.

## 3.4 Propiedades Ópticas no lineales.

El diseño de los compuestos descritos anteriormente se ha realizado con el propósito de estudiar las propiedades *ONL* de tercer orden, no obstante, también se han evaluado las propiedades de segundo orden mediante la técnica *Kurtz Powder*.

### *ONL* de 2º Orden: *Kurtz Powder*.

Observaciones preliminares, utilizando radiaciones de diferentes longitudes de onda y diferentes pulsos, muestran que todos los compuestos son transparentes a la longitud de onda fundamental (1064 *nm*) y para la generación del segundo armónico (532 *nm*), por lo que fue necesario la utilización de otro láser de distinta longitud de onda. Los resultados obtenidos se midieron utilizando una radicación fundamental de 1300 *nm* y son los que se muestran en la tabla 3.2.

***Table 3.2***

*Resultados de los estudios de ONL.* [a] *Medidas realizadas en THF.* [b] *Técnica Kurtz powder a 1.3 $\mu m$.* [c] *Z-scan a 800 nm, referencia: silice $n_2 = 3 \times 10^{-16}$ $cm^2$ $W^{-1}$.* [d] *No observado.* [e] *Insoluble.*

| *Compuesto* | $\lambda_{máx}$ *(nm)* [$\varepsilon$ ($10^4$ $M^{-1}$ $cm^{-1}$)] | *SHG*[b] *(urea = 1)* | $\gamma_r$[c] *($10^{-36}$ esu)* | $\gamma_i$[c] *($10^{-36}$ esu)* | $\lvert\gamma\rvert$ *($10^{-36}$ esu)* |
|---|---|---|---|---|---|
| **4**-*(E,E)* | 495 [0.47] | 0.28 | e | e | e |
| **4**-*(E,Z)* | 488 [0.56] | d | 840 ± 400 | 770 ± 200 | 1140 ± 430 |
| **4**-*(Z,Z)* | 481 [0.30] | d | 600 ± 300 | 0 ± 50 | 600 ± 300 |
| **5**-*(E,E)* | 492 [0.34] | 0.24 | 280 ± 150 | 30 ± 20 | 280 ± 150 |
| **5**-*(E,Z)* | 469 [0.33] | d | 310 ± 200 | 50 ± 30 | 310 ± 200 |
| **6** | 457 [0.45] | d | 640 ± 300 | 30 ± 20 | 640 ± 300 |
| **7** | 455 [0.31] | 0.14 | 850 ± 300 | 95 ± 30 | 860 ± 300 |

Los compuestos **4**-(*E,Z*), **4**-(*Z,Z*) y **5**-(*E,Z*) no presentan *SHG*, pero se observa una emisión *relativamente* fuerte con una componente azul significante, lo cual es una indicación de que algún proceso óptico no lineal esta ocurriendo. Los compuestos **4**-(*E,E*) y **5**-(*E,E*) muestran *SHG*, aunque el valor sea bastante pequeño. El compuesto **5**-(*E,E*) cristaliza en un grupo espacial no centrosimétrico, pero si observamos el empaquetamiento, los cromóforos se alinean de tal modo que producen una cancelación del momento dipolar total, figura 3.4. Esta es la causa de que el valor de *SHG* de estos compuestos sea tan pequeño.

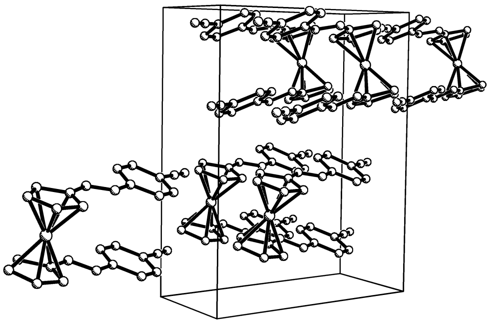


***Figura 3.4***

*Empaquetamiento del compuesto* **5**-*(E,E) en donde se observa la cancelación de los momentos dipolares.*

El compuesto **6** no muestra ninguna *SHG,* en cambio, para el compuesto **7** (que tiene el fragmento -$Cr(CO)_3$ enlazado por vía $\pi$ al fenilo) presenta un valor bajo pero distinto de cero a pesar de cristalizar en grupo espacial centrosimétrico. Este no es el único ejemplo de compuesto centrosimétrico que presenta *SHG*, si bien el resultado es bastante sorprendente. Este fenómeno, también se ha observado en compuestos del *tipo* $[Ru(C{=}CPhN{=}N\text{-}4\text{-}C_6H_4OMe)(PPh_3)_2(\eta^5\text{-}C_5H_5)]BF_4$.[31] La *SHG* se debe a efectos no centrosimétricos producidos en la superfice del cristal, pequeñas contribuciones de fases no centrosimétricas y a ligeras desviaciones del empaquetamiento centrosimétrico.

### *ONL* de 3º Orden: *Z-scan*.

Las propiedades *ONL* de tercer orden han sido evaluadas utilizando la técnica *Z-scan*[32] a 800 *nm* y los valores de $|\gamma|$ son del mismo orden de magnitud que los encontrados para otros derivados conjugados de ferroceno utilizando la técnica *DFWM* (*Degenerate Four-Wave Mixing*).[33] Las hiperpolarizabilidades cúbicas son mayores para los derivados de ferroceno que contienen el grupo nitro que para los correspondientes nitrilos, tal y como se observaba en los valores de $\beta$. Los errores experimentales no permiten comentar el efecto producido por los distintos esteroisómeros.

El compuesto **6** presenta un valor de $\gamma_r$ y $|\gamma|$ elevado. Las propiedades *ONL* de tercer orden de este compuesto también han sido evaluadas utilizando la técnica *DFWM* (504 ± 32 x $10^{-36}$ *esu*)[33] llegando a un resultado análogo. La única diferencia reside en que en nuestro caso la estereoquímica del compuesto es *E,E*, mientras que en el descrito en la literatura no se especifica la estereoquímica. La incorporación el fragmento -$Cr(CO)_3$ conduce a un aumento de $\gamma_r$ y $|\gamma|$. Estudios recientes han demostrado que este fragmento puede actuar como aceptor o dador de densidad electrónica en determinados arenos conjugados.[26] En nuestro caso, los estudios electroquímicos ponen de manifiesto que este fragmento actúe como dador de densidad electrónica, ya que es más fácil de oxidar que el compuesto **6**. Esta composición dador-dador-dador aumenta la facilidad de polarización de la densidad electrónica de la molécula contribuyendo a un aumento de la respuesta óptica no lineal.

## 4. REFERENCIAS

(1) *Nonlinear Optical Properties of Organic and Polymeric Materials*; Williams, D. J., Ed.; ACS Symp. Ser.: **1983**.

(2) *Materials for Nonlinear Optics: Chemical Prespectives*; Marder, S. R.; Sohn, J. E.; Stucky, G. D., Eds.; ACS Symp. Ser:, **1991**.

(3) Chen, C.; Liu, G. *Rev. Mater. Sci.* **1986**, *16*, 203.

(4) Oudar, J. L.; Chemla, D. S. *J. Chem. Phys.* **1977**, *66*, 2664.

(5) Moylan, C. R.; Twieg, R. J.; Lee, V. Y.; Swanson, S. A.; Betterton, K. M.; Miller, R. D. *J. Am. Chem. Soc* **1993**, *115*, 12599.

(6) Green, M. L. H.; Marder, S. R.; Thompson, M. E.; Bandy, J. A.; Bloor, D.; Kolinsky, P. V.; Jones, R. J. *Lett. Nature* **1987**, *26*, 360.

(7) Togni, A.; Rihs, G. *Organomet.* **1993**, *12*, 3368.

(8) Behrens, U.; Brussaard, H.; Hagenau, U.; Heck, J.; Hendrickx, E.; Körnich, J.; vanderLinden, J. G. M.; Persoons, A.; Spek, A. L.; Veldman, N.; Voss, B.; Wong, H. *Chem. Eur. J.* **1996**, *1*, 98.

(9) Loucifsaibi, R.; Delaire, J. A.; Bonazzola, L.; Doisneau, G.; Balavoine, G.; Fillebeenkhan, T.; Ledoux, I.; Puccetti, G. *Chem. Phys.* **1992**, *167*, 369.

(10) Calabrese, J. C.; Cheng, L. T.; Green, J. C.; Marder, S. R.; Tam, W. *J. Am. Chem. Soc* **1991**, *113*, 7227.

(11) Cheng, L. T.; Tam, W.; Meredith, G. R.; Marder, S. R. *Mol. Cryst. Liq. Cryst.* **1990**, *189*, 137.

(12) Houbrechts, S.; Clays, K.; Persoons, A.; Cadierno, V.; Gamasa, M. P.; Gimeno, J. *Organomet.* **1996**, *15*, 5266.

(13) Whittall, I. R.; Humphrey, M. G.; Houbrechts, S.; Persoons, A. *Organomet.* **1996**, *15*, 5741.

(14) Hsung, R. P.; Chidsey, C. E. D.; Sita, L. R. *Organomet.* **1995**, *14*, 4808.

(15) Bunting, H. E.; Green, M. L. H.; Marder, S. R.; Thompson, M. E.; Bloor, D.; Kolinsky, P. V.; Jones, R. J. *Polyhedron* **1992**, *11*, 1489.

(16) Dos Santos, D. A.; Kogej, T.; Bredas, J. L.; Boutton, C.; Hendrickx, E.; Houbrechts, S.; Clays, K.; Persoons, A.; Xhang, J. X.; Dubois, P.; Jerome, R. *J. Mol. Struc.* **2000**, *521*, 221.

(17) Barlow, S.; Bunting, H. E.; Ringham, C.; Green, J. C.; Bublitz, G. U.; Boxer, S. G.; Perry, J. W.; Marder, S. R. *J. Am. Chem. Soc* **1999**, *121*, 3715.

(18) Balavoine, G. G. A.; Daran, J. C.; Iftime, G.; Lacroix, P. G.; Manoury, E.; Delaire, J. A.; Maltey-Fanton, I.; Nakatani, K.; Di Bella, S. *Organomet.* **1999**, *18*, 21.

(19) Wong, H.; Meyer-Friedrichsen, T.; Farrell, T.; Mecker, C.; Heck, J. *Eur. J. Inorg. Chem.* **2000**, 631.

(20) Zhang, J. X.; Dubois, P.; Jerome, R. *J. Chem. Soc. Perkin Trans. 2* **1997**, 1209.

(21) Marder, S. R.; Gorman, C. B.; Tiemann, B. G.; Cheng, L. T. *J. Am. Chem. Soc.* **1993**, *115*, 3006.

(22) Marder, S. R.; Perry, J. W.; Tiemann, B. G.; Schaefer, W. P. *Organomet.* **1991**, *10*, 1896.

(23) Cifuentes, M. P.; Driver, J.; Humphrey, M. G.; Asselberghs, I.; Persoons, A.; Samoc, M.; Luther-Davies, B. *J. Organomet. Chem.* **2000**, *607*, 72.

(24) D. Woollins, J. *Inorganic Experiments*; VCH: Weinheim, **1994**.

(25) Müller, T. J. J. *J. Organomet. Chem.* **1999**, *578*, 95.

(26) Müller, T. J. J.; Netz, A.; Ansorge, M.; Schmalzlin, E.; Brauchle, C.; Meerholz, K. *Organomet.* **1999**, *18*, 5066.

(27) Heck, J.; Dabek, S.; Meyer-Friedrichsen, T.; Wong, H. *Coord. Chem. Rev.* **1999**, *192*, 1217.

(28) Togni, A.; Hayashi, T. *Ferrocenes*; VCH Verlagsgesellschaft mbH: Weinheim, Germany, **1995**.

(29) Lee, I. S.; Chung, Y. K.; Mun, J.; Yoon, C. S. *Organomet.* **1999**, *18*, 5080.

(30) Braga, D.; Grepioni, F.; Desiraju, G. R. *Chem. Rev.* **1998**, *98*, 1375.

(31) Whittall, I. R.; Cifuentes, M. P.; Costigan, M. J.; Humphrey, M. G.; Goh, S. C.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1994**, *471*, 193.

(32) Sheikbahae, M.; Said, A. A.; Wei, T. H.; Hagan, D. J.; Vanstryland, E. W. *Ieee Journal of Quantum Electronics* **1990**, *26*, 760.

(33) Ghosal, S.; Samoc, M.; Prasad, P. N.; Tufariello, J. J. *J. Phys. Chem.* **1990**, *94*, 2847.

Journal of Organometallic Chemistry 562 (1998) 197–202

# Synthesis and characterization of new ferrocenyl heterobimetallic compounds with high NLO responses

Jose Mata [a], Santiago Uriel [a], Eduardo Peris [a,*], Rosa Llusar [b], Stephan Houbrechts [c], André Persoons [c]

[a] *Departamento de Química Inorgánica y Orgánica, Universitat Jaume I, E-12080 Castellón, Spain*
[b] *Dpto. de Ciencies Experimentals, Universitat Jaume I, E-12080 Castellón, Spain*
[c] *Centre for Research on Molecular Electronics and Photonics, Laboratory of Chemical and Biological Dynamics, University of Leuven, Celestijnenlaan 200D, B-3001 Leuven, Belgium*

Received 19 January 1998; received in revised form 11 March 1998

**Abstract**

Several ferrocenyl based heterobimetallic compounds have been obtained and characterized, and their NLO responses have been measured. We find that the observed $\beta$ values are among the highest of the organometallic based materials reported up to date. © 1998 Elsevier Science S.A. All rights reserved.

*Keywords:* Ferrocenes; NLO; Heterobimetalic; Metal-carbonyl; Electrochemistry

## 1. Introduction

In the last ten years, the incorporation of metals to NLO systems have given a new dimension to the study and design of new chromophores [1]. Although a large number of organometallic complexes have been studied, just a few examples can be found in which clear design criteria are applied for the optimization of the nonlinear responses [2]. It has been stated that the use of organometallic compounds in NLO has a wide fan of advantages [1] that make them appropiate in the field of non linear optics. One of these advantages is that the electronic properties of the metal fragment can be tuned, so that the NLO response can be modulated. The use of heterobimetallic organometallic complexes in which the electron-accepting and donating properties of two organometallic fragments are combined in order to obtain high first hyperpolarizabilities is rare, and only recently some examples have been reported [3]. The introduction of two metal centres in the NLO chromophore can allow us to tune both, electron-donor and electron-acceptor fragments by modifying their electronic properties.

In the search of new combinations of organometallic fragments we have chosen a typical donor fragment (ferrocene), and a series of electron accepting moieties derived from $M(CO)_6$ ($M = Cr$ or Mo). The ferrocenyl ligands were prepared according to conventional organic synthesis, and we have developed a synthetic route to ligands with long conjugated chains. We have studied the electrochemical properties of our compounds and relate them to their NLO responses. These bimetallic compounds exhibit static hyperpolarizabilities up to $164 \times 10^{-30}$ esu, the largest measured to date for ferrocenyl derivatives.

## 2. Experimental section

### 2.1. General details

All reactions were carried out under a nitrogen atmo-

---

* Corresponding author. Fax: +34 964 345747.

*PII* S0022-328X(98)00569-5

sphere using standard Schlenck techniques. Solvents for synthesis and electrochemical measurements were dried and degassed by standard methods before use. Chromatographic work was performed on Silica gel 60 Å or Alumina columns.

Compound **1** was obtained according to literature methods [4]. We report modified methods to the obtaintion of compounds **2** [5], **5**, **8** and **9** [6] in which we have simplified the work up and improved the yields.

Proton-NMR spectra were recorded on a Varian Gemini 200 MHz, using $CDCl_3$ as solvent unless otherwise stated. IR spectra were recorded on a Perkin Elmer System 2000 FT-IR using NaCl pellets. Cyclic voltammetry experiments were performed with a ECHOCHEMIE PGSTAT 20 electrochemical analyzer. All measurements were carried out at room temperature with a conventional three-electrode configuration consisting of platinum working and auxiliary electrodes and a Ag/AgCl reference electrode containing aqueous 3 M KCl. The solvent in all experiments was $CH_2Cl_2$, which was obtained in HPLC grade from sds. The supporting electrolite was 0.1 M tetrabutylammonium hexafluorophosphate, obtained from Sigma or synthesized by metathesis of tetrabutylammonium bromide and $HPF_6$, recrystallized from ethanol and dried under vacuum. $E_{1/2}$ values were determined as $1/2(E_{p,a}+E_{p,c})$, where $E_{p,a}$ and $E_{p,c}$ are the anodic and cathodic peak potentials, respectively. All potentials reported are not corrected for the junction potential.

### 2.2. NLO measurements

Details of the HRS set-up have been discussed previously [7,8]. All measurements are performed in chloroform and the known hyperpolarizability of para-nitroaniline in this solvent ($23\times10^{-30}$ esu) is used as a reference [9]. The samples are passed through a 0.45 μm filter for contaminated samples often produce spurious signals, and are checked for multiphoton fluorescence that can interfere with the HRS signal [10–12]. IR-laser pulses generated with an injection seeded, Q-switched Nd:YAG laser (Quanta-Ray GCR-5, 1064 nm, 10 ns pulses, 10 Hz) are focused into a cylindrical cell containing the solution (7 ml). The fundamental intensity is altered by rotation of a half-wave plate placed between crossed polarizers, and measured with a photodiode. An efficient condenser system is used to collect the light scattered at the harmonic frequency (532 nm) that is detected by a photomultiplier. Discrimination of the second-harmonic light from the fundamental light is accomplished by a low-pass filter and a 532 nm interference filter. Actual values for the intensities are retrieved by using gated integrators. In all experiments the incident light was vertically polarized along the $z$ axis.

### 2.3. Syntheses of the ferrocenyl ligands **3**, **5** and **9**

To an ice-cold solution of (1-(triphenylphosphinomethyl)ferrocenyl]iodine (3 g, 5.1 mmol) in THF (50 ml) was added potassium tert-butoxide (850 mg, 7.6 mmol) and the resulting solution stirred for 30 min to form the ylide. The corresponding aldehyde, *t*-ciannamaldehyde (2.5 ml, 20.4 mmol for the synthesis of **3**), 4-pyridinecarboxaldehyde (1.5 ml, 15.3 mmol for the synthesis of **5**) and 4-cyanobenzaldehyde (1.2 g, 15.3 mmol for the synthesis of **9**), was added and the resulting mixture stirred for ca. 24 h. After removing the solvent under reduced pressure, the product was extracted with $CH_2Cl_2$ and purified by column chromatography on silica gel with hexane/$CH_2Cl_2$ (8:2) for compound **3** and hexane/$CH_2Cl_2$/acetone (12:8:1) for compounds **5** and **9** as eluent. Recrystallization from $CH_2Cl_2$/hexane mixtures afforded pure compounds. Yields: 47% (for **3**), 60% (for **5**), 44% (for **9**). Proton-NMR spectrum for compound **3**: $\delta$ 7.41–7.18 (m, 5H, $C_6H_5$), 6.88–6.76 (m, 2H, CH=CH); 6.60–6.36 (m, 2H, CH=CH); 4.37 (s, 2H, $C_5H_4$); 4.25 (s, 2H, $C_5H_4$); 4.09 (s, 5H, $C_5H_5$)**;** Proton-NMR spectrum for compound **5**: $\delta$ 8.45 (d, 2H, $^3J_{H-H}=5.04$ Hz, $C_5H_4N$); 7.21 (d, 2H, $^3J_{H-H}=5.88$ Hz, $C_5H_4N$); 7.06 (d, 1H, $^3J_{H-H}=16.12$ Hz, CH=CH); 6.53 (d, 1H, $^3J_{H-H}=16.08$, CH=CH); 4.43 (s, 2H, $C_5H_4$); 4.29 (s, 2H, $C_5H_4$); 4.09 (s, 5H, $C_5H_5$); Proton-NMR spectrum for compound **9**: $\delta$ 7.53 (d, 2H, $^3J_{H-H}=8.43$ Hz, $C_6H_4$); 7.42 (d, 2H, $^3J_{H-H}=8.36$ Hz, $C_6H_4$); 7.20 $CDCl_3$; 6.96 (d, 1H, $^3J_{H-H}=16.12$ Hz, CH=CH); 6.60 (d, 1H, $^3J_{H-H}=16.14$ Hz, CH=CH); 4.43 (s, 2H, $C_5H_4$); 4.29 (s, 2H, $C_5H_4$); 4.09 (s, 5H, $C_5H_5$). Elemental Anal. Calc. for compound **3**, $C_{20}H_{18}Fe$, Mw = 314.21: C, 76.5; H, 5.8. Found: C, 76.6; H, 6.0. Elemental Anal. Calc. for compound **5**, $C_{17}H_{15}FeN$, Mw = 289.26: C, 70.6; H, 5.2; N, 4.8. Found: C, 71.1; H, 5.0; N, 4.8. Elemental Anal. Calc. for compound **9**, $C_{19}H_{15}FeN$, Mw = 313.18: C,72.9; H, 4.8; N, 4.5. Found: C, 72.1; H, 5.0; N, 4.4.

### 2.4. Syntheses of **2** and **4**

$Cr(CO)_6$ (500 mg, 2.3 mmol) and compound **1** (265 mg, 0.9 mmol) or compound **3** (283 mg, 0.9 mmol) were refluxed in buthyl ether (40 ml) overnight. After cooling the mixture to r.t., the solution was filtered and the solvent removed under reduced pressure. Purification by column chromatography on alumina with $CH_2Cl_2$/hexane (4:1) afforded pure compounds **2** (Yield: 45%) and **4** (Yield: 57%). Proton-NMR spectrum for compound **2**: $\delta$ 6.82 (d, 1H, $^3J_{H-H}=16.25$ Hz, CH=CH), 6.20 (d, 1H, $^3J_{H-H}=16.16$ Hz, CH=CH); 5.47 (s, 5H, $C_5H_5$); 4.44 (s, 2H $C_5H_4$); 4.34 (s, 2H $C_5H_4$); 4.18 (s, 5H, $C_5H_5$); Carbon-NMR spectrum for compound **2**: $\delta$ 233.30 (3C, CO); 130.52 (1C, CH=CH); 121.24 (1C, CH=CH); 107.66 (1C, $C_6H_5$); 93.42 (2C, $C_6H_5$); 90.56 (1C, $C_6H_5$); 89.87 (2C, $C_6H_5$); 81.27 (1C, $C_5H_4$); 69.78 (2C, $C_5H_4$); 69.56 (5C, $C_5H_5$); 67.30 (2C, $C_5H_4$)). Proton-NMR spectrum for compound **4**: $\delta$ 6.4–6.6 (m, CH=CH); 6.45 (d, 1H, $^3J_{H-H} = 16.16$ Hz, CH=CH); 6.05 (d, 1H, $^3J_{H-H} = 16.16$ Hz, CH=CH); 5.15–5.50 (m, 5H, $C_6H_5$); 4.37 (s, 2H $C_5H_4$); 4.27 (s, 2H $C_5H_4$); 4.18 (s, 5H, $C_5H_5$). Carbon-NMR spectrum for compound **4**: $\delta$ 233.24 (3C, CO); 134.83 (1C, CH=CH); 132.37 (1C, CH=CH); 125.31 (1C, CH=CH); 125.18 (1C, CH=CH); 107.13 (1C, $C_6H_5$); 82.03 (1C, $C_5H_4$); 69.46 (2C, $C_5H_4$); 69.21 (5C, $C_5H_5$); 67.21 (2C, $C_5H_4$). Elemental Anal. Calc. for compound **2**, $C_{21}H_{16}FeO_3Cr$, Mw = 424.20: C, 59.5; H, 3.8. Found: C,59.3; H, 3.5. Elemental Anal. Calc. for compound **4**, $C_{23}H_{18}FeO_3Cr$, Mw = 450.24: C, 61.4; H, 4.0. Found: C,61.2; H, 4.4.

### 2.5. Syntheses of **6** and **10**

$Cr(CO)_6$ (176 mg, 0.8 mmol) and $Me_3NO$ (88.9 mg, 0.8 mmol) were dissolved in THF (20 ml) and the resulting solution was stirred for 20 min. Compound **5** (231 mg, 0.8 mmol) or compound **9** (250 mg, 0.8 mmol) was then added to the above solution for the preparation of **6** or **10**, respectively. The reaction mixture was stirred for another 20 min, the solution was filtered and the solvent removed under reduced pressure. Purification by column chromatography on alumina with $CH_2Cl_2$/hexane (1:1) afforded pure compounds **6** (Yield: 40%) and **10** (Yield: 20%). Proton-NMR spectrum for compound **6**: $\delta$ 8.34 (d, 2H, $^3J_{H-H} = 5.7$ Hz, $C_5H_4N$); 7.08 (d, 2H, $^3J_{H-H} = 5.9$ Hz, $C_5H_4N$); 7.13 (d, 1H, $^3J_{H-H} = 16.08$ Hz, CH=CH); 6.46 (d, 1H, $^3J_{H-H} = 16.1$, CH=CH); 4.45 (s, 2H $C_5H_4$); 4.35 (s, 2H, $C_5H_4$); 4,09 (s, 5H, $C_5H_5$); Carbon-NMR spectrum for compound **6**: $\delta$ 214.55 (1C, *trans* CO); 211.53 (4C, *cis* CO); 155.29 (2C, Py); 146.30 (1C, Py); 135.65 (2C, Py); 120.86 (2C, CH=CH); 80.96 (1C, $C_5H_4$); 70.52 (2C, $C_5H_4$); 69.54 (5C, $C_5H_5$); 67.85 (2C, $C_5H_4$); Proton-NMR spectrum for compound **10**: $\delta$ 7.52 (d, 2H, $^3J_{H-H} = 8.07$ Hz, $C_6H_4$); 7.41 (d, 2H, $^3J_{H-H} = 8.10$ Hz, $C_6H_4$); 6.96 (d, 1H, $^3J_{H-H} = 15.98$ Hz, CH=CH); 6.60 (d, 1H, $^3J_{H-H} = 16.12$, CH=CH); 4.43 (s, 2H, $C_5H_4$); 4.29 (s, 2H, $C_5H_4$); 4.09 (s, 5H, $C_5H_5$); Carbon-NMR spectrum for compound **10**: $\delta$ 219.41 (1C, *trans* CO); 214.05 (4C, *cis* CO); 143.31 (1C, $C_6H_4$); 132.78 (2C, $C_6H_4$); 128.97 (1C, $C_6H_4$); 126.20 (2C, $C_6H_4$); 123.95 (1C, CH=CH); 123.60 (1C, CH=CH); 107.86 (1C, CN); 81.71 (1C, $C_5H_4$); 70.10 (2C, $C_5H_4$); 69.89 (5C, $C_5H_5$); 67.53 (2C, $C_5H_4$). Elemental Anal. Calc. for compound **6**, $C_{22}H_{15}NFeO_5Cr$, Mw = 481.21: C, 54.9; H, 3.1; N, 2.9. Found: C, 54.3; H, 3.5; N, 3.1. Elemental Anal. Calc. for compound **10**, $C_{24}H_{15}NFeO_5Cr$, Mw = 505.23: C, 57.1; H, 3.0; N, 2.8. Found: C, 57.3; H, 3.4; N, 2.9.

### 2.6. Syntheses of **7**, **8** and **11**

Compounds **7**, **8** and **11** were prepared by the same general method than **6** and **10** from $Mo(CO)_6$ and $W(CO)_6$, respectively. Yield for **7**, 10%, yield for **8**, 63% and yield for **11**, 25%. Proton-NMR spectrum for compound **7**: $\delta$ 8.41 (d, 2H, $^3J_{H-H} = 6.23$ Hz, $C_5H_4N$); 7.08 (d, 2H, $^3J_{H-H} = 5.9$ Hz, $C_5H_4N$); 7.13 (d, 1H, $^3J_{H-H} = 16.08$ Hz, CH=CH); 6.46 (d, 1H, $^3J_{H-H} = 16.1$, CH=CH); 4.45 (s, 2H, $C_5H_4$); 4.35 (s, 2H, $C_5H_4$), 4.09 (s, 5H, $C_5H_5$); Carbon-NMR spectrum for compound **7**: $\delta$ 214.57 (1C, *trans* CO); 204.50 (4C, *cis* CO); 154.78 (2C, Py); 146.30 (1C, Py); 135.65 (2C, Py); 120.86 (2C, CH=CH); 80.96 (1C, $C_5H_4$); 70.52 (2C, $C_5H_4$); 69.54 (5C, $C_5H_5$); 67.85 (2C, $C_5H_4$); Proton-NMR spectrum for compound **8**: $\delta$ 8.54 (d, 2H, $^3J_{H-H} = 6.5$ Hz, $C_5H_4N$); 7.27 (d, 1H, $^3J_{H-H} = 16.5$ CH=CH); 7.23 (2H, $^3J_{H-H} = 6.6$ Hz, $C_5H_4N$); 6.49 (d, 1H, $^3J_{H-H} = 16.4$ Hz, CH=CH); 4.47 (s, 2H, $C_5H_4$); 4.37 (s, 2H, $C_5H_4$); 4.10 (s, 5H, $C_5H_5$); Proton-NMR spectrum for compound **11**: $\delta$ 7.56 (d, 2H, $^3J_{H-H} = 8.06$ Hz, $C_6H_4$); 7.47 (d, 2H, $^3J_{H-H} = 8.16$ Hz, $C_5H_4$); 7.04 (d, 1H, $^3J_{H-H} = 16.10$ Hz, CH=CH); 6.61 (d, 1H, $^3J_{H-H} = 16.02$, CH=CH); 4.45 (s, 2H, $C_5H_4$); 4.33 (s, 2H, $C_5H_4$); 4.11 (s, 5H, $C_5H_5$); Carbon-NMR spectrum for compound **11**: $\delta$ 199.92 (1C, *trans* CO); 196.11 (4C, *cis* CO); 143.45 (1C, $C_6H_4$); 132.85 (2C, $C_6H_4$); 125.95 (2C, $C_6H_4$); 125.01 (1C, $C_6H_4$); 123.18 (2C, CH=CH); 106.56 (1C, CN); 81.29 (1C, $C_5H_4$); 69.87 (2C, $C_5H_4$); 69.19 (5C, $C_5H_5$); 67.26 (2C, $C_5H_4$). Elemental Anal. Calc. for compound **7**, $C_{22}H_{15}NFeO_5Mo$, Mw = 525.15: C, 50.3; H, 2.9; N, 2.7. Found: C, 51.3; H, 3.4; N, 2.8. Elemental Anal. Calc. for compound **8**, $C_{22}H_{15}NFeO_5W$, Mw = 613.06: C, 43.1; H, 2.5; N, 2.3. Found: C, 43.7; H, 2.5; N, 2.1. Elemental Anal. Calc. for compound **11**, $C_{24}H_{15}NFeO_5W$, Mw = 637.08: C, 45.2; H, 2.4; N, 2.2. Found: C, 44.3; H, 2.3; N, 2.1.

## 3. Results and discussion

### 3.1. Synthesis and characterization of the ferrocenyl compounds

The new ferrocenyl compounds were prepared by conventional organic synthetic procedures (Wittig reactions), or modification of the literature methods. All the compounds were characterized by means of IR-, $^1H$- and $^{13}C$-NMR spectroscopy and satisfactory microanalyses. The $\pi$ bonded $\eta^6$ compounds (**2** and **4**) were obtained refluxing the corresponding ferrocenyl ligands (**1** or **3**) with chromium hexacarbonyl for 12 h in butyl ether. Fig. 1 shows the general procedure to the obtention of compounds **2, 4, 5**–**11**. The coordination of the ferrocenyl cyano and pyridyl derivatives were carried out by previously reacting $Me_3NO$ with the correspond-

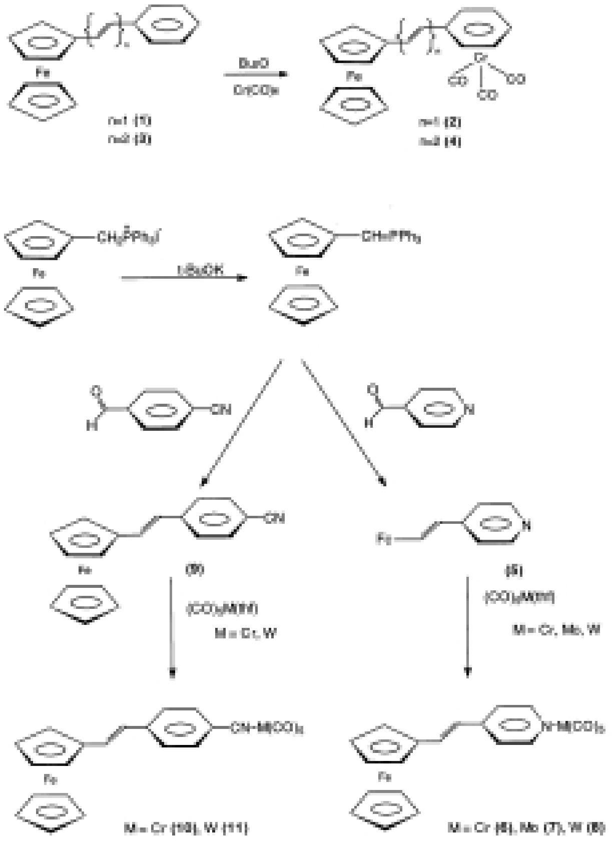


Fig. 1. Reaction scheme for the syntheses of compounds **2**, **4**, **5–11**.

ing metal hexacarbonyl, and then adding the ferrocenyl ligand. This method showed better results than any other photochemical or thermal reaction used.

The pyridyl and cyano ferrocenyl ligands were obtained in moderate high yields, with high selectivities on the trans isomers, as stated in Section 2.

Comparison of the IR spectra of the $\sigma$-bonded cyano and pyridyl ferrocene derivatives (**6**, **7**, **8**, **10**, **11**) shows that the compounds containing W have lower values of $\nu$(CO), meaning that W is more capable than Cr and Mo of reducing its electron density by $\pi$ back-donation to CO. As we comment in the NLO section, this fact supports the observation of the larger hyperpolarizabilities found for our compounds containing W. Similar results have been reported for group 6 metal Fischer type carbenes [14].

### 3.2. Cyclic voltammetry

Electrochemical data obtained for the compounds studied are summarized in Table 1.

Cyclic voltammetric investigations for the ferrocene derivatives CpFe($\eta^5$-$C_5H_4$)–(CH=CH)–($C_6H_5$) (**1**), CpFe($\eta^5$-$C_5H_4$)–$(CH=CH)_2$-($C_6H_5$) (**3**), CpFe($\eta^5$-$C_5H_4$)–(CH=CH)-py (**5**) and CpFe($\eta^5$-$C_5H_4$)–(CH=CH)–($C_6H_4$)–CN (**9**) show a redox behavior analogous to the one observed for ferrocene, that is, an electrochemically quasireversible one-electron oxidation.

The half wave potential of the quasireversible wave for compounds **1** and **3** is sligthly lower than that shown for ferrocene, indicating that the oxidation is favoured by the delocalization of the charge along the conjugated system of the ligand ($E_{1/2}$(**3**) < $E_{1/2}$(**1**), as expected from the longer conjugated chain of **3**). The rest of the compounds show half wave potentials for the ferrocene center, that are higher than that shown for ferrocene, meaning that ferrocenyl ligands connected to electronegative/electron-accepting fragments show some electron transfer between the iron and the pyridyl or cyano fragments. Coordination to the metal carbonyl implies an additional increase on the half wave pontential of the ferrocene center in all the cases, indicating that the carbonyl metal attached to the ferrocenyl ligands promotes an additional increase of the electron transfer in the direction $Fe \rightarrow M(CO)_n$. On the other hand, the second oxidation step for **2** and **4** displays complete electrochemical irreversibility with an anodic peak potential $E_{p,a}$ showing a slight cathodic shift with respect to $E_{1/2}$ for $(\eta^6\text{-}C_6H_6)Cr(CO)_3$, in spite of the positive charge in $\mathbf{2}^+$ and $\mathbf{4}^+$.

In contrast, the cyclic voltammetric experiments for $CpFe(\eta^5\text{-}C_5H_4){-}CH{=}CH\text{-py-}Cr(CO)_5$ (**6**) show two electrochemical quasireversible oxidation waves. Both processes are coupled with a reduction on the reverse sweep. The peak separation, 75 and 77 mV, and the virtually equal peak currents suggest that we are observing two quasireversible one-electron oxidations. The half wave potential $E_{1/2}$ for $\mathbf{6}^+/\mathbf{6}$ shows an anodic shift of 30 mV relative to that of $\mathbf{5}^+/\mathbf{5}$ as expected based on the electron-withdrawing nature of the $(C_6H_5)Cr(CO)_3$ moiety. Compounds **7** and **8** display complete electrochemical irreversibility for the oxidation of Mo and W respectively, as reported previously for **8** ([5]b).

The chromium based compound **10**, shows two electrochemical quasireversible oxidation waves. Both processes are coupled with a reduction on the reverse sweep. The related tungsten based compound **11**, displays complete electrochemical irreversibility for the oxidation of W. This result is consistent with those studies reported before where chromium and tungsten ferrocenyl derivatives show quasireversible and complete irreversible oxidation waves respectively [5,13].

Table 1
Cyclic voltammetric data for compounds **1**–**11**

| Compound | $E_{1/2}$(V) (ΔEp (mV)) Fe-based | $E_{1/2}$(V) (ΔEp (mV)) M-based[a] |
|---|---|---|
| Ferrocene | 0.446 (106) | – |
| **1** | 0.440 (85) | – |
| **2** | 0.481 (74) | 0.808[b] |
| **3** | 0.436 (87) | – |
| **4** | 0.448 (91) | 0.784[b] |
| **5** | 0.498 (70) | – |
| **6** | 0.520 (75) | 0.928 (77) |
| **7** | 0.518 (83) | 1.110[b] |
| **8** | 0.530 (77) | 1.125[b] |
| **9** | 0.482 (82) | – |
| **10** | 0.499 (72) | 0.981 (66) |
| **11** | 0.495 (68) | 1.146[b] |

[a] M = Cr, Mo, W.

[b] Irreversible peak, measured at 100 mV $s^{-1}$.

Table 2
Experimental nonlinear response of the compounds synthetised previously; [a]$\beta$ and $\beta_0$ in $10^{-30}$ esu

| Compound | $\lambda_{max}$ (nm) | $\beta$ | $\beta_0$[b] |
|---|---|---|---|
| **2** | 304 | 193 | 119 |
| **4** | 334 | 300 | 164 |
| **5** | 468 | 21 | 4 |
| **6** | 401 | 63 | 23 |
| **7** | 487 | 95 | 12 |
| **8** | 491 | 101 | 12 |
| **9** | 473 | 203 | 34 |
| **10** | 481 | 271 | 39 |
| **11** | 487 | 375 | 48 |

[a] Measured in chloroform by the HRS method and calculated with respect to $\beta$ of PNA in chloroform ($23\times10^{-30}$ esu). HRS at 1.06 mm. Values ± 15%.

[b] Calculated from the two level model.

### 3.3. NLO properties

The UV–vis spectra of compounds **1**–**11** show low absorption in the region where second harmonic is generated (1064 nm) in the solvent where the nonlinear response was studied by the hyper Rayleigh scattering method (chloroform). Table 2 shows the values of $\beta$ obtained for compounds **1**–**11**. These values are comparable in magnitude to those obtained for the bimetallic cationic compounds reported by Heck et al. ([3]a,b) The simple two-level method allowed us to calculate the static hyperpolarizabilities, $\beta_0$; for compounds **7**–**11**, the differences between $\beta$ and $\beta_0$ are rather large because the maximum of absorption of these compounds are relatively close to 532 nm. Since the molecules that we have studied display several optical transitions, the static hyperpolarizabilities given are only a crude estimation. In their estimations (two level model) we have only taken into account the transition closest to the harmonic frequency, and damping has been neglected. Compounds **2**, **4**, **6**, **7**, **8**, **10** and **11**, being a combination of two neutral fragments show the electron-accepting capability of the chromium carbonyl moiety through both $\pi$- and a $\sigma$-bonding to the electron donating ferrocene derivative. It is noteworthy pointing out that previous studies have shown that a series of $(\eta^6$-arene)tricarbonylchromium derivatives show low values of $\beta$ ([2]d), while $\sigma$-bonded derivatives of $(CO)_5Cr(p\text{-X-py})$ (X = H, $NH_2$, $C_6H_5$, CHO, $COCH_3$) gave interesting results [14]. Compound **9** shows a higher value of $\beta$ than **5**, probably because of the longer chain separating the donor and acceptor fragments. As seen from Table 2, $\pi$-donation affords a much higer value of the hyperpolarizability than that shown of the ligands upon $\sigma$-donation. The result can be interpreted in terms of the linkage to the carbonyl fragment. In the case of the $\pi$-bonded compounds (**2** and **4**), the orbitals participating in the conjugated delocalization of the charge are the same used in the formation of the bond to chromium. The lower increase of $\beta$ in the $\sigma$-bonded complexes can be explained in terms of the role of the metal in lowering the energy of the pyridyl acceptor orbital and this way to increase the accepting properties of the pyridyl ligand [15].

There is a considerable increase in the value of $\beta$ when we change the metal, in the order $W > Mo > Cr$, probably due to the decrease of the Pauling electronegativity in the same direction and to the higher backdonation capability of W compared to Cr and Mo. As we have previously mentioned, all the ferrocenyl-metalcarbonyl compounds that we report in the present work, show higher half wave potentials (based on the iron center), than that shown for ferrocene. We interprete this result as a consequence of a partial charge transfer to the metalcarbonyl fragment.

In summary, we have presented a series of heterobimetallic compounds showing large values of $\beta$. These compounds are easy-to-make, stable and soluble in most common organic solvents, showing low absorption in the second harmonic generation region. The electronic and optical properties of these compounds can be easily tuned by modifying the chainlength, bonding to the metal and change of the metal.

## Acknowledgements

We thank the Generalitat Valenciana for the financial support of this work (GV-C-CN-09-071-96) and the Belgian National Fund for Scientific Research-Flanders (G.0308.96), the Belgian Government (IUAP-P4-11) and the University of Leuven (GOA/1/95). We would also like to thank Professor Robert H. Crabtree for his valuable help and wise advices, and to Professor Miguel Carda for the design of the organic pathways to obtain the ligands. S.H. is a Research Assistant of the Belgian National Fund for Scientific Research.

## References

[1] (a) N.J. Long, Angew. Chem. Int. Ed. Engl. 34 (1995) 21–38. (b) I.R. Whittall, A.M. McDonagh, M.G. Humphrey, M. Samoc, Adv. Organomet. Chem. 42 (1997) 291. (c) T. Verbiest, S. Houbrechts, M. Kauranen, K. Clays, A. Persoons, J. Mater. Chem. 7 (1997) 2175.

[2] See for example: (a) I.R. Whittall, M.G. Humphrey, A. Persoons, S. Houbrechts, Organometallics 15 (1996) 1935. (b) M. Tamm, A. Grzegorzewski, Th. Steiner, Th. Jentzsch, W. Werncke, Organometallics 15 (1996) 4984. (c) I.R. Whittall, M.G. Humphrey, A. Persoons, S. Houbrechts, D.C.R. Hockless, Organometallics 15 (1996) 5738. (d) L.T. Cheng, W. Tam, G.R. Meredith, S.R. Marder, Mol. Cryst. Liq. Cryst. 189 (1990) 137. (e) B.J. Coe, J.A. Harris, L.J. Harrington, J.C. Jeffery, L.H. Rees, S. Houbrechts, A. Persoons, Inorg. Chem submitted, (1997). (f) B.J. Coe, J.P. Essex-Lopresti, S. Houbrechts, A. Persoons. J.C.S., Chem. Commun. (1997) 1645. (g) S. Di Bella, I. Fragalà, T. Marks, M.A. Ratner, J. Am. Chem. Soc. 118 (1996) 12747. (h) S. Di Bella, I. Fragalà, I. Ledoux, T.J. Marks. J. Am. Chem. Soc. 117 (1995) 9481.

[3] (a) U. Behrens, H. Brussard, U. Hagenau, J. Heck, E. Hendrickx, J. Kornich, J.G.M. van der Linden, A. Persoons, A.L. Spek, N. Veldman, B. Voss, H. Wong, Chem. Eur. J. 2 (1996) 98. (b) U. Hagenau, J. Heck, E. Hendrickx, A. Persoons, T. Schuld, H. Wong, Inorg. Chem. 35 (1996) 7863. (c) R. Loucif-Saiba, J.A. Delaire, L. Bonazzola, G. Doisneau, G. Balavoine, T. Fillebeen-Khan, I. Ledoux, G. Puccetti, Chem. Phys. 167 (1992) 369. (d) S. Houbrechrts, K. Clays, A. Persoons, V. Cadierno, M.P. Gamasa, J. Gimeno, Organometallics 15 (1996) 5266.

[4] P.L. Pauson, W.E. Watts, J. Organomet. Chem. (1963) 2990.

[5] (a) M.M. Bhadbhade, A. Das, J.C. Jeffery, J. McCleverty, J.A. Navas, M.D. Ward. J. Chem. Dalton Trans. (1995) 2769. (b) S. Sakanishi, D.A. Bardwell, S. Couchman, J.C. Jeffery, J.A. McCleverty, M.D. Ward. J. Organomet. Chem. 528 (1997) 35–45. (c) S. Toma, A. Gaplovosky, P. Elecko, Chem. Pap. 39 (1985) 115.

[6] C. Degrand, A. Radecki-sudre, J. Organomet. Chem. 268 (1984) 63 and references cited therein.

[7] E. Hendrickx, K. Clays, A. Persoons, C. Dehu, J.L. Brédas, J. Am. Chem. Soc. 117 (1995) 3547.

[8] S. Houbrechts, K. Clays, A. Persoons, Z. Pikramenou, J.-M. Lehn, Chem. Phys. Lett. 258 (1996) 485.

[9] K. Clays, A. Persoons, Rev. Sci. Instrum. 63 (1992) 3285.

[10] E. Hendrickx, C. Dehu, K. Clays, J.L. Brédas, A. Persoons, in: G.A. Lindsay, K.D. Singer, Polymers for Second-Order Nonlinear Optics, American Chemical Society, Washington DC, 1995, pp. 82–94.

[11] M.C. Flipse, R. de Jonge, R.H. Woudenberg, A.W. Marsman, C.A. van Walree, L.W. Jenneskens, Chem. Phys. Lett. 245 (1995) 297.

[12] I.D. Morrison, R.G. Denning, W.M. Laidlaw, M.A. Stammers, Rev. Sci. Instrum. 67 (1996) 1445.

[13] (a) L.K. Yeung, J.E. Kim, Y.K. Chung, P.H. Rieger, D.A. Sweigart, Organometallics 15 (1996) 3298. (b) I.P. Gubin, V.S. Khandkarova, J. Organomet. Chem. 22 (1970) 449.

[14] L.T. Cheng, W. Tam, D.F. Eaton, Organometallics 9 (1990) 2856.

[15] (a) D.R. Kanis, M.A. Ratner, T.J. Marks, J. Am. Chem. Soc. 114 (1992) 10338. (b) D.R. Kanis, P.G. Lacroix, M.A. Ratner, T.J. Marks, J. Am. Chem. Soc. 116 (1994) 10089. (c) D.R.M.A. Ratner, T.J. Marks, Chem. Rev. 94 (1994) 195.

www.elsevier.nl/locate/jorganchem

Journal of Organometallic Chemistry 616 (2000) 80–88

# Preparation, properties and coordination of new conjugated ferrocenyl-based ligands with an end-capped nitrile

José A. Mata [a], Eva Falomir [a], Rosa Llusar [b], Eduardo Peris [a,*]

[a] *Dpto. de Química Inorgánica y Orgánica, Universitat Jaume I, E-12080 Castellón, Spain*
[b] *Dpto. de Ciencias Experimentales, Universitat Jaume I, E-12080 Castellón, Spain*

Received 17 April 2000; accepted 24 July 2000

## Abstract

New ferrocenyl-nitrile conjugated ligands have been obtained by several routes in which we combined Wittig and Horner–Emmons–Wadsworth (HEW) reactions, being the latter the one that shows better results both in yield and selectivity for the *E* isomers. The coordination capabilities of these new ligands have been proved using different metal carbonyls and the electronic spectra of the compounds have been studied, showing a clear dependence on the length of the conjugated chain and in the nature of the coordinated metal carbonyl fragment. © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* Ferrocenes; Metal containing oligomers; Heterobimetallic complexes; Metal carbonyl; Electrochemistry

## 1. Introduction

The synthesis and characterization of new ferrocenyl-based compounds has become an intriguing area of research [1], specially because of their potential applications in fields such as organic synthesis, catalysis and material science. The preparation of ferrocenyl-conjugated systems offers the possibility of electronic communication between terminal subunits, this being of particular interest in either nonlinear optics, magnetism, molecular sensors or liquid crystals. Molecular wires, that is, mixed-valence bimetallic compounds with a conjugating bridging ligand that allow electronic communication between the two termini, have also been the subject of extensive research during the last decade [2]. These systems can be formed by oligoene bridging ligands between ruthenium pentamine complexes or between simple ferrocenes, where the electronic coupling has been experimentally verified for up to 40 Å [3,4].

The introduction of a metallocene unit into one-dimensional oligomers promotes a large range of properties that differ from those shown by conventional organic polymers. Although a large number of works have been reported in which metallocene-based oligomers are obtained [5], there is still a lack of systematic descriptions of synthesis leading to useful starting materials. All the reported metal-containing polymers have in common that they are only conducting if charge carriers can be delocalized over both the metal and the organic fragments.

We and others have used ferrocenyl-based conjugated ligands in order to obtain bimetallic and heterometallic push–pull complexes [6–8]. In fact, some heterobimetallic complexes, not all of them ferrocenyl-based, have shown high non linear optical responses, although the list of such compounds used in NLO is still scarce [9]. We have recently reported the syntheses, characterization and NLO behavior of new ferrocenyl heterobimetallic neutral compounds with a series of electron-accepting moieties derived from $M(CO)_6$ ($M =$ Cr, Mo or W) [6]. These compounds exhibited static hyperpolarizabilities up to $164 \times 10^{-30}$ esu, which are among the largest measured up to date for ferrocenyl-based derivatives.

We now report, based on our previous findings, several efficient routes to the preparation of ferrocenyl conjugated compounds with an end-capped nitrile group. These compounds are obtained by combined

---

* Corresponding author. Fax: + 34-964-728214.
*E-mail address:* eperis@qio.uji.es (E. Peris).

PII: S0022-328X(00)00557-X

Wittig and/or Horner–Emmons–Wadsworth (HEW) reactions, for which the corresponding ferrocenyl-aldehydes have also been obtained. The electrochemistry of the compounds and the electronic spectra has also been investigated.

## 2. Results and discussion

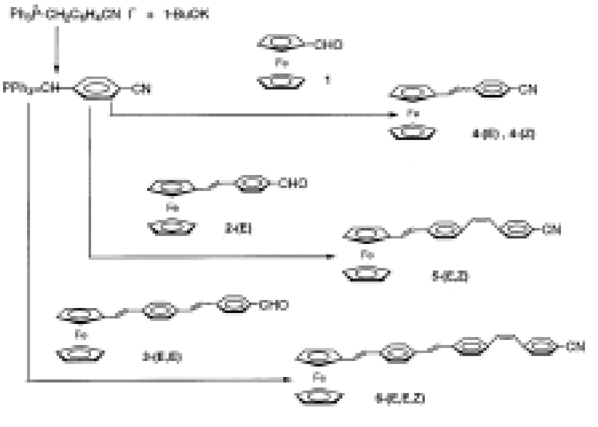
### 2.1. Synthesis and characterization of the compounds

Most of the ferrocenyl-based oligomers reported to date, have been obtained by conventional Wittig reactions but these reactions usually lead to the formation of *E* and *Z* isomer mixtures [4b,9a,10]. Several authors have reported the advantages of the *E*-type isomers over the *Z*-type for effective electronic coupling [10c,11]. The lack of coplanarity between donor and acceptor groups in the *Z* isomers leads to a decrease in their coupling. In addition, the reduction of the through space distance (in the *Z*-type) between donor and acceptor results in the change in dipole per unit charge separation being less. Since most of the times the aim of the synthetic procedures is to obtain linear oligomers with effective electronic coupling, the *E* isomers are the ones that are mainly pursued, but the separation of the mixtures of the *E* and *Z* isomers is not always easy. However, in some cases, effective *Z* to *E* isomerizations have been reported for some conjugated ferrocenyl compounds [10].

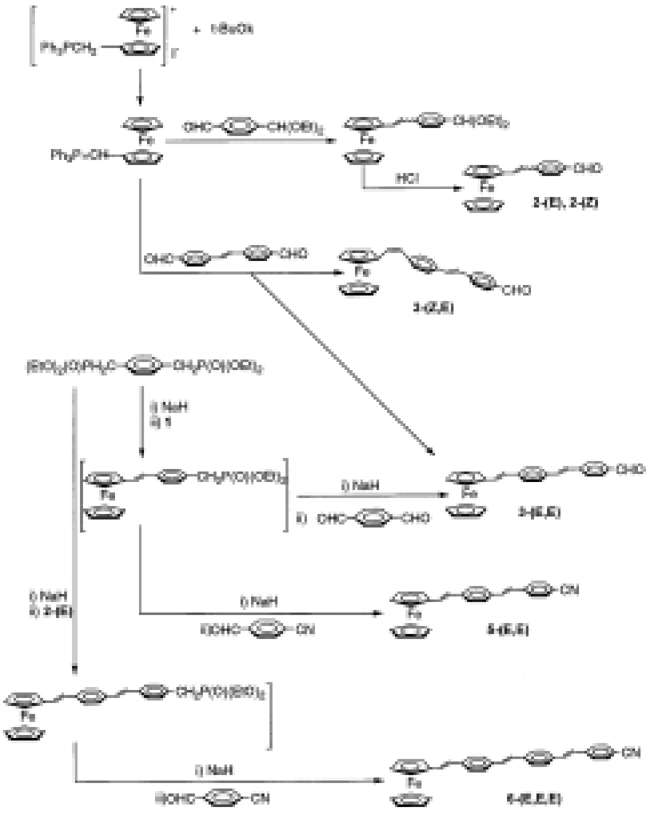
We have obtained several ferrocenyl-nitrile derivatives, following different synthetic procedures, as shown in Schemes 1 and 2. We have used Wittig–Horner (WH) reaction in previous works, this being the most appropriate method for the short-length chained complexes **2** and **4** [6,10d]. Usually this procedure led to reasonable yields of both *Z*- and *E*-isomers which could be separated by column chromatography, as described in Section 4.

When we used the same reaction (WH) in order to obtain the longer chained compounds **5** and **6**, we unexpectedly observed that the only characterizable spectroscopically and isolable compound were the (*E*,*Z*) and (*E*,*E*,*Z*) isomers. (The first lyric always corresponds to the double bond nearest to the ferrocenyl group). For reasons that we still unknow, the stereolinear isomers (*E*,*E*) and (*E*,*E*,*E*) were not obtained by this procedure. In order to obtain these isomers we performed the corresponding HEW reaction that stereoselectively lead to the formation of double bonds in the *E*-configuration [13]. As it is shown in Scheme 2 compounds **5-(*E*,*E*)** and **6-(*E*,*E*,*E*)** were obtained by double olefination of *p*-xylenebis(diethylphosphonate) with the ferrocenyl–aldehyde compound **1** or **2-(*E*)** and 4-cyanobenzaldehyde. This procedure leads to reasonably good yields for compound **5-(*E*,*E*)**, but compound **6-(*E*,*E*,*E*)** was only obtained in very low yield and it could only be characterized spectroscopically. We tried to obtain the *E*-isomers by isomerization of the *Z* isomers using *N*-Bromosuccinimide and $I_2$ or with basic alumina, but no conversion was observed.

Another problem that we found in the preparation of the ferrocenyl-nitrile complexes, came from the synthetic routes to the carboxaldehyde intermediates **2-(*E*)** and **3-(*E*,*E*)**. The synthetic routes for such complexes in most cases lead to moderate to poor yields [4b], and the separation workups make the overall process complicated. In order to simplify the preparation of these intermediates, we modified their synthesis as it is shown in Scheme 2. The use of terephtalaldehydemono-(diethylacetal) [*p*-OHC–$C_6H_4$–CH(OEt)$_2$] instead of the more widely used terephtaldehyde (*p*-OHC–$C_6H_4$–



Scheme 1.



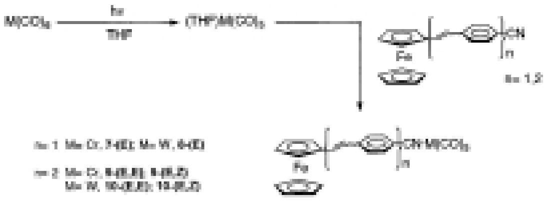
Scheme 2.

CHO), avoids the obtaintion of 1,4-bis(ferrocenyl)-ethenylbenzene as one of the major side-products of these types of reactions. The ferrocenyl–acetal complex so synthesized, can be transformed into the carboxaldehyde compound **2**, by simply reacting the acetal derivative in a solution of hydrochloric acid as has already been reported [10d].

Compound **3-(*E*,*E*)** can be obtained in a one pot reaction from a HEW reaction using *p*-xylenebis(diethylphosphonate) [12] ferrocenecarboxaldehyde and terephtaldehyde. In this reaction we avoid the formation of any *Z* isomer, since the HEW process unambiguously leads to the *E* isomers. Compound **3** can also be obtained in a one-pot reaction, by using (*E*)-1,2-bis(*p*-phenylcarboxaldehyde)ethene and [1-(triphenylphosphinomethyl)ferrocenyl]iodide in a WH reaction, giving rise to moderate yields of **3** although a mixture of the (*E*,*E*) and (*Z*,*E*) isomers were obtained. The bisaldehyde compound (*E*)-1,2-bis(*p*-phenylcarboxaldehyde)ethene, was obtained according to the method that we describe in Section 4.

In order to obtain push–pull heterobimetallic complexes from the ferrocenyl compounds obtained, we have coordinated compounds **4** and **5** to metal carbonyl fragments $M(CO)_5$ ($M = Cr, W$). The synthesis of these compounds is summarized in Scheme 3 (the coordination of **4** has already been reported and the resulting compounds characterized) [6]. These compounds decompose after several days in solution, but not decomposition was observed in the solid state.

In all cases, the vinyl protons of the *E* isomers appear as doublets with coupling constants of 16 Hz, in accord with the expected trans stereochemistry. The *Z* isomers show lower coupling constants for the vinyl protons (ca. 12 Hz), this being a good method of determining the stereochemistry of the compounds obtained. Besides, the effect of the electronwithdrawing acceptor group is also witnessed in the $^1$H chemical shifts of the



Scheme 3.

substituted $C_5H_5$ ring. These signals appear at higher frequencies in those compounds with *E* conformation, where the electronic communication between the ferrocenyl and the electronaccepting group is more effective.

The IR spectra of the heterobimetallic compounds are virtually identical, indicating the presence of a metal pentacarbonyl moiety, the bands being readily assigned to the two $A_1$, $B_2$ and $E$ modes for the pseudo $C_{4v}$ metal center, by comparison with other monosubstituted metal carbonyl derivatives [14]. The $^{13}$C-NMR clearly shows the two carbonyl inequivalent sites of the pentacarbonyl fragments, so confirming the proposed geometry of the compounds. Comparison of the IR spectra of the heterobimetallic compounds shows that the compounds containing W have lower values of $\nu$(CO), meaning that W is more capable than Cr of reducing its electron density by $\pi$ back-donation to CO.

Electrospray mass spectra were recorded using a Micromass Quattro LC instrument, using $CH_3CN$ and/or $CH_3OH$ as the mobile phase solvent. Cone voltage were typically varied from 15 to 90 V in order to investigate the effect of higher voltages on fragmentation pathways of parent ions. The peaks in the ESMS are identified by the most intense $m/z$ value within the isotopic mass distribution. Isotope patterns were compared with theoretical patterns obtained using the MassLynx NT software package. In all cases there was good agreement between the experimental and calculated isotopic mass distribution.

### 2.2. Electronic spectra

The electronic absorption spectra of the new ferrocenyl nitrile compounds were taken in different solvents and the results are shown in Table 1. Electronic absorption spectra of these compounds show a maximum of two strong bands between 250 and 320 nm and between 370 and 470 nm. The higher energy band was assigned to the $\pi$–$\pi$* band according to the reported data in the literature for similar ferrocenyl compounds [7d,16]. The lower energy band is assigned to a MLCT band, this being strongly influenced by the nature of the ligand (chainlength, electron acceptor moiety) and metal coordinated fragment ((M(CO)$_5$). This assignment is in accordance to the theoretical results reported by Barlow et al. and to other experimental results [7,16], although we are aware that some controversy about this assignation has been reported. For most ferrocene derivatives the charge transfer bands usually gains significantly in oscillator strength as the acceptor strength increases [7d,11c,15]. This band was found to increasingly red-shifted with increasing chain length, as expected for a lowering of the energy of the $\pi$* orbital of the ligand. Red shift is also achieved for the cases in which an electron-accepting moiety is coordinated to the ligand, as in complexes **9-(*E,E*)**, **9-(*E,Z*)**, **10-(*E,E*)**, **10-(*E,Z*)**, these changes being much more appreciable for the (E,E) isomers, according to their greater charge transfer capabilities. Thus, while compound **4-(*E*)** exhibits a $\lambda_{max}$ at 329 nm, this value progressively shifts to longer wavelengths in going to **5-(*E,Z*)** 340 nm, to **5-(*E,E*)** 369 nm and finally to **6-(*E,E,Z*)** 380 nm. Similar trends are observed for other families of ferrocenyl phenylethynyl compounds [16]. The lower hypsochromic shifts for the *Z* configured isomers may be justified for their trend to disturb from coplanarity due to enhanced allylic strain [17]. The much weaker d–d transitions substantially overlap the MLCT bands and are not assigned.

According to the tabulated UV–vis data (Table 2) the solvachromicities of the ferrocenyl(styryl)nitrile compounds are fairly small. This result is not surprising, since the CN group is not a powerful acceptor. For

Table 1
Electronic spectra data of ferrocenyl-nitriles

| Compound | $\lambda_{max}$ (nm, MLCT) | | | | |
|---|---|---|---|---|---|
| | $CHCl_3$ | Acetone | $CH_2Cl_2$ | THF | MeOH |
| **4-(*E*)** | 329 | – | 329 | 327 | 327 |
| **5-(*E,Z*)** | 340 | 339 | 340 | 341 | 345 |
| **5-(*E,E*)** | 369 | 364 | 368 | 364 | 364 |
| **6-(*E,E,Z*)** | 380 | 373 | 375 | 376 | 380 |
| **6-(*E,E,E*)** | – | – | – | – | – |
| **9-(*E,Z*)** | 345 | 349 | 340 | 343 | 341 |
| **9-(*E,E*)** | 380 | 378 | 382 | 383 | 364 |
| **10-(*E,Z*)** | 344 | 341 | 344 | 344 | 341 |
| **10-(*E,E*)** | 394 | 382 | 389 | 386 | 362 |

Table 2
Cyclic voltammetric data for compounds **1**–**10**

| Compound | $E_{1/2}$ (mV) ($\Delta E_p$ (mV)) Ferrocene-based | $E_{1/2}$ (mV) ($\Delta E_p$ (mV)) M [c]-based |
|---|---|---|
| Ferrocene | 445 (105) | – |
| **1** | 460 (70) | – |
| **2-(*E*)** | 500 (105) | – |
| **3-(*E*,*E*)** | 450 (95) | – |
| **3-(*Z*,*E*)** | 460 (100) | – |
| **4-(*E*)** [a] | 480 (80) | – |
| **5-(*E*,*E*)** | 440 (70) | – |
| **5-(*E*,*Z*)** | 445 (70) | – |
| **6-(*E*,*E*,*E*)** [d] | – | – |
| **6-(*E*,*E*,*Z*)** | 420 (85) | – |
| **7-(*E*)** [a] | 500 (70) | 980 (66) |
| **8-(*E*)** [a] | 495 (70) | 1150 [b] |
| **9-(*E*,*E*)** | 435 (80) | 965 (70) |
| **9-(*E*,*Z*)** | 450 (85) | 965 (75) |
| **10-(*E*,*E*)** | 435 (85) | 965 [b] |
| **10-(*E*,*Z*)** | 450 (70) | 1160 [b] |

[a] Data from Ref. [6].
[b] Irreversible peak, measured at 100 mV $s^{-1}$.
[c] M = Cr, W
[d] Not measured.

the heterobimetallic complexes **9-(*E*,*E*)**, **9-(*E*,*Z*)**, **10-(*E*,*E*)** and **10-(*E*,*Z*)**, the solvatochromic behavior is more important, so confirming the stronger electron-accepting capabilities of the metal-carbonyl units. This result gives us an idea of the dipole moments in the ground and in the excited states, which have a direct relation to hyperpolarizability. The charge transfer band $\lambda_{max}$ shifts upon changing the solvent from $CH_2Cl_2$ to MeOH. These hypsochromic shifts mean that the dipole moment in the excited state is lower than in the ground state. In addition this effect is greater in the cases were all the double bonds are *E* [18].

### 2.3. Cyclic voltammetry

The electrochemical data obtained for the compounds studied are summarized in Table 2. All the complexes display the chemically reversible ferrocene/ferricinium couple in $CH_2Cl_2$. The peak to peak separation are, however, significantly greater than the ideal value of 60 mV $s^{-1}$ for a fully reversible one-electron process. This may be due to a combination of uncompensated solution resistance and slightly slow electron-transfer kinetics. The half-wave potential of the ferrocenyl moieties for the aldehydes derivatives **2** and **3-(*E*,*E*)** are more anodic than that measured for ferrocene, meaning some degree of electron transfer between the iron center and the electron accepting aldehyde fragment. Similar anodic shift has also been reported for the nitrile derivative **4-(*E*)** [6]. However, the halfwave potential of the nitrile derivatives with longer conjugated chains are similar to that shown for ferrocene, compounds **5-(*E*,*Z*)** and **5-(*E*,*E*)** or even more lower, compound **6-(*E*,*E*,*Z*)** indicating that the oxidation is favored by the delocalization of the charge along the longer conjugated system of the ligand. This cathodic shift is larger for the waves in which the increase of the chain is achieved in a linear form (*E*-isomers).

Coordination of the neutral unit $M(CO)_5$, to the ferroceny nitrile ligands, does not have any significant effect on the redox potential of the ferrocene center. However, the coordination of this unit to the shorter chain ferrocenyl nitrile derivative **4-(*E*)** comes an increase of the redox potential for both Cr and W in agreement with an electron transfer in the direction $Fc \rightarrow M(CO)_5$. These results are in accordance to those reviewed by Heck et al. in which the redox shift depends in opposite directions of both the strength of the electron-accepting moiety and the length of the conjugated chain. [8]. The wave associated to the $M(CO)_5$/$[M(CO)_5]^+$ couple is reversible for the Cr case and irreversible for W, as seen in some other examples [6,7f]. The oxidation potential of the second step ascribed to the metal-carbonyl fragment depends on the metal present, this being higher for the W complexes compared to the Cr complexes.

## 3. Conclusions

In summary, a series of ferrocenyl-based oligomers have been obtained using Wittig and HEM reactions. These compounds proved to be good electronic messengers along the (up to 25 Å) conjugated chain, as seen from the data obtained from the cyclic voltammetry and electronic spectra. This gives an easy way that allows one to design suitable molecules for electron transfer studies and nonlinear optical studies. Through electronic spectroscopy and electrochemical studies we have shown that chain-lengthening and coordination of the compounds clearly influence the values of the reduction potential and the energies of the charge transfer bands in the electronic spectra.

## 4. Experimental

### 4.1. General details

All reactions were carried out under a nitrogen atmosphere using standard Schlenck techniques. Solvents for synthesis and electrochemical measurements were dried and degassed by standard methods before use. Chromatographic work was performed on silica gel 60 Å or neutral alumina columns.

Compound **2** was obtained according to literature methods [19]. Compounds **1**, $Cr(CO)_6$ and $W(CO)_6$ were purchased from Aldrich Chemicals and used without further purification.

NMR spectra were recorded on a Varian Innova 300 MHz and 500 MHz, using $CDCl_3$ as solvent unless otherwise stated. IR spectra were recorded on a Perkin–Elmer System 2000 FT-IR using NaCl pellets. Electronic absorption spectra were obtained on a UV-1603 Shimazdzu spectrophotometer. Elemental analyses were performed on a EA 1108 CHNS-O Carlo Erba Instruments. Cyclic voltammetry experiments were performed with a Echochemie pgstat 20 electrochemical analyzer. All measurements were carried out at room temperature (r.t.) with a conventional three-electrode configuration consisting of platinum working and auxiliary electrodes and a Ag/AgCl reference electrode containing aqueous 3 M KCl. The solvent in all experiments was $CH_2Cl_2$, which was obtained in HPLC grade. The supporting electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate, synthesized by metathesis of tetrabutylammonium bromide and $HPF_6$, recrystallized from ethanol and dried under vacuum. $E_{1/2}$ values were determined as $1/2(E_{p,a} + E_{p,c})$, where $E_{p,a}$ and $E_{p,c}$ are the anodic and cathodic peak potentials, respectively. All potential reported are not corrected for the junction potential. Electrospray mass spectra were recorded using a Micromass Quattro LC instrument, using $CH_3CN$ and/or $CH_3OH$ as the mobile phase solvent. The samples were added to give a mobile phase of approximate concentration 0.1 mM. This solution was injected into the spectrometer via a Rheodyne injector fitted a 10 µl sample loop, and nitrogen was employed as a drying and nebulising gas.

### *4.2. Synthesis of (E)-1,2-bis(p-phenylaldehyde)ethene*

To a solution of sodium hydride 60% dispersion in mineral oil (650 mg, 21 mmol) in THF (25 ml) it was added at r.t. 4-bromobenzyltriphenylphosphonium bromide (10 g, 20 mmol) in THF (100 ml). After stirring the reaction mixture for 1 h at r.t. was added *p*-bromebenzaldehyde (3.7 mg, 20 mmol) in THF (70 ml) and the resulting solution was stirred for 4 h. After removing the solvent under reduced pressure, the product was extracted with $CH_2Cl_2$–$H_2O$–$NH_4Cl$ and dried over $Na_2SO_4$. Purification by column chromatography on silica gel using hexane–AcOEt (9:1) as eluent afforded pure compound (*E*)-1,2-bis(*p*-phenylbromide)ethene. Yield: 70%. Then, to a solution of (*E*)-1,2-bis(*p*-phenylbromide)ethene (2.5 g, 7.4 mmol) in THF (75 ml) at −78°C BuLi (8.1 ml, 22.2 mmol) was added and the reaction mixture stirred at −78°C for 1 h and at 0°C for 2 h. After cooling again to −78°C *N*-formylmorpholine (3.2 ml, 41 mmol) was added and stirred at r.t. overnight. After removing the solvent under reduced pressure, the product was extracted with $CH_2Cl_2$–HCl (5%) and dried over $Na_2SO_4$. Purification by column chromatography on silica gel using hexane–AcOEt (9:1) as eluent afforded pure compound (*E*)-1,2-bis(*p*-phenylaldehyde)ethene. Yield: 75%.

$^1$H-NMR (300 MHz, $CDCl_3$): $\delta$ 9.99 (s, 2H, CHO); 7.87 (d, 4H, $^3J_{H-H} = 7.8$ Hz, $C_6H_4$); 7.66 (d, 4H, $^3J_{H-H} = 7.8$ Hz, $C_6H_4$); 7.24 (s, 2H, CH=CH). $^{13}$C-NMR (300 MHz, $CDCl_3$): $\delta$ 127.9, 130.8, 131.2 (10C, CH=CH and $C_6H_4$); 136.4, 142.9 (4Cq, $C_6H_4$); 192.0 (2C, CHO).

### *4.3. Synthesis of **3-(Z,E)** and **3-(E,E)***

#### *4.3.1. Using (E)-1,2-bis(p-phenylaldehyde)ethene*

To an ice-cold solution of (1-(triphenylphosphinomethyl)ferrocenyl]iodide (3 g, 5.1 mmol) in THF (50 ml) potassium *tert*-butoxide (850 mg, 7.6 mmol) was added and the resulting solution stirred for 30 min to form the ylide. The aldehyde (*E*)-1,2-bis(*p*-phenylaldehyde)ethene (2.5 ml, 20.4 mmol) was added and the resulting mixture stirred for ca. 24 h. After removing the solvent under reduced pressure, the product was extracted with $CH_2Cl_2$–$H_2O$–$NaHCO_3$ and purified by column chromatography on silica gel with hexane–$CH_2Cl_2$ (4:1). Recrystallization from $CH_2Cl_2$–hexane mixtures afforded pure compounds. Yields: 10% (for **3-(*Z*,*E*)**), 35% (**3-(*E*,*E*)**).

#### *4.3.2. Using the Horner–Emmons–Wadsworth reaction*

To an ice-cold solution of *p*-xylenebis(diethylphosphonate) (4.0 g, 10.6 mmol) in THF (75 ml) was added sodium hydride 60% dispersion in mineral oil (500 mg, 12.5 mmol) and the resulting solution stirred for 45 min at 0°C and 60 min at r.t. The aldehyde **1** (1.8 g, 8.4 mmol) was added at 0°C and the resulting solution stirred 5 h at r.t. Then, sodium hydride 60% dispersion in mineral oil (575 mg, 14.4 mmol) was added at 0°C and the reaction mixture stirred for 45 min. Finally, terephtaldehyde (1.5 g, 11.2 mmol) was added at 0°C and the reaction mixture stirred for 5 h at r.t. After removing the solvent under reduced pressure, the product was extracted with $CH_2Cl_2$–$H_2O$–$NaHCO_3$ and dried over $MgSO_4$. Purification by column chromatography on silica gel using hexane–$CH_2Cl_2$ (2:5) as eluent. Recrystallization from $CH_2Cl_2$–hexane mixtures afforded pure compound **3-(*E*,*E*)**. Yield: 40%.

$^1$H-NMR for compound **3-(*Z*,*E*)** (300 MHz, $CDCl_3$): $\delta$ 7.79 (d, 2H, $^3J_{H-H} = 8.4$ Hz, $C_6H_4$); 7.26 (d, 2H, $^3J_{H-H} = 8.4$ Hz, $C_6H_4$); 7.19 (d, 2H, $^3J_{H-H} = 8.4$ Hz, $C_6H_4$); 7.08 (d, 2H, $^3J_{H-H} = 8.1$ Hz, $C_6H_4$); 6.85 (d, 1H, $^3J_{H-H} = 12.2$ Hz, CH=CH); 6.77 (d, 1H, $^3J_{H-H} = 12.0$ Hz, CH=CH); 6.50 (d, 1H, $^3J_{H-H} = 16.0$ Hz, CH=CH); 6.34 (d, 1H, $^3J_{H-H} = 16.0$ Hz, CH=CH); 4.34 (s, 2H, $C_5H_4$); 4.25 (s, 2H, $C_5H_4$); 4.14 (s, 5H, $C_5H_5$). $^{13}$C-NMR (300 MHz, $CDCl_3$): $\delta$ 67.8, 69.8 (4C, $C_5H_4$); 69.9 (5C, $C_5H_5$); 83.4 (1Cq, $C_5H_4$); 125.3, 125.7, 127.8, 129.6, 130.5, 130.9, 131.7, 133.0 (12C, CH=CH and $C_6H_4$); 132.4, 135.3, 138.8, 144.0 (4Cq, $C_6H_4$); 190.1 (1C, CHO). IR ($cm^{-1}$): 1670 (vs), 1654 (s), 1405 (w), 1273(w). Anal. Calc. for compound **3-(*Z*,*E*)**, $C_{27}H_{22}FeN$ ($M_w = 418.32$): C, 77.50; H, 5.30. Found: C, 77.33; H, 5.53%.

$^1$H-NMR for compound **3-(*E*,*E*)** (300 MHz, $CDCl_3$): $\delta$ 7.88 (d, 2H, $^3J_{H-H} = 8.1$ Hz, $C_6H_4$); 7.67 (d, 2H, $^3J_{H-H} = 8.4$ Hz, $C_6H_4$); 7.53 (d, 2H, $^3J_{H-H} = 8.4$ Hz, $C_6H_4$); 7.46 (d, 2H, $^3J_{H-H} = 8.4$ Hz, $C_6H_4$); 7.27 (d, 1H, $^3J_{H-H} = 16.2$ Hz, CH=CH); 7.15 (d, 1H, $^3J_{H-H} = 16.2$ Hz, CH=CH); 6.94 (d, 1H, $^3J_{H-H} = 16.2$ Hz, CH=CH); 6.71 (d, 1H, $^3J_{H-H} = 15.9$ Hz, CH=CH); 4.49 (t, 2H, $^3J_{H-H} = 1.8$ Hz $C_5H_4$); 4.32 (s, 2H, $^3J_{H-H} = 1.8$ Hz $C_5H_4$); 4.16 (s, 5H, $C_5H_5$). $^{13}$C-NMR (300 MHz, $CDCl_3$): $\delta$ 67.7, 69.6 (4C, $C_5H_4$); 69.6 (5C, $C_5H_5$); 83.8 (1Cq, $C_5H_4$); 125.9, 126.7, 127.2, 127.4, 127.9, 128.4, 130.9, 132.5 (12C, CH=CH and $C_6H_4$); 135.5, 135.7, 138.8, 144.1 (4Cq, $C_6H_4$); 192.1 (1C, CO). IR ($cm^{-1}$): 1678 (vs), 1660 (s), 1452 (w), 1243(w), 1028(w), 811 (w). Anal. Calc. for compound **3-(*E*,*E*)**, $C_{27}H_{22}FeN$ ($M_w = 418.32$): C, 77.50; H, 5.30. Found: C, 77.10; H, 5.18%.

### 4.4. Synthesis of **5-(*E*,*Z*)**

To an ice-cold solution of *p*-[(triphenylphosphinomethyl)-benzonitrile] iodine (2.5 g, 5.5 mmol) in THF (75 ml) potassium *tert*-butoxide (539 mg, 4.8 mmol) was added and the resulting solution stirred for 30 min at 0°C and 45 min at r.t. The aldehyde **2-(*E*)** (1.6 g, 5.0 mmol) was added at 0°C and the resulting solution stirred overnight at r.t. After removing the solvent under reduced pressure, the product was extracted with $CH_2Cl_2$–$H_2O$–$NaHCO_3$ and dried over $MgSO_4$. The title compound was purified by column chromatography on silica gel using hexane–$CH_2Cl_2$ (1:1) as eluent. Recrystallization from $CH_2Cl_2$–hexane mixtures afforded pure compound **5-(*E*,*Z*)**. Yield: 45%. $^1$H-NMR (500 MHz, $CDCl_3$): $\delta$ 7.52 (d, 2H, $^3J_{H-H} = 8.5$ Hz, $C_6H_4$); 7.38 (d, 2H, $^3J_{H-H} = 8.0$ Hz, $C_6H_4$); 7.30 (d, 2H, $^3J_{H-H} = 7.5$ Hz, $C_6H_4$); 7.15 (d, 2H, $^3J_{H-H} = 8.5$ Hz, $C_6H_4$); 6.87 (d, 1H, $^3J_{H-H} = 16.0$, CH=CH); 6.65 (d, 1H, $^3J_{H-H} = 16.0$, CH=CH); 6.71 (d, 1H, $^3J_{H-H} = 12.0$, CH=CH); 6.55 (d, 1H, $^3J_{H-H} = 12.0$, CH=CH); 4.45 (t, 2H, $^3J_{H-H} = 1.5$ Hz, $C_5H_4$); 4.29 (t, 2H, $^3J_{H-H} = 1.5$ Hz, $C_5H_4$); 4.14 (s, 5H, $C_5H_5$). $^{13}$C-NMR (500 MHz, $CDCl_3$): $\delta$ 67.4, 69.6 (4C, $C_5H_4$); 69.6 (5C, $C_5H_5$); 83.3 (1Cq, $C_5H_4$); 110.1 (1C, CN); 125.6, 126.1, 126.7, 128.5, 129.0, 129.3, 133.1, 135.0 (12C, CH=CH and $C_6H_4$); 120.0, 135.1, 137.6, 140.1 (4Cq, $C_6H_4$). IR ($cm^{-1}$): 2207 (s), 1300 (w), 1117 (w). Anal. Calc. for compound **5-(*E*,*Z*)**, $C_{27}H_{21}FeN$ ($M_w = 415.32$): C, 78.10; H, 5.10; N, 3.37. Found: C, 78.12; H, 5.07; N, 3.39%. Electrospray MS. Cone 64 V. *m*/*z* (fragment): 415, $M^+$.

### 4.5. Synthesis of **5-(*E*,*E*)**

To an ice-cold solution of *p*-xylenebis(diethylphosphonate) (2.0 g, 5.3 mmol) in THF (75 ml) sodium hydride 60% dispersion in mineral oil (212 mg, 5.3 mmol) was added and the resulting solution stirred for 45 min at 0°C and 60 min at r.t. The aldehyde **1** (1.1 g, 5.0 mmol) was added at 0°C and the resulting solution stirred 5 h at r.t. Then, sodium hydride 60% dispersion in mineral oil (212 mg, 5.3 mmol) was added at 0°C and the mixture stirred for 45 min at r.t. Finally, 4-cyanobenzaldehyde (917.9 mg, 7.0 mmol) was added and the reaction mixture was stirred overnight at r.t. After removing the solvent under reduced pressure, the product was extracted with $CH_2Cl_2$–$H_2O$–$NaHCO_3$ and dried over $MgSO_4$. The title compound was purified by column chromatography on silica gel washing with hexane–$CH_2Cl_2$ (4:1) first and using hexane–$CH_2Cl_2$ (1:2) as eluent. Recrystallization from $CH_2Cl_2$–hexane mixtures afforded pure compound. Yield: 47%. $^1$H-NMR (500 MHz, $CDCl_3$): $\delta$ 7.64 (d, 2H, $^3J_{H-H} = 8.0$ Hz, $C_6H_4$); 7.59 (d, 2H, $^3J_{H-H} = 8.0$ Hz, $C_6H_4$); 7.50 (d, 2H, $^3J_{H-H} = 8.0$ Hz, $C_6H_4$); 7.45 (d, 2H, $^3J_{H-H} = 8.0$ Hz, $C_6H_4$); 7.21 (d, 1H, $^3J_{H-H} = 16.5$, CH=CH); 7.10 (d, 1H, $^3J_{H-H} = 16.0$, CH=CH); 6.94 (d, 1H, $^3J_{H-H} = 16.0$, CH=CH); 6.71 (d, 1H, $^3J_{H-H} = 16.0$, CH=CH); 4.49 (s, 2H, $C_5H_4$); 4.32 (s, 2H, $C_5H_4$); 4.16 (s, 5H, $C_5H_5$). $^{13}$C-NMR (500 MHz, $CDCl_3$): $\delta$ 67.4, 69.7 (4C, $C_5H_4$); 69.7 (5C, $C_5H_5$); 83.5 (1Cq, $C_5H_4$); 110.9 (1C, CN); 125.8, 126.4, 126.6, 127.2, 127.8, 128.4, 132.6, 132.9 (12C, CH=CH and $C_6H_4$); 119.5, 135.2, 138.9, 142.5 (4Cq, $C_6H_4$). IR ($cm^{-1}$): 2211 (s), 1590 (w), 967 (w). Anal. Calc. for compound **5-(*E*,*E*)**, $C_{27}H_{21}FeN$ ($M_w = 415.32$): C, 78.10; H, 5.10; N, 3.37. Found: C, 78.18; H, 5.00; N, 3.33%. Electrospray MS. Cone 84 V. *m*/*z* (fragment): 415, $M^+$.

### 4.6. Synthesis of **6-(*E*,*E*,*Z*)**

This compound was obtained following the general procedure described for compound **5-(*E*,*Z*)** and using the aldehyde **3-(*E*,*E*)** (2.1 g, 5.0 mmol) instead of **2-(*E*)**. The purification was made by column chromatography on silica gel using hexane–$CH_2Cl_2$ (2:1) as eluent. Yield: 25%. $^1$H-NMR (500 MHz, $CDCl_3$): $\delta$ 7.53–7.37 (m, 10H); 7.14 (d, 2H, $^3J_{H-H} = 8.5$ Hz, $C_6H_4$); 7.10 (d, 1H, $^3J_{H-H} = 16.5$, CH=CH); 7.06 (d, 1H, $^3J_{H-H} = 16.5$, CH=CH); 6.90 (d, 1H, $^3J_{H-H} = 16.5$, CH=CH); 6.70 (d, 1H, $^3J_{H-H} = 16.0$, CH=CH); 6.74 (d, 1H, $^3J_{H-H} = 12.0$, CH=CH); 6.58 (d, 1H, $^3J_{H-H} = 12.0$, CH=CH); 4.48 (s, 2H, $C_5H_4$); 4.30 (s, 2H, $C_5H_4$); 4.15 (s, 5H, $C_5H_5$). $^{13}$C-NMR (500 MHz, $CDCl_3$): $\delta$ 67.7, 69.9 (4C, $C_5H_4$); 69.9 (5C, $C_5H_5$); 84.0 (1Cq, $C_5H_4$); 111.2 (1C, CN); 126.3, 126.8, 127.1, 127.6, 128.0, 129.0, 129.7, 130.0, 130.2, 132.7, 133.6 (18C, CH=CH and $C_6H_4$); 119.6, 136.0, 136.3, 137.8, 138.2, 142.9 (6Cq, $C_6H_4$). IR (cm$^{-1}$): 2218 (s), 1248 (w). Anal. Calc. for compound **6-(*E*,*E*,*Z*)**, $C_{35}H_{27}F_6FeN$ ($M_w = 517.45$): C, 81.20; H, 5.26; N, 2.71. Found: C, 81.84; H, 5.63; N, 2.73%. Electrospray MS. Cone 77 V. $m/z$ (fragment): 517, M$^+$.

### *4.7. Syntheses of the compound* ***6-(E,E,E)***

This compound was obtained following the general procedure described for compound **5-(*E*,*E*)** and using the aldehyde **2-(*E*)** (1.6 g, 5.0 mmol) instead of **1**. Purification was made by column chromatography on silica gel using hexane–$CH_2Cl_2$ (1:4) as eluent. $^1$H-NMR (500 MHz, $CDCl_3$): $\delta$ 7.64 (d, 2H, $^3J_{H-H} = 8.0$ Hz, $C_6H_4$); 7.58 (d, 2H, $^3J_{H-H} = 8.0$ Hz, $C_6H_4$); 7.43 (d, 2H, $^3J_{H-H} = 8.0$ Hz, $C_6H_4$); 7.34 (d, 2H, $^3J_{H-H} = 8.0$ Hz, $C_6H_4$); 7.32 (d, 2H, $^3J_{H-H} = 8.5$ Hz, $C_6H_4$); 7.26 (d, 2H, $^3J_{H-H} = 8.0$ Hz, $C_6H_4$); 7.19 (d, 1H, $^3J_{H-H} = 16.0$, CH=CH); 7.08 (d, 1H, $^3J_{H-H} = 17.0$, CH=CH); 6.88 (d, 1H, $^3J_{H-H} = 16.0$, CH=CH); 6.68 (d, 1H, $^3J_{H-H} = 16.0$, CH=CH); 6.62 (d, 1H, $^3J_{H-H} = 17.0$, CH=CH); 6.59 (d, 1H, $^3J_{H-H} = 17.0$, CH=CH); 4.47 (s, 2H, $C_5H_4$); 4.30 (s, 2H, $C_5H_4$); 4.15 (s, 5H, $C_5H_5$).$^{13}$C-NMR (500 MHz, $CDCl_3$): $\delta$ 67.6, 70.0 (4C, $C_5H_4$); 69.9 (5C, $C_5H_5$); 83.7 (1Cq, $C_5H_4$); 111.2 (1C, CN); 126.3, 127.2, 127.4, 127.6, 127.9, 130.0, 130.2, 131.4, 132.8, 133.0, 133.8 (18C, CH=CH and $C_6H_4$); 119.5, 135.8, 136.3, 137.7, 138.7, 142.6 (6Cq, $C_6H_4$). IR (cm$^{-1}$): 2211 (s), 1308 (w). Electrospray MS. Cone 76 V. $m/z$ (fragment): 517, M$^+$.

### *4.8. Syntheses of the compounds* ***9-(E,E)*** *and* ***9-(E,Z)***

Chromium hexacarbonyl (176 mg, 0.8 mmol) was dissolved in THF (30 ml) and the resulting solution was irradiated using a Hg lamp for 1 h. Compound **5-(*E*,*Z*)** (150 mg, 0.4 mmol) or compound **5-(*E*,*E*)** (150 mg, 0.4 mmol) were added to the yellow solution formed upon irradiation in order to obtain compounds **9-(*E*,*Z*)** or **9-(*E*,*E*)**, respectively. The reaction mixture was stirred for another 30 min, filtered to remove the solid, and the solvent was removed under reduced pressure. Purification by column chromatography on neutral alumina with $CH_2Cl_2$–hexane (1:1) afforded pure compounds **9-(*E*,*Z*)** yield 40% or **9-(*E*,*E*)** yield 60%.

$^1$H-NMR for compound **9-(*E*,*Z*)** (300 MHz, $CDCl_3$): $\delta$ 7.54 (d, 2H, $^3J_{H-H} = 8.4$ Hz, $C_6H_4$); 7.39 (d, 2H, $^3J_{H-H} = 8.4$ Hz, $C_6H_4$); 7.32 (d, 2H, $^3J_{H-H} = 8.4$ Hz, $C_6H_4$); 7.17 (d, 2H, $^3J_{H-H} = 8.1$ Hz, $C_6H_4$); 6.72 (d, 1H, $^3J_{H-H} = 16.2$ Hz, CH=CH); 6.49 (d, 1H, $^3J_{H-H} = 16.2$ Hz, CH=CH); 6.55 (d, 1H, $^3J_{H-H} = 12.0$ Hz, CH=CH); 6.38 (d, 1H, $^3J_{H-H} = 12.0$ Hz, CH=CH); 4.47 (t, 2H, $^3J_{H-H} = 1.8$ Hz, $C_5H_4$); 4.31 (t, 2H, $^3J_{H-H} = 1.8$ Hz, $C_5H_4$); 4.15 (s, 5H, $C_5H_5$). $^{13}$C-NMR (300 MHz, $CDCl_3$): $\delta$ 67.9, 69.9 (4C, $C_5H_4$); 69.9 (5C, $C_5H_5$); 83.7 (1Cq, $C_5H_4$); 109.5 (1C, CN); 125.8, 126.4, 128.5, 129.8, 130.1, 130.4, 132.7, 132.9 (12C, CH=CH and $C_6H_4$); 129.1, 134.3, 138.3, 143.9 (4Cq, $C_6H_4$); 214.3 (4C, CO); 219.1 (1C, CO). IR (cm$^{-1}$): 2209 (s), 2074 (s), 1934 (vs). Anal. Calc. for compound **9-(*E*,*Z*)**, $C_{32}H_{21}FeNO_5Cr$ ($M_w = 607.37$): C, 63.30; H, 3.45; N, 2.31. Found: C, 61.7; H, 3.83; N, 2.29%.

$^1$H-NMR for compound **9-(*E*,*E*)** (500 MHz, $CDCl_3$): $\delta$ 7.64 (d, 2H, $^3J_{H-H} = 8.0$ Hz, $C_6H_4$); 7.57 (d, 2H, $^3J_{H-H} = 8.0$ Hz, $C_6H_4$); 7.51 (d, 2H, $^3J_{H-H} = 7.5$ Hz, $C_6H_4$); 7.46 (d, 2H, $^3J_{H-H} = 7.5$ Hz, $C_6H_4$); 7.24 (d, 1H, $^3J_{H-H} = 16.0$ Hz, CH=CH); 7.09 (d, 1H, $^3J_{H-H} = 16.5$ Hz, CH=CH); 6.95 (d, 1H, $^3J_{H-H} = 16.0$ Hz, CH=CH); 6.71 (d, 1H, $^3J_{H-H} = 15.5$ Hz, CH=CH); 4.49 (s, 2H, $C_5H_4$); 4.33 (s, 2H, $C_5H_4$); 4.16 (s, 5H, $C_5H_5$). $^{13}$C-NMR (300 MHz, $CDCl_3$): $\delta$ 67.7, 69.9 (4C, $C_5H_4$); 69.9 (5C, $C_5H_5$); 83.7 (1Cq, $C_5H_4$); 108.7 (1C, CN); 125.8, 126.1, 126.8, 127.3, 127.9, 132.7, 133.0, 133.3 (12C, CH=CH and $C_6H_4$); 128.8, 135.2, 139.1, 143.4 (4Cq, $C_6H_4$); 214.4 (4C, CO); 219.7 (1C, CO). IR (cm$^{-1}$): 2213 (s), 2074 (s), 1942 (vs). Anal. Calc. for compound **9-(*E*,*E*)**, $C_{32}H_{21}FeNO_5Cr$ ($M_w = 607.37$): C, 63.30; H, 3.45; N, 2.31. Found: C, 62.6; H, 3.50; N, 2.32%. Electrospray MS. Cone 27 V. $m/z$ (fragment): 607, M$^+$.

### *4.9. Syntheses of* ***10-(E,E)*** *and* ***10-(E,Z)***

These compounds were obtained using the general procedure described for **9** but using tungsten hexacarbonyl (281.5 mg, 0.8 mmol) instead of chromium hexacarbonyl. Yield for compound **10-(*E*,*Z*)** 40% and for compound **10-(*E*,*E*)** 70%.

$^1$H-NMR for compound **10-(*E*,*Z*)** (300 MHz, $CDCl_3$): $\delta$ 7.57 (d, 2H, $^3J_{H-H} = 8.7$ Hz, $C_6H_4$); 7.45 (d, 2H, $^3J_{H-H} = 8.1$ Hz, $C_6H_4$); 7.32 (d, 2H, $^3J_{H-H} = 8.1$ Hz, $C_6H_4$); 7.16 (d, 2H, $^3J_{H-H} = 8.1$ Hz, $C_6H_4$); 6.90 (d, 1H, $^3J_{H-H} = 16.2$ Hz, CH=CH); 6.66 (d, 1H, $^3J_{H-H} = 16.2$ Hz, CH=CH); 6.78 (d, 1H, $^3J_{H-H} = 12.0$ Hz, CH=CH); 6.58 (d, 1H, $^3J_{H-H} = 12.0$ Hz, CH=CH); 4.47 (t, 2H, $^3J_{H-H} = 1.8$ Hz, $C_5H_4$); 4.32 (t, 2H, $^3J_{H-H} = 1.8$ Hz, $C_5H_4$); 4.15 (s, 5H, $C_5H_5$). $^{13}$C-NMR (500 MHz, $CDCl_3$): $\delta$ 67.7, 69.9 (4C, $C_5H_4$); 69.9 (5C, $C_5H_5$); 83.7 (1Cq, $C_5H_4$); 108.7 (1C, CN); 125.9, 126.5, 128.2, 128.7, 129.9, 130.6, 133.3, 134.7 (12C, CH=CH and $C_6H_4$); 125.4, 134.9, 138.5, 144.6 (4Cq, $C_6H_4$); 197.0 (4C, CO); 200.7 (1C, CO). IR (cm$^{-1}$): 2073 (s), 1928 (vs). Anal. Calc. for compound **10-(*E*,*Z*)**, $C_{32}H_{21}FeNO_5W$ ($M_w = 739.23$): C, 52.00; H, 2.86; N, 1.89. Found: C, 52.03; H, 2.99; N, 1.91%.

$^1$H-NMR for compound **10-(*E*,*E*)** (500 MHz, $CDCl_3$): $\delta$ 7.68 (d, 2H, $^3J_{H-H} = 8.5$ Hz, $C_6H_4$); 7.65 (d, 2H, $^3J_{H-H} = 8.0$ Hz, $C_6H_4$); 7.52 (d, 2H, $^3J_{H-H} = 8.0$ Hz, $C_6H_4$); 7.47 (d, 2H, $^3J_{H-H} = 8.0$ Hz, $C_6H_4$); 7.27 (d, 1H, $^3J_{H-H} = 16.5$ Hz, CH=CH); 7.11 (d, 1H, $^3J_{H-H} = 16.5$ Hz, CH=CH); 6.95 (d, 1H, $^3J_{H-H} = 16.5$ Hz, CH=CH); 6.72 (d, 1H, $^3J_{H-H} = 16.0$ Hz, CH=CH); 4.49 (s, 2H, $C_5H_4$); 4.33 (s, 2H, $C_5H_4$); 4.16 (s, 5H, $C_5H_5$). $^{13}$C-NMR (300 MHz, $CDCl_3$): $\delta$ 67.7, 70.1 (4C, $C_5H_4$); 69.9 (5C, $C_5H_5$); 83.7 (1Cq, $C_5H_4$); 108.5 (1C, CN);

125.8, 126.1, 126.8, 127.6, 128.1, 128.8, 133.7, 133.8 (12C, CH=CH and $C_6H_4$); 127.9, 134.9, 139.3, 143.9 (4Cq, $C_6H_4$); 196.8 (4C, CO); 200.5 (1C, CO). IR (cm$^{-1}$): 2075 (s), 1976 (sh), 1922 (vs). Anal. Calc. for compound **10-(*E*,*E*)**, $C_{32}H_{21}FeNO_5W$ ($M_w = 739.23$): C, 52.00; H, 2.86; N, 1.89. Found: C, 53.24; H, 2.74; N, 1.81%. Electrospray MS. Cone 30 V. $m/z$ (fragment): 739, $M^+$.

## Acknowledgements

We thank the Generalitat Valenciana for the financial support of this work (GV-C-CN-09-071-96) and BANCAIXA (P1B98-07). We also thank the Generalitat Valenciana for a fellowship (J.M.).

## References

[1] For excellent recent reviews on ferrocene-based compounds, see: (a) A. Togni, T. Hayashi (Eds.), Ferrocenes: Homogeneous Catalysis – Organic Synthesis Materials – Science,VCH, Weinheim, Germany, 1995. (b) A. Togni, R.L. Halterman (Eds.), Metallocenes, Wiley-VCH, Weinheim, Germany, 1998. (c) N.J. Long, Metallocenes: A Introduction to Sandwich Complexes, Blackwell Science, Oxford, 1998.

[2] (a) J.P. Launay (Ed.), Molecular Electronics, Gauthier-Villars, Paris, 1991. (b) J.P. Launay, New J. Chem. 1 (1991) 97.

[3] (a) A.C. Ribou, J.P. Launay, K. Takashashi, T. Nihira, S. Tarutani, C.W. Spangler, Inorg. Chem. 33 (1994) 1325. (b) S. Woitellier, J.P. Launay, C.W. Spangler, Inorg. Chem. 28 (1989) 758.

[4] (a) A.C. Ribou, J.P. Launay, M.L. Sachtleben, H. Li, C.W. Spangler, Inorg. Chem. 35 (1996) 3735. (b) A. Hradsky, B. Bildstein, N. Schuler, H. Schottenberger, P. Jaitner, K.H. Ongania, K. Wurst, J.P. Launay, Organometallics 16 (1997) 392.

[5] (a) N.J.Long, A.J. Martin, R. Vilar, A.J.P. White, D.J. Williams, M. Younus, Organometallics 18 (1999) 4261. (b) S. Barlow, D. O'Hare, Chem. Rev. 97 (1997) 637. (c) Y. Zhu, O. Clot, O. Wolf, G.P.A. Yap, J. Am. Chem. Soc. 120 (1998) 1812. (d) O. Lavastre, L. Ollivier, P.H. Dixneuf, S. Sibandhit, Tetrahedron 51 (1996) 1683. (e) M.C.B. Colbert, J. Lewis, N.J. Long, P.R. Raithby, A.J.P. White, D.J. Williams, J. Chem. Soc. Dalton Trans. 99 (1997) 99. (f) O. Lavastre, M. Even, P.H. Dixneuf, A. Pacreau, J.P. Vairon, Organometallics 15 (1996) 1530.

[6] J. Mata, S. Uriel, E. Peris, R. Llusar, S. Houbrechts, A. Persoons, J. Organomet. Chem. 562 (1998) 197.

[7] (a) J.T. Lin, J.J. Wu, Ch. Sh. Li, Y.S. Wen, K.J. Lin, Organometallics 15 (1996) 5028. (b) A. Togni, G. Rins, Organometallics 12 (1993) 3368. (c) G. Doineau, G. Balavoine, T. Fillebeen-Khan, J.C. Clinet, J. Delaire, I. Ledoux, R. Loucif, G. Puccetti, J. Organomet. Chem. 421 (1991) 299. (d) I.S. Lee, S.S. Lee, Y.K. Chung, D. Kim, N.W. Song, Inorg. Chim. Acta 279 (1998) 243. (e) K.N. Jayaprakash, P.C. Ray, I. Matsuoka, M.M. Bhadbhade, V.G. Puranik, P.K. Das, H. Nishihara, A. Sarklar, Organometallics 18 (1999) 3851. (f) S. Sakanishi, D.A. Badrdwell, S. Couchman, J.C. Jeffrey, J.A. McCleverty, M.D. Ward, J. Organomet. Chem. 528 (1997) 35. (g) S. Barlow, H.E. Bunting, C. Ringham, J.C. Green, G.U. Bublitz, S.G. Boxer, J.W. Perry, S.R. Marder, J. Am. Chem. Soc. 121 (1999) 3715.

[8] J. Heck, S. Dabeck, T. Meyer-Fridrichsen, H. Wong, Coord. Chem. Rev. 190-192 (1999) 1217.

[9] (a) I.S. Lee, H. Seo, Y.K. Chung, Organometallics 18 (1999) 1091. (b) V. Cadierno, S. Conejero, M.P. Gamasa, J. Gimeno, I. Asselberghs, S. Houbrechts, K. Clays, A. Persoons, J. Borge, S. García-Granda, Organometallics 18 (1999) 582. (c) U. Behrens, H. Brussard, U. Hagenau, J. Heck, E. Hendrickx, J. Kornich, J.G.M. Van der Linden, A. Persoons, A.L. Spek, N. Veldman, B. Voss, H. Wong, Chem. Eur. J. 2 (1996) 98. (d) U. Hagenau, J. Heck, E. Hendrickx, A. Persoons, T. Schuld, H. Wong, Inorg. Chem. 35 (1996) 7863; 35 (1996) 7863. (e) R. Loucif-Saiba, J.A. Delaire, L. Bonazzola, G. Doisneau, G. Balavoine, T. Fillebeen-Khan, L. Ledoux, G. Puccetti, Chem. Phys. 167 (1992) 369. (f) S. Houbrechrts, K. Clays, A. Persoons, V. Cadierno, M.P. Gamasa, J. Gimeno, Organometallics 15 (1996) 5266.

[10] (a) G.G.A. Balavoine, J.C. Daran, G. Iftime, P.G. Lacroix, E. Manoury, A. Delaire, I.J. Maltey-Fanbton, K. Nakatani, Organometallics 18 (1999) 21. (b) M.M. Bhadbhade, A. Das, J.C. Jeffrey, J.A. McCleverty, J.A. Navas-Badiola, M.D. Ward, J. Chem. Soc. Dalton Trans. (1995) 2769. (c) K.R.J. Thomas, J.T. Lin, Y.S. Wen, J. Organomet. Chem. 575 (1999) 301. (d) H.E. Bunting, M.L.H. Green, S.R. Marder, M.E. Thompson, D. Bloor, P.V. Kolinsky, R.J. Jones, Polyhedron 11 (1992) 1489.

[11] (a) A. Houlton, J.R. Miller, J. Silver, N. Jassim, T.L. Axon, D. Bloor, G.H. Cross, Inorg. Chim. Acta 205 (1993) 67. (b) J.C. Calabrese, L. Cheng, J.C. Green, S.R. Marder, W. Tam, J. Am. Chem. Soc. 113 (1991) 7227. (c) A. Houlton, N. Jasim, R.M.G. Roberts, J. Silver, D. Cunningham, P. McArdle, T. Higgins, J. Chem. Soc. Dalton Trans. (1992) 2235.

[12] J.K. Lee, R.R. Schrock, D.R. Baigent, R.H. Friend, Macromolecules 28 (1995) 1966.

[13] (a) J. Boutagy, R. Thomas, Chem. Rev. 74 (1974) 87. (b) W.S. Jr. Wadsworth, Org. React. 25 (1997) 73. (c) B.E. Maryanoff, A.B. Reitz, Chem. Rev. 89 (1989) 863. (d) M.S. Paley, J.M. Harris, J. Org. Chem. 56 (1991) 368.

[14] (a) E. Peris, J.A. Mata, V.J. Moliner, J. Chem. Soc. Dalton Trans. (1999) 3898. (b) P.S. Bratterman, Metal Carbonyl Spectra, Academic Press, New York, 1975.

[15] (a) J.T. Lin, S.S. Sun, L. Lee, K.J. Lin, Y.F. Huang, Inorg. Chem. 34 (1995) 2323. (b) V. Alain, A. Fort, M. Barzoukas, C.T. Chen, M. Blanchard-Desce, S. Marder, J.W. Perry, Inorg. Chim. Acta 97 (1996) 43.

[16] (a) J.S. Schumm, D.L. Pearson, J.M. Tom, Angew. Chem. Int. Ed. Engl. 33 (1994) 1360. (b) R.P. Hsung, C.E.D. Chidsey, L.R. Sita, Organometallics 14 (1995) 4808.

[17] J.A. Mata, S. Uriel, R. Llusar, E.V. Peris, Organometallics 19 (2000) 3797.

[18] C. Runser, A. Fort, M. Barzoukas, C. Combellas, C. Suba, A.R. Thiebault Graff, J.P. Kintzinger, Chem. Phys. 193 (1995) 309.

[19] S. Toma, A. Gaplovsky, P. Elecko, Chem. Papers 39 (1985) 115.

*Organometallics* **2000,** *19,* 3797−3802

# Preparation, Properties, and Crystal Structure of New Conjugated Oligomers with a Pendant Ferrocenyl and an End-Capped Pyridine

José A. Mata,[†] Santiago Uriel,[†] Rosa Llusar,[‡] and Eduardo Peris*,[†]

*Departamento de Química Inorgánica y Orgánica and Departamento de Ciencias Experimentales, Universitat Jaume I, E-12080 Castellón, Spain*

*Received March 14, 2000*

New ferrocenyl−pyridine conjugated ligands have been obtained by several routes in which we combined Wittig and Horner−Emmons−Wadsworth (HEW) reactions, the latter showing better results both in yield and selectivity for the *E* isomers. Methylation of the ferrocenyl−pyridyl compounds yields cationic ferrocenyl−pyridinium compounds, whose electronic properties have been studied. The crystal structures of several of the described complexes are reported, showing a conjugated pathway of up to 27 Å.

## Introduction

Metal-containing long-chain conjugated systems have emerged as an important category of materials. The impetus for developing these materials is based on the premise that conjugated chains containing metals are expected to possess properties significantly different from those of conventional organic conjugated oligomers. Examples of these properties include electrical conductivity, magnetic behavior, thermal stability, nonlinear optical (NLO) effects, and even superconductivity. Because of the special electronic and chemical properties of ferrocene, many efforts have been directed toward the incorporation of a ferrocene moiety into a polymer,[1] in order to investigate novel properties such as those mentioned above. Besides, the preparation of ferrocenyl conjugated systems offers the possibility of electronic communication between terminal subunits, this being of particular interest in terms of modulating the electronic properties of the material.

Although many studies have been reported in which metallocene-based oligomers are obtained,[2] there is still a lack of systematic descriptions of synthesis leading to useful starting materials. All the reported metal-containing polymers have in common that they are only conducting if charge carriers can be delocalized over both the metal and the organic fragments.

We and others have used ferrocenyl-based conjugated ligands in order to obtain bimetallic and heterometallic push−pull complexes.[3] Most of the problems regarding the synthesis of such complexes are the difficulties found when trying to increase the conjugated chain in a multistep synthetic procedure. Bildstein et al. have published excellent results regarding the synthesis of ferrocenyl “molecular wires”, in which the metal-to-metal distance reaches up to 40 Å.[4] Since the electronic and optical responses of the materials seem to be highly influenced by the length of the conjugated chain connecting the electron-donating and electron-accepting termini of the molecule, we focused our efforts on obtaining long-chain oligomers with a pendant ferrocene fragment. We have recently reported the preparation and properties of new conjugated ferrocenyl-based ligands with an end-capped nitrile, with an estimated distance between the iron atom and the nitrile group of up to 23 Å.[5] These complexes showed interesting electronic and spectroscopic properties that made them good candidates for NLO measurements. However, the step-by-step syntheses of these compounds sometimes are tedious and complicated, and the yields are usually poor.

Some conjugated pyridines with end-capping ferrocene have been reported by Lin et al.,[3b] and their electronic and coordinative properties have been described. We now report, on the basis of our previous findings, several routes to the preparation of ferrocenyl conjugated compounds with an end-capped pyridine ring. These compounds are obtained by combined Wittig and/or Horner−Emmons−Wadsworth (HEW) reactions.

---

[†] Departamento de Química Inorgánica y Orgánica.

[‡] Departamento de Ciencias Experimentales.

[1] (a) Long, N. J. In *Metallocenes: An Introduction to Sandwich Complexes*; Blackwell Science: Oxford, U.K., 1998; Chapter 6. (b) Togni, A.; Hayashi, T. *Ferrocenes*; VCH: New York, 1995; Chapter 10.

[2] (a) Long, N. J.; Martin, A. J.; Vilar, R.; White, A. J. P.; Williams, D. J.; Younus, M. *Organometallics* **1999**, *18*, 4261. (b) Barlow, S.; O'Hare, D. *Chem. Rev.* **1997**, *97*, 637. (c) Zhu, Y.; Clot, O.; Wolf, O.; Yap, G. P. A. *J. Am. Chem. Soc.* **1998**, *120*, 1812. (d) Lavastre, O.; Ollivier, L.; Dixneuf, P. H.; Sibandhit, S. *Tetrahedron* **1996**, *51*, 1683. (e) Colbert, M. C. B.; Lewis, J.; Long, N. J.; Raithby, P. R.; White, A. J. P.; Williams, D. J. *J. Chem. Soc., Dalton Trans.* **1997**, 99. (f) Lavastre, O.; Even, M.; Dixneuf, P. H.; Pacreau, A.; Vairon, J.-P. *Organometallics* **1996**, *15*, 1530.

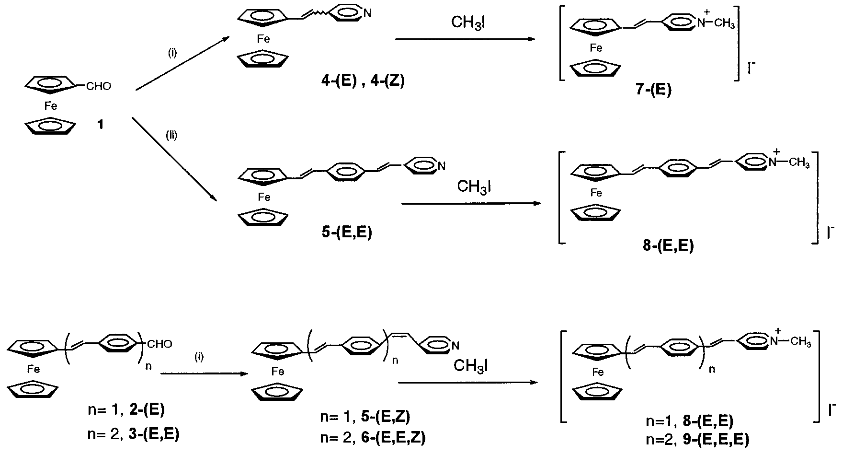
[3] (a) Mata, J.; Uriel, S.; Peris, E.; Llusar, R.; Houbrechts, S.; Persoons, A. *J. Organomet. Chem.* **1998**, *562*, 197. (b) Lin, J. T.; Wu, J. J.; Li, C.-S.; Wen, K.-J.; Lin, Y. S. *Organometallics* **1996**, *15*, 5028. (c) Togni, A.; Rins, G. *Organometallics* **1993**, *12*, 3368. (d) Doineau, G.; Balavoine, G.; Fillebeen-Khan, T.; Clinet, J. C.; Delaire, J.; Ledoux, I.; Loucif, R.; Puccetti, G. *J. Organomet. Chem.* **1991**, *421*, 299. (e) Lee, I. S.; Lee, S. S.; Chung, Y. K.; Kim, D.; Song, N. W. *Inorg. Chim. Acta* **1998**, *279*, 243. (f) Jayaprakash, K. N.; Ray, P. C.; Matsuoka, I.; Bhadbhade, M. M.; Puranik, V. G.; Das, P. K.; Nishihara, H.; Sarklar, A. *Organometallics* **1999**, *18*, 3851. (g) Sakanishi, S.; Badrdwell, D. A.; Couchman, S.; Jeffrey, J. C.; McCleverty, J. A.; Ward, M. D. *J. Organomet. Chem.* **1997**, *528*, 35. (h) Hsung, R. P.; Chidsey, C. E. D.; Sita, L. R. *Organometallics* **1995**, *14*, 4808. (i) Thomas, K. R. J.; Lin, J. T.; Lin, K. J. *Organometallics* **1999**, *18*, 5285.

[4] Hradsky, A.; Bildstein, B.; Schuler, N.; Schottenberger, H.; Jaitner, P.; Ongania, K.-H.; Wurst, K.; Launay, J.-P. *Organometallics* **1997**, *16*, 392.

[5] Mata, J. A.; Falomir, E.; Llusar, R.; Peris, E. *J. Organomet. Chem.*, submitted for publication.

10.1021/om000228v CCC: $19.00

**Scheme 1**[a]



[a] Legend: (i) $[Ph_3P^+CH_2py]Cl^-$/BuOK; (ii) (1) *p*-$(EtO)_2P(O)CH_2C_6H_4CH_2P(O)(OEt)_2$/NaH, (2) NaH (3) *p*-$OHCC_6H_4CHO$.

Methylation of the pyridyl compounds with $CH_3I$ leads to the corresponding *N*-methylpyridinium derivatives. These compounds are very interesting, since the related compound (*E*)-$[CpFe(\eta^5\text{-}C_5H_4)CH{=}CHC_5H_4N^+CH_3]I^-$ has proved to be one of the most effective NLO chromophores reported to date.[6] The electrochemistry of the compounds and the electronic spectra are also investigated.

## Results and Discussion

Most of the ferrocenyl-based oligomers reported to date have been obtained by conventional Wittig reactions, but these reactions usually lead to the formation of *E* and *Z* isomer mixtures.[4,7] Several authors have reported the advantages of the *E* type isomers over the *Z* type for effective electronic coupling.[7c,8] The lack of coplanarity between donor and acceptor groups in the *Z* isomers leads to a decrease in their electronic communication. In addition, the reduction of the through-space distance (in the *Z*-type) between donor and acceptor results in a lower change in dipole per unit charge separation. Since most of the time the aim of the synthetic procedures is to obtain linear oligomers with effective electronic coupling, the *E* isomers are the ones that are mainly pursued, but the separation of the mixtures of the *E* and *Z* isomers is not always easy. We recently reported the preparation and characterization of new ferrocenyl-based ligands with an end-capping nitrile. The syntheses of these complexes showed an increasing difficulty upon lengthening the connection between the ferrocenyl and nitrile units and, in the case of the longest ligand, this being (*E*,*E*,*E*)-$(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)CH{=}CH(C_6H_4)CH{=}CH(C_6H_4)CH{=}CH(C_6H_4)CN$, the synthetic procedure led to such a low yield that only spectroscopic characterization of the compound could be achieved.

In the synthesis of the new ferrocenyl compounds connected to a pyridyl unit by a conjugated chain, we used conventional Wittig and HEW reactions, as shown in Scheme 1. The ferrocenyl aldehydes **2**-(*E*) and **3**-(*E*,*E*) were obtained according to the methods reported in the literature.[3a,5] Compounds **4**-(*E*) and **4**-(*Z*) have already been reported, and their coordination capabilities and electronic properties have been extensively described.[3a,e] The olefination of the aldehyde **2**-(*E*) by conventional Wittig reaction leads to a mixture of *Z* and *E* isomers, the *E* isomer being the major one. However, the olefination of the aldehyde **3**-(*E*,*E*) leads selectively to the formation of the *Z* isomer **6**-(*E*,*E*,*Z*).

The use of *p*-xylenebis(diethylphosphonate) in the HEW reactions leads unambiguously to the formation of the *E* isomer **5**-(*E*,*E*). However, the same reaction did not lead to favorable results in the case of the olefination of the aldehyde **3**-(*E*,*E*) for reasons that we still do not know. In fact, we believe that this unfavorable result may be due to the low solubility of compound **6**-(*E*,*E*,*E*), which would be formed by this procedure. This low solubility, probably due to the rigid-row geometry derived from the all-*E* configuration, complicates the characterization of the compound (**6**-(*E*,*E*,*E*), if formed) by conventional methods and, furthermore, would explain the loss of the aforementioned compound during the extraction of compounds made in the last step of the olefination reaction. A similar effect was reported by Bildstein et al.[4] when elongating the conjugated chains of some permethylated ferrocenyl complexes. Conventional methods for the isomerization of the *Z* to *E* double bonds (such as using N-bromosuccinimide and

---

(6) Marder, S. R.; Perry, J. W.; Tiemann, B. G.; Schaefer, W. P. *Organometallics* **1991**, *10*, 1896.

(7) (a) Balavoine, G. G. A.; Daran, J.-C.; Iftime, G.; Lacroix, P. G.; Manoury, E.; Delaire, A.; Maltey-Fanbton, I. J.; Nakatani, K. *Organometallics* **1999**, *18*, 21. (b) Bhadbhade, M. M.; Das, A.; Jeffrey, J. C.; McCleverty, J. A.; Navas-Badiola, J. A.; Ward, M. D. *J. Chem. Soc., Dalton Trans.* **1995**, 2769. (c) Thomas, K. R. J.; Lin, J. T.; Wen, Y. S. *J. Organomet. Chem.* **1999**, *575*, 301. (d) Bunting, H. E.; Green, M. L. H.; Marder, S. R.; Thompson, M. E.; Bloor, D.; Kolinsky, P. V.; Jones, R. J. *Polyhedron* **1992**, *11*, 1489.

(8) (a) Houlton, A.; Miller, J. R.; Silver, J.; Jassim, N.; Axon, T. L.; Bloor, D.; Cross, G. H. *Inorg. Chim. Acta* **1993**, *205*, 67. (b) Calabrese, J. C.; Cheng, L.; Green, J. C.; Marder, S. R.; Tam, W. *J. Am. Chem. Soc.* **1991**, *113*, 7227.

$I_2$ or with basic alumina) were tried, but no conversion was observed.

Methylation of the pyridine complexes led to the corresponding cationic ferrocenyl−methyl−pyridinium salts. The corresponding methylated salts showed an *E* conformation even when the starting pyridyl complex corresponded to the *Z* conformation, this indicating that an isomerization process had occurred during the methylation. This effect was especially observed for the reactions of **5**-(*E*,*Z*) to **8**-(*E*,*E*) and **6**-(*E*,*E*,*Z*) to **9**-(*E*,*E*,*E*).

The electronic absorption spectra of the ferrocenylpyridyl compounds **4**−**6** and the ferrocenyl−methyl−pyridinium salts **7**−**9** were taken in different solvents. In general, the electronic absorption spectra of the neutral compounds show two prominent bands at 300 and 370 nm assigned to the $\pi-\pi^*$ transitions, according to the reported data in the literature for substituted ferrocenyl compounds.[3e,9] The weaker band at about 450 nm is assigned to a ferrocenyl-based MLCT band. Another weak band at higher wavelengths (about 500 nm), assigned to a d−d transition, is only discernible in some cases as a shoulder of the other MLCT band. The MLCT band is strongly influenced by the nature of the ancillary ligand, showing a hypsochromic shift upon lengthening the conjugated chain. This result is not surprising, since the more intense $\pi-\pi^*$ band also shows a clear dependence on the nature of the ligand, probably because elongating the conjugation length lowers the energy of the $\pi^*$ orbital. However, a nonlinear increase in $\lambda_{\max}$ is observed when going from **7**-(*E*) to **8**-(*E*,*E*) and **9**-(*E*,*E*,*E*), suggesting different net contributions for each additional phenylene−vinylene subunit. These data (although limited to only three points) suggest that an effective limit for conjugation may be envisaged, this being supported by the results reported by Hsung et al.,[3h] where again, a nonlinear shift of $\lambda_{\max}$ is observed upon elongating the chain of a series of ferrocenyl-based phenylethynyl oligomers. The methylation of the complexes to the cationic methylpyridinium compounds increases the $\lambda_{\max}$ values by 40 nm ($\pi-\pi^*$) and 60 nm (MLCT), confirming that the generation of the cationic site located on the nitrogen atom of the pyridine results in an inductive electron-accepting character.

Ferrocenyl−pyridine compounds show moderate solvatochromic behavior. This result gives us an idea of the dipole moments in the ground and in the excited states, which have a direct relation to hyperpolarizability. The $\pi-\pi^*$ charge-transfer band shifts upon changing the solvent from $CHCl_3$ to MeOH. These hypsochromic shifts mean that the dipole moment in the excited state is lower than in the ground state. In addition, this effect is greater in the cases where all the double bonds are *E*.

The electrochemical data for these compounds were measured using the same setup, except the ferrocenyl−methyl−pyridinium salts that were measured in acetone instead of $CH_2Cl_2$ because of the low solubility of these salts in the latter solvent. In all cases we observed the chemically reversible ferrocene/ferrocenium couple with $i_{p,a}/i_{p,c} \cong 1$. As previously reported, the half-wave potencial of the ferrocenyl moieties for the aldehyde derivatives **1**, **2**-(*E*), and **3**-(*E*,*E*) and for pyridyl derivatives **4**-(*E*) and **7**-(*E*) are more anodic than that measured for ferrocene, indicating some degree of electron transfer between the iron center and the electron-accepting fragment.[5] Elongation of the chain promotes a decrease in the redox potential, probably due to the stabilization of the positive charge of the oxidized species along the conjugated chain. This cathodic shift is particularly significant (ca. 200 mV) when going from compound **7**-(*E*) to **8**-(*E*,E) but is much less important when adding a new vinyl−phenylene subunit to obtain **9**-(*E*,*E*,*E*).

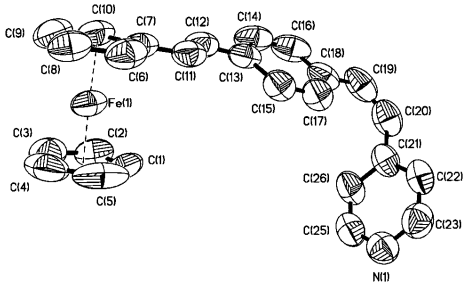


**Figure 1.** Molecular structure of **5**-(*E*,*Z*) showing the atom-numbering scheme. Hydrogen atoms are omitted for clarity. Distances: Fe−N(through space) = 9.74 Å and Fe−N(through bonds) = 18.74 Å. Torsion angle: Cp−Cp-(substituted) = 2.39(0.35)°. Thermal ellipsoids are drawn at 50% probability.

Humphrey has reported that stepwise elongation of the conjugated chain in ruthenium acetylides leads to an increase in the NLO responses of the material, but this increase is gradually reduced until an asymptotic or limit situation is achieved, in which elongation of the chain does not lead to any further increase in the NLO responses.[12] This observation, together with our results, suggests that conjugation may actually reach a limiting effective length.

The ORTEP drawings and selected bond distances and angles of the ferrocenyl−vinylene−phenylene−pyridyl and methylpyridinium (as $PF_6$ salts) complexes **5**-(*E*,*Z*), **8**-(*E*,*E*), and **9**-(*E*,*E*,*E*) are displayed in Figures 1−3, respectively. The molecular structure of compound **5**-(*E*,*E*) was also resolved, being very similar to that of **8**-(*E*,*E*) (all data are included in the Supporting Information). In all cases the two cyclopentadienyl rings are sligthly tilted (2.4−6.5°) with respect to each other. The iron distances to the substituted and unsubstituted rings and the C−C distances within these rings lie in the expected ranges. **5**-(*E*,*E*) presents a disorder in a 1:1 ratio with regard to the orientation of the trans olefinic moieties. This kind of disorder has been observed in similar molecules.[3g,4] Except for compound **5**-(*E*,*Z*), with a *Z* olefinic geometry, the phenylene and pyridyl rings are roughly coplanar with the substituted

---

(9) (a) Schumm, J. S.; Pearson, D. L.; Tom, J. M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1360. (b) Hsung, R. P.; Chidsey, C. E. D.; Sita, L. R. *Organometallics* **1995**, *14*, 4808.

(10) Blanchard-Desce, M.; Runser, C.; Fort, A.; Barzoukas, M.; Lehn, J. M.; Bloy, V.; Alain, V. *Chem. Phys.* **1995**, *199*, 253.

(11) (a) SAINT, version 5.0; Bruker Analytical X-ray Systems, Madison, WI. (b) Sheldrick, G. M. SADABS Empirical Absorption Program; University of Göttingen, Göttingen, Germany, 1996.

(12) Whittall, I. R.; McDonagh, A. M.; Humphrey, M. G.; Samoc, M. *Adv. Organomet. Chem.* **1999**, *43*, 349.

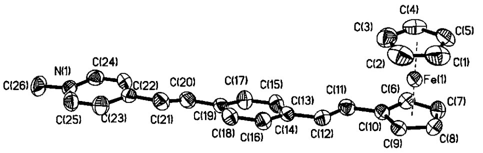


**Figure 2.** Molecular structure of **8**-(*E*,*E*) showing the atom-numbering scheme. Hydrogen atoms are omitted for clarity. The counteranion $PF_6$ has also been omitted for clarity. Distances: Fe−N(through space) = 14.41 Å and Fe−N(through bonds) = 18.77 Å. Torsion angles: Cp−Cp-(substituted) = 5.36(0.41)°; Ph−Cp(substituted) = 11.96-(0.43)°; Py−Cp(substituted) = 1.91(0.36)°. Thermal ellipsoids are drawn at 50% probability.

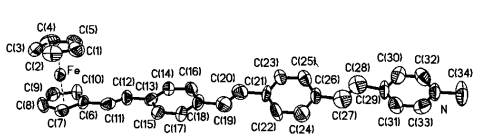


**Figure 3.** Molecular structure of **9**-(*E*,*E*,*E*) showing the atom-numbering scheme. Hydrogen atoms are omitted for clarity. The counteranion $PF_6$ has also been omitted for clarity. Distances: Fe−N(through space) = 21.03 Å and Fe−N(through bonds) = 27.13 Å. Torsion angles: Cp−Cp-(substituted) = 6.49(1.08)°; Ph1−Cp(substituted) = 8.73-(0.94)°; Ph2−Cp(substituted) = 29.66(0.74)°; Py−Cp-(substituted) = 18.77(0.88)°. Thermal ellipsoids are drawn at 50% probability.

Cp ring. In **5**-(*E*,*E*) the through-space Fe−N distance equals 14.8 Å and the sum of the bond lengths corresponding to the conjugation pathway from Fe to N is 18.88 Å. Almost the same through-space distance between the Fe and N atoms is observed for the methylated compound **8**-(*E*,*E*) (14.4 Å), indicating that no significant modification of the conjugated backbone has occurred upon methylation.

The pyridinium compound **9**-(*E*,*E*,*E*) shows Fe−N distances of 21.03 Å (through space) and 27.13 Å (through conjugated bonds). A clear loss of coplanarity with respect to the substituted Cp ring is observed, which may be due to solid-state effects, although a loss of coplanarity cannot be discarded in solution, regarding the electronic spectra and electrochemical behavior of the compound.

It is important to point out that both ferrocenyl−pyridinium complexes **8**-(*E*,*E*) and **9**-(*E*,*E*,*E*) show an eclipsed disposition of the Cp rings of the ferrocenyl fragment, in contrast to the staggered disposition in the pyridyl complexes **5**-(*E*,*E*) and **5**-(*E*,*Z*). This effect has already been described for other systems, and it has been pointed out that the electronic perturbation induced by oxidation of the iron atom or, in our case, the effective electronic communication from the positively charged pyridinium moiety and the ferrocenyl fragment may promote this change in the relative conformation of the two Cp rings in order to relieve steric strain induced by electronic perturbation.[1b]

## Experimental Section

NMR spectra were recorded on Varian Innova 300 and 500 MHz instruments, using $CDCl_3$ as solvent unless otherwise stated. IR spectra were recorded on a Perkin-Elmer System 2000 FT-IR using NaCl pellets. Electronic absorption spectra were obtained on a Shimadzu UV-1603 spectrophotometer. Cyclic voltammetry experiments were performed with a Echochemie PGSTAT 20 electrochemical analyzer. All measurements were carried out at room temperature with a conventional three-electrode configuration consisting of platinum working and auxiliary electrodes and a Ag/AgCl reference electrode containing aqueous 3 M KCl. The supporting electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate. All potential data reported are not corrected for the junction potential. Electrospray mass spectra were recorded using a Micromass Quattro LC instrument, using $CH_3CN$ and/or $CH_3OH$ as the mobile-phase solvent. The samples were added to give a mobile phase of approximate concentration 0.1 mM. Ferrocenealdehyde (**1**) was used as purchased (Aldrich); (*E*)-(ferrocenylethenyl)benzaldehyde (**2**-(*E*)) and (*E*,*E*)-(ferrocenylethenyl)-4-formylstilbene (**3**-(*E*,*E*)) were obtained according to literature methods[3a,5] or by the method reported by Bildstein et al. for the permethylated ferrocenyl derivatives.[4] **7**-(*E*) was also obtained by the method described in the literature.[6]

**Synthesis of {(*E*,*Z*)-($\eta^5$-$C_5H_5$)Fe($\eta^5$-$C_5H_4$)(CH=CH)($C_6H_4$)-(CH=CH)($C_5H_4N$)} (5-(*E*,*Z*)).** To an ice-cold solution of *p*-[(triphenylphosphino)methyl]pyridinium iodide (1 g, 2.6 mmol) in THF (75 mL) was added potassium *tert*-butoxide (393 mg, 3.5 mmol), and the resulting solution was stirred for 30 min at 0 °C and for 45 min at room temperature. The aldehyde **2**-(*E*) (758 mg, 2.4 mmol) was added at 0 °C, and the resulting solution was stirred overnight at room temperature. After the solvent was removed under reduced pressure, the product was extracted with $CH_2Cl_2/H_2O/NaHCO_3$ and dried over $MgSO_4$. The title compound was purified by column chromatography on silica gel, washing with hexane/$CH_2Cl_2$ (1:1) first and using $CH_2Cl_2$ as eluent. Recrystallization from $CH_2Cl_2$/hexane mixtures afforded pure **5**-(*E*,*Z*). Yield: 15%. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 8.51 (d, 2H, $^3J_{H-H} = 4.5$ Hz, $C_5H_4N$); 7.19 (m, 4H, $C_5H_4N$, $C_6H_4$); 7.32 (d, 2H, $^3J_{H-H} = 8.5$ Hz, $C_6H_4$); 6.89 (d, 1H, $^3J_{H-H} = 16.0$ Hz, CH=CH); 6.67 (d, 1H, $^3J_{H-H} = 16.0$ Hz, CH=CH); 6.75 (d, 1H, $^3J_{H-H} = 12.0$ Hz, CH=CH); 6.49 (d, 1H, $^3J_{H-H} = 12.0$ Hz, CH=CH); 4.47 (t, 2H, $^3J_{H-H} = 1.8$ Hz, $C_5H_4$); 4.30 (t, 2H, $^3J_{H-H} = 1.8$ Hz, $C_5H_4$); 4.15 (s, 5H, $C_5H_5$). $^{13}$C NMR (300 MHz, $CDCl_3$): $\delta$ 67.6, 69.8 (4C, $C_5H_4$); 69.9 (5C, $C_5H_5$); 83.7 (1$C_q$, $C_5H_4$); 124.1, 125.9, 126.3, 127.6, 128.3, 129.8, 134.3, 150.4 (12C, CH=CH and $C_6H_4$); 134.9, 138.1, 145.8 (3$C_q$, $C_6H_4$). IR (cm$^{-1}$): 1592 (w), 1411 (w), 815 (w). Anal. Calcd for **5**-(*E*,*Z*), $C_{25}H_{21}FeN$, $M_w = 391.30$: C, 76.7; H, 5.41; N, 3.58. Found: C, 75.9; H, 5.49; N, 3.48. Electrospray MS (*m/z* (fragment)): cone 70 V, 392 ($M^+$); cone 110 V, 392 ($M^+$), 326 ($M^+ -$ Cp).

**Synthesis of {(*E*,*E*)-($\eta^5$-$C_5H_5$)Fe($\eta^5$-$C_5H_4$)(CH=CH)($C_6H_4$)-(CH=CH)($C_5H_4N$)} (5-(*E*,*E*)).** To an ice-cold solution of *p*-xylenebis(diethylphosphonate) (2.0 g, 5.3 mmol) in THF (75 mL) was added sodium hydride (212 mg, 5.3 mmol), and the resulting solution was stirred for 45 min at 0 °C and 60 min at room temperature. The aldehyde **1** (1.1 g, 5.0 mmol) was added at 0 °C and the resulting solution was stirred for 5 h at room temperature. Then, sodium hydride (212 mg, 5.3 mmol) was added at 0 °C and the mixture stirred for 45 min at room temperature. Finally, 4-pyridinecarboxaldehyde (643 mg, 6.0 mmol) was added, and the reaction mixture was stirred overnight at room temperature. After the solvent was removed under reduced pressure, the product was extracted with $CH_2Cl_2/H_2O/NaHCO_3$ and dried over $MgSO_4$. The title compound was purified by column chromatography on silica gel, washing with hexane/$CH_2Cl_2$ (1:4) first and using $CH_2Cl_2$/acetone (1:1) as eluent. Recrystallization from $CH_2Cl_2$/hexane mixtures afforded pure compound **5**-(*E*,*E*). Yield: 35%. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 8.60 (s, 2H, $C_5H_4N$); 7.38 (d, 2H, $^3J_{H-H} = 4.0$ Hz, $C_5H_4N$); 7.51 (d, 2H, $^3J_{H-H} = 8.0$ Hz, $C_6H_4$); 7.45 (d, 2H, $^3J_{H-H} = 7.5$ Hz, $C_6H_4$); 7.29 (d, 1H, $^3J_{H-H} = 16.0$ Hz, CH=CH); 7.02 (d, 1H, $^3J_{H-H} = 16.0$ Hz, CH=CH); 6.94 (d, 1H, $^3J_{H-H}$

**Table 1. Crystallographic Data**

| | **5**-(*E*,*Z*) | **5**-(*E*,*E*) | **8**-(*E*,*E*)PF$_6$ | **9**-(*E*,*E*,*E*)PF$_6$ |
|---|---|---|---|---|
| empirical formula | $C_{25}H_{21}FeN$ | $C_{25}H_{21}FeN$ | $C_{26}H_{24}F_6FeNP$ | $C_{34}H_{30}FeNPF_6$ |
| fw | 391.28 | 391.28 | 551.28 | 653.41 |
| temp (K) | 293(2) | 293(2) | 293(2) | 293(2) |
| wavelength (Å) | 0.710 73 | 0.710 73 | 0.710 73 | 0.710 73 |
| cryst syst | monoclinic | monoclinic | monoclinic | monoclinic |
| space group | $P2_1/c$ | $P2_1$ | $P2_1/c$ | $P2_1/c$ |
| $a$ (Å) | 17.7672(18) | 6.2814(4) | 12.0649(9) | 14.1378(9) |
| $b$ (Å) | 10.0114(9) | 7.7253(6) | 15.7470(12) | 17.6844(11) |
| $c$ (Å) | 11.3680(11) | 19.3917(14) | 12.5267(9) | 12.6401(8) |
| α (deg) | 90 | 90 | 90 | 90 |
| $\beta$ (deg) | 106.027(2) | 95.394(2) | 95.150(2) | 110.748(2) |
| $\gamma$ (deg) | 90 | 90 | 90 | 90 |
| $V$ (Å$^3$) | 1943.5(3) | 936.83(12) | 2370.3(3) | 2955.3(3) |
| $Z$ | 4 | 4 | 4 | 4 |
| calcd density (Mg m$^{-3}$) | 1.337 | 1.387 | 1.545 | 1.469 |
| abs coeff (mm$^{-1}$) | 0.784 | 0.813 | 0.767 | 0.628 |
| no. of rflns collected | 7085 | 4833 | 11387 | 11043 |
| final $R$ indices ($I > 2\sigma(I)$) | R1 = 0.0318,<br>wR2 = 0.0835 | R1 = 0.0411,<br>wR2 = 0.0896 | R1 = 0.0548,<br>wR2 = 0.1356 | R1 = 0.1035,<br>wR2 = 0.3046 |
| goodness of fit on $F^2$ | 1.023 | 0.974 | 1.060 | 1.232 |

= 16.0, CH═CH); 6.71 (d, 1H, $^3J_{H-H}$ = 16.0 Hz, CH═CH); 4.49 (s, 2H, $C_5H_4$); 4.32 (s, 2H, $C_5H_4$); 4.16 (s, 5H, $C_5H_5$). $^{13}$C NMR (300 MHz, $CDCl_3$): $\delta$ 67.7, 69.7 (4C, $C_5H_4$); 69.7 (5C, $C_5H_5$); 83.7 (1C$_q$, $C_5H_4$); 121.4, 125.8, 125.9, 126.7, 128.0, 128.6, 133.5, 150.7 (12C, CH═CH and $C_6H_4$); 135.1, 139.1, 145.3 (3C$_q$, $C_6H_4$). IR (cm$^{-1}$): 1588 (w), 1409 (w), 821 (w). Anal. Calcd for **5**-(*E*,*E*), $C_{25}H_{21}FeN$, $M_w$ = 391.30: C, 76.7; H, 5.41; N, 3.58. Found: C, 76.5; H, 5.43; N, 3.56. Electrospray MS (*m*/*z* (fragment)): cone 70 V, 392.1 (M$^+$); cone 110 V, 392.1 (M$^+$), 326.1 (M$^+$ −Cp).

**Synthesis of {(*E*,*E*,*Z*)-($\eta^5$-$C_5H_5$)Fe($\eta^5$-$C_5H_4$)(CH═CH)-($C_6H_4$)(CH═CH)($C_6H_4$)(CH═CH)($C_5H_4N$)} (6-(*E*,*E*,*Z*)).** This compound was obtained by following the general procedure described for **5**-(*E*,*Z*) and using the aldehyde **3**-(*E*,*E*) (1 g, 2.4 mmol) instead of **2**-(*E*). The purification was carried out by column chromatography on silica gel using hexane/$CH_2Cl_2$ (1:1) as eluent. Yield: 25%. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 8.50 (s, 2H, $C_5H_4N$); 7.54−7.40 (m, 6H, $C_6H_4$); 7.25−7.16 (m, 4H, $C_6H_4$, $C_5H_4N$); 7.10 (d, 1H, $^3J_{H-H}$ = 16.5 Hz, CH═CH); 7.09 (d, 1H, $^3J_{H-H}$ = 16.5 Hz, CH═CH); 6.91 (d, 1H, $^3J_{H-H}$ = 16.2 Hz, CH═CH); 6.71 (d, 1H, $^3J_{H-H}$ = 15.9 Hz, CH═CH); 6.78 (d, 1H, $^3J_{H-H}$ = 12.3 Hz, CH═CH); 6.51 (d, 1H, $^3J_{H-H}$ = 12.3 Hz, CH═CH); 4.49 (s, 2H, $C_5H_4$); 4.31 (s, 2H, $C_5H_4$); 4.16 (s, 5H, $C_5H_5$). $^{13}$C NMR (300 MHz, $CDCl_3$): $\delta$ 67.6, 69.8 (4C, $C_5H_4$); 69.9 (5C, $C_5H_5$); 83.9 (1C$_q$, $C_5H_4$); 126.2, 126.7, 127.0, 127.2, 127.5, 127.8, 127.9, 128.0, 129.5, 129.8, 134.2, 150.4 (18C, CH═CH and $C_6H_4$); 135.8, 136.2, 137.7, 138.1, 145.7 (5C$_q$, $C_6H_4$). Anal. Calcd for **6**-(*E*,*E*,*Z*), $C_{33}H_{27}FeN$, $M_w$ = 493.43: C, 80.3; H, 5.52; N, 2.84. Found: C, 80.7; H, 5.61; N, 2.88. Electrospray MS (*m*/*z* (fragment)): cone 70 V, 494 (M$^+$), cone 110 V, 494 (M$^+$), 428 (M$^+$ − Cp).

**Synthesis of {(*E*,*E*)-($\eta^5$-$C_5H_5$)Fe($\eta^5$-$C_5H_4$)(CH═CH)($C_6H_4$)-(CH═CH)($C_5H_4N$)$CH_3$}$PF_6$ (8-(*E*,*E*)).** To a solution of **5**-(*E*,*Z*) or **5**-(*E*,*E*) (100 mg, 0.26 mmol) in toluene (45 mL) was added iodomethane (63.9 mg, 0.45 mmol), and the reaction mixture was warmed to 100 °C for 3 days. After the solution was cooled to room temperature, a wine red solid was obtained. This compound was purified by column chromatography on silica gel, washing with $CH_2Cl_2$ and eluting with acetone or a solution of $KPF_6$ in acetone. Recrystallization from acetone/hexane mixtures afforded the pure compound **8**-(*E*,*E*)PF$_6$. Yield: 85%. $^1$H NMR for **8**-(*E*,*E*)PF$_6$ (300 MHz, $d_6$-acetone): $\delta$ 8.81 (d, 2H, $^3J_{H-H}$ = 6.5 Hz, $C_5H_4N$); 8.37 (d, 2H, $^3J_{H-H}$ = 6.5 Hz, $C_5H_4N$); 7.90 (d, 2H, $^3J_{H-H}$ = 8.5 Hz, $C_6H_4$); 7.74 (d, 2H, $^3J_{H-H}$ = 8.0 Hz, $C_6H_4$); 8.14 (d, 1H, $^3J_{H-H}$ = 16.0 Hz, CH═CH); 7.66 (d, 1H, $^3J_{H-H}$ = 16.5 Hz, CH═CH); 7.32 (d, 1H, $^3J_{H-H}$ = 16.0 Hz, CH═CH); 6.99 (d, 1H, $^3J_{H-H}$ = 16.0 Hz, CH═CH); 4.73 (t, 2H, $^3J_{H-H}$ = 1.5 Hz, $C_5H_4$); 4.48 (t, 2H, $^3J_{H-H}$ = 1.5 Hz, $C_5H_4$); 4.29 (s, 5H, $C_5H_5$); 4.57 (s, 3H, $CH_3$). $^1$H NMR for **8**-(*E*,*E*)I (300 MHz, $d_6$-acetone): $\delta$ 8.49 (d, 2H, $^3J_{H-H}$ = 6.3 Hz, $C_5H_4N$); 8.05 (d, 2H, $^3J_{H-H}$ = 6.9 Hz, $C_5H_4N$); 7.75 (d, 2H, $^3J_{H-H}$ = 8.4 Hz, $C_6H_4$); 7.63 (d, 2H, $^3J_{H-H}$ = 9.3 Hz, $C_6H_4$); 7.86 (d, 1H, $^3J_{H-H}$ = 16.2 Hz, CH═CH); 7.40 (d, 1H, $^3J_{H-H}$ = 16.2 Hz, CH═CH); 7.18 (d, 1H, $^3J_{H-H}$ = 16.2 Hz, CH═CH); 6.88 (d, 1H, $^3J_{H-H}$ = 16.2 Hz, CH═CH); 4.62 (s, 2H, $C_5H_4$); 4.42 (s, 2H, $C_5H_4$); 4.22 (s, 5H, $C_5H_5$); 4.24 (s, 3H, $CH_3$). Anal. Calcd for **8**-(*E*,*E*), $C_{26}H_{24}FeNPF_6$, $M_w$ = 551.29: C, 56.6; H, 4.39; N, 2.54. Found: C, 57.1; H, 4.54; N, 2.48. Electrospray MS (*m*/*z* (fragment)): cone 70 V, 406 (M$^+$), cone 130 V, 406 (M$^+$), 391 (M$^+$ − $CH_3$).

**Synthesis of {(*E*,*E*,*E*)-($\eta^5$-$C_5H_5$)Fe($\eta^5$-$C_5H_4$)(CH═CH)-($C_6H_4$)(CH═CH)($C_6H_4$)(CH═CH)($C_5H_4N$)$CH_3$}$PF_6$(9-(*E*,*E*,*E*)).** This compound was obtained by following the general procedure described for **8**-(*E*,*E*) and using **6**-(*E*,*E*,*Z*) (100 mg, 0.20 mmol) instead of **5**-(*E*,*Z*) or **5**-(*E*,*E*). Yield: 80%. $^1$H NMR (300 MHz, $d_6$-acetone): $\delta$ 8.83 (d, 2H, $^3J_{H-H}$ = 6.3 Hz, $C_5H_4N$); 8.26 (d, 2H, $^3J_{H-H}$ = 6.3 Hz, $C_5H_4N$); 8.03 (d, 1H, $^3J_{H-H}$ = 16.2 Hz, CH═CH); 7.80 (d, 2H, $^3J_{H-H}$ = 8.1 Hz, $C_6H_4$); 7.73 (d, 2H, $^3J_{H-H}$ = 7.8 Hz, $C_6H_4$); 7.61 (d, 2H, $^3J_{H-H}$ = 8.4 Hz, $C_6H_4$); 7.52 (m, 3H, $C_6H_4$, CH═CH); 7.37 (d, 1H, $^3J_{H-H}$ = 16.5 Hz, CH═CH); 7.31 (d, 1H, $^3J_{H-H}$ = 16.5 Hz, CH═CH); 7.06 (d, 1H, $^3J_{H-H}$ = 16.2 Hz, CH═CH); 6.81 (d, 1H, $^3J_{H-H}$ = 16.2 Hz, CH═CH); 4.56 (s, 2H, $C_5H_4$); 4.31 (s, 2H, $C_5H_4$); 4.14 (s, 5H, $C_5H_5$); 4.46 (s, 3H, $CH_3$). Anal. Calcd for **9**-(*E*,*E*,*E*), $C_{34}H_{30}FeNPF_6$, $M_w$ = 653.43: C, 62.5; H, 4.63; N, 2.14. Found: C, 62.9; H, 4.57; N, 2.19. Electrospray MS (*m*/*z* (fragment)): cone 70 V, 508 (M$^+$); cone 160 V, 508 (M$^+$), 493 (M$^+$ − $CH_3$), 428 (M$^+$ − Cp − $CH_3$).

**X-ray Diffraction Studies.** Single crystals were grown by slow diffusion of hexane into concentrated $CH_2Cl_2$ solutions and mounted on a glass fiber in a random orientation. Data collection was performed at room temperature on a Siemens Smart CCD diffractometer using graphite-monochromated Mo Kα radiation ($\lambda$ = 0.710 73 Å) with a nominal crystal to detector distance of 4.0 cm. A hemisphere of data was collected on the basis of three $\omega$-scan runs (starting $\omega = -28°$) at values $\phi$ = 0, 90, and 180° with the detector at $2\theta = 28°$. At each of these runs, frames (606, 435, and 230, respectively) were collected at 0.3° intervals and 40 s per frame for **5**-(*E*,*Z*) and **5**-(*E*,*E*) and 60 s per frame for **8**-(*E*,*E*) and **9**-(*E*,*E*,E). Space group assignments are based on systematic absences, *E* statistics, and successful refinement of the structures. Structures were solved by direct methods with the aid of successive difference Fourier maps and were refined using the SHELXTL 5.1 software package. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned to ideal positions and refined using a riding model. Details of the data collection and cell dimensions are given in Table 1.

The diffraction frames were integrated using the SAINT package and corrected for absorption with SADABS.[12]

**Acknowledgment.** We thank the CICYT (PB98-1044) and BANCAIXA (P1B98-07) for financial support. We also thank the Generalitat Valenciana for a fellowship (J.A.M.).

**Supporting Information Available:** Tables of crystallographic data and structure refinement details, atomic coordinates with equivalent isotropic displacement parameters, anisotropic displacement parameters, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates with isotropic displacement parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

OM000228V

# Large second-order NLO properties of new conjugated oligomers with a pendant ferrocenyl and an end-capped pyridine

José A. Mata,[a] Eduardo Peris,*[a] Inge Asselberghs,[b] Roel Van Boxel[b] and André Persoons[b]

[a] *Departemento de Química Inorgánica y Orgánica, Universitat Jaume I, E-12080 Castellón, Spain*
[b] *Centre for Research on Molecular Electronics and Photonics, Laboratory of Chemical and Biological Dynamics, University of Leuven, Celestijnenlaan 200D, B-3001 Leuven, Belgium*

***Received (in Strasbourg, France) 29th March 2001, Accepted 17th May 2001***
***First published as an Advance Article on the web 4th July 2001***

The NLO properties of a series of vinylenephenylene complexes with a pendant ferrocene and an end-capping pyridine have been evaluated by the HRS method. The NLO responses ($\beta$) are clearly dependent on both the nature of the electron-accepting fragment and the length of the conjugated chain. As seen in some previous works on other organometallic complexes, the spectroscopic properties and electrochemical behavior of our compounds provide efficient diagnostics for the nonlinear optical behavior.

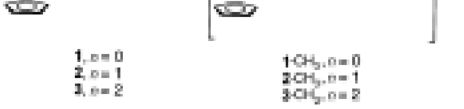
The increasing interest in the preparation of new chromophores suitable for electro-optical applications has initiated a search for new synthetic procedures leading to highly polarizable organometallic complexes. Many studies reporting nonlinear optical (NLO) properties of an enormous number of organic, inorganic and organometallic complexes have been published and some common structural features have been deduced. For example, in most cases the backbone of the chromophore consists of an electron-donating group connected to an electron-accepting group by a conjugated $\pi$-bridge. It is widely accepted that the NLO response of the chromophore is greatly increased upon chain lengthening of the conjugated $\pi$-bridge. On the other hand, it has been suggested that this increase gradually diminishes until an asymptotic or limiting situation is achieved, in which elongation of the chain does not lead to any further increase in the NLO response.[1]

We and other groups have used ferrocenyl-based conjugated ligands in order to obtain bimetallic and heterometallic push–pull complexes.[2,3] Most of the problems regarding the synthesis of such complexes are encountered when trying to extend the conjugated chain in a multi-step synthetic procedure. In fact, the list of such long conjugated metal-based ligands used in nonlinear optics is still short, despite their high NLO responses.[3e,4] Since the electronic and optical responses of these materials seem to be highly influenced by the length of the conjugated chain connecting the electron-donating and electron-accepting termini of the molecule, we focused our efforts on obtaining long-chain oligomers with a pendant ferrocene fragment. We have recently reported the preparation and electronic properties of new conjugated ferrocenyl-based ligands based on end-capped nitrile,[2b] pyridine[5a] and nitro[5b] fragments with distances between the iron atom and the heteroatom of up to 27 Å.[5a] These complexes show interesting electronic and spectroscopic properties that make them good candidates for NLO measurements. Among all the compounds that we have already reported, we opted for pendant pyridines for several reasons: (i) there is a precedent[6] as extremely high NLO responses have been reported in the compound *E*-[CpFe($\eta^5$-$C_5H_4$–CH=CH–$C_5H_4N^+$–$CH_3$)]$I^-$, (ii) the coordination properties of the pyridines allow us to obtain several complexes in which the electronic properties of the electron-accepting moiety can be fine-tuned, (iii) the lone pair on the nitrogen atom of the pyridine allows protonation and methylation, converting the compound into a cation with a positive charge located at the nitrogen atom and hence increasing the electron-accepting character of the ancillary ligand and (iv) the coplanarity observed in the molecular structures of the complexes,[5a] together with their redox and electronic properties, show efficient communication between the donor and acceptor groups.

Based on the above-mentioned premises, we have studied the NLO properties of several ferrocenyl oligomers with pyridine pendant groups and have shown their dependence upon chain lengthening, coordination capabilities and methylation of the pyridine groups. The NLO results obtained, together with the results obtained in our previous papers,[2a,5] allow us to confirm that spectroscopic and electrochemical data are an excellent way to qualitatively diagnosis NLO behavior.

## Results and discussion

We recently reported the synthesis and characterization of new ferrocenyl oligomers connected to a pyridyl group through a $\pi$-conjugated bridge[5a] of the type CpFe($\eta^5$-$C_5H_4\{CH{=}CHC_6H_4\}_nCH{=}CHC_5H_4N$) and [CpFe($\eta^5$-$C_5H_4$-$\{CH{=}CHC_6H_4\}_nCH{=}CHC_5H_4NCH_3$)]$PF_6$ ($n = 0$, 1 and 2, Scheme 1). The molecular structures of these compounds show an almost perfect coplanarity of all the aromatic rings for the all-*E* conformation. This coplanarity suggests that the conjugated bridge is an effective electronic pathway between the ferrocenyl fragment and the pyridyl ring. Although it is difficult to relate solid state structures to those in solution, in the case of highly conjugated systems such as ours, a large



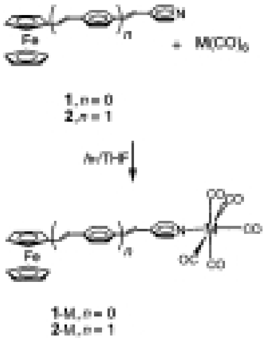
Scheme 1

contribution from the coplanar structure is expected as a consequence of the effective overlap of the carbon $p_z$ orbitals to form the extended π system. This is confirmed by other physical properties of the compounds such as the electrochemical behavior and the electronic spectra.[5a]

The coordination capabilities of pyridine allow us to obtain a series of group 6 carbonyl compounds, which have proved to act as a very effective electron-accepting moiety in several NLO chromophores. Scheme 2 shows the general procedure to obtain such complexes in the case of $n = 1$. The NLO behavior of some of these complexes ($n = 0$) was reported simultaneously to our results[2a] by Lee *et al.*,[3d] who found $\beta$ values significantly different from ours, probably because they used a different solvent for their measurements.

**Physical properties of the complexes**

Table 1 shows the physical properties of the complexes under study. Regarding the spectroscopic data, in general, the electronic absorption spectra of the neutral compounds show one prominent band between 300 and 400 nm assigned to the π–π* transitions, according to the reported data in the literature for monosubstituted ferrocenyl compounds.[3d,g,h,7a,e] The weaker band at about 450–500 nm is assigned to a ferrocenyl-based MLCT band. Another weak band at higher wavelengths (about 500 nm), assigned to a d–d transition, is only discernible in some cases as a shoulder on the other MLCT band and is not listed in Table 1. In our pyridine-based compounds, the MLCT band is strongly influenced by the nature of the ancillary ligand, showing a hypsochromic shift upon lengthening the conjugated chain. It has been shown that this band gains in oscillator strength as the electron-accepting capabilities of the ancillary ligand are increased.[3d] In our case, the hypsochromic shift is difficult to justify without any further theoretical MO studies, but it may imply that this band contributes less to $\beta$. We have observed the same tendency for –CN–M(CO)$_5$ (M = Cr, Mo, W) terminated complexes,[2b] and other examples have been reported in which this trend is also observed.[3e] In other similar complexes reported by us, terminated by –CN[2b] and –NO$_2$[5b], we observed a bathochromic shift; this is the opposite variation upon chain lengthening, so it is difficult to establish a clear correlation between band energy and effective conjugation when using the MLCT band. Much more informative are the data derived from the more intense π–π* band, which in all the cases that we[2b,5b] and others[3a,e,g,4e] have reported, shows a clear bathochromic shift when elongating the conjugation chain, which most likely lowers the energy of the π* orbital. In all the complexes that we have studied, the addition of one vinylenephenylene unit when going from $n = 1$ to $n = 2$ results in a positive shift of 40–60 nm. Addition of one vinylenephenylene unit when going from $n = 2$ to $n = 3$ (**2**-CH$_3$ to **3**-CH$_3$), results in a much smaller bathochromic shift (20 nm).



**Scheme 2**

Electrochemistry offers the possibility to examine trends in LUMO energies. Addition of an electron-accepting fragment to ferrocene results in an increase in the redox potential compared to that of unsubstituted ferrocene (445 mV). This effect is clearly seen in our pyridine complexes and agrees with the general trend observed for our other related oligomers.[2,5] The effect has been studied in detail by Barlow *et al.*[8] Chain lengthening promotes a decrease in the redox potential, due to the stabilization of the positive charge of the oxidized species along the conjugated chain. According to our present and previous results,[2,5] the addition of each vinylenephenylene unit leads to a linear decrease in the redox potential of 50–90 mV for all the py, –CN, –CHO, M(CO)$_5$ (M = Cr, Mo, W) and NO$_2$ terminated complexes. This correlation is not observed for the cationic complexes **1**-CH$_3$, **2**-CH$_3$ and **3**-CH$_3$, for which a very large decrease is observed when going from **1**-CH$_3$ to **2**-CH$_3$ (190 mV) and much smaller from **2**-CH$_3$ to **3**-CH$_3$ (30 mV). This, together with the spectroscopic results described before, suggests that for these complexes, conjugation may be reaching a limiting effective length.[1,5a]

**Nonlinear optical properties of the complexes**

All the compounds were analysed by the hyper-Rayleigh scattering (HRS) technique.[9] The hyperpolarizabilities $\beta$ for the pyridine-based compounds are reported in Table 1. The neutral compounds were measured in chloroform, while

**Table 1** Experimental nonlinear response and electrochemical properties of the conjugated oligomers with a pendant ferrocenyl and an end-capped pyridine

| | $\lambda_{max}$/nm | | | $E_{1/2}$/mV ($\Delta E_p$/mV) | |
|---|---|---|---|---|---|
| Compound | π–π* | MLCT | $\beta$[a] | Ferrocene-based | M-based |
| Ferroceno | | | | 445 (105)[b]<br>450 (100)[c] | |
| **1** | 315 | 468 | 21[d] | 500 (70)[b] | — |
| **2** | 386 | 459 | 146[d] | 440 (65)[b] | — |
| **1**-CH$_3$ | 359 | 553 | 40[c] | 595 (85)[c] | — |
| **2**-CH$_3$ | 399 | 503 | 197[c] | 385 (80)[c] | — |
| **3**-CH$_3$ | 417 | 462 | 458[c] | 355 (65)[c] | — |
| **1**-Cr[e] | 330 | 477 | 63[d] | 520 (75)[b] | 930 (75) |
| **1**-Mo[e] | 345 | 487 | 95[d] | 520 (85)[b] | 1110[f] |
| **1**-W[e] | 362 | 491 | 101[d] | 530 (75)[b] | 1125[f] |
| **2**-Cr | 374 | 462 | 369[d] | 440 (75)[b] | 906 (70) |
| **2**-Mo | 389 | 476 | 448[d] | 450 (75)[b] | 1120[f] |
| **2**-W | 405 | 487 | 535[d] | 440 (70)[b] | 1125[f] |

[a] All $\beta$ values are in $10^{-30}$ e.s.u. and the experimental error is $\pm 15\%$ of the value. [b] Measured in CH$_2$Cl$_2$. [c] Measured in Acetone. [d] Measured in CHCl$_3$. [e] Values are taken from ref. 2(*a*). [f] Irreversible peak, measured at 100 mV s$^{-1}$.

acetone was used for the ionic methylpyridinium compounds due to their low solubility in the former solvent. In order to compare the NLO results in the same solvent, we also tried to measure the neutral compounds **1**-M and **2**-M (M = Cr, Mo, W) in acetone, but found that they decomposed, probably because of replacement of the pyridine ligand by acetone in the metal carbonyl fragments. It has been shown that both the MLCT and the π–π* transitions lead to changes in $\beta$,[7] so a two-level model may not be appropriate when considering metallocenes, therefore we have not estimated the static hyperpolarizability values.

Some important structure–property relationships can be derived from the NLO values. As expected, the increase in the conjugation length by *n* multiple bonds results in a rather dramatic increase in the $\beta$ values, as seen for the methylpyridinium compounds **1**-$CH_3$, **2**-$CH_3$ and **3**-$CH_3$ (Table 1). A similar trend is observed for the neutral pyridyl complexes and from our previously reported data on $NO_2$ terminated complexes,[5b] although different increases in the $\beta$ values are observed for each vinylenephenylene unit added in the three series of complexes [–py, –py–$M(CO)_5$ and –$NO_2$]. The metal carbonyl moieties enhance the push–pull character as compared to the uncoordinated pyridyl species and even to the methylpyridinium compounds, as reflected by the higher $\beta$ values observed. However, this point has to be considered as a crude estimate, since first hyperpolarizabilities of organometallic push–pull complexes often exhibit a significant solvent polarity dependence, which enhances $\beta$ when the polarity increases. In this sense, it is observed that the stronger acceptor (cationic –$CH_3$ terminated complexes) does not lead to the largest nonlinearities. This observation is rather surprising, although it has been pointed out that long π-chain complexes with better acceptors do not necessarily show higher nonlinear responses.[7a]

According to theoretical calculations, a linear dependence between $\beta$ and the length of the conjugated chain must not be expected.[7b,c] In extended conjugated systems, the number of excited states contributing to $\beta$ increases upon chain lengthening.[7d] In an effort to quantify the NLO dependence on the chain length, Jayaprakash *et al.* found that the equation $\beta = an^b$ (where *a* and *b* are constants and *n* the number of double bonds),[3e] gives a good correlation for their compounds. Although a limited amount of data is available for our compounds, we compared the different *b* values obtained using the same relationship. We found that the exponent *b* is 2.27 for the methylpyridinium complexes and 2.8 for the uncoordinated neutral pyridyl ones. For the metal carbonyl substituted compounds, the values are 2.6, 2.2 and 2.4 for Cr, Mo and W, respectively. For the $NO_2$ terminated complexes reported in our previous paper,[5b] *b* is 3.6. These values are considerably higher than those obtained by Jayaprakash *et al.* in their study,[3e] showing that they seem to be highly dependent on the nature of the electron-accepting fragment, although in an apparently random manner.

In general, we have observed that electrochemical and spectroscopic studies give a good idea of the trends in NLO behavior in a series of similar complexes. In this sense, we always observe that while maintaining the same electron-accepting and electron-donating groups, chain lengthening promotes a bathochromic shift of the π–π* band, reduction of the redox potential, and an enhancement of the NLO response. These results confirm that the ferrocenyl derivatives follow the same qualitative design rules that have evolved for π-electron organic chromophores. However, our attempts to make quantitative predictions or good correlations between these physical properties and the hyperpolarizability values failed, probably due to the increase in the number of excited states contributing to $\beta$ upon chain lengthening, thus making simple models to interpret the experimental data (such as the two-level model) poor approximations.

## Experimental

### General details

NMR spectra were recorded on Varian Innova 300 and 500 MHz instruments, using $CDCl_3$ as solvent, unless otherwise stated. IR spectra were recorded on a Perkin Elmer System 2000 FT-IR from NaCl pellets. Electronic absorption spectra were obtained on a UV-1603 Shimadzu spectrophotometer. Cyclic voltammetry experiments were performed with a Echochemie pgstat 20 electrochemical analyzer. All measurements were carried out at room temperature with a conventional three-electrode configuration consisting of platinum working and auxiliary electrodes and an Ag/AgCl reference electrode containing aqueous 3 M KCl. The supporting electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate. All potential data reported are not corrected for the junction potential. Electrospray mass spectra were recorded using a Micromass Quattro LC instrument, using $CH_3CH_2OH$ as the mobile phase solvent. The samples were added to give a mobile phase of approximate concentration 0.1 mM. The synthesis and characterization of the ferrocenyl derivatives with a pendant end-capped pyridine is described in our previous works.[5]

### NLO measurements

Details of the HRS set-up have been discussed previously.[9] All measurements are performed in chloroform and the known hyperpolarizability of *para*-nitroaniline ($\beta = 23 \times 10^{-30}$ esu in chloroform)[10] is used as an external reference. The samples were passed through a 0.45 μm filter, since contaminated samples often produce spurious signals, and were checked for multiphoton fluorescence that can interfere with the HRS signal.[11] IR laser pulses generated with an injection seeded, Q-switched Nd : YAG laser (Quanta-Ray GCR-5, 1064 nm, 10 ns pulses, 10 Hz) were focused into a cylindrical cell containing the solution (7 ml). The fundamental intensity was altered by rotation of a half-wave plate placed between crossed polarizers, and measured with a photodiode. An efficient condenser system was used to collect the light scattered at the harmonic frequency (532 nm), which was detected by a photomultiplier. Discrimination of the second-harmonic light from the fundamental light was accomplished by a low-pass filter and a 532 nm interference filter. Actual values for the intensities were retrieved by using gated integrators. In all experiments the incident light was vertically polarized along the *z* axis.

### Synthesis

**[(*E*,*E*)-($\eta^5$-$C_5H_5$)Fe{$\eta^5$-$C_5H_4CH{=}CHC_6H_4CH{=}CHC_5H_4N$-$Cr(CO)_5$}], 2-Cr.** Chromium hexacarbonyl (220 mg, 1.0 mmol) was dissolved in dry THF (30 ml) and the resulting solution was irradiated using a Hg lamp for 1 h. Compound **2** (200 mg, 0.5 mmol) was added to the yellow solution formed upon irradiation in order to obtain **2**-Cr. The reaction mixture was stirred for another 30 min, filtered to remove the solid, and the solution was concentrated under reduced pressure. Purification by column chromatography on neutral alumina with $CH_2Cl_2$–hexane (1 : 1) afforded pure **2**-Cr. Yield 45%. $^1$H-NMR (500 MHz, $CDCl_3$): $\delta$ 8.48 (d, 2H, $^3J_{H-H} = 5.0$, $C_5H_4N$); 7.26 (m, 2H, $C_5H_4N$); 7.51 (d, 2H, $^3J_{H-H} = 8.0$, $C_6H_4$); 7.47 (d, 2H, $^3J_{H-H} = 8.0$, $C_6H_4$); 7.31 (d, 1H, $^3J_{H-H} = 16.5$, CH=CH); 6.95 (m, 1H, CH=CH); 6.95 (m, 1H, CH=CH); 6.71 (d, 1H, $^3J_{H-H} = 16.5$ Hz, CH=CH); 4.50 (s, 2H, $C_5H_4$); 4.36 (s, 2H, $C_5H_4$); 4.16 (s, 5H, $C_5H_5$). $^{13}$C-NMR (300 MHz, $CDCl_3$): $\delta$ 67.8, 70.1 (4C, $C_5H_4$); 70.0 (5C, $C_5H_5$); 83.5 (1Cq, $C_5H_4$); 122.1, 123.7, 125.6, 126.8, 128.4, 129.2, 135.8, 155.9 (12C, CH=CH and $C_6H_4$); 139.8, 146.7 (2Cq, $C_6H_4$); 214.9

(4Cq, CO); 221.3 (1Cq, CO). IR ($\nu$/cm$^{-1}$): 2071 (s), 1976 (s), 1885 (vs). Elem. anal. calc. for **2**-Cr: $C_{30}H_{21}FeCrNO_5$, $M_w$ = 583.34: C, 61.8; H, 3.63; N, 2.4; found: C, 61.6; H, 3.62; N, 2.4%. Electrospray MS (cone 70 V) *m*/*z* (fragment): 584 [M]$^+$; 392 [M − Cr(CO)$_5$].$^+$

**[(*E*,*E*)-($\eta^5$-$C_5H_5$)Fe{$\eta^5$-$C_5H_4CH{=}CHC_6H_4CH{=}CHC_5H_4N$-Mo(CO)$_5$}], 2-Mo.** This compound was obtained following the general procedure described for **2**-Cr using molybdenum hexacarbonyl (264 mg, 1.0 mmol) instead of chromium hexacarbonyl. Purification was achieved by column chromatography on neutral alumina using hexane–$CH_2Cl_2$ (3 : 2) as eluent. Yield: 55%. $^1$H-NMR (300 MHz, $CDCl_3$): $\delta$ 8.55 (d, 2H, $^3J_{H–H}$ = 6.3, $C_5H_4N$); 7.30 (m, 2H, $C_5H_4N$); 7.53 (d, 2H, $^3J_{H–H}$ = 7.0, $C_6H_4$); 7.47 (d, 2H, $^3J_{H–H}$ = 8.4, $C_6H_4$); 7.30 (m, 1H, CH=CH); 7.00 (m, 1H, CH=CH); 7.00 (m, 1H, CH=CH); 6.72 (d, 1H, $^3J_{H–H}$ = 15.9 Hz, CH=CH); 4.50 (s, 2H, $C_5H_4$); 4.34 (s, 2H, $C_5H_4$); 4.17 (s, 5H, $C_5H_5$). $^{13}$C-NMR (300 MHz, $CDCl_3$): $\delta$ 67.8, 70.1 (4C, $C_5H_4$); 70.0 (5C, $C_5H_5$); 83.5 (1Cq, $C_5H_4$); 122.1, 123.8, 125.7, 126.8, 128.4, 129.3, 136.0, 155.3 (12C, CH=CH and $C_6H_4$); 134.3, 139.9, 146.9 (3Cq, $C_6H_4$); 204.8 (4Cq, CO); 214.5 (1Cq, CO). IR ($\nu$/cm$^{-1}$): 2070 (s), 1977 (s), 1900 (vs). Elem. anal. calc. for **2**-Mo: $C_{30}H_{21}FeMoNO_5$, $M_w$ = 627.29: C, 57.4; H, 3.37; N, 2.2; found: C, 57.5; H, 3.36; N, 2.2%. Electrospray MS (cone 60 V) *m*/*z* (fragment): 628 [M]$^+$; 392 [M − Mo(CO)$_5$]$^+$

**[(*E*,*E*)-($\eta^5$-$C_5H_5$)Fe{$\eta^5$-$C_5H_4CH{=}CHC_6H_4CH{=}CHC_5H_4N$-W(CO)$_5$}], 2-W.** This compound was obtained following the general procedure described for **2**-Cr using tungsten hexacarbonyl (352 mg, 1.0 mmol) instead of chromium hexacarbonyl. The purification was achieved by column chromatography on neutral alumina using hexane–$CH_2Cl_2$ (1 : 1) as eluent. Yield: 60%. $^1$H-NMR (500 MHz, $CDCl_3$): $\delta$ 8.71 (d, 2H, $^3J_{H–H}$ = 6.5, $C_5H_4N$); 7.30 (d, 2H, $^3J_{H–H}$ = 6.5 $C_5H_4N$); 7.53 (d, 2H, $^3J_{H–H}$ = 8.0, $C_6H_4$); 7.48 (d, 2H, $^3J_{H–H}$ = 8.0, $C_6H_4$); 7.36 (d, 1H, $^3J_{H–H}$ = 16.0, CH=CH); 6.99 (m, 1H, CH=CH); 6.99 (m, 1H, CH=CH); 6.72 (d, 1H, $^3J_{H–H}$ = 16.0 Hz, CH=CH); 4.50 (s, 2H, $C_5H_4$); 4.34 (s, 2H, $C_5H_4$); 4.17 (s, 5H, $C_5H_5$). $^{13}$C-NMR (300 MHz, $CDCl_3$): $\delta$ 67.8, 70.1 (4C, $C_5H_4$); 70.0 (5C, $C_5H_5$); 83.5 (1Cq, $C_5H_4$); 122.7, 123.6, 125.6, 126.8, 128.5, 129.4, 136.3, 156.4 (12C, CH=CH and $C_6H_4$); 134.2, 140.0, 146.8 (3Cq, $C_6H_4$); 199.3 (4Cq, CO); 202.9 (1Cq, CO). IR ($\nu$/cm$^{-1}$): 2069 (s), 1969 (s), 1895 (vs). Elem. anal. calc. for **2**-W: $C_{30}H_{21}FeWNO_5$, $M_w$ = 715.21: C, 50.4; H, 2.96; N, 1.9; found: C, 50.2; H, 2.97; N, 1.9%. Electrospray MS, (cone 70 V) *m*/*z* (fragment): 715 [M]$^+$; 392 [M − W(CO)$_5$]$^+$.

## Acknowledgements

We thank the CICYT (PB98-1044) and BANCAIXA (P1B98-07) for financial support and the Generalitat Valenciana for a fellowship (J. M.). We also thank the University of Leuven (GOA 2000/03), the Belgian Government (IUAP IV/11) and the Fund for Scientific Research-Flanders (FWO-V G.0407.98 and G.0338.98).

## References

1 I. R. Whittall, A. M. McDonagh, M. G. Humphrey and M. Samoc, *Adv. Organomet. Chem.*, 1999, **43**, 349.

2 (*a*) J. A. Mata, S. Uriel, E. Peris, R. Llusar, S. Houbrechts and A. Persoons, *J. Organomet. Chem.*, 1998, **562**, 197; (*b*) J. A. Mata, E. Falomir, R. Llusar and E. Peris, *J. Organomet. Chem.*, 2000, **616**, 80.

3 (*a*) J. T. Lin, J. J. Wu, Ch.-Sh. Li, K.-J. Wen and Y. S. Lin, *Organometallics*, 1996, **15**, 5028; (*b*) A. Togni and G. Rins, *Organometallics*, 1993, **12**, 3368; (*c*) G. Doisneau, G. Balavoine, T. Fillebeen-Khan, J. C. Clinet, J. Delaire, I. Ledoux, R. Loucif and G. Puccetti, *J. Organomet. Chem.*, 1991, **421**, 299; (*d*) I. S. Lee, S. S. Lee, Y. K. Chung, D. Kim and N. W. Song, *Inorg. Chim. Acta*, 1998, **279**, 243; (*e*) K. N. Jayaprakash, P. C. Ray, I. Matsuoka, M. M. Bhadbhade, V. G. Puranik, P. K. Das, H. Nishihara and A. Sarklar, *Organometallics*, 1999, **18**, 3851; (*f*) S. Sakanishi, D. A. Bardwell, S. Couchman, J. C. Jeffrey, J. A. McCleverty and M. D. Ward, *J. Organomet. Chem.*, 1997, **528**, 35; (*g*) R. P. Hsung, C. E. D. Chidsey and L. R. Sita, *Organometallics*, 1995, **14**, 4808; (*h*) J. S. Schumm, D. L. Pearson and J. M. Tom, *Angew. Chem.*, *Int. Ed. Engl.*, 1994, **33**, 1360; (*i*) K. R. J. Thomas, J. T. Lin and K. J. Lin, *Organometallics*, 1999, **18**, 5285; (*j*) U. Behrens, H. Brussaard, U. Hagenau, J. Heck, E. Hendrickx, J. Körnich, J. G. M. van der Linden, A. Persoons, A. L. Spek, N. Veldman, B. Voss and H. Wong, *Chem. Eur. J.*, 1996, **2**, 29.

4 See, for example: (*a*) Th. J. J. Müller, A. Netz, M. Ansorge, E. Schmälzlin, Ch. Bräuchle and K. Meerholz, *Organometallics*, 1999, **18**, 1999; (*b*) I. R. Whittall, M. P. Cifuentes, M. G. Humphrey, B. Luther-Davies, M. Samoc, S. Houbrechts, A. Persoons, G. Heath and D. Bogsányi, *Organometallics*, 1997, **16**, 2631; (*c*) I. R. Whittall, M. G. Humphrey, A. Persoons and S. Houbrechts, *Organometallics*, 1996, **15**, 1935; (*d*) O. Briel, K. Sünkel, I. Krossing, H. Nöth, E. Schmälzlin, K. Meerholz, Ch. Bräuchle and W. Beck, *Eur. J. Inorg. Chem.*, 1999, 483; (*e*) V. Alain, A. Fort, M. Barzoukas, C.-T. Chen, M. Blanchard-Desce, S. R. Marder and J. W. Perry, *Inorg. Chim. Acta*, 1996, **242**, 43.

5 (*a*) J. A. Mata, S. Uriel, R. Llusar and E. Peris, *Organometallics*, 2000, **19**, 3797; (*b*) J. A. Mata, E. Peris, I. Asselberghs, R. V. Boxer and A. Persoons, *New J. Chem.*, 2001, **25**, 299.

6 S. R. Marder, J. W. Perry, B. G. Tiemann and W. P. Schaefer, *Organometallics*, 1991, **10**, 1896.

7 (*a*) S. R. Marder, G. B. Gorman, B. G. Tiemann and L. T. Cheng, *J. Am. Chem. Soc.*, 1993, **115**, 3006; (*b*) S. Ramasesha and P. K. Das, *Chem. Phys.*, 1990, **145**, 343; (*c*) I. D. L. Albert, P. K. Das and S. Ramasesha, *Chem. Phys. Lett.*, 1990, **168**, 454; (*d*) G. B. Gorman and S. R. Marder, *Proc. Natl. Acad. Sci. U.S.A.*, 1993, **90**, 11297; (*e*) J. C. Calabrese, L.-T. Cheng, J. C. Green, S. R. Marder and W. Tam, *J. Am. Chem. Soc.*, 1991, **113**, 7227.

8 S. Barlow, H. E. Bunting, C. Ringham, J. C. Green, G. U. Bublitz, S. G. Boxer, J. W. Perry and S. R. Marder, *J. Am. Chem. Soc.*, 1999, **121**, 3715.

9 K. Clays and A. Persoons, *Rev. Sci. Instrum.*, 1992, **63**, 3285.

10 M. Stähelin, D. M. Burland and J. E. Rice, *Chem. Phys. Lett.*, 1992, **191**, 245.

11 E. Hendrickx, C. Dehu, K. Clays, J. L. Brédas and A. Persoons, in *Polymers for Second-Order Nonlinear Optics*, ed. G. A. Lindsay and K. D. Singer, American Chemical Society, Washington, DC, 1995, pp. 82–94.

# Syntheses, characterization and second-order nonlinear optical behavior of new ferrocenyl-terminated phenylethenyl oligomers with a pendant nitro group

**Jose A. Mata,[a] Eduardo Peris,*[a] Inge Asselberghs,[b] Roel Van Boxel[b] and André Persoons*[b]**

[a] *Departamento de Química Inorgánica y Orgánica, Universitat Jaume I, E-12080 Castellón, Spain. E-mail: eperis@qio.uji.es*

[b] *Center for Research on Molecular Electronics and Photonics, Laboratory of Chemical and Biological Dynamics, University of Leuven, Celestijnenlaan 200D, B-3001 Leuven, Belgium*

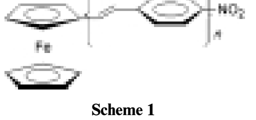
***Received (in Strasbourg, France) 8th September 2000, Accepted 3rd November 2000***
***First published as an Advance Article on the web 11th January 2001***

Several ferrocenyl-based oligomers with a pendant nitro group have been synthesized and characterized. The crystal structure of the compound ($E$)-($\eta^5$-$C_5H_5$)Fe($\eta^5$-$C_5H_4$)–CH=CHC$_6$H$_4$NO$_2$ is described, showing a centrosymmetric arrangement as already proposed by several authors. The nonlinear optical properties of the compounds have been measured by means of the HRS technique, showing the highest $\beta$ values for any organometallic compound with a pendant nitro group reported to date.

Since Green *et al.* published their results on the nonlinear optical (NLO) responses of the ferrocene complex ($Z$)-1-ferrocenyl-2-(4-nitrophenyl)ethylene[1] there has been a large number of publications reporting the NLO properties of ferrocene-based donor–acceptor materials.[2] On the other hand, metal-containing long-chain conjugated systems have emerged as an important category of materials due to the fact that these kinds of complexes are expected to posses properties significantly different from organic conjugated oligomers.[3]

Although a large number of reports have appeared in which metallocene-containing long-chain conjugated systems are presented,[3] systematic descriptions of syntheses leading to useful starting materials are still required. In fact, the bottleneck to the development of organometallic push-pull oligomers is the lack of a systematic approach to the synthesis of long-chain conjugated systems. All of the reported metal-containing polymers have a common feature: they are conducting only if charge carriers can be delocalized over both the metal and the organic fragments. In this regard, we have focused our attention on the fabrication, characterization and study of the physical properties of ferrocene-terminated conjugated oligomers connected to an electron-accepting fragment such as –CN, pyr, or metal carbonyl moieties of the type M(CO)$_n$ (M = Cr, Mo, W; $n$ = 3, 6).[4] High yielding routes to these complexes are nowadays one of the most challenging targets, since the step-by-step traditional synthetic procedures unambiguously lead to poor yields and complicated work-ups.

Herein we report a synthetic scheme that has been successfully employed to provide members of the ($C_5H_5$)Fe($C_5H_4$)–(CH=CHC$_6$H$_4$)$_n$–NO$_2$ series (Scheme 1) for $n$ = 1–3, in which the electron-accepting moiety is –NO$_2$. The redox and electronic behavior of the compounds are also described. The NLO behavior of these complexes is discussed, showing large hyperpolarizability values, which are highly influenced by the length of the ancillary ligand. We also describe the crystal structure of ($E$)-($\eta^5$-$C_5H_5$)Fe($\eta^5$-$C_5H_4$)–CH=CHC$_6$H$_4$NO$_2$, which has been the object of discussion by several authors,[5] although we have no knowledge of its report up to now.



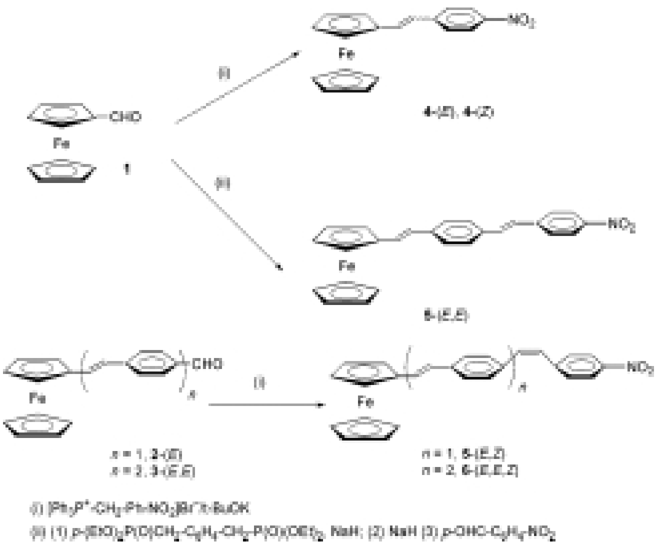
Scheme 1

## Results and discussion

### Synthesis and characterization of the ferrocenyl compounds

We recently reported the preparation and characterization of new ferrocenyl- based oligomers with an end-capped nitrile[4b] and pyridine.[4c] In these two previous reports, we described the advantages of using the Hornes–Emmons–Wadsworth (HEW) reactions over the conventional Wittig/Wittig–Horner processes, when the olefines pursued need to have the $E$ configuration. The HEW method has also been used by other authors in order to obtain all-$E$ configurations.[3h,3k] In fact, most of the authors have pointed out the advantages of the $E$-type isomers over the $Z$-type for effective electronic coupling.[5] The lack of coplanarity between donor and acceptor groups in the $Z$ isomers leads to a decrease in their electronic communication and hence these compounds are less suitable for potential applications.

In the synthesis of the new ferrocenyl compounds connected to a nitro group by a conjugated chain, we used conventional Wittig and HEW reactions, as shown in Scheme 2. The ferrocenyl aldehydes **2**-($E$) and **3**-($E$,$E$) were obtained according to the methods reported in the literature.[4,6] Compounds **4**-($E$) and **4**-($Z$) have already been reported and their electronic and nonlinear optical responses have been extensively discussed.[1,5b] The olefination of the aldehydes **2**-($E$) and **3**-($E$,$E$) by conventional Wittig reaction leads to the $Z$ isomers **5**-($E$,$Z$) and **6**-($E$,$E$,$Z$), respectively, and no evidence for formation of the all-$E$ isomers was shown by this method. In the beginning, we thought that this result could be due to the use of the base in the Wittig reaction ($t$-BuOK), since this is one of the main factors that contribute to the different $E$ : $Z$ ratios in this type of reaction. However, changing the base did not lead to any differences with respect to the formation of the all-$E$ complexes, and only yields in **5**-($E$,$Z$) and **6**-($E$,$E$,$Z$) were slightly influenced by the nature of the base.



Scheme 2

The use of *p*-xylenebis(diethylphosphonate) in the HEW reactions leads to the formation of *E* isomers, like **5**-(*E*,*E*). However, the same reaction did not lead to favorable results in the case of the olefination of the aldehyde **3**-(*E*,*E*). As we have previously reported for other long conjugated systems,[4c] we believe that this unfavorable result may be due to the low solubility of compound **6**-(*E*,*E*,*E*) that would be formed by this procedure. This low solubility, probably due to the rigid-rod geometry of the all-*E* configuration, complicates the characterization of the compound [**6**-(*E*,*E*,*E*), if formed] by conventional methods and, furthermore, would explain the loss of the aforementioned compound during the extraction of compounds made in the last step of the olefination reaction. A similar effect was reported by Hradsky *et al.*[6] when elongating the conjugated chains of some permethylated ferrocenyl complexes. On the other hand, this reaction did not show any tendency to give the *Z* isomer, so we believe that most of the reaction products were lost in the extraction and purification processes. Conventional methods for the isomerization of the *Z* to *E* double bonds (such as using *N*-bromosuccinimide and $I_2$ or with basic alumina) were tried, but no conversion was observed.

Characterization of the products was achieved by means of $^1$H and $^{13}$C NMR spectroscopy, elemental analysis and electrospray mass spectrometry. $^1$H NMR spectroscopy has been shown to be a very effective tool for unambiguously determining the geometrical configuration of olefinated compounds, since in all cases, the vinyl protons of the *E* isomers appear as doublets with coupling constants of 16 Hz, in accord with the expected *trans* stereochemistry. The *Z* isomers show lower coupling constants for the vinyl protons (*ca.* 12 Hz).

## Electronic spectra

The current interest in the uses of organic and organometallic materials in second-order nonlinear optics prompted us to determine the suitability of these ferrocenyl derivatives by carefully studying their electronic spectra. Solvatochromic effects can hint at the magnitude of the expected nonlinear optical properties, since they reflect the polarizability of a chromophore.[3h,7] The electronic absorption spectra of compounds **4**–**6** (Fig. 1) were taken in different solvents and the results are shown in Table 1. In general, the electronic absorption spectra of the ferrocenyl monosubstituted compounds show one prominent band between 310 and 390 nm assigned to π–π* transitions, according to the data in the literature.[4,5,8–10] Another weaker band at higher wavelengths (about 500 nm), is attributed to a metal-to-ligand charge-transfer (MLCT) band, and d–d transitions are only discernible in some cases as a shoulder on the MLCT band. This assignment is in accordance with the theoretical results reported by Barlow *et al.* (model III in ref. 10) and to other experimental results,[4,5,8,9] although we are aware that there is some controversy about this assignment.[11] In the compounds that we report here, only one band for the π–π* transitions is clearly observed, which is strongly influenced by the length of the conjugated ancillary ligand. The band is redshifted with increasing polyenic length only in the cases in which the addi-

**Table 1** Physical properties of **4**–**6**, including the electronic spectra (λ in nm), electrochemistry and NLO

| | MEOH | | THF | | $CHCl_3$ | | | |
|---|---|---|---|---|---|---|---|---|
| | MLCT | π–π* | MLCT | π–π* | MLCT | π–π* | Ferrocene-based $E_{1/2}$/mV ($\Delta E_p$/mV)[a] | β/$10^{-30}$ esu |
| **4**-(*E*) | 502 | 358 | 503 | 360 | 511 | 363 | 500 (100) | 31 (EFISH)[b] |
| **5**-(*E*,*Z*) | — | 313 | — | 315 | — | 315 | 450 (105) | 122 (HRS)[c] |
| **5**-(*E*,*E*) | — | 386 | — | 388 | — | 387 | 445 (100) | 403 (HRS)[c] |
| **6**-(*E*,*E*,*Z*) | — | 360 | — | 364 | — | 364 | 430 (75) | 209 (HRS)[c] |

[a] In $CH_2Cl_2$. Redox potential for ferrocene/ferricinium = 445 mV. [b] From ref. 5*a*. [c] Calculated with respect to $\beta$ of PNA in chloroform ($23 \times 10^{-30}$ esu). HRS at 1.06 nm. Values ±15%.

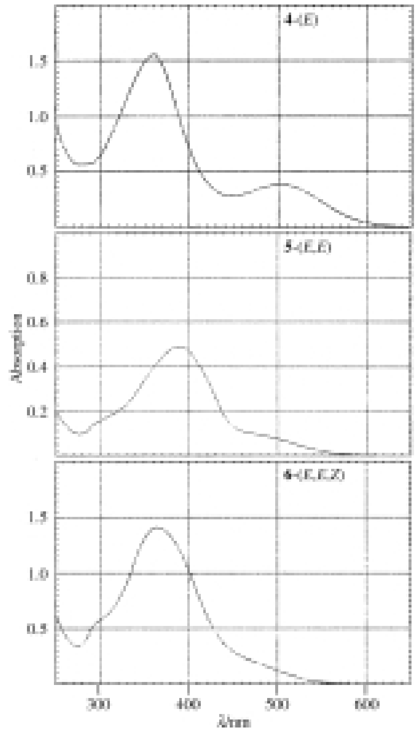


**Fig. 1** UV-Vis spectra of compounds **4**-(*E*), **5**-(*E*,*E*) and **6**-(*E*,*E*,*Z*) in THF.

tion of the phenylene-vinylene unit produces the E form [*i.e.* **4**-(*E*) compared to **5**-(*E*,*E*) and **5**-(*E*,*Z*) compared to **6**-(*E*,*E*,*Z*)]. This result indicates that elongation of the conjugation length lowers the energy of the $\pi^*$ orbital only if the elongation is produced in the *E* form. On going from the *E* to the *Z* isomers, we observe that there is a bathochromic shift of the $\pi$–$\pi^*$ transition, which indicates that for these oligomers the $\pi^*$ orbital is less stabilized in the *Z* isomer than in the *E* isomers, due to a partial loss of the conjugation as a consequence of the non-coplanar geometry imposed by the configuration of the complex. The lower energy band (MLCT) also shows a clear dependence on the chain length of the polyenic ligand, but the effect is of lower magnitude than for the higher energy band ($\pi$–$\pi^*$). As a result, the two bands overlap for long-chain ferrocene oligomers, preventing clear assignment of a frequency to the MLCT transitions.

In the literature, we have found that smaller shifts in $\lambda$ are observed for the high-energy band ($\pi$–$\pi^*$) upon changing the solvent,[9] whilst larger solvatochromic shifts are observed for the low-energy bands. The same effect is seen for the ferrocenylnitro compounds **4**–**6**. A small and negative solvatochromic effect is observed for the $\pi$–$\pi^*$ transition band (higher energy band) in all the compounds that we studied. This effect is also observed for the lower energy band (MLCT), this band being more solvatochromic than the higher energy one, although it could only be quantified for the **4**-(*E*) compound for the reasons discussed above.

### Cyclic voltammetry

The electrochemical data obtained for the compounds studied are summarized in Table 1. All the compounds were measured in $CH_2Cl_2$ using the same setup. In all cases we observed the chemically reversible ferrocene/ferricinium couple with $i_{pa}/i_{pc} \simeq 1$. Although the peak-to-peak separations in all compounds are greater than the ideal value for a fully reversible one-electron process, this difference ($E_{pc} - E_{pa}$) is similar to that measured for ferrocene under the conditions of the experiment. Electrochemistry offers the possibility to examine trends in LUMO energies. Addition of the electron-accepting fragment to ferrocene in compound **4** results in an increase of the redox potential compared to that of unsubstituted ferrocene (445 mV). This effect has been studied in detail by Barlow *et al.*[10] Chain lengthening promotes a decrease in the redox potential, probably due to the stabilization of the positive charge of the oxidized species along the conjugated chain. This effect is especially seen in the *E*-type complexes, for which the stabilization of the positive charge along the conjugated chain is favored as observed by the larger decrease of the redox potential than that observed for the Z-type oligomers.

### Crystal structure of 4-*E*

Since Green *et al.*[1] reported the NLO properties and crystal structure of (*Z*)-($\eta^5$-$C_5H_5$)Fe($\eta^5$-$C_5H_4$)–CH=$CHC_6H_4NO_2$ [**4**-(Z) in our nomenclature], many authors have referred to the crystal structure of its *trans* isomer (*E*)-($\eta^5$-$C_5H_5$)Fe($\eta^5$-$C_5H_4$)–CH=$CHC_6H_4NO_2$ [**4**-(*E*)] and to the fact that the low efficiency in the bulk NLO response is due to its centrosymmetry. However, we have not found in the literature nor in the CSD the reported crystal structure of **4**-(*E*). Compound **4**-(*E*) crystallizes in the centrosymmetric space group $P2_1/c$. As seen in Fig. 2, the molecule has an almost perfect coplanar arrangement between the ferrocenyl donor and the nitrophenyl moiety. The dimer pairs adopt a head-to-tail (DAAD) alignment in which the molecular dipoles mutually cancel each other out. Regarding this molecular structure and other *E*-type ferrocenyl structures reported to date,[6] it can be expect that the longer complex **5**-(*E*,*E*) and the hypothetical **6**-(*E*,*E*,*E*) will maintain an almost ideal coplanar arrangement, which facilitates the conjugation between the donor and acceptor groups and hence enhances the molecular nonlinear optical response of the compound.

### NLO properties

In chloroform (used for the NLO experiments) the UV-vis specta of compounds **4**–**6** show low absorption in the region where the second harmonic signal is generated (532 nm). The nonlinear response was studied by the hyper-Rayleigh scattering method. Table 1 shows the values of $\beta$ obtained. These values are higher than any other ferrocenyl compounds with a nitro pendant group reported to date.[5] Since two transitions are observed for the complexes and these two bands must have an effect on the nonlinear response of the compounds

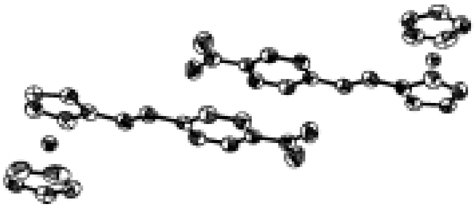


**Fig. 2** View of the dimer pairs of **4**-(*E*) showing a head-to-tail (DAAD) alignment. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Distances: Fe–$NO_2$ (through space) = 9.38 Å and Fe–$NO_2$ (through bonds) = 11.89 Å. Torsion angles: Cp–Cp(substituted) = 1.83(0.18); Cp(substituted)–Ph = 1.63(0.16)°.

under study, we are unable to calculate the static hyperpolarizability $\beta_0$ of these compounds, especially since the two bands overlap and a clear determination is thereby difficult. We have to assume that the values of $\beta$ that we obtained must be affected by resonance enhancement. We have found a good agreement between the linear and nonlinear spectroscopic data. The loss of conjugation between **5**-(*E*,*E*) and **5**-(*E*,*Z*) results in a spectacular decrease in hyperpolarizability, although this increase may be less in terms of static hyperpolarizability due to the high resonance enhancement of $\beta$ in **5**-(*E*,*E*), which shows some absorption at 532 nm. Extending the conjugation pathway by an *E*-elongation only results in a redshift of the CT band, which is clearly reflected in the observed $\beta$ values. These results are in good agreement with the spectroscopic and electrochemical data that we report in the present paper, confirming that these characterization methods constitute excellent diagnostics for the nonlinear optical behavior of molecular species.

## Experimental section

### General procedures

All reactions were carried out under a nitrogen atmosphere using standard Schlenck techniques. Solvents for synthesis and electrochemical measurements were dried and degassed by standard methods before use. Chromatographic work was performed on silica gel (60 Å) or neutral alumina columns.

NMR spectra were recorded on Varian Innova 300 MHz and 500 MHz instrument, using $CDCl_3$ as solvent unless otherwise stated. IR spectra were recorded on a Perkin Elmer System 2000 FT-IR using NaCl pellets. Electronic absorption spectra were obtained on a UV-1603 Shimazdzu spectrophotometer.

Cyclic voltammetry experiments were performed with an Echochemie pgstat 20 electrochemical analyzer. All measurements were carried out at room temperature with a conventional three-electrode configuration consisting of platinum working and auxiliary electrodes and an Ag/AgCl reference electrode containing aqueous 3 M KCl. The solvents used in all experiments were $CH_2Cl_2$ or acetone, which were obtained in HPLC grade. The supporting electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate, synthesized by metathesis of tetrabutylammonium bromide and $HPF_6$, recrystallized from ethanol and dried under vacuum. $E_{1/2}$ values were determined as $1/2(E_{p,a} + E_{p,c})$, where $E_{p,a}$ and $E_{p,c}$ are the anodic and cathodic peak potentials, respectively. All potentials reported are uncorrected for the junction potential.

Electrospray mass spectra were recorded using a Micromass Quattro LC instrument, using $CH_3CN$ and/or $CH_3OH$ as the mobile phase solvent. The samples were added to give a mobile phase concentration of approximately 0.1 mM. This solution was injected into the spectrometer *via* a Rheodyne injector fitted with a 10 μL sample loop, and nitrogen was employed as a drying and nebulizing gas.

Ferrocenealdehyde, **1**, was used as purchased (Aldrich), (*E*)-ferrocenylethenylbenzaldehyde, **2**-(*E*) and (*E*,*E*)-ferrocenylethenyl-4-formylstilbene, **3**-(*E*,*E*), were obtained according to literature methods[4] or by the method reported by Hradsky *et al.* for the permethylatedferrocenyl derivatives.[7]

### NLO measurements

Details of the HRS set-up have been discussed previously.[12,13] All measurements were performed in chloroform and the known hyperpolarizability of *para*-nitroaniline (PNA; $\beta = 23 \times 10^{-30}$ esu in chloroform[14]) was used as an external reference. The samples were passed through a 0.45 μm filter as contaminated samples often produce spurious signals, and were checked for multiphoton fluorescence that can interfere with the HRS signal.[15] IR-laser pulses generated with an injection seeded, Q-switched Nd:YAG laser (Quanta-Ray GCR-5, 1064 nm, 10 ns pulses, 10 Hz) were focused into a cylindrical cell containing the solution (7 ml). The fundamental intensity was altered by rotation of a half-wave plate placed between crossed polarizers, and measured with a photodiode. An efficient condenser system was used to collect the light scattered at the harmonic frequency (532 nm) that was detected by a photomultiplier. Discrimination of the second-harmonic light from the fundamental light was accomplished by a low-pass filter and a 532 nm interference filter. Actual values for the intensities were retrieved by using gated integrators. In all experiments the incident light was vertically polarized along the *z* axis.

### Syntheses

**(*E*,*Z*)-($\eta^5$-$C_5H_5$)Fe($\eta^5$-$C_5H_4$)[(CH=CH)($C_6H_4$)]$_2$$NO_2$, 5-(*E*,*Z*).** To an ice-cold solution of *p*-[(triphenylphosphinomethyl) nitrobenzene] bromide (956 g, 2.0 mmol) in THF (75 ml) potassium *tert*-butoxide (235 mg, 2.1 mmol) was added and the resulting solution stirred for 30 min at 0 °C and 45 min at room temperature. The aldehyde **2**-(*E*) (569 g, 1.8 mmol) was added at 0 °C and the resulting solution stirred overnight at room temperature. After removing the solvent under reduced pressure, the product was extracted with 50 ml $CH_2Cl_2$ and 50 ml of a saturated aqueous solution of $NaHCO_3$ and dried over $MgSO_4$. The title compound was purified by column chromatography on silica gel using hexane–$CH_2Cl_2$ (1:2) as eluent. Recrystallization from a 1 : 1 $CH_2Cl_2$–hexane mixture afforded pure compound **5**-(*E*,*Z*). Yield: 48%. $^1$H-NMR (300 MHz, $CDCl_3$): $\delta$ 8.12 (d, 2H, $^3J_{H–H} = 8.7$, $C_6H_4$); 7.45 (d, 2H, $^3J_{H–H} = 8.7$, $C_6H_4$); 7.33 (d, 2H, $^3J_{H–H} = 8.4$, $C_6H_4$); 7.18 (d, 2H, $^3J_{H–H} = 8.1$, $C_6H_4$); 6.90 (d, 1H, $^3J_{H–H} = 16.2$, CH=CH); 6.67 (d, 1H, $^3J_{H–H} = 15.9$, CH=CH); 6.78 (d, 1H, $^3J_{H–H} = 12.0$, CH=CH); 6.61 (d, 1H, $^3J_{H–H} = 12.3$, CH=CH); 4.48 (t, 2H, $^3J_{H–H} = 1.6$, $C_5H_4$); 4.31 (t, 2H, $^3J_{H–H} = 1.6$ Hz, $C_5H_4$); 4.15 (s, 5H, $C_5H_5$). $^{13}$C-NMR (300 MHz, $CDCl_3$): $\delta$ 67.6, 69.9 (9C, $C_5H_4$ and $C_5H_5$); 83.7 (1Cq, $C_5H_4$); 124.2, 125.8, 126.4, 128.1, 128.4, 129.8, 130.2, 134.2 (12C, CH=CH and $C_6H_4$); 134.9, 138.0, 145.0, 147.0 (4Cq, $C_6H_4$). Anal. calc. for $C_{26}H_{21}FeNO_2$, MW = 435.32: C, 71.7; H, 4.86; N, 3.22%. Found: C, 71.68; H, 5.02; N, 3.16%. ESI-MS (cone 85 V) *m*/*z* (fragment): 435 ($M^+$).

**(*E*,*E*)-($\eta^5$-$C_5H_5$)Fe($\eta^5$-$C_5H_4$)[(CH=CH)($C_6H_4$)]$_2$$NO_2$, 5-(*E*,*E*).** To an ice-cold solution of *p*-xylenebis(diethylphosphonate) (2 g, 5.3 mmol) in THF (75 ml) sodium hydride (240 mg, 6.0 mmol) was added and the resulting solution stirred for 45 min at 0 °C and 60 min at room temperature. The aldehyde **1** (800 mg, 3.7 mmol) was added at 0 °C and the resulting solution stirred 5 h at room temperature. Then, sodium hydride (280 mg, 7.0 mmol) was added at 0 °C and the mixture stirred for 45 min at room temperature. Finally, 4-nitrobenzaldehyde (565 mg, 3.7 mmol) was added and the reaction mixture was stirred overnight at room temperature. After removing the solvent under reduced pressure, the product was extracted with 50 ml $CH_2Cl_2$ and 50 ml of a saturated aqueous solution of $NaHCO_3$ and dried over $MgSO_4$. The title compound was purified by column chromatography on silica gel washing with hexane–$CH_2Cl_2$ (4 : 1) first and using hexane–$CH_2Cl_2$ (1 : 2) as eluent. Recrystallization from a 1 : 1 $CH_2Cl_2$–hexane mixture afforded pure compound **5**-(*E*,*E*). Yield: 62%. $^1$H–NMR (500 MHz, $CDCl_3$): $\delta$ 8.23 (d, 2H, $^3J_{H–H} = 8.0$, $C_6H_4$); 7.64 (d, 2H, $^3J_{H–H} = 8.5$, $C_6H_4$); 7.52 (d, 2H, $^3J_{H–H} = 7.5$, $C_6H_4$); 7.47 (d, 2H, $^3J_{H–H} = 8.0$, $C_6H_4$); 7.28 (d, 1H, $^3J_{H–H} = 16.0$, CH=CH); 7.15 (d, 1H, $^3J_{H–H} = 16.0$, CH=CH); 6.95 (d, 1H, $^3J_{H–H} = 16.5$, CH=CH); 6.72 (d, 1H, $^3J_{H–H} = 15.5$ Hz, CH=CH); 4.49 (s, 2H, $C_5H_4$); 4.33 (s, 2H, $C_5H_4$); 4.16 (s, 5H, $C_5H_5$). $^{13}$C-NMR (500

**Table 2** Crystallographic data

| | |
|---|---|
| Compound | **4**-(*E*) |
| Empirical formula | $C_{18}H_{15}FeNO_2$ |
| Formula weight | 333.16 |
| $T$/K | 293 |
| Crystal system | Monoclinic |
| Space group | $P2_1/c$ |
| $a$/Å | 18.0285(13) |
| $b$/Å | 10.6208(7) |
| $c$/Å | 7.7084(5) |
| $\beta$/° | 98.223(2) |
| $\mu$ Å$^3$ | 1460.81(17) |
| $Z$ | 4 |
| $\mu$ mm$^{-1}$ | 1.038 |
| Total reflect. | 9051 |
| Indep. Reflect. | 2990 |
| | $R$(int) = 0.0364 |
| Final $R_1$, $wR_2$ [$I > 2\sigma(I)$] | 0.0306, 0.0679 |
| $R_1$, $wR_2$ (all data) | 0.0591, 0.0833 |

MHz, $CDCl_3$): $\delta$ 67.7, 70.0 (9C, $C_5H_4$ and $C_5H_5$); 83.7 (1Cq, $C_5H_4$); 124.9, 126.0, 126.2, 126.9, 127.4, 128.1, 128.9, 133.8 (12C, CH=CH and $C_6H_4$); 135.3, 139.3, 144.8, 146.2 (4Cq, $C_6H_4$). Anal. calc. for $C_{26}H_{21}FeNO_2$, MW = 435.32: C, 71.7; H, 4.86; N, 3.22%. Found: C, 71.08; H, 5.00; N, 3.33%. ESI-MS (cone 84 V) $m/z$ (fragment): 435 ($M^+$).

**(*E*,*E*,*Z*)-($\eta^5$-$C_5H_5$)Fe($\eta^5$-$C_5H_4$)[(CH=CH)($C_6H_4$)]$_3$$NO_2$, 6-(*E*,*E*,*Z*).** This compound was obtained following the general procedure described for compound **5**-(*E*,*Z*) and using the aldehyde **3**-(*E*,*E*) (753 mg, 1.8 mmol) instead of **2**-(*E*). The purification was made by column chromatography on silica gel using hexane–$CH_2Cl_2$ (1 : 1) as eluent. Yield: 33%. $^1$H-NMR (500 MHz, $CDCl_3$): $\delta$ 8.11 (d, 2H, $^3J_{H-H} = 9.0$, $C_6H_4$); 7.49–7.7.40 (m, 8H, $C_6H_4$); 7.21 (d, 2H, $^3J_{H-H} = 7.5$, $C_6H_4$); 7.11 (d, 1H, $^3J_{H-H} = 16.5$, CH=CH); 7.07 (d, 1H, $^3J_{H-H} = 16.5$, CH=CH); 6.91 (d, 1H, $^3J_{H-H} = 16.0$, CH=CH); 6.71 (d, 1H, $^3J_{H-H} = 16.0$, CH=CH); 6.84 (d, 1H, $^3J_{H-H} = 12.5$, CH=CH); 6.63 (d, 1H, $^3J_{H-H} = 12.0$ Hz, CH=CH); 4.48 (s, 2H, $C_5H_4$); 4.31 (s, 2H, $C_5H_4$); 4.16 (s, 5H, $C_5H_5$). $^{13}$C-NMR $\delta$ (300 MHz, $CDCl_3$): 67.4, 69.9 (9C, $C_5H_4$ and $C_5H_5$); 84.0 (1Cq, $C_5H_4$); 124.4, 126.3, 126.8, 127.2, 127.6, 128.0, 128.6, 129.8, 129.9, 130.4, 134.23 (12C, CH=CH and $C_6H_4$); 135.9, 136.3, 137.9, 138.3, 145.0, 147.3 (6Cq, $C_6H_4$). Anal. calc. for $C_{34}H_{27}FeNO_2$, MW = 537.44: C, 76.0; H, 5.06; N, 2.61%. Found: C, 76.1; H, 5.60; N, 2.84%. ESI-MS. (cone 85 V) $m/z$ (fragment): 537 ($M^+$).

### X-Ray diffraction studies

Single crystals of **4**-(*E*) were grown by slow diffusion of hexane into concentrated $CH_2Cl_2$ solutions and mounted on a glass fiber in a random orientation. Data collection was performed at room temperature on a Siemens Smart CCD diffractometer using graphite monochromated Mo-K$\alpha$ radiation ($\lambda = 0.71073$ Å). The diffraction frames were integrated using the SAINT package and corrected for absorption with SADABS.[16] Space group assignments are based on systematic absences, $E$ statistics and successful refinement of the structures. Structures were solved by direct methods with the aid of successive difference Fourier maps and were refined using the SHELXTL 5.1 software package. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned to ideal positions and refined using a riding model. Some details of the data collection, cell dimensions and structure refinement are given in Table 2.

CCDC reference number 440/239. http://www.rsc.org/suppdata/nj/b0/b007411j/ for crystallographic files in .cif format.

## Acknowledgements

We thank the CICYT (PB98-1044) and BANCAIXA (P1B98-07) for financial support and the Generalitat Valenciana for a fellowship (J. A. M.). We would also like to thank the University of Leuven (GOA/2000/03), the Belgian government (IUAP-IV-11) and the Fund for Scientific Research, Flanders (FWO-V G.0407.98s) for financial support.

## References

1 M. L. H. Green, S. R. Marder, M. E. Thompson, J. A. Bandy. D. Bloor, P. V. Kolinsky and R. J. Jones, *Nature* (*London*), 1987, **26**, 360.

2 See, for example: (*a*) I. R. Whittall, A. M. McDonagh, M. G. Humphrey and M. Samoc, *Adv. Organomet. Chem.*, 1999, **43**, 349; (*b*) I. R. Whittall, A. M. McDonagh, M. G. Humphrey and M. Samoc, *Adv. Organomet. Chem.*, 1998, **42**, 291; (*c*) N. J. Long, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 21.

3 (*a*) N. J. Long, A. J. Martin, R. Vilar, A. J. P. White, D. J. Williams and M. Younus, *Organometallics*, 1999, **18**, 4261; (*b*) S. Barlow and D. O'Hare, *Chem. Rev.*, 1997, **97**, 637; (*c*) Y. Zhu, O. Clot, O. Wolf and G. P. A. Yap, *J. Am. Chem. Soc.*, 1998, **120**, 1812; (*d*) O. Lavastre, L. Ollivier, P. H. Dixneuf and S. Sibandhit, *Tetrahedron*, 1996, **51**, 1683; (*e*) M. C. B. Colbert, J. Lewis, N. J. Long, P. R. Raithby, A. J. P. White and D. J. Williams, *J. Chem. Soc., Dalton Trans.*, 1997, 99; (*f*) O. Lavastre, M. Even, P. H. Dixneuf, A. Pacreau and J. P. Vairon, *Organometallics*, 1996, **15**, 1530; (*g*) K. N. Jayaprakash, P. C. Ray, I. Matsuoka, M. M. Bhadbhade, V. G. Puranik, P. K. Das, H. Nishihara and A. Sarkar, *Organometallics*, 1999, **18**, 3851; (*h*) H. Wong, T. Meyer-Friedrischen, T. Farrell, Ch. Mecker and J. Heck, *Eur. J. Inorg. Chem.*, 2000, 631; (*i*) O. Briel, K. Sünkel, I. Krossing, H. Nöth, E. Schmälzlin, K. Meerholz, Ch. Bräuchle and W. Beck, *Eur. J. Inorg. Chem.*, 1999, 483; (*j*) J. Heck, S. Dabek, T. Meyer-Friedrichsen and H. Wong, *Coord. Chem. Rev.*, 1999, **190–192**, 1217; (*k*) Th. J. J Müller, A. Netz, M. Ansorge, E. Schmälzlin, Ch. Bräuchle and K. Meerholz, *Organometallics*, 1999, **18**, 1999; (*l*) I. R. Whittall, M. P. Cifuentes, M. G. Humphrey, B. Luther-Davies, M. Samoc, S. Houbrechts, A. Persoons, G. Heath and D. Bogsanyi, *Organometallics*, 1997, **16**, 2631; (*m*) I. R. Whittall, M. G. Humphrey, A. Persoons and S. Houbrechts, *Organometallics*, 1996, **15**, 1935; (*n*) Th. J. J. Müller, *J. Organomet. Chem.*, 1999, **578**, 95.

4 (*a*) J. A. Mata, S. Uriel, E. Peris, R. Llusar, S. Houbrechts and A. Persoons, *J. Organomet. Chem.*, 1998, **562**, 197; (*b*) J. A. Mata, E. Falomir, R. Llusar and E. Peris, *J. Organomet. Chem.*, 2000, **616**, 80; (*c*) J. A. Mata, S. Uriel, R. Llusar and E. Peris, *Organometallics*, 2000, **19**, 3797.

5 (*a*) J. C. Calabrese, L.-T. Cheng, J. C. Green, S. R. Marder and W. Tam, *J. Am. Chem. Soc.*, 1991, **113**, 7227; (*b*) H. E. Bunting, M. L. H. Green, S. R. Marder. M. E. Thompson, D. Bloor, P. V. Kolinsky and R. J. Jones, *Polyhedron*, 1992, **11**, 1489; (*c*) G. G. Balavoine, J.-C Daran, G. Iftime, P. G. Lacroix, E. Manoury, J. A. Delaire, I. Maltey-Fanton and K. Nakatani, *Organometallics*, 1999, **18**, 21; (*d*) H. Nock and H. Schottenberger, *J. Org. Chem.*, 1993, **58**, 7045; (*e*) A. Togni and G. Rihs, *Organometallics*, 1993, **12**, 3368.

6 A. Hradsky, B. Bildstein, N. Schuler, H. Schottenberger, P. Jaitner, K.-H. Ongania, K. Wurst and J.-P. Launay, *Organometallics*, 1997, **16**, 3926.

7 (*a*) M. S. Paley and J. M. Harris, *J. Org. Chem.*, 1989, **54**, 3774; (*b*) E. G. McRae, *J. Phys. Chem.*, 1957, **61**, 562.

8 A. Houlton, J. R. Miller, J. Silver, N. Jassim, T. L. Axon, D. Bloor and G. H. Cross, *Inorg. Chim. Acta*, 1993, **205**, 67.

9 (*a*) J. S. Schumm, D. L. Pearson and J. M. Tom, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1360; (*b*) R. P. Hsung, C. E. D. Chidsey and L. R. Sita, *Organometallics*, 1995, **14**, 4808; (*c*) A. Houlton, N. Jasim, R. M. G. Roberts, J. Silver, D. Cunningham, P. McArdle and T. Higgins, *J. Chem. Soc., Dalton Trans.*, 1992, 2235; (*d*) V. Alain, A. Fort, M. Barzoukas, C.-T. Chen, M. Blanchard–Desce, S. R. Marder and J. W. Perry, *Inorg. Chim. Acta*, 1996, **242**, 43.

10 S. Barlow, H. E. Bunting, C. Ringham, J. C. Green, G. U. Bublitz, S. G. Boxer, J. W. Perry and S. R. Marder, *J. Am. Chem. Soc.*, 1999, **121**, 3715.

11 D. R. Kanis, M. A. Ratner and T. J. Marks, *J. Am. Chem. Soc.*, 1992, **114**, 10338.

12 E. Hendrickx, K. Clays, A. Persoons, C. Dehu and J. L. Brédas, *J. Am. Chem. Soc.*, 1995, **117**, 3547.

13 S. Houbrechts, K. Clays, A. Persoons, Z. Pikramenou and J.-M. Lehn, *Chem. Phys. Lett.*, 1996, **258**, 485.
14 K. Clays and A. Persoons, *Rev. Sci. Instrum.*, 1992, **63**, 3285.
15 E. Hendrickx, C. Dehu, K. Clays, J. L. Brédas and A. Persoons, in *Polymers for Second-Order Nonlinear Optics*, ed. G. A. Lindsay and K. D. Singer, American Chemical Society, Washington, DC, 1995, pp. 82–94.
16 (*a*) SAINT, v. 5.0, Bruker Analytical X-Ray Systems, Madison, WI; (*b*) G. M. Sheldrick, SADABS, Empirical Absorption Program, University of Göttingen, Göttingen, Germany, 1996.

PERGAMON

Polyhedron 20 (2001) 2083–2088

POLYHEDRON
www.elsevier.com/locate/poly

# Preparation and properties of new ferrocenyl heterobimetallic complexes with counterion dependent NLO responses

José A. Mata [a], Eduardo Peris [a,*], Santiago Uriel [b], Rosa Llusar [b], Inge Asselberghs [c], André Persoons [c,*]

[a] *Departamento de Química Inorgánica y Orgánica, Universitat Jaume I, E-12080 Castellon, Spain*
[b] *Departamento de Ciencias Experimentales, Universitat Jaume I, E-12080 Castellon, Spain*
[c] *Laboratory of Chemical and Biological Dynamics, Centre for Research on Molecular Electronics and Photonics, University of Leuven, Celestijnenlaan 200D, B-3001 Leuven, Belgium*

Received 8 December 2000; accepted 12 April 2001

**Abstract**

New ferrocenyl-based bimetallic cationic compounds of the type of ($E$)-[CpFe($\eta^5$-$C_5H_4$)–(CH=CH)–($C_6H_4$)–CN–RuCp($PPh_3$)$_2$]X (X = $PF_6$, $BF_4$) and of ($E$)-[CpFe($\eta^5$-$C_5H_4$)–(CH=CH)–($C_6H_4$)–CN–FeCp(CO)$_2$]$PF_6$ have been obtained and characterized. The crystal structure of ($E$)-[CpFe($\eta^5$-$C_5H_4$)–(CH=CH)–($C_6H_4$)–CN–RuCp($PPh_3$)$_2$]$BF_4$ has been established by means of X-ray diffractometry. The NLO responses of the compounds have been studied by the hyper-Rayleigh scattering technique and the hyperpolarizability is found to be dependent on the nature of the counterion. © 2001 Elsevier Science Ltd. All rights reserved.

*Keywords:* Ferrocenes; NLO; Bimetallic complexes; Electrochemistry

## 1. Introduction

The synthesis and characterization of new ferrocenyl based compounds has become an intriguing area of research [1], especially because of their potential applications in fields such as organic synthesis, catalysis and material science. The preparation of ferrocenyl conjugated systems offers the possibility of electronic communication between terminal subunits, this being of particular interest in nonlinear optics, magnetism, molecular sensors and liquid crystals.

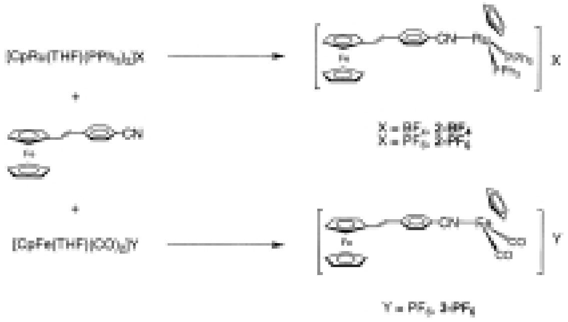
The increasing interest in the preparation of new chromophores suitable for electrooptical applications has initiated an eager search of new synthetic procedures leading to highly polarizable organometallic complexes. Since many studies have been published reporting NLO properties of a large number of organic, inorganic and organometallic complexes, some common structural features have been deduced, such that the backbone of the chromophore usually consists of an electron-donating group connected to an electron-accepting group by a conjugated π-bridge. In the last decade, there has been a large number of publications reporting the NLO properties of ferrocene-based donor–acceptor materials [2,3] but their potential as NLO materials is yet to be fully explored. The use of heterobimetallic organometallic complexes, in which the electron-accepting and -donating properties of two organometallic fragments are combined in order to obtain high first hyperpolarizabilities, is giving a new dimension to the study and design of new chromophores [4,5]. We have reported the syntheses, characterization and NLO behavior of new ferrocenyl heterobimetallic neutral compounds with a series of electron-accepting moieties derived from $M(CO)_6$ (M = Cr, Mo or W) [5]. These compounds exhibited static hyperpolarizabilities up to $164 \times 10^{-30}$ esu, which are among the largest measured till date for ferrocenyl-based derivatives.

We now report, based on our previous findings, the preparation of mixed ferrocenyl (Fc) complexes of the type Fc/Fe(II) and Fc/Ru(II), where the accepting moiety is cationic; this clearly enhances the NLO response

---

* Corresponding authors. Fax: + 34-964-728-214.
*E-mail address:* eperis@qio.uji.es (E. Peris).

PII: S0277-5387(01)00808-7



Scheme 1.

of the system. The value of the static hyperpolarizability is dependent on the nature of the counterion.

## 2. Results and discussion

### 2.1. Synthesis and characterization of the ferrocenyl bimetallic compounds

The new ferrocenyl bimetallic compounds were prepared by coordination of the ferrocenyl–nitrile compound 1-ferrocenyl-2-*E*-(4-cyanophenyl)ethylene, (*E*)-CpFe($\eta^5$-$C_5H_4$)–(CH=CH)–($C_6H_4$)–CN (**1**) [5a,6] to [CpFe(THF)$(CO)_2$]$PF_6$ and [CpRu(THF)$(PPh_3)_2$]$PF_6$ (Scheme 1). The two cationic fragments were generated in THF by addition of $TlPF_6$ to [CpFeI$(CO)_2$] or [CpRuCl$(PPh_3)_2$]. The reaction of CpFe($\eta^5$-$C_5H_4$)–(CH=CH)–($C_6H_4$)–CN with each of the cationic fragments yielded [CpFe($\eta^5$-$C_5H_4$)–(CH=CH)–($C_6H_4$)–CN–RuCp$(PPh_3)_2$]$PF_6$ (**2-PF$_6$**) and [CpFe($\eta^5$-$C_5H_4$)–(CH=CH)–($C_6H_4$)–CN–FeCp$(CO)_2$]$PF_6$ (**3-PF$_6$**). These compounds were characterized by means of IR, $^1$H and $^{13}$C NMR spectroscopy and satisfactory microanalyses. We thought that it could be interesting to test what would be the influence of the counterion on the NLO properties of the compounds and so we obtained the compound (*E*)-[CpFe($\eta^5$-$C_5H_4$)–(CH=CH)–($C_6H_4$)–CN–RuCp$(PPh_3)_2$]$BF_4$ (**2-BF$_4$**) from the reaction of **1** with [CpRu(THF)$(PPh_3)_2$]$BF_4$. The reaction of [CpRuCl$(PPh_3)_2$] with $AgBF_4$ in THF afforded [CpRu(THF)$(PPh_3)_2$]$BF_4$. Attempts to obtain the compound (*E*)-CpFe($\eta^5$-$C_5H_4$)–(CH=CH)–($C_6H_4$)–CN–FeCp$(CO)_2$]$BF_4$ (**3-BF$_4$**) by the same method failed due to reasons that we still do not know.

### 2.2. Cyclic voltammetry

The electrochemical data obtained for the compounds studied are summarized in Table 1. All the complexes display the chemically reversible ferrocene/ferricinium couple in $CH_2Cl_2$ analogous to the one observed for ferrocene. The half-wave potential of the ferrocenyl moieties for **2-PF$_6$**, **2-BF$_4$** and **3-PF$_6$** are more anodic than that measured for **1** and also for ferrocene, meaning some degree of electron transfer between the ferrocenyl moiety and the electron-accepting fragment. This behavior is similar to the one observed in our previous works, in which **1** was connected to a neutral acceptor fragment, $M(CO)_5$ where M = Cr or W 4-Cr, 4-W[5]. The half-wave potential for the Fc/Fc$^+$ couple for **3-PF$_6$** is the highest among the compounds studied, probably due to the combined effects of the cationic charge of the complex and the electron-withdrawing nature of the carbonyl ligands.

Table 1
Electrochemical potentials vs. an Ag/AgCl reference electrode

| Compound | $E_{1/2}$ (mV) ($\Delta E_p$ (mV)) | |
|---|---|---|
| | Fe-based | M-based [a] |
| Ferrocene | 445 (105) | |
| **1** | 480 (80) [b] | |
| **2-PF$_6$** | 485 (85) | |
| **2-BF$_4$** | 495 (85) | |
| **3-PF$_6$** | 515 (90) | |
| **4-Cr** | 500 (70) [b] | 980 (65) [b] |
| **4-W** | 495 (70) [b] | 1150 [b,c] |

[a] M = Cr, W.

[b] Data obtained from Ref. [5a].

[c] Irreversible peak, measured at 100 mV s$^{-1}$.

All compounds were measured between 0 and 1.25 V using $CH_2Cl_2$.

Table 2
Crystallographic data for **2-BF$_4$**

| | |
|---|---|
| Compound | **2-BF$_4$** |
| Empirical formula | $C_{60}H_{50}BF_4FeNRuP_2$ |
| Formula weight (g mol$^{-1}$) | 1090.68 |
| Temperature (K) | 293 |
| Wavelength (Å) | 0.71073 |
| Crystal system | monoclinic |
| Space group | $P2_1/n$ |
| Unit cell dimensions | |
| $a$ (Å) | 11.3280(7) |
| $b$ (Å) | 29.5349(17) |
| $c$ (Å) | 16.7223(9) |
| $\alpha$ (°) | 90 |
| $\beta$ (°) | 95.778(2) |
| $\gamma$ (°) | 90 |
| $V$ (Å$^3$) | 5566.4(6) |
| $Z$ | 4 |
| $D_{calc}$ (Mg m$^{-3}$) | 1.301 |
| Absorption coefficient (mm$^{-1}$) | 0.640 |
| $F$(000) | 2232 |
| Crystal size (mm) | $0.32 \times 0.18 \times 0.05$ |
| $2\theta$ Range (°) | 1.38–23.28 |
| Index ranges | $-12 \leq h \leq 12$, $-32 \leq k \leq 21$, $-18 \leq l \leq 18$ |
| Reflections collected | 27 054 |
| Independent reflections | 8026 [$R_{int} = 0.0872$] |
| Data/restrains/parameters | 8026/0/598 |
| Final $R$ indices [$I > 2\sigma(I)$] | $R_1 = 0.0785$, $wR_2 = 0.2264$ |
| $R$ indices (all data) | $R_1 = 0.1370$, $wR_2 = 0.2572$ |
| Goodness-of-fit-on $F^2$ | 1.195 |
| Largest difference peak and hole (e Å$^{-3}$) | 1.660 and −0.859 |

### 2.3. Molecular structure of *2-BF$_4$*

The crystal structure of compound **2-BF$_4$** reveals that this compound crystallizes in the centrosymmetric monoclinic space group $P2_1/n$. A summary of the crystal data, data collection and processing parameters is given in Table 2. Selected bond distances and angles are displayed in Table 3. The two cyclopentadienyl groups of the ferrocene are tilted slightly (3.95°) with respect to each other. The iron distances to the substituted and unsubstituted rings and the C–C distances and angles lie in the expected ranges [7]. In contrast to the crystal structure of other ferrocenyl derivatives [8], a lack of coplanarity between the cyclopentadienyl (Cp) of the ferrocene and the phenyl (Ph) group is observed, probably due to the interaction of the counteranion between one of the protons of the Ph group and one of the protons of the $PPh_3$. An ORTEP drawing of this compound is displayed in Fig. 1.

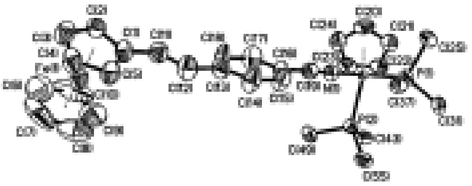


Fig. 1. Molecular structure of **2-BF$_4$** showing the atom-numbering scheme. Hydrogen atoms, phenyl (Ph) rings and the counteranion **BF$_4$**$^-$ are omitted for clarity. Thermal ellipsoids are drawn at 50% of probability.

### 2.4. NLO properties

The UV–Vis spectra of the compounds studied show low absorption in the region where the second-harmonic signal is generated (532 nm) in the measuring solvent (chloroform). The nonlinear response was studied by the hyper-Rayleigh scattering method, and the results are summarized in Table 4 [9]. The static hyperpolarizabilities ($\beta_0$) were evaluated using the two-level model [9]. The nonlinear responses are comparable in magnitude to those obtained before in our group [5]. A remarkable characteristic of these compounds is the influence of the counterion. The use of **BF$_4$**$^-$ instead of **PF$_6$**$^-$ produces an increase in the nonlinear optical response. Marder et al. have studied the influence of the

Table 3
Selected bond distances (Å) and angles (°) for compound **5**-($E$,$Z$)

| | | | |
|---|---|---|---|
| *Bond distances* | | | |
| Fe(1)–Cp (substituted) (centroid) | 1.656 | Ru(1)–Cp (centroid) | 1.857 |
| Fe(1)–Cp (centroid) | 1.636 | Ru(1)–N(1) | 2.027(8) |
| Ru(1)–P(1) | 2.348(3) | Ru(1)–P(2) | 2.352(3) |
| C(1)–C(11) | 1.450(14) | C(11)–C(12) | 1.302(14) |
| C(12)–C(13) | 1.491(15) | C(16)–C(19) | 1.447(14) |
| C(19)–N(1) | 1.134(11) | P(1)–C(25) | 1.828(10) |
| Fe(1)–Ru(1) | 12.4 | Fe(1)–Ru(1) (bonds) | 15.1 |
| *Bond angles* | | | |
| C(1)–C(11)–C(12) | 127.0(12) | C(11)–C(12)–C(13) | 125.9(12) |
| C(19)–N(1)–Ru(1) | 173.1(8) | P(1)–Ru(1)–P(2) | 102.72(9) |
| *Planes* | | | |
| Cp–Cp (substituted) | 3.95(1.00) | Cp(substituted)–Ph | 27.47(0.55) |
| Ph–Cp(C21, . . .) | 69.48(0.43) | | |

counterion in a series of salts of the form (*E*)-[CpFe($\eta^5$-$C_5H_4$)–(CH=CH)–(4-$C_5H_4$N-1-$CH_3$)]$^+X^-$ [10a]. In their work, the **$BF_4^-$** derivatives show larger SHG (Kurtz powder) than the related $PF_6^-$ compounds. The differences were attributed to the different packing of both species. In our case, the measurements have been carried out in solution, and we attribute the larger $\beta$ values of **2-$BF_4$** $^-$ to the lack of center of symmetry of **$BF_4$** $^-$, which leads to an enhanced contribution of the nonlinear optical response.

It could be argued that the extent of ion pairing may also contribute to the NLO response of these complexes. In fact, the extent of this pairing is unknown, although it is likely to be negligible in the solvent used. In order to check this point, we tried to measure the quadratic polarizabilities of the sodium salts of **$BF_4^-$** and **$PF_6^-$**, but we found that the solubilities of the salts were too low to allow the measurement to be reliable. Humphrey et al. [10b] have observed a similar effect in a series of aryldiazovinylidene complexes and they conclude that the contribution of the anion and cation to the observed nonlinearities of the salts should be largely independent, this confirms our previous suggestion.

## 3. Experimental

### 3.1. General details

All the reactions were carried out under a nitrogen atmosphere using standard Schlenck techniques. Solvents for synthesis and electrochemical measurements were dried and degassed by standard methods before use. Chromatographic work was performed on silica gel 60 Å or alumina columns.

Compound (*E*)-[CpFe($\eta^5$-$C_5H_4$)–(CH=CH)–($C_6H_4$)–CN] (**1**) was obtained according to literature methods [5a].

$^1$H NMR spectra were recorded on a Varian Gemini 300 MHz or Varian Gemini 500 MHz, using $CDCl_3$ as solvent unless otherwise stated. IR spectra were recorded on a Perkin–Elmer System 2000 FTIR using NaCl pellets. Cyclic voltammetry experiments were performed with an Echochemie PGSTAT 20 electrochemical analyzer. All measurements were carried out at room temperature (r.t.) with a conventional three-electrode configuration consisting of platinum working and auxiliary electrodes and a Ag/AgCl reference electrode containing aqueous 3 M KCl. The solvent in all experiments was $CH_2Cl_2$, which was obtained in HPLC grade from SDS. The supporting electrolyte was 0.1 M *tert*-butylammonium hexafluorophosphate, obtained from Sigma or synthesized by metathesis of *tert*-butylammonium bromide and $HPF_6$, recrystallized from ethanol and dried under vacuum. $E_{1/2}$ values were determined as $1/2(E_{pa}+E_{pc})$, where $E_{pa}$ and $E_{pc}$ are the anodic and cathodic peak potentials, respectively. All potential values reported are not corrected for the junction potential. Electrospray ionization (ESI) mass spectra were collected on a Quattro LC (Micromass) instrument, using dilute $CH_3CN$ and/or $CH_3OH$ solutions of the title compounds.

Table 4
Experimental nonlinear response; $\beta$ and $\beta_0$ in $10^{-30}$ esu

| Compound | $\lambda_{max}$ (nm) | $\beta$ [a] | $\beta_0$ [b] |
|---|---|---|---|
| **1** | 473 [c] | 203 [c] | 34 [c] |
| **2-$PF_6$** | 485 | 186 | 25 |
| **2-$BF_4$** | 484 | 325 | 44 |
| **3-$PF_6$** | 474 | 171 | 28 |
| **4-Cr** | 481 [c] | 271 [c] | 39 [c] |
| **4-W** | 487 [c] | 375 [c] | 48 [c] |

[a] Measured in chloroform by the HRS method and calculated with respect to $\beta$ of *p*-nitroaniline in chloroform ($23\times10^{-30}$ esu). HRS at 1064 nm. Values ±15%.

[b] Calculated using the two level model.

[c] Data obtained from Ref. [5a].

### 3.2. NLO measurements

Details of the HRS setup have been discussed previously [11]. All measurements are performed in chloroform and the known hyperpolarizability of *p*-nitroaniline in this solvent ($23\times10^{-30}$ esu) [12] is used as a reference. The samples are passed through a 0.45 μm filter for contaminated samples often produce spurious signals, and are checked for multiphoton fluorescence that can interfere with the HRS signal [13]. IR-laser pulses generated with an injection seeded, Q-switched Nd:YAG laser (Quanta-Ray GCR-5, 1064 nm, 10 ns pulses, 10 Hz) are focused into a cylindrical cell containing the solution (7 ml). The fundamental intensity is altered by rotation of a half-wave plate placed between crossed polarizers, and measured with a photodiode. An efficient condenser system is used to collect the light scattered at the harmonic frequency (532 nm) that is detected by a photomultiplier. Discrimination of the second-harmonic light from the fundamental light is accomplished by a low-pass filter and a 532 nm interference filter. Actual values for the intensities are retrieved by using gated integrators. In all experiments the incident light was polarized vertically along the *z*-axis.

### 3.3. *Syntheses of (E)-[CpFe($\eta^5$-$C_5H_4$)–(CH=CH)–($C_6H_4$)–CN–RuCp($PPh_3$)$_2$]$PF_6$ (**2-$PF_6$**) and (E)-[CpFe-($\eta^5$-$C_5H_4$)–(CH=CH)–($C_6H_4$)–CN–RuCp($PPh_3$)$_2$]$BF_4$ (**2-$BF_4$**)*

To a solution of CpRu($PPh_3$)$_2$Cl (404 mg, 0.56 mmol) in $CH_2Cl_2$–MeOH (5:1; 20 ml), was added

$TlPF_6$ (196 mg, 0.56 mmol). After stirring the mixture for about 30 min, a white powder was filtered off. probably this precipitate could correspond to the formation of TlCl. Then, **1** was added (176 mg, 0.56 mmol) and the reaction was followed by TLC. No reaction was observed after 45 min of stirring. Finally, the solvent was removed under reduced pressure; the product was extracted with $CH_2Cl_2$ and purified by column chromatography on alumina, using a mixture of acetone–$CH_2Cl_2$ (1:1). By this method pure compound **2-PF$_6$** was obtained. Compound **2-PF$_6$** was recrystallized using EtOH–hexane, giving 410 mg of a deep red microcrystalline powder. Yield: 64%.

Compound **2-BF$_4$** was obtained in the same manner as compound **2-PF$_6$** but using $AgBF_4$ instead of $TlPF_6$; $CpRu(PPh_3)_2Cl$ (463 mg, 0.64 mmol), $AgBF_4$ (124 mg, 0.64 mmol) and **1** (200 mg, 0.64 mmol). Yield: 52%.

$^1H$ NMR spectrum for compound **2-PF$_6$**: $\delta$ 7.24–6.90 (m, 35H, $C_6H_5$, $C_6H_4$, CH=CH), 6.46 (d, 1H, $^3J_{H-H} =$ 16.0 Hz, CH=CH), 4.36 (s, 5H, $C_5H_5$), 4.32 (s, 2H, $C_5H_4$), 4.18 (s, 2H, $C_5H_4$), 3.98 (s, 5H, $C_5H_5$). $^{13}C$ NMR: $\delta$? 142.3, 137.1, 136.9, 135.6, 133.1, 132.1, 130.6, 129.5, 129.3, 128.8, 128.4, 127.3, 126.9, 125.6 (44C, $C_6H_5$, $C_6H_4$, CH=CH), 109.4 (1C, CN), 84.7 (5C, $C_5H_5$), 82.6 (1C, $C_5H_4$), 70.1 (2C, $C_5H_4$), 69.9 (5C, $C_5H_5$), 68.2 (2C, $C_5H_4$). IR ($cm^{-1}$): 1593 (w), 1481 (w), 1435 (w), 1054 (s). *Anal.* Found: C, 63.01; H, 4.43; N, 1.21. Calc. for **2-PF$_6$**, $C_{60}H_{50}F_6FeNP_3Ru$ (MW 1148.87): C, 62.73; H, 4.39; N, 1.22%. EI MS; *m/z* (fragment, relative intensity): 1004 (**2-PF$_6^+$**, 18); 691 ($CpRu^+(PPh_3)_2$, 100). *Anal.* Found: C, 67.18; H, 4.77; N, 1.24. Calc. for **2-BF$_4$**, $C_{60}H_{50}F_4BFeNP_2Ru$ (MW 1090.71): C, 66.07; H, 4.62; N, 1.28%. EI MS: *m/z* (fragment, relative intensity): 1004 (**2-BF$_4^+$**, 18), 691 ($CpRu^+(PPh_3)_2$, 100).

### 3.4. Synthesis of (E)-[CpFe($\eta^5$-$C_5H_4$)–(CH=CH)–($C_6H_4$)–CN–FeCp(CO)$_2$]$PF_6$ (3-PF$_6$)

This compound was obtained using the same general procedure described for **2-PF$_6$**, with the following reagents: $CpFe(CO)_2I$ (182 mg, 0.6 mmol), $TlPF_6$ (210 mg, 0.6 mmol), and **1** (200 mg, 0.6 mmol). Yield: 47%.

$^1H$ NMR spectrum for compound **2-PF$_6$**: $\delta$ 7.60 (d, 2H, $^3J_{H-H} =$ 8.4 Hz, $C_6H_4$), 7.49 (d, 2H, $^3J_{H-H} =$ 8.4 Hz, $C_6H_4$), 7.03 (d, 2H, $^3J_{H-H} =$ 15.9 Hz, CH=CH), 6.67 (d, 2H, $^3J_{H-H} =$ 16.2 Hz, CH=CH), 5.05 (s, 5H, $C_5H_5$), 4.51 (s, 2H, $C_5H_4$), 4.37 (s, 2H, $C_5H_4$), 4.17 (s, 5H, $C_5H_5$). $^{13}C$ NMR spectrum: $\delta$ 230.3 (2C, CO), 143.1 (1C, $C_6H_4$), 133.2 (2C, $C_6H_4$), 132.3 (1C, CH=CH), 126.7 (2C, $C_6H_4$), 124.6 (1C, CH=CH), 120.1 (1C, $C_6H_4$), 110.1 (1C, CN), 84.9 (5C, $C_5H_4$), 70.6 (2C, $C_5H_4$), 70.1 (5C, $C_5H_5$), 68.1 (2C, $C_5H_4$). IR ($cm^{-1}$): 2035 (vs), 1989 (vs). *Anal.* Found: C, 49.85; H, 3.59; N, 2.23. Calc. for **2-PF$_6$**, $C_{26}H_{20}F_6Fe_2NO_2P$ (MW 635.10): C, 49.17; H, 3.17; N, 2.21%.

### 3.5. X-ray diffraction studies

Single crystals of **2-BF$_4$** were grown by slow diffusion of hexane into concentrated $CH_2Cl_2$–toluene solutions and mounted on a glass fiber in a random orientation. Data collection was performed at r.t. on a Siemens SMART CCD diffractometer using graphite monochromated Mo K$\alpha$ radiation ($\lambda = 0.71073$ Å) with a nominal crystal to detector distance of 4.0 cm. A hemisphere of data was collected based on three $\omega$-scans runs (starting $\omega = -28°$) at values $\phi = 0$, 90 and 180° with the detector at $2\theta = 28°$. At each of these runs, frames (606, 435 and 230, respectively) were collected at 0.3° intervals and 15 s per frame. Space group assignment was based on systematic absences, E statistics and successful refinement of the structures. The structure was solved by direct methods with the aid of successive difference Fourier maps and were refined using the SHELXTL 5.1 software package. All non-hydrogens were refined anisotropically. Hydrogen atoms were assigned to ideal positions and refined using a riding model. Details of the data collection, cell dimensions and structure refinements are given in Table 2.

The diffraction frames were integrated using the SAINT package and corrected for absorption with SADABS [14].

## 4. Supplementary material

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC no. 150162 for compound **2-BF$_4$**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

## Acknowledgements

We thank the DGESIC (PB98-1044) and BANCAIXA (P1B98-07) for financial support and the Generalitat Valenciana for a fellowship (J. Mata). We would also like to thank the University of Leuven (GOA/2000/03), the Belgian Government (IUAP-IV-11) and the fund for scientific research, Flanders (FWO-V G.0407.98 and G.0338.98).

## References

[1] For excellent recent reviews on ferrocene-based compounds, see: (a) A. Togni, T. Hayashi (Eds.), Ferrocenes: Homogeneous Catalysis — Organic Synthesis — Materials Science, VCH, Weinheim, 1995.

(b) A. Togni, R.L. Halterman, Metallocenes, Wiley–VCH, Weinheim, 1998.
(c) N.J. Long, Metallocenes: an Introduction to Sandwich Complexes, Blackwell Science, Oxford, 1998.

[2] See for example: (a) I.R. Whittall, A.M. McDonagh, M.G. Humphrey, M. Samoc, Adv. Organomet. Chem. 43 (1999) 349;
(b) I.R. Whittall, A.M. McDonagh, M.G. Humphrey, M. Samoc, Adv. Organomet. Chem. 42 (1998) 291;
(c) N.J. Long, Angew. Chem., Int. Ed. Engl. 34 (1995) 21;
(d) S. Barlow, S.R. Marder, Chem. Commun. (2000) 1555.

[3] (a) J.T. Lin, J.J. Wu, Ch.Sh. Li, Y.S. Wen, K.J. Lin, Organometallics 15 (1996) 5028;
(b) A. Togni, G. Rins, Organometallics 12 (1993) 3368;
(c) G. Doineau, G. Balavoine, T. Fillebeen-Khan, J.C. Clinet, J. Delaire, I. Ledoux, R. Loucif, G. Puccetti, J. Organomet. Chem. 421 (1991) 299;
(d) I.S. Lee, S.S. Lee, Y.K. Chung, D. Kim, N.W. Song, Inorg. Chim. Acta 279 (1998) 243;
(e) K.N. Jayaprakash, P.C. Ray, I. Matsuoka, M.M. Bhadbhade, V.G. Puranik, P.K. Das, H. Nishihara, A. Sarklar, Organometallics 18 (1999) 3851;
(f) S. Sakanishi, D.A. Badrdwell, S. Couchman, J.C. Jeffrey, J.A. McCleverty, M.D. Ward, J. Organomet. Chem. 528 (1997) 35;
(g) S. Barlow, H.E. Bunting, C. Ringham, J.C. Green, G.U. Bublitz, S.G. Boxer, J.W. Perry, S.R. Marder, J. Am. Chem. Soc. 121 (1999) 3715;
(h) J. Heck, S. Dabeck, T. Meyer-Fridrichsen, H. Wong, Coord. Chem. Rev. 190–192 (1999) 1217.

[4] (a) I.S. Lee, H. Seo, Y.K. Chung, Organometallics 18 (1999) 1091;
(b) V. Cadierno, S. Conejero, M.P. Gamasa, J. Gimeno, I. Asselberghs, S. Houbrechts, K. Clays, A. Persoons, J. Borge, S. García-Granda, Organometallics 18 (1999) 582;
(c) U. Behrens, H. Brussard, U. Hagenau, J. Heck, E. Hendrickx, J. Kornich, J.G.M. Van der Linden, A. Persoons, A.L. Spek, N. Veldman, B. Voss, H. Wong, Chem. Eur. J. 2 (1996) 98;
(d) U. Hagenau, J. Heck, E. Hendrickx, A. Persoons, T. Schuld, H. Wong, Inorg. Chem. 35 (1996) 7863;
(e) R. Loucif-Saiba, J.A. Delaire, L. Bonazzola, G. Doisneau, G. Balavoine, T. Fillebeen-Khan, L. Ledoux, G. Puccetti, Chem. Phys. 167 (1992) 369;
(f) S. Houbrechts, K. Clays, A. Persoons, V. Cadierno, M.P. Gamasa, J. Gimeno, Organometallics 15 (1996) 5266;
(g) T. Farrell, T. Meyer-Friedrichsen, J. Heck, A.R. Manning, Organometallics 19 (2000) 3410.

[5] (a) J. Mata, S. Uriel, E. Peris, R. Llusar, S. Houbrechts, A. Persoons, J. Organomet. Chem. 562 (1998) 197;
(b) J.A. Mata, E. Falomir, R. Llusar, E. Peris, J. Organomet. Chem. 616 (2000) 80.

[6] H.E. Bunting, M.L.H. Green, S.R. Marder, M.E. Thompson, D. Bloor, P.V. Kolinsky, R.J. Jones, Polyhedron 11 (1992) 1489.

[7] (a) B.V. Lee, H. Moon, Y.K. Chung, N. Jeong, G.B. Carpenter, Organometallics 12 (1993) 3879;
(b) S.G. Lee, H.K. Lee, G.S. Lee, Y.K. Chung, Organometallics 16 (1997) 304;
(c) S. Lee, Y.K. Chung, J. Mun, C.S. Yoon, Organometallics 18 (1999) 5080.

[8] J.A. Mata, S. Uriel, R. Llusar, E. Peris, Organometallics 19 (2000) 3797.

[9] (a) J.L. Oudar, D.S. Chemla, Chem. Phys. 66 (1977) 2664;
(b) E. Hendrickx, K. Clays, A. Persoons, C. Dehu, J.L. Bredas, J. Am. Chem. Soc. 363 (1995) 58.

[10] (a) S.R. Marder, J.W. Perry, B.G. Tiemann, W.P. Schaefer, Organometallics 10 (1991) 1896;
(b) M.P. Cifuentes, J. Driver, M.G. Humphrey, I. Asselberghs, A. Persoons, M. Samoc, B. Luther-Davies, J. Organomet. Chem. 607 (2000) 72.

[11] (a) K. Clays, A. Persoons, Phys. Rev. Lett. 66 (1991) 2980;
(b) K. Clays, E. Hendrickx, T. Verbiest, A. Persoons, Adv. Mater. 10 (1998) 643;
(c) K. Clays, A. Persoons, Rev. Sci. Instrum. 63 (1992) 3285.

[12] K. Clays, A. Persoons, Rev. Sci. Instrum. 63 (1992) 3285.

[13] (a) E. Hendrickx, C. Dehu, K. Clays, J.L. Bredas, A. Persoons, in: G.A. Lindsay, K.D. Singer (Eds.), Polymers for Second-order Nonlinear Optics, American Chemical Society, Washington, DC, 1995, pp. 82–94;
(b) M.C. Filipse, R. de Jonge, R.H. Woudenberg, A.W. Marsman, C.A. van Walree, L.J. Jenneskens, Chem. Phys. Lett. 245 (1995) 297;
(c) I.D. Morrison, R.G. Denning, W.M. Laidlaw, M.A. Stammers, Rev. Sci. Instrum. 67 (1996) 1445.

[14] (a) SAINT version 5.0, Bruker Analytical X-ray Systems, Madison, WI;
(b) G.M. Sheldrick, SADABS Empirical Absorption Program, University of Göttingen, 1996.

FULL PAPER

# Syntheses, Structures and Nonlinear Optical Properties of Ferrocenyl Complexes with Arylethenyl Substituents

**José A. Mata,[a] Eduardo Peris,*[a] Rosa Llusar,[b] Santiago Uriel,[b] Marie P. Cifuentes,[c] Mark G. Humphrey,*[c] Marek Samoc,[d] and Barry Luther-Davies[d]**

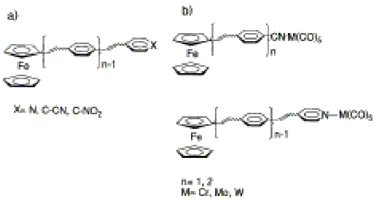
**Keywords:** Ferrocene / NLO / Bimetallic compounds / Crystal structure

The complexes (*E*)- and (*Z*)-Fe($\eta^5$-$C_5H_4CHO$)($\eta^5$-$C_5H_4CH$=CH–$C_6H_4$-4-$NO_2$) [**2**-(*E*) and **2**-(*Z*), respectively], (*E*)- and (*Z*)-Fe($\eta^5$-$C_5H_4CHO$)($\eta^5$-$C_5H_4CH$=CH–$C_6H_4$-4-CN) [**3**-(*E*) and **3**-(*Z*), respectively], (*E*,*E*)-, (*E*,*Z*)-, and (*Z*,*Z*)-Fe($\eta^5$-$C_5H_4CH$=$CHC_6H_4$-4-$NO_2$)$_2$ [**4**-(*E*,*E*), **4**-(*E*,*Z*), and **4**-(*Z*,*Z*), respectively], (*E*,*E*)-, (*E*,*Z*)-, and (*Z*,*Z*)-Fe($\eta^5$-$C_5H_4CH$=$CHC_6H_4$-4-CN)$_2$ [**5**-(*E*,*E*), **5**-(*E*,*Z*), and **5**-(*Z*,*Z*), respectively], and Fe($\eta^5$-$C_5H_5$)[$\eta^5$-$C_5H_4$–(*E*)-CH=CH–4-[($\eta^6$-$C_6H_4$)Cr(CO)$_3$]–(*E*)-CH=CH–$\eta^5$-$C_5H_4$)Fe($\eta^5$-$C_5H_5$) (**7**) have been synthesized. Structural studies on **2**-(*E*), **4**-(*E*,*Z*), **5**-(*E*,*E*), Fe[$\eta^5$-$C_5H_5$)($\eta^5$-$C_5H_4$–(*E*)-CH=CH–4-$C_6H_4$–(*E*)-CH=CH–$\eta^5$-$C_5H_4$]Fe($\eta^5$-$C_5H_5$) (**6**) and **7** have been performed. Electrochemical studies of **2**–**5** reveal trends in the oxidation potentials which are consistent with the more effective conjugation of the (*E*) isomers, and the better electron-accepting character of $NO_2$ than CN and of CHO than H. Powder SHG measurements by the Kurtz technique using fs pulses at the telecommunications wavelength of 1.3 μm reveal low responses for **4**-(*E*,*E*), **5**-(*E*,*E*), and **7**. Third-order NLO measurements by Z-scan using fs pulses at 800 nm suggest an increase in |γ| on increasing the electron-acceptor strength [when proceeding from **5**-(*E*,*Z*) to **4**-(*E*,*Z*), CN is replaced by $NO_2$], and on introduction of the Cr(CO)$_3$ unit, when proceeding from **6** to **7**.

## Introduction

Ferrocene is a versatile building block. Its excellent thermal and photochemical stability, and combination of useful redox properties and chemical versatility, provides access to materials with potentially useful physical and chemical properties.[1–3] With the importance of ferrocene in the field of material science, there is currently great interest in the chemistry of ferrocenyl-based oligomers and ferrocenyl-containing conjugated compounds. The former contain the ferrocene building block in the repeat unit, and the latter couple ferrocene to a potentially π-delocalizable system. These complexes are of interest because of, amongst other things, their nonlinear optical (NLO) properties; the significant electron-donating strength of the ferrocenyl group has made it a good candidate for the design of chromophores with high NLO responses.

We previously reported on the syntheses, characterization, and molecular quadratic NLO behavior of ferrocene-containing conjugated compounds with pyridine, nitro, and nitrile pendant groups. This allowed us to obtain heterobimetallic complexes containing a series of electron-accepting moieties derived from M(CO)$_6$ (M = Cr, Mo, W) [Scheme 1 (a) and (b)].[4–6] Electrochemical studies together with the planar conformation of the molecular structures suggested effective electron delocalization along the conjugated chains. In a continuation of these studies, we have now synthesized a series of ferrocenyl 1,1′-bis-substituted complexes with nitro and nitrile pendant groups, whose electronic and solid-state structural properties have been studied. The results from these studies are reported herein. Similar 1,1′-bis-substituted ferrocenyl complexes with pendant pyridine groups have been reported by Lee et al., and show very interesting structural features.[7]



Scheme 1

We have also investigated arylethenyl-linked biferrocenes, with and without the presence of bridge arene-ligated Cr(CO)$_3$ units, the syntheses of which were reported by Müller et al.[8] while the current studies were underway. We

---

[a] Departamento de Química Inorgánica y Orgánica, Universitat Jaume I
Ctra. Borriol S/N, 12080 Castellón, Spain,
Fax: (internat.) +34 964/72 8214
E-mail: eperis@qio.uji.es
[b] Departamento de cc. Experimentales, Universitat Jaume I
Castellón, Spain
[c] Department of Chemistry, Australian National University
Canberra, ACT 0200, Australia
Fax: (internat.) +61 2/6125 0760
E-mail: Mark.Humphrey@anu.edu.au
[d] Australian Photonics Cooperative Research Centre, Laser Physics Centre, Research School of Physical Sciences and Engineering, Australian National University
Canberra, ACT 0200, Australia

report herein a modified synthesis of the $Cr(CO)_3$-ligated complex, together with X-ray structural studies of both complexes.

Although the number of studies reporting second-order NLO responses of ferrocenyl complexes is very high, comparatively fewer studies exist in which third-order NLO responses are reported.[9] Since the effective delocalization in the molecular structures of our complexes fulfill a basic requirement for third-order NLO-active materials, we have measured and report herein on their cubic hyperpolarizabilities at 800 nm by Z-scan. While the bulk second-order susceptibilities of many ferrocenyl complexes have been reported,[10] much extant data has been obtained at wavelengths close to those of material resonances, resulting in significant resonance enhancement of the response. We therefore also report the bulk susceptibilities for these complexes by the Kurtz powder method at wavelengths remote from electronic absorption bands, thus enabling an assessment of off-resonance nonlinearity to be obtained.

## Results and Discussion

### Syntheses of 2−5

Based on our previous experience[4−6] we have synthesized compounds **2−5** by conventional Wittig and Horner−Emmons−Wadsworth methods (Scheme 2). The first step of the two-step reaction procedure afforded the bis-substituted complexes **2** and **3** with (*Z*) and (*E*) stereochemistry, together with small amounts of the bis-olefinated complexes (**4** and **5** in all their isomeric forms). Compounds **2** and **3** may be of interest in the design of new materials, since the presence of the carboxaldehyde group may provide access to a variety of functional groups. Complexes **2** and **3** undergo further olefination in the second step to yield **4** and **5** in all their isomeric forms [**4** and **5** exist as three isomers by combination of the (*E*) and (*Z*) dispositions of the vinylic group, i.e. (*E*,*E*), (*E*,*Z*) and (*Z*,*Z*)]. All three isomers were fully characterized for both the nitro and nitrile derivatives. Higher yields of the bis-substituted compounds **4** and **5** were obtained when performing the one-step (direct reaction) procedure. In all cases, separation of the (*E*) and (*Z*) isomers was easily achieved by column chromatography. Reaction of any of the complexes in refluxing toluene in the presence of iodine leads to the all-*E*-isomers in almost quantitative yields (see Experimental section).

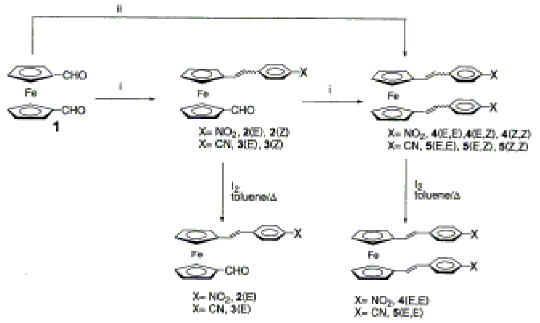
### Synthesis of 7

The synthesis of **6** was again based on Horner−Emmons−Wadsworth (HEW) olefinations using the corresponding phosphonate reagent. A synthesis of **7** was reported while the present studies were underway,[8] and involved olefination by HEW reaction of an $\eta^6$-coordinated carbonylchromium phenylene-bisphosphonate with ferrocenecarboxaldehyde. In the present study, $\eta^6$-coordination of the tri(carbonyl)chromium moiety to the phenylene bridging group of **6** was performed by heating compound **6** with $Cr(CO)_6$ in refluxing butyl ether (Scheme 3).

### X-ray Structural Studies of 2-(*E*), 4-(*E*,*Z*), 5-(*E*,*E*), 6, and 7

The identities of **2**-(*E*) (ORTEP plots in Figures 1 and 2), **4**-(*E*,*Z*) (Figure 3), **5**-(*E*,*E*) (Figures 4 and 5), **6** (Figure 6), and **7** (Figure 7) were confirmed by single-crystal X-ray studies; crystallographic data are summarized in Table 5, and selected bond angles and distances are listed in Tables 1 and 2.

The structural studies reveal a number of interesting features. Complexes **2**-(*E*), **4**-(*E*,*Z*), and **5**-(*E*,*E*) provide the opportunity to assess the impact of π-system chain lengthening, stereochemistry, and acceptor modification on metrical parameters and crystal packing preference. In



Scheme 2. Syntheses of **2−5**. (i) 1.5 $(PPh_3CH_2-C_6H_4\text{-}4\text{-}NO_2)Br/KO\mathit{t}Bu$ or 1.5 $(PPh_3CH_2-C_6H_4\text{-}4\text{-}CN)Br/KO\mathit{t}Bu$. (ii) 3 $(PPh_3CH_2-C_6H_4\text{-}4\text{-}NO_2)Br/KO\mathit{t}Bu$, or 3 $(PPh_3CH_2-C_6H_4\text{-}4\text{-}CN)Br/KO\mathit{t}Bu$.

Scheme 3

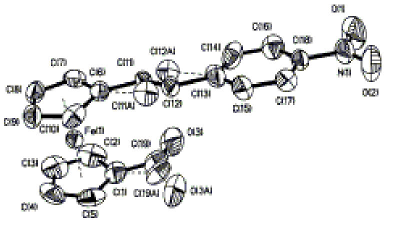


Figure 1. Molecular structure and atomic labeling scheme for **2**-(*E*), Fe($\eta^5$-C$_5$H$_4$CHO){$\eta^5$-C$_5$H$_4$−(*E*)-CH=CHC$_6$H$_4$-4-NO$_2$}, with 50% anisotropic displacement ellipsoids

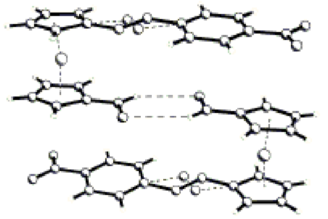


Figure 2. Crystal packing of compound **2**-(*E*) showing the hydrogen-bonding through the aldehydes of two different molecules. The distance between H···O is ca. 2.7 A

ferrocenyl complexes, it has been reported that two molecular motions relieve steric strain:[1] (i) the rotation from an eclipsed to a staggered disposition of the two Cp rings and (ii) their tilting from a parallel disposition. For these three complexes, little tilting is observed; the two cyclopentadienyl rings are slightly tilted (dihedral angles 2.7−4.3°) with respect to each other. Compounds **2**-(*E*), **4**-(*E*,*Z*), and **5**-(*E*,*E*) show *syn* conformations with respect to the two ancillary ligands, with a perfect eclipsed disposition of the Cp rings of the ferrocene unit in **2**-(*E*) and **5**-(*E*,*E*).

The distances from iron to the cyclopentadienyl rings and the C−C distances within the rings in these three structures, lie in the expected range. As seen in Figures 1, 2, 3, and 4, all the molecules with (*E*) stereochemistry have an almost idealized coplanar arrangement between the ferrocenyl donor and the vinylene-phenylene functionalized fragment. The two ancillary ligands in compound **5**-(*E*,*E*) show intra-

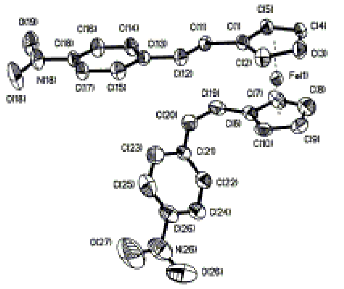


Figure 3. Molecular structure and atomic labeling scheme for **4**-(*E*,*Z*), Fe{$\eta^5$-C$_5$H$_4$−(*Z*)-CH=CHC$_6$H$_4$-4-NO$_2$}{$\eta^5$-C$_5$H$_4$−(*E*)-CH=CHC$_6$H$_4$-4-NO$_2$}, with 50% anisotropic displacement ellipsoids

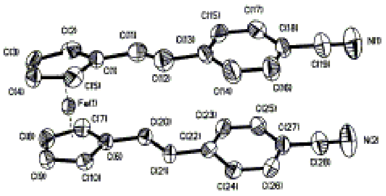


Figure 4. Molecular structure and atomic labeling scheme for **5**-(*E*,*E*), Fe{$\eta^5$-C$_5$H$_4$−(*E*)-CH=CHC$_6$H$_4$-4-CN}$_2$, with 50% anisotropic displacement ellipsoids

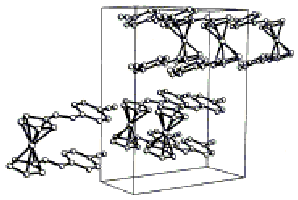


Figure 5. Cell packing diagram for **5**-(*E*,*E*), Fe{$\eta^5$-C$_5$H$_4$−(*E*)-CH=CHC$_6$H$_4$-4-CN}$_2$

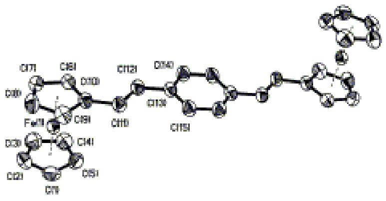


Figure 6. Molecular structure and atomic labeling scheme for **6**, Fe($\eta^5$-$C_5H_5$)($\eta^5$-$C_5H_4$−(*E*)-CH=CH−4-$C_6H_4$−(*E*)-CH=CH−$\eta^5$-$C_5H_4$)Fe($\eta^5$-$C_5H_5$), with 50% anisotropic displacement ellipsoids

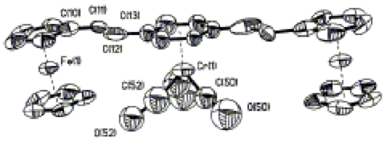


Figure 7. Molecular structure and atomic labeling scheme for **7**, Fe($\eta^5$-$C_5H_5$)($\eta^5$-$C_5H_4$−(*E*)-CH=CH−4-{($\eta^6$-$C_6H_4$)Cr(CO)$_3$}-(*E*)-CH=CH−$\eta^5$-$C_5H_4$)Fe($\eta^5$-$C_5H_5$) with 50% anisotropic displacement ellipsoids

Table 1. Selected bond lengths and angles for **2**-(*E*), **4**-(*E,Z*), and **5**-(*E,E*)

| | | | |
|---|---|---|---|
| **2**-(*E*) | | | |
| N1−O1 | 1.216(3) | Fe1−N1 (space) | 9.42 |
| N1−O2 | 1.212(3) | Fe1−N1 (bonds) | 11.9 |
| C19−O3 | 1.188(10) | | |
| C19A−O3A | 1.135(18) | | |
| plane Cp(1−5)−Cp(6−10) | | 4.28(0.21) | |
| plane Cp(1−5)−Ph | | 7.18(0.20) | |
| **4**-(*E,Z*) | | | |
| N18−O18 | 1.221(3) | Fe1−N18 (space) | 9.41 |
| N18−O19 | 1.218(4) | Fe1−N26 (space) | 7.97 |
| N26−O26 | 1.225(4) | Fe1−N18 (bonds) | 11.90 |
| N26−O27 | 1.208(4) | Fe1−N26 (bonds) | 11.92 |
| plane Cp(1−5)−Cp(6−10) | | 3.01(0.24) | |
| plane Cp(1−5)−Ph(13−18) | | 9.51(0.19) | |
| **5**-(*E,E*) | | | |
| C11−C20 | 3.44 | Fe1−N1 (space) | 10.46 |
| C12−C21 | 3.71 | Fe1−N2 (space) | 10.56 |
| C19−C28 | 3.89 | Fe1−N1 (bonds) | 13.0 |
| N1−N2 | 3.92 | Fe1−N2 (bonds) | 13.0 |
| plane Cp(1−5)−Cp(6−10) | | 2.75(0.16) | |
| plane Cp(1−5)−Ph(13−18) | | 10.93(0.16) | |
| plane Cp(6−10)−Ph(22−27) | | 7.57(0.17) | |
| plane Ph(13−18)−Ph(22−27) | | 2.30(0.13) | |

Table 2. Selected bond lengths and angles for **6** and **7**

| | **6** | **7** |
|---|---|---|
| Fe−C (Cp subs.) | 2.047[10] | 2.024[25] |
| Fe−C (Cp non subs.) | 2.041[1] | 2.022[40] |
| C−C (Cp subs.) | 1.417 [10] | 1.403[25] |
| C−C (Cp non subs.) | 1.407[5] | 1.401[8] |
| C(10)−C(11) | 1.464(2) | 1.34(2) |
| C(11)−C(12) | 1.323(2) | 1.37(3) |
| C(12)−C(13) | 1.469(2) | 1.40(3) |
| Cr1−C(CO) | – | 1.72[9] |
| C(CO)−O(CO) | – | 1.24[10] |
| Fe−Fe (space) | 13.49 | 12.85 |
| Fe−Fe (bonds) | 17.86 | 16.46 |
| Fe−Cr (space) | – | 6.14 |
| Fe−Cr (bonds) | – | 8.15 |
| C(10)−C(11)−C(12) | 124.59(18) | 121(2) |
| C(11)−C(12)−C(13) | 128.02(18) | 122(3) |
| plane Cp−Cp(subs) | 1.46(16) | 0.29(0.73) |
| plane Ph−Cp(subs) | 3.37(25) | 5.03(1.11) |

molecular π-stacking, as can be clearly seen in Figure 4; the two ligands smoothly increase their separation from 3.44 [C(20)−C(11)] to 3.92 Å [N(1)−N(2)]. In the crystal lattice of compound **2**-(*E*), centrosymmetric dimer pairs are connected by hydrogen-bonding through the oxygen and hydrogen atoms of the aldehyde group (Figure 2). This hydrogen-bond of the type C−H···O is pervasive in crystalline organometallic transition metal complexes, especially when the C−H is of the sp$^2$ type.[11] In our case, the oxygen atom of the aldehyde polarizes the C−H bond enhancing its H-donor capabilities. Compound **5**-(*E,E*) crystallizes in the noncentrosymmetric space group $P2_1$. The crystal arrangement of **5**-(*E,E*) (Figure 5), despite being noncentrosymmetric, reveals an anti-parallel alignment of the molecular dipoles, therefore low second-harmonic generation (SHG) is expected for the bulk material. This canceling of the molecular dipoles has also been observed for other noncentrosymmetric ferrocenyl compounds.[12]

Compounds **6** and **7** both crystallize in the centrosymmetric space group $P2_1/c$, the inversion center for compound **6** is located in the middle of the phenyl ring. The crystallographic inversion center lies very close to the chromium atom, generating another molecule with a face to face disposition when compared with the previous one, thus resulting in disorder. The bond lengths and angles in **6** lie in the expected range,[13] with the ferrocenyl units adopting the sterically less hindered *anti* conformation. The cyclopentadienyl and phenyl rings in **6** are roughly coplanar (maximum dihedral angle 3.37°). The bond lengths and angles in **7** lie in the expected range, except the Cr−C−O angles which are significantly distorted from linearity (ca. 167°). The most significant structural feature of **7** is the *syn/syn* conformation adopted by the two ferrocenyl and the tri(carbonyl)chromium units. The two substituted-cyclopentadienyl rings and the phenyl group are more distorted from coplanarity (maximum dihedral angle 5.03°) than the similar rings in compound **6**.

The Fe−Cr distances in **7** are 6.1 Å (through space) and 8.2 Å (through bonds), so a direct bonding effect must be discounted. In the absence of conclusive theoretical calculations, we believe that the more sterically hindered disposition of the ligated metal units may be due to packing effects. In fact, this kind of disposition has also been observed in other related compounds.[14]

### Cyclic Voltammetry

The electrochemical data obtained for complexes **2−5** are summarized in Table 3. In all cases, we observed the chemically reversible ferrocene/ferrocenium couple with $i_{pa}/i_{pc}$ = 1. Although the peak to peak separations in all the compounds are greater than the ideal value for a fully reversible one-electron process, this difference ($E_{pc} - E_{pa}$) is similar to that measured for ferrocene under the conditions of the experiment. When compared with the previously reported ferrocenyl derivatives with one 4-nitrophenylethenyl or 4-cyanophenylethenyl substituent,[4−6] the bis-substituted complexes show a more anodic half-wave potential (ca. 100 mV), suggesting that the extra electron-accepting substituent has an important electronic effect on the ferrocenyl fragment. When comparing complexes with analogous stereochemical features, the nitro compounds **4** have a higher oxidation potential than the homologous nitrile derivatives **5**, thus confirming the better electron-accepting nature of the nitro group. The complexes with a higher degree of (*E*) stereochemistry (i.e. *E,E* > *E,Z* > *Z,Z*) possess a lower half-wave potential than those with a higher degree of (*Z*) stereochemistry (half-wave potential **4**-(*E,E*) < **4**-(*E,Z*) < **4**-(*Z,Z*) and **5**-(*E,E*) < **5**-(*E,Z*) < **5**-(*Z,Z*)]. This is in good agreement with the greater stabilization of the positive charge corresponding to the more effective conjugation of the (*E*) isomers, and indicates a higher degree of charge transfer from the metal center to the polyene backbone.[5,6,15] The aldehydes **2** and **3** possess a much higher half-wave potential than the ferrocenyl complexes with one 4-nitrophenylethenyl or 4-cyanophenylethenyl substituent,[4−6] perhaps due to the electron-accepting nature of the aldehyde group. The substitution of the aldehyde group by the corresponding conjugated ligand to give **4** and **5**, results in a shift to more cathodic potentials, probably as a consequence of the enhanced stabilization of the positive charge of the resultant ferrocenium species at the two conjugated ancillary ligands.

Literature electrochemical data suggest that biferrocene complexes similar to **6** and **7** do not show effective electronic communication between the two ferrocene moieties.[8,13] For such complexes, and homologues with pentamethylcyclopentadienyl ligands, only one peak is observed for the oxidation of the iron atoms. However, the potential for this two-electron oxidation is sensitive to modification of the bridging unit; electrochemical data for compound **7** shows that the oxidation of the iron atom is clearly influenced by the carbonyl fragment. A shift from 455 mV in compound **6** to 351 mV in **7** is consistent with oxidation of the ferrocene centers which is facilitated by incorporation of the chromium carbonyl unit.[8] In fact, one would expect that the electron-accepting nature of chromium tricarbonyl should increase the oxidation potential of the compound in contrast to what we observed. The same effect has been described by Müller for compound **7** and other related ferrocenyl-chromium tricarbonyl complexes[8] and, in fact, may be justified by the amphoteric character of $Cr(CO)_3$ proposed by the same author and his co-workers.[16]

Table 3. Electrochemical and linear optical data for complexes **2−5**

| | λmax (nm) | | | | | | $E_{1/2}(\Delta E_p)$/mV (Ferrocene based)[a] |
|---|---|---|---|---|---|---|---|
| | $CHCl_3$ | | MeOH | | THF | | |
| Compd. | MLCT | π-π* | MLCT | π-π* | MLCT | π-π* | |
| **2**-(*E*) | – | 309 | – | 356 | – | 358 | 755(74) |
| **2**-(*Z*) | – | 308 | – | 325 | – | 329 | 790(170) |
| **3**-(*E*) | – | 327 | – | 329 | – | 329 | 775(127) |
| **4**-(*E,E*) | 494 | 358 | 497 | 358 | 495 | 355 | 545(89) |
| **4**-(*E,Z*) | 493 | 350 | 487 | 353 | 488 | 352 | 555(74) |
| **4**-(*Z,Z*) | 481 | 335 | – | 337 | 481 | 343 | 585(155) |
| **5**-(*E,E*) | – | 342 | – | 340 | 492 | 340 | 500(100) |
| **5**-(*E,Z*) | 473 | 334 | 473 | 333 | 469 | 335 | 545(115) |
| **5**-(*Z,Z*) | – | 318 | – | 312 | – | 319 | 565(79) |
| **6** | | | | | | | 455 |
| **7** | 436[b] | 306[b] | | | | | 351[b] |

[a] Ferrocene half-wave potential = 445(105) mV. – [b] Data taken from ref. [8].

### Electronic Spectra

Table 3 contains the electronic spectroscopic data for the bis-substituted complexes **2−5**. In a typical electronic spectrum of substituted ferrocenyl complexes, two prominent bands are often observed in the range of 500 to 300 nm. The more energetic band (300−360 nm) is assigned to a π−π* intra-ligand transition, and the less energetic band (400−500 nm) is assigned to a metal to ligand charge-transfer band (MLCT). A weak band at higher wavelengths (about 500 nm), assigned to a *d-d* transition, is only discernible in some cases as a shoulder on the MLCT band, and is not shown in Table 3. This assignment is in accordance to the theoretical results reported by Barlow et al. (model III in ref.[17]) and to other experimental results,[5,6,12,18−23] although we are aware that some controversy about this assignment has been reported.[24] The MLCT band is influenced by the nature of the ancillary ligand, showing a hypsochromic shift on increasing the (*E*) character of the complex. The more intense π-π* band shows a similar dependence on the nature of the ligand; this is because the (*E*) stereochemistry promotes a more effective conjugation than the (*Z*) stereochemistry, thus lowering the energy of the π* orbital. Solvatochromism affords an idea of the dipole moments in the ground and in the excited states. These are related to hyperpolarizability, and therefore solvatochromism is a useful indicator for the potential for second-order NLO behavior. The bis-substituted ferrocenyl complexes show moderate solvatochromic behavior across the solvents surveyed.

### Kurtz Powder Studies

Kurtz powder measurements were performed on **4**-(*E,Z*), **4**-(*Z,Z*), **4**-(*E,E*), **5**-(*E,Z*), **5**-(*E,E*), **6**, and **7**. Initial studies using ns pulses at 1.064 µm suggested the doubling of the frequency for a number of samples (green flashes were observed when the samples were irradiated), but absorption associated with the MLCT bands in these complexes rendered these results qualitative at best. A second qualitative test at the important telecommunications wavelength of 1.3 µm using fs pulses again suggested the doubling of the frequency (red flashes were observed for most complexes). A third qualitative test at 1.4 µm confirmed this result. Importantly, all complexes are transparent at both the fundamental and second-harmonic frequencies corresponding to the wavelength of 1.3 µm, so the SHG merit of these complexes was quantified against an urea standard, the results for which are summarized in Table 4.

Complexes **4**-(*E,Z*), **4**-(*Z,Z*), and **5**-(*E,Z*) showed a relatively strong emission with a significant blue component; this may be due to other NLO processes, and it masks any SHG which may be present, rendering further discussion of these complexes unwarranted. The ferrocene-containing conjugated compounds **4**-(*E,E*) and **5**-(*E,E*) both gave significant responses. Noncentrosymmetric crystal packing is a requirement for observable SHG, therefore it is worthy to note that the structural study of **5**-(*E,E*) reveals a lack of a center of symmetry in the crystal lattice. Complex **6** shows no observable SHG at 1.3 µm, in contrast to the $Cr(CO)_3$-ligated complex **7**. Both complexes crystallize in the centrosymmetric space group $P2_1/c$. The observed SHG for the centrosymmetric **7** is not unique; similar observations for $[Ru(C{-}CPhN{-}N{-}4\text{-}C_6H_4OMe)(PPh_3)_2(\eta^5\text{-}C_5H_5)]BF_4$[25] and $[(\eta^5\text{-}C_5H_5)(CO)_2Fe(\mu\text{-}CO)\{\mu\text{-}(E)\text{-}CH{=}CH{-}4\text{-}C_6H_4\text{-}NMe_2\}Fe(CO)_2(\eta\text{-}C_5H_5)]BF_4$,[26] both of which pack in centrosymmetric space groups, were assigned to effects originating in the noncentrosymmetric crystal surface, small contributions from a noncentrosymmetric phase, or minor deviations from centrosymmetry. Electron diffraction studies to resolve this ambiguity were similarly inconclusive.

The results of the present series of samples emphasize the challenges inherent in translating significant molecular nonlinearities to useful bulk susceptibilities. Thus, while $Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4{-}(Z)\text{-}CH{=}CH{-}4\text{-}C_6H_4NO_2)$ is reported to give SHG with an efficiency 62 times that of urea,[19,26–28] incorporation of a further 4-nitrophenylethenyl group in proceeding to **4**-(*E,Z*) or **4**-(*Z,Z*), results in complexes for which observable SHG could not be determined unambiguously.

### Third-Order NLO Studies

Third-order nonlinearities of **4**-(*Z,Z*), **5**-(*E,E*), **6**, and **7** were evaluated by the Z-scan technique at 800 nm;[29] the results of these measurements are given in Table 4. Complex **4**-(*E,E*) was insufficiently soluble, in both dichloromethane and THF, to afford useful data.

Early studies of ferrocenyl complexes by optical power limiting afforded very high nonlinearities ($10^{-32}$ to $10^{-31}$ esu),[30–32] but this technique is carried out on a ns time scale, and contributions from thermal effects may exist. For structure-activity studies, it is more useful to use Z-scan with fs pulses, as in the present study. The cubic nonlinearities $|\gamma|$ of these new ferrocenyl complexes are of the same magnitude as those of related conjugated ferrocenyl complexes examined by degenerate four-wave mixing (DFWM).[33]

One advantage of Z-scan relative to DFWM is that one can readily determine the real and imaginary components of the cubic hyperpolarizabilities, (these are also listed in Table 4). We have previously used Z-scan to study the cubic hyperpolarizabilities of acetylide complexes,[34–40] for which most real components are large and negative, and imaginary components are large, indicative of significant two-photon dispersion effects. The real components of the nonlinearities $\gamma_r$ for the present series of complexes are large and positive and, with the exception of **4**-(*E,Z*), the imaginary components $\gamma_i$ are small; two-photon effects are therefore likely to be minor, permitting cautious comment on the effect of structural variation on cubic NLO merit. Replace-

Table 4. Linear optical and nonlinear optical response parameters for **4**-(*Z,Z*), **4**-(*E,Z*), **4**-(*E,E*), **5**-(*E,Z*), **5**-(*E,E*), **6**, and **7**

| Complex | $\lambda_{max}$ (nm)[a] [$\varepsilon$ ($10^4$ M$^{-1}$ cm$^{-1}$)] | SHG[b] (urea = 1) | $\gamma_r$[c] ($10^{-36}$ esu) | $\gamma_i$[c] ($10^{-36}$ esu) | $\lvert\gamma\rvert$ ($10^{-36}$ esu) |
|---|---|---|---|---|---|
| $Fe\{\eta^5\text{-}C_5H_4\text{-}(E)\text{-}CH{=}CHC_6H_4.4.NO_2\}_2$ [**4**-(*E,E*)] | 495 [0.47] | 0.28 | [e] | [e] | [e] |
| $Fe\{\eta^5\text{-}C_5H_4\text{-}(E)\text{-}CH{=}CHC_6H_4.4.NO_2\}\text{-}\{\eta^5\text{-}C_5H_4\text{-}(Z)\text{-}CH{=}CHC_6H_4.4.NO_2\}$ [**4**-(*E,Z*)] | 488 [0.56] | [d] | 840 ± 400 | 770 ± 200 | 1140 ± 430 |
| $Fe\{\eta^5\text{-}C_5H_4\text{-}(Z)\text{-}CH{=}CHC_6H_4.4.NO_2\}_2$ [**4**-(*Z,Z*)] | 481 [0.30] | [d] | 600 ± 300 | 0 ± 50 | 600 ± 300 |
| $Fe\{\eta^5\text{-}C_5H_4\text{-}(E)\text{-}CH{=}CHC_6H_4.4.CN\}_2$ [**5**-(*E,E*)] | 492 [0.34] | 0.24 | 280 ± 150 | 30 ± 20 | 280 ± 150 |
| $Fe\{\eta^5\text{-}C_5H_4\text{-}(E)\text{-}CH{=}CHC_6H_4.4.CN\}\text{-}\{\eta^5\text{-}C_5H_4\text{-}(Z)\text{-}CH{=}CHC_6H_4.4.CN\}$ [**5**-(*E,Z*)] | 469 [0.33] | [d] | 310 ± 200 | 50 ± 30 | 310 ± 200 |
| $Fe(\eta\text{-}C_5H_5)\{\eta^5\text{-}C_5H_4\text{-}(E)\text{-}CH{=}CH\text{-}4\text{-}C_6H_4\text{-}(E)\text{-}CH{=}CH\text{-}\eta^5\text{-}C_5H_4\}Fe(\eta^5\text{-}C_5H_5)$ (**6**) | 457 [0.45] | [d] | 640 ± 300 | 30 ± 20 | 640 ± 300 |
| $Fe(\eta\text{-}C_5H_5)(\eta^5\text{-}C_5H_4\text{-}(E)\text{-}CH{=}CH\text{-}4\text{-}\{(\eta^6\text{-}C_6H_4)\text{-}Cr(CO)_3\}\text{-}(E)\text{-}CH{=}CH\text{-}\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)$ (**7**) | 455 [0.31] | 0.14 | 850 ± 300 | 95 ± 30 | 860 ± 300 |

[a] All solution measurements (linear optical spectra, third-order NLO studies) in THF as solvent. All complexes are optically transparent at 1.3 µm and 800 nm. – [b] Bulk second-order responses by the Kurtz powder method at 1.3 µm. – [c] Third-order NLO measurements by Z-scan at 800 nm, referenced to the nonlinear refractive index of silica $n_2 = 3 \cdot 10^{-16}$ cm$^2$·W$^{-1}$. – [d] Not determined unambiguously. – [e] Insufficiently soluble.

ment of CN by $NO_2$ in proceeding from **5**-(*E,Z*) to **4**-(*E,Z*), leads to a significant increase in both $\gamma_r$ and $|\gamma|$; increase in acceptor-strength leads to increased quadratic nonlinearity in dipolar organometallic complexes,[10] and a similar increase in cubic nonlinearity for the present complexes on increasing acceptor-strength is not unexpected. Errors do not permit comment on the effect of bridge stereochemistry modification on $\gamma_r$ and $|\gamma|$. The linked complex **6** has substantial $\gamma_r$ and $|\gamma|$ values despite the absence of a molecular dipole; a large cubic nonlinearity ($\gamma = 504 \pm 52 \times 10^{-36}$ esu, as measured by DFWM at 0.60 μm) was reported for a complex with this composition in earlier work, although the bridge stereochemistry was not specified.[33] Interestingly, incorporation of the bridge-ligated $Cr(CO)_3$ unit in proceeding from **6** to **7**, results in an increase in both $\gamma_r$ and $|\gamma|$. Recent studies concluded that the $Cr(CO)_3$ unit behaves as an electronically amphoteric auxochrome in chromium carbonyl arene complexes with conjugated side-chains,[16] resulting in significant quadratic nonlinearities for complexes with donor- or acceptor- substituents on the side-chain. In the present system, complex **6** has a donor-bridge-donor composition, whereas our electrochemistry studies suggest that **7** has a donor-donor-donor composition; the increase in the ease of oxidation in proceeding from **6** to **7** probably correlates with an increase in the ease of polarization of electron density, and may be responsible for the increased cubic nonlinearity.

## Experimental Section

**General Remarks:** All reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques. Solvents for synthesis and electrochemical measurements were dried and deoxygenated by standard methods before use. Chromatographic work was performed on silica gel 60 Å or neutral alumina columns.

NMR spectra were recorded on Varian Innova 300 MHz and 500 MHz spectrometers, using $CDCl_3$ as solvent unless otherwise stated. – IR spectra were recorded on a Perkin−Elmer System 2000 FT-IR using NaCl pellets. – Electronic absorption spectra were obtained on a UV-1603 Shimadzu spectrophotometer. – Elemental analyses were performed on a EA 1108 CHNS-O Carlo Erba instrument. – Cyclic voltammetry experiments were performed with a Echochemie pgstat 20 electrochemical analyzer. All measurements were carried out at room temperature with a conventional three-electrode configuration consisting of platinum working and auxiliary electrodes and a Ag/AgCl reference electrode containing aqueous 3 M KCl. The solvent used in all experiments was $CH_2Cl_2$, which was obtained in HPLC grade and used as received. The supporting electrolyte was 0.1 M tetra-*n*-butylammonium hexafluorophosphate, synthesized by reaction of tetra-*n*-butylammonium bromide and $HPF_6$, recrystallized from ethanol and dried under vacuum. $E_{1/2}$ values were determined as $(E_{p,a} + E_{p,c})/2$, where $E_{p,a}$ and $E_{p,c}$ are the anodic and cathodic peak potentials, respectively. All reported potentials are not corrected for the junction potential. – Electrospray mass spectra were recorded using a Micromass Quattro LC instrument, using $CH_3CN$ and/or $CH_3OH$ as the mobile phase solvent. The samples were added to give a mobile phase with an approximate concentration of 0.1 mM. This solution was injected into the spectrometer via a Rheodyne injector fitted with a 10 μL sample loop, and nitrogen was employed as a drying and nebulizing gas. – $Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4-(E)\text{-}CH=CH-4\text{-}C_6H_4-(E)\text{-}CH=CH-\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)$ (**6**) was synthesized by literature procedures.[41,42]

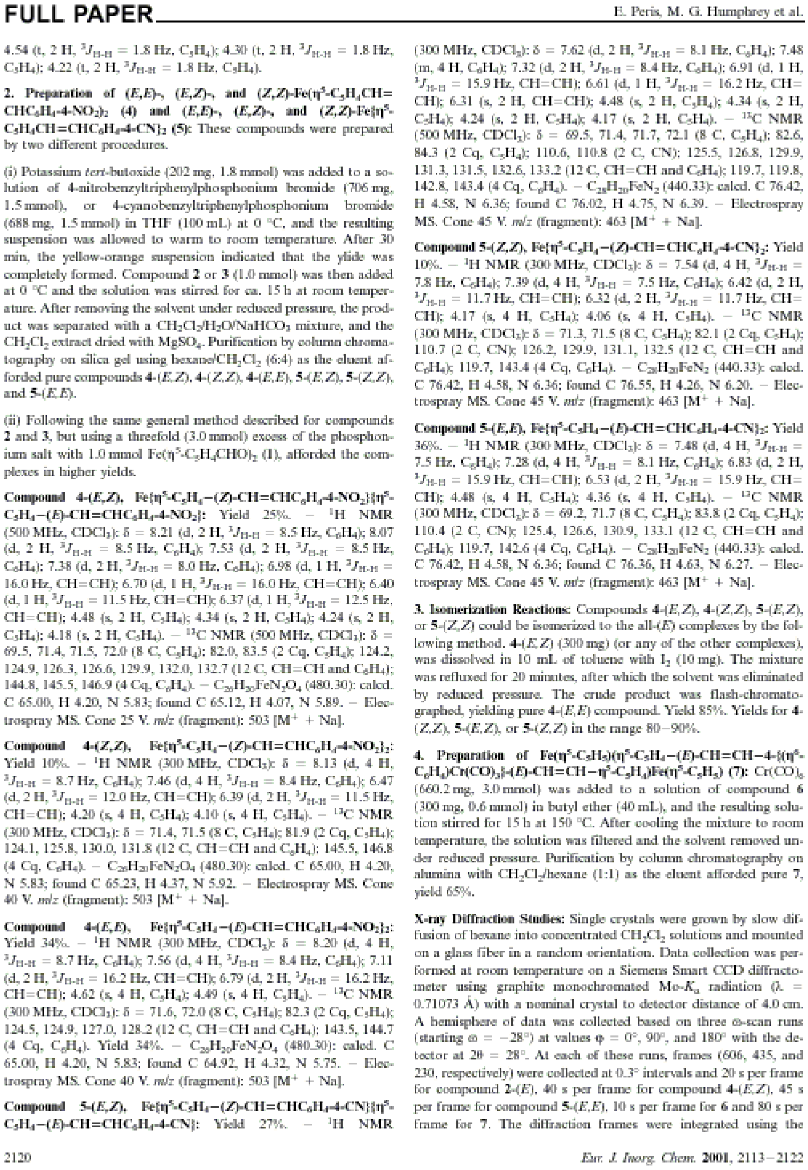
**1. Preparation of (*E*)- and (*Z*)-$Fe(\eta^5\text{-}C_5H_4CHO)(\eta^5\text{-}C_5H_4CH=CH-C_6H_4\text{-}4\text{-}NO_2)$ (2) and (*E*)-and (*Z*)-$Fe(\eta^5\text{-}C_5H_4CHO)(\eta^5\text{-}C_5H_4CH=CH-C_6H_4\text{-}4\text{-}CN)$ (3):** Potassium *tert*-butoxide (258 mg, 2.3 mmol) was added to a solution of 4-nitrobenzyltriphenylphosphonium bromide (988 mg, 2.1 mmol), or 4-cyanobenzyltriphenylphosphonium bromide (963 mg, 2.1 mmol) in THF (100 mL) at 0 °C, and the resulting suspension was allowed to warm to room temperature. After 30 min, the yellow-orange suspension indicated that the ylide was completely formed. 1,1′-Ferrocenebis(carboxaldehyde), **1** (500 mg, 2.1 mmol), was then added at 0 °C and the solution was stirred for ca. 15 h at room temperature. After removing the solvent under reduced pressure, the product was separated with a $CH_2Cl_2/H_2O/NaHCO_3$ mixture and the dichloromethane extract dried with $MgSO_4$. Purification by column chromatography on silica gel using hexane/$CH_2Cl_2$ (3:7) as the eluent afforded pure **2**-(*E*), **2**-(*Z*), **3**-(*E*), and **3**-(*Z*), although **3**-(*Z*) was obtained in such a low yield that only spectroscopic characterization could be achieved.

**Compound 2-(*E*), $Fe(\eta^5\text{-}C_5H_4CHO)\{\eta^5\text{-}C_5H_4-(E)\text{-}CH=CH-C_6H_4\text{-}4\text{-}NO_2\}$:** Yield 35%. – $^1H$ NMR (500 MHz, $CDCl_3$): $\delta$ = 9.90 (s, 1 H, CHO); 8.20 (d, 2 H, $^3J_{H-H}$ = 8.4 Hz, $C_6H_4$); 7.56 (d, 2 H, $^3J_{H-H}$ = 8.1 Hz, $C_6H_4$); 6.96 (d, 1 H, $^3J_{H-H}$ = 16.2 Hz, CH=CH); 6.76 (d, 1 H, $^3J_{H-H}$ = 15.9 Hz, CH=CH); 4.78 (s, 2 H, $C_5H_4$); 4.62 (s, 2 H, $C_5H_4$); 4.58 (s, 2 H, $C_5H_4$); 4.46 (s, 2 H, $C_5H_4$). – $^{13}C$ NMR (500 MHz, $CDCl_3$): $\delta$ = 69.4, 71.5, 71.9, 75.0 (8 C, $C_5H_4$); 80.6, 84.3 (2 Cq, $C_5H_4$); 124.8, 126.2, 126.9, 131.2 (6 C, CH=CH and $C_6H_4$); 144.3, 146.9 (2 Cq, $C_6H_4$); 194.1 (1 C, CHO). – $C_{19}H_{15}FeNO_3$ (361.18): calcd. C 63.20, H 4.19, N 3.88; found C 63.53, H 4.27, N 3.80.

**Compound 2-(*Z*), $Fe(\eta^5\text{-}C_5H_4CHO)\{\eta^5\text{-}C_5H_4-(Z)\text{-}CH=CH-C_6H_4\text{-}4\text{-}NO_2\}$:** Yield 17%. – $^1H$ NMR (500 MHz, $CDCl_3$): $\delta$ = 9.87 (s, 1 H, CHO); 8.14 (d, 2 H, $^3J_{H-H}$ = 8.5 Hz, $C_6H_4$); 7.43 (d, 2 H, $^3J_{H-H}$ = 8.0 Hz, $C_6H_4$); 6.55 (d, 1 H, $^3J_{H-H}$ = 12.0 Hz, CH=CH); 6.39 (d, 1 H, $^3J_{H-H}$ = 12.0 Hz, CH=CH); 4.74 (s, 2 H, $C_5H_4$); 4.54 (s, 2 H, $C_5H_4$); 4.31 (s, 2 H, $C_5H_4$); 4.23 (s, 2 H, $C_5H_4$). – $^{13}C$ NMR (500 MHz, $CDCl_3$): $\delta$ = 71.3, 71.4, 71.5, 75.0 (8 C, $C_5H_4$); 81.1, 83.0 (2 Cq, $C_5H_4$); 124.2, 127.4, 130.1, 130.4 (6 C, CH=CH and $C_6H_4$); 145.2, 147.2 (2 Cq, $C_6H_4$); 193.8 (1 C, CHO). – $C_{19}H_{15}FeNO_3$ (361.18): calcd. C 63.20, H 4.19, N 3.88; found C 63.01, H 4.07, N 3.79.

**Compound 3-(*E*), $Fe(\eta^5\text{-}C_5H_4CHO)\{\eta^5\text{-}C_5H_4-(E)\text{-}CH=CH-C_6H_4\text{-}4\text{-}CN\}$:** Yield 40%. – $^1H$ NMR (500 MHz, $CDCl_3$): $\delta$ = 9.90 (s, 1 H, CHO); 7.62 (d, 2 H, $^3J_{H-H}$ = 7.5 Hz, $C_6H_4$); 7.52 (d, 2 H, $^3J_{H-H}$ = 8.0 Hz, $C_6H_4$); 6.89 (d, 1 H, $^3J_{H-H}$ = 16.0 Hz, CH=CH); 6.72 (d, 1 H, $^3J_{H-H}$ = 16.0 Hz, CH=CH); 4.79 (s, 2 H, $C_5H_4$); 4.60 (s, 2 H, $C_5H_4$); 4.58 (s, 2 H, $C_5H_4$); 4.44 (s, 2 H, $C_5H_4$). – $^{13}C$ NMR (500 MHz, $CDCl_3$): $\delta$ = 69.3, 71.5, 71.7, 74.9 (8 C, $C_5H_4$); 80.7, 84.6 (2 Cq, $C_5H_4$); 110.9 (1 C, CN); 126.8, 127.1, 130.1, 133.3 (6 C, CH=CH and $C_6H_4$); 119.8, 142.4 (2 Cq, $C_6H_4$); 194.2 (1 C, CHO). – $C_{20}H_{15}FeNO$ (341.19): calcd. C 70.43, H 4.43, N 4.11; found C 70.12, H 4.17, N 4.25. – Electrospray MS. Cone 60 V. *m/z* (fragment): 364 $[M^+ + Na]$.

**Compound 3-(*Z*), $Fe(\eta^5\text{-}C_5H_4CHO)\{\eta^5\text{-}C_5H_4-(Z)\text{-}CH=CH-C_6H_4\text{-}4\text{-}CN\}$:** $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ = 9.86 (s, 1 H, CHO); 7.56 (d, 2 H, $^3J_{H-H}$ = 8.1 Hz, $C_6H_4$); 7.38 (d, 2 H, $^3J_{H-H}$ = 8.4 Hz, $C_6H_4$); 6.50 (d, 1 H, $^3J_{H-H}$ = 12.0 Hz, CH=CH); 6.33 (d, 1 H, $^3J_{H-H}$ = 12.0 Hz, CH=CH); 4.73 (t, 2 H, $^3J_{H-H}$ = 1.8 Hz, $C_5H_4$);



4.54 (t, 2 H, $^{3}J_{H\text{-}H}$ = 1.8 Hz, $C_5H_4$); 4.30 (t, 2 H, $^{3}J_{H\text{-}H}$ = 1.8 Hz, $C_5H_4$); 4.22 (t, 2 H, $^{3}J_{H\text{-}H}$ = 1.8 Hz, $C_5H_4$).

**2. Preparation of (*E,E*)-, (*E,Z*)-, and (*Z,Z*)-Fe($\eta^5$-$C_5H_4CH{=}CHC_6H_4$-4-$NO_2$)$_2$ (4) and (*E,E*)-, (*E,Z*)-, and (*Z,Z*)-Fe{$\eta^5$-$C_5H_4CH{=}CHC_6H_4$-4-CN}$_2$ (5):** These compounds were prepared by two different procedures.

(i) Potassium *tert*-butoxide (202 mg, 1.8 mmol) was added to a solution of 4-nitrobenzyltriphenylphosphonium bromide (706 mg, 1.5 mmol), or 4-cyanobenzyltriphenylphosphonium bromide (688 mg, 1.5 mmol) in THF (100 mL) at 0 °C, and the resulting suspension was allowed to warm to room temperature. After 30 min, the yellow-orange suspension indicated that the ylide was completely formed. Compound **2** or **3** (1.0 mmol) was then added at 0 °C and the solution was stirred for ca. 15 h at room temperature. After removing the solvent under reduced pressure, the product was separated with a $CH_2Cl_2/H_2O/NaHCO_3$ mixture, and the $CH_2Cl_2$ extract dried with $MgSO_4$. Purification by column chromatography on silica gel using hexane/$CH_2Cl_2$ (6:4) as the eluent afforded pure compounds **4**-(*E,Z*), **4**-(*Z,Z*), **4**-(*E,E*), **5**-(*E,Z*), **5**-(*Z,Z*), and **5**-(*E,E*).

(ii) Following the same general method described for compounds **2** and **3**, but using a threefold (3.0 mmol) excess of the phosphonium salt with 1.0 mmol Fe($\eta^5$-$C_5H_4CHO$)$_2$ (**1**), afforded the complexes in higher yields.

**Compound 4-(*E,Z*), Fe{$\eta^5$-$C_5H_4$−(*Z*)-$CH{=}CHC_6H_4$-4-$NO_2$}{$\eta^5$-$C_5H_4$−(*E*)-$CH{=}CHC_6H_4$-4-$NO_2$}:** Yield 25%. − $^1H$ NMR (500 MHz, $CDCl_3$): δ = 8.21 (d, 2 H, $^{3}J_{H\text{-}H}$ = 8.5 Hz, $C_6H_4$); 8.07 (d, 2 H, $^{3}J_{H\text{-}H}$ = 8.5 Hz, $C_6H_4$); 7.53 (d, 2 H, $^{3}J_{H\text{-}H}$ = 8.5 Hz, $C_6H_4$); 7.38 (d, 2 H, $^{3}J_{H\text{-}H}$ = 8.0 Hz, $C_6H_4$); 6.98 (d, 1 H, $^{3}J_{H\text{-}H}$ = 16.0 Hz, CH=CH); 6.70 (d, 1 H, $^{3}J_{H\text{-}H}$ = 16.0 Hz, CH=CH); 6.40 (d, 1 H, $^{3}J_{H\text{-}H}$ = 11.5 Hz, CH=CH); 6.37 (d, 1 H, $^{3}J_{H\text{-}H}$ = 12.5 Hz, CH=CH); 4.48 (s, 2 H, $C_5H_4$); 4.34 (s, 2 H, $C_5H_4$); 4.24 (s, 2 H, $C_5H_4$); 4.18 (s, 2 H, $C_5H_4$). − $^{13}C$ NMR (500 MHz, $CDCl_3$): δ = 69.5, 71.4, 71.5, 72.0 (8 C, $C_5H_4$); 82.0, 83.5 (2 Cq, $C_5H_4$); 124.2, 124.9, 126.3, 126.6, 129.9, 132.0, 132.7 (12 C, CH=CH and $C_6H_4$); 144.8, 145.5, 146.9 (4 Cq, $C_6H_4$). − $C_{26}H_{20}FeN_2O_4$ (480.30): calcd. C 65.00, H 4.20, N 5.83; found C 65.12, H 4.07, N 5.89. − Electrospray MS. Cone 25 V. *m/z* (fragment): 503 [$M^+$ + Na].

**Compound 4-(*Z,Z*), Fe{$\eta^5$-$C_5H_4$−(*Z*)-$CH{=}CHC_6H_4$-4-$NO_2$}$_2$:** Yield 10%. − $^1H$ NMR (300 MHz, $CDCl_3$): δ = 8.13 (d, 4 H, $^{3}J_{H\text{-}H}$ = 8.7 Hz, $C_6H_4$); 7.46 (d, 4 H, $^{3}J_{H\text{-}H}$ = 8.4 Hz, $C_6H_4$); 6.47 (d, 2 H, $^{3}J_{H\text{-}H}$ = 12.0 Hz, CH=CH); 6.39 (d, 2 H, $^{3}J_{H\text{-}H}$ = 11.5 Hz, CH=CH); 4.20 (s, 4 H, $C_5H_4$); 4.10 (s, 4 H, $C_5H_4$). − $^{13}C$ NMR (300 MHz, $CDCl_3$): δ = 71.4, 71.5 (8 C, $C_5H_4$); 81.9 (2 Cq, $C_5H_4$); 124.1, 125.8, 130.0, 131.8 (12 C, CH=CH and $C_6H_4$); 145.5, 146.8 (4 Cq, $C_6H_4$). − $C_{26}H_{20}FeN_2O_4$ (480.30): calcd. C 65.00, H 4.20, N 5.83; found C 65.23, H 4.37, N 5.92. − Electrospray MS. Cone 40 V. *m/z* (fragment): 503 [$M^+$ + Na].

**Compound 4-(*E,E*), Fe{$\eta^5$-$C_5H_4$−(*E*)-$CH{=}CHC_6H_4$-4-$NO_2$}$_2$:** Yield 34%. − $^1H$ NMR (300 MHz, $CDCl_3$): δ = 8.20 (d, 4 H, $^{3}J_{H\text{-}H}$ = 8.7 Hz, $C_6H_4$); 7.56 (d, 4 H, $^{3}J_{H\text{-}H}$ = 8.4 Hz, $C_6H_4$); 7.11 (d, 2 H, $^{3}J_{H\text{-}H}$ = 16.2 Hz, CH=CH); 6.79 (d, 2 H, $^{3}J_{H\text{-}H}$ = 16.2 Hz, CH=CH); 4.62 (s, 4 H, $C_5H_4$); 4.49 (s, 4 H, $C_5H_4$). − $^{13}C$ NMR (300 MHz, $CDCl_3$): δ = 71.6, 72.0 (8 C, $C_5H_4$); 82.3 (2 Cq, $C_5H_4$); 124.5, 124.9, 127.0, 128.2 (12 C, CH=CH and $C_6H_4$); 143.5, 144.7 (4 Cq, $C_6H_4$). Yield 34%. − $C_{26}H_{20}FeN_2O_4$ (480.30): calcd. C 65.00, H 4.20, N 5.83; found C 64.92, H 4.32, N 5.75. − Electrospray MS. Cone 40 V. *m/z* (fragment): 503 [$M^+$ + Na].

**Compound 5-(*E,Z*), Fe{$\eta^5$-$C_5H_4$−(*Z*)-$CH{=}CHC_6H_4$-4-CN}{$\eta^5$-$C_5H_4$−(*E*)-$CH{=}CHC_6H_4$-4-CN}:** Yield 27%. − $^1H$ NMR (300 MHz, $CDCl_3$): δ = 7.62 (d, 2 H, $^{3}J_{H\text{-}H}$ = 8.1 Hz, $C_6H_4$); 7.48 (m, 4 H, $C_6H_4$); 7.32 (d, 2 H, $^{3}J_{H\text{-}H}$ = 8.4 Hz, $C_6H_4$); 6.91 (d, 1 H, $^{3}J_{H\text{-}H}$ = 15.9 Hz, CH=CH); 6.61 (d, 1 H, $^{3}J_{H\text{-}H}$ = 16.2 Hz, CH=CH); 6.31 (s, 2 H, CH=CH); 4.48 (s, 2 H, $C_5H_4$); 4.34 (s, 2 H, $C_5H_4$); 4.24 (s, 2 H, $C_5H_4$); 4.17 (s, 2 H, $C_5H_4$). − $^{13}C$ NMR (500 MHz, $CDCl_3$): δ = 69.5, 71.4, 71.7, 72.1 (8 C, $C_5H_4$); 82.6, 84.3 (2 Cq, $C_5H_4$); 110.6, 110.8 (2 C, CN); 125.5, 126.8, 129.9, 131.3, 131.5, 132.6, 133.2 (12 C, CH=CH and $C_6H_4$); 119.7, 119.8, 142.8, 143.4 (4 Cq, $C_6H_4$). − $C_{28}H_{20}FeN_2$ (440.33): calcd. C 76.42, H 4.58, N 6.36; found C 76.02, H 4.75, N 6.39. − Electrospray MS. Cone 45 V. *m/z* (fragment): 463 [$M^+$ + Na].

**Compound 5-(*Z,Z*), Fe{$\eta^5$-$C_5H_4$−(*Z*)-$CH{=}CHC_6H_4$-4-CN}$_2$:** Yield 10%. − $^1H$ NMR (300 MHz, $CDCl_3$): δ = 7.54 (d, 4 H, $^{3}J_{H\text{-}H}$ = 7.8 Hz, $C_6H_4$); 7.39 (d, 4 H, $^{3}J_{H\text{-}H}$ = 7.5 Hz, $C_6H_4$); 6.42 (d, 2 H, $^{3}J_{H\text{-}H}$ = 11.7 Hz, CH=CH); 6.32 (d, 2 H, $^{3}J_{H\text{-}H}$ = 11.7 Hz, CH=CH); 4.17 (s, 4 H, $C_5H_4$); 4.06 (s, 4 H, $C_5H_4$). − $^{13}C$ NMR (300 MHz, $CDCl_3$): δ = 71.3, 71.5 (8 C, $C_5H_4$); 82.1 (2 Cq, $C_5H_4$); 110.7 (2 C, CN); 126.2, 129.9, 131.1, 132.5 (12 C, CH=CH and $C_6H_4$); 119.7, 143.4 (4 Cq, $C_6H_4$). − $C_{28}H_{20}FeN_2$ (440.33): calcd. C 76.42, H 4.58, N 6.36; found C 76.55, H 4.26, N 6.20. − Electrospray MS. Cone 45 V. *m/z* (fragment): 463 [$M^+$ + Na].

**Compound 5-(*E,E*), Fe{$\eta^5$-$C_5H_4$−(*E*)-$CH{=}CHC_6H_4$-4-CN}$_2$:** Yield 36%. − $^1H$ NMR (300 MHz, $CDCl_3$): δ = 7.48 (d, 4 H, $^{3}J_{H\text{-}H}$ = 7.5 Hz, $C_6H_4$); 7.28 (d, 4 H, $^{3}J_{H\text{-}H}$ = 8.1 Hz, $C_6H_4$); 6.83 (d, 2 H, $^{3}J_{H\text{-}H}$ = 15.9 Hz, CH=CH); 6.53 (d, 2 H, $^{3}J_{H\text{-}H}$ = 15.9 Hz, CH=CH); 4.48 (s, 4 H, $C_5H_4$); 4.36 (s, 4 H, $C_5H_4$). − $^{13}C$ NMR (300 MHz, $CDCl_3$): δ = 69.2, 71.7 (8 C, $C_5H_4$); 83.8 (2 Cq, $C_5H_4$); 110.4 (2 C, CN); 125.4, 126.6, 130.9, 133.1 (12 C, CH=CH and $C_6H_4$); 119.7, 142.6 (4 Cq, $C_6H_4$). − $C_{28}H_{20}FeN_2$ (440.33): calcd. C 76.42, H 4.58, N 6.36; found C 76.36, H 4.63, N 6.27. − Electrospray MS. Cone 45 V. *m/z* (fragment): 463 [$M^+$ + Na].

**3. Isomerization Reactions:** Compounds **4**-(*E,Z*), **4**-(*Z,Z*), **5**-(*E,Z*), or **5**-(*Z,Z*) could be isomerized to the all-(*E*) complexes by the following method. **4**-(*E,Z*) (300 mg) (or any of the other complexes), was dissolved in 10 mL of toluene with $I_2$ (10 mg). The mixture was refluxed for 20 minutes, after which the solvent was eliminated by reduced pressure. The crude product was flash-chromatographed, yielding pure **4**-(*E,E*) compound. Yield 85%. Yields for **4**-(*Z,Z*), **5**-(*E,Z*), or **5**-(*Z,Z*) in the range 80−90%.

**4. Preparation of Fe($\eta^5$-$C_5H_5$)($\eta^5$-$C_5H_4$−(*E*)-CH=CH−4-{($\eta^6$-$C_6H_4$)Cr(CO)$_3$}-(*E*)-CH=CH−$\eta^5$-$C_5H_4$)Fe($\eta^5$-$C_5H_5$) (7):** $Cr(CO)_6$ (660.2 mg, 3.0 mmol) was added to a solution of compound **6** (300 mg, 0.6 mmol) in butyl ether (40 mL), and the resulting solution stirred for 15 h at 150 °C. After cooling the mixture to room temperature, the solution was filtered and the solvent removed under reduced pressure. Purification by column chromatography on alumina with $CH_2Cl_2$/hexane (1:1) as the eluent afforded pure **7**, yield 65%.

**X-ray Diffraction Studies:** Single crystals were grown by slow diffusion of hexane into concentrated $CH_2Cl_2$ solutions and mounted on a glass fiber in a random orientation. Data collection was performed at room temperature on a Siemens Smart CCD diffractometer using graphite monochromated Mo-$K_\alpha$ radiation ($\lambda$ = 0.71073 Å) with a nominal crystal to detector distance of 4.0 cm. A hemisphere of data was collected based on three ω-scan runs (starting ω = −28°) at values φ = 0°, 90°, and 180° with the detector at 2θ = 28°. At each of these runs, frames (606, 435, and 230, respectively) were collected at 0.3° intervals and 20 s per frame for compound **2**-(*E*), 40 s per frame for compound **4**-(*E,Z*), 45 s per frame for compound **5**-(*E,E*), 10 s per frame for **6** and 80 s per frame for **7**. The diffraction frames were integrated using the

Table 5. Crystallographic Data

| Compound | **2**-(E) | **4**-(*E,Z*) | **5**-(*E,E*) | **6** | **7** |
|---|---|---|---|---|---|
| Empirical formula | C[illegible]H[illegible]FeNO[illegible] | C[illegible]H[illegible]FeN[illegible]O[illegible] | C[illegible]H[illegible]FeNFeN[illegible] | C[illegible]H[illegible]Fe[illegible] | C[illegible]H[illegible]Fe[illegible]CrO[illegible] |
| Molecular weight [g·mol$^{-1}$] | 361.17 | 480.29 | 440.31 | 498.21 | 634.24 |
| Temperature [K] | 293(2) | 293(2) | 293(2) | 293(2) | 293(2) |
| Wavelength [Å] | 0.71073 | 0.71073 | 0.71073 | 0.71073 | 0.71073 |
| Crystal System | Monoclinic | Triclinic | Monoclinic | Monoclinic | Monoclinic |
| Space group | $P2_1/n$ | $P\bar{1}$ | $P2_1$ | $P2_1/c$ | $P2_1/c$ |
| $a$ [Å] | 7.6532(5) | 7.5874(17) | 6.2114(4) | 12.7324(4) | 17.131(3) |
| $b$ [Å] | 7.6518(5) | 10.569(2) | 14.0877(8) | 7.7128(2) | 7.4568(13) |
| $c$ [Å] | 26.6880(17) | 14.416(3) | 12.1250(7) | 11.6266(5) | 10.7432(19) |
| α [deg.] | 90 | 100.919(5) | 90 | 90 | 90 |
| β [deg.] | 91.328(2) | 103.232(5) | 102.3550(10) | 98.5460(10) | 99.780(4) |
| γ [deg.] | 90 | 101.555(6) | 90 | 90 | 90 |
| Volume [Å$^3$] | 1562.45(18) | 1068.5(4) | 1036.42(11) | 1129.08(7) | 1352.4(4) |
| $Z$ | 4 | 2 | 2 | 2 | 2 |
| Density [calcd. Mg·m$^{-3}$] | 1.535 | 1.493 | 1.411 | 1.465 | 1.557 |
| Absorption Coef. [mm$^{-1}$] | 0.982 | 0.743 | 0.746 | 1.300 | 1.487 |
| $F$(000) | 744 | 496 | 456 | 516 | 648 |
| Crystal Size [mm$^3$] | 0.28×0.23×0.16 | 0.26×0.11×0.10 | 0.49×0.44×0.02 | 0.46×0.14×0.03 | 0.046×0.042×0.011 |
| θ range [deg.] | 1.53 to 30.55 | 1.50 to 30.59 | 1.72 to 30.53 | 1.62 to 30.85 | 1.21 to 24.70 |
| Index Ranges | $-9 \le h \le 10$<br>$-10 \le k \le 10$<br>$-37 \le l \le 25$ | $-8 \le h \le 10$<br>$-15 \le k \le 14$<br>$-20 \le l \le 15$ | $-8 \le h \le 8$<br>$-18 \le k \le 20$<br>$-16 \le l \le 17$ | $-18 \le h \le 17$<br>$-11 \le k \le 11$<br>$-16 \le l \le 16$ | $-11 \le h \le 11$<br>$-7 \le k \le 7$<br>$-7 \le l \le 12$ |
| Reflections Collected | 12775 | 9110 | 8466 | 12797 | 4327 |
| Independent Reflections | 4766 [$R$(int.) = 0.0617] | 6400 [$R$(int.) = 0.0553] | 4917 [$R$(int.) = 0.0313] | 3395 [$R$(int.) = 0.0439] | 1353 [$R$(int.) = 0.0790] |
| Data/Restraints/Parameters | 4766/0/245 | 6400/0/298 | 4917/1/281 | 3395/0/145 | 1353/0/182 |
| Goodness-of-fit-on $F^2$ | 0.868 | 0.844 | 0.876 | 0.916 | 1.082 |
| Final $R$ indices [$I > 2\sigma(I)$] | $R1 = 0.0454$, $wR2 = 0.0850$ | $R1 = 0.0572$, $wR2 = 0.0943$ | $R1 = 0.0422$, $wR2 = 0.0720$ | $R1 = 0.0328$, $wR2 = 0.0669$ | $R1 = 0.0699$, $wR2 = 0.1749$ |
| $R$ indices (all data) | $R1 = 0.1366$, $wR2 = 0.1027$ | $R1 = 0.1679$, $wR2 = 0.1191$ | $R1 = 0.0867$, $wR2 = 0.0805$ | $R1 = 0.0748$, $wR2 = 0.0760$ | $R1 = 0.1034$, $wR2 = 0.2006$ |
| ρ max, ρ min. [e Å$^{-3}$] | 0.529, −0.261 | 0.758, −0.599 | 0.428, −0.246 | 0.303, −0.229 | 0.456, −0.507 |

SAINT package and corrected for absorption with SADABS.[43,44] Space group assignments are based on systematic absences, E statistics, and successful refinement of the structures. Structures were solved by direct methods with the aid of successive difference Fourier maps and were refined using the SHELXTL 5.1 software package. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned to ideal positions and refined using a riding model. Data collection parameters are given in Table 5.

**Kurtz Powder Studies:** Samples were ungraded powders placed in the circular cavity (10 mm diameter × 0.5 mm depth) of a microscope slide with a cover slip. Powder SHG efficiencies were measured using the Kurtz technique.[45] Studies utilizing the fundamental output of a Q-switched Quanta-Ray GC-130 Nd:YAG laser (1.06 µm) were inconclusive due to material resonances at the second-harmonic frequency. The powder measurements were therefore performed at 1.3 and 1.4 µm using a Light Conversion Topas optical parametric generator pumped with a Clark MXR regenerative amplifier. This afforded approximately 150 fs pulses at a 1 kHz repetition rate which were directed onto the sample as an unfocussed beam (spot size about 5 mm; energy per pulse: up to 20 mJ). The intensity of the generated powder SHG was determined using a Coolsnap Photometric CCD camera. Measurements thus made were compared with those of a urea powder sample.

**Z-scan Measurements:** Z-scan measurements were performed at 800 nm using 100 fs pulses from a system consisting of a Coherent Mira Ti-sapphire laser pumped with a Coherent Innova or Coherent Verdi cw pump and a Ti-sapphire regenerative amplifier pumped with a frequency-doubled Q-switched pulsed YAG laser (Spectra Physics GCR) at 30 Hz and employing chirped pulse amplification. Tetrahydrofuran solutions were examined in a glass cell with a 0.1 cm path length. The Z-scans were recorded at three concentrations for each compound [two concentrations for **4**-(*E,E*), **4**-(*Z,Z*), and **5**-(*E,E*)] and the real and imaginary part of the nonlinear phase change determined by numerical fitting.[29] The real and imaginary part of the hyperpolarizability of the solute was then calculated assuming linear concentration dependencies of the nonlinear phase shifts. The nonlinearities and light intensities were calibrated using measurements of a 1 mm thick silica plate for which the nonlinear refractive index $n_2 = 3{\cdot}10^{-16}$ cm$^2$·W$^{-1}$ was assumed.

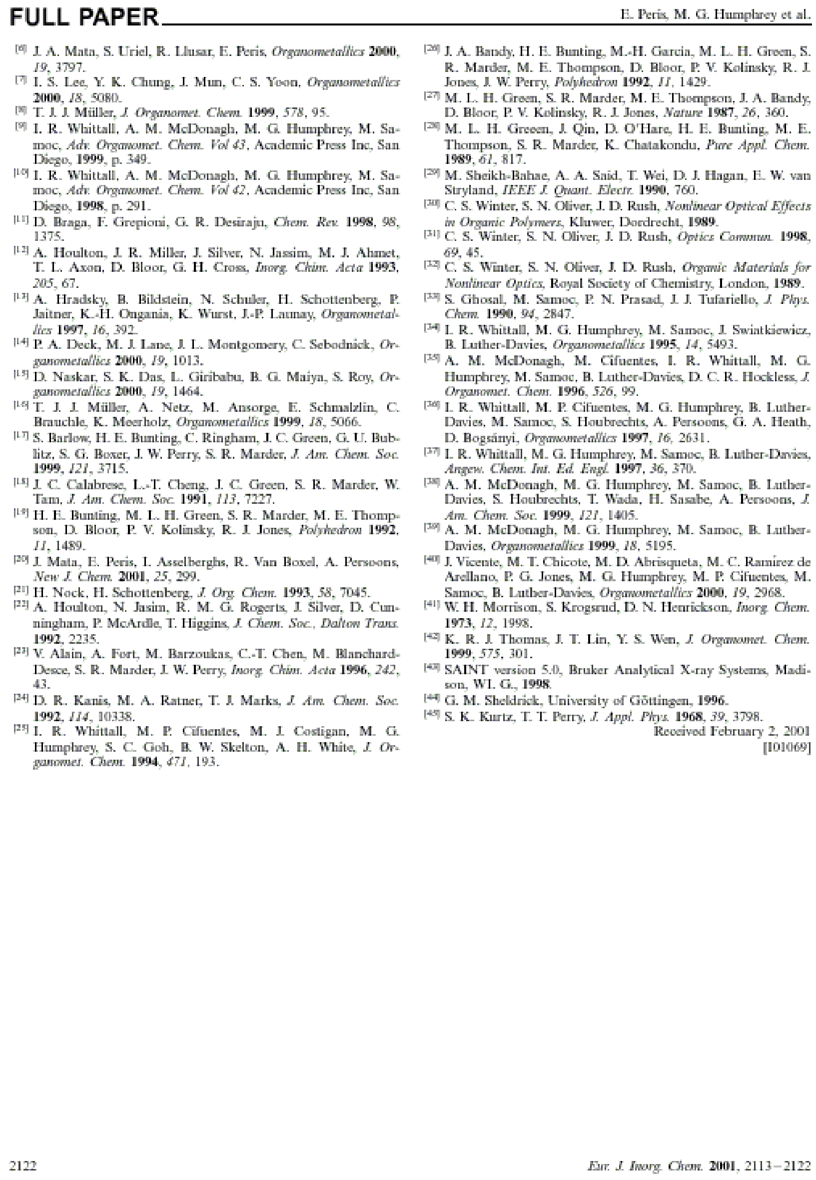
**Supplementary Data:** Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-152432 for compound **2**-(*E*), CCDC-152433 for compound **4**-(*E,Z*), CCDC-152434 for compound **5**-(*E,E*), CCDC-152435 for compound **6**, and CCDC-152436 for compound **7**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. [Fax: (internat.) +44−1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

## Acknowledgments

We thank the DGESIC (PB98-1044), BANCAIXA (P1B98-07) and the Australian Research Council (ARC) for financial support. J. A. M. thanks the Generalitat Valenciana for a fellowship, and MGH thanks the ARC for a Senior Research Fellowship.

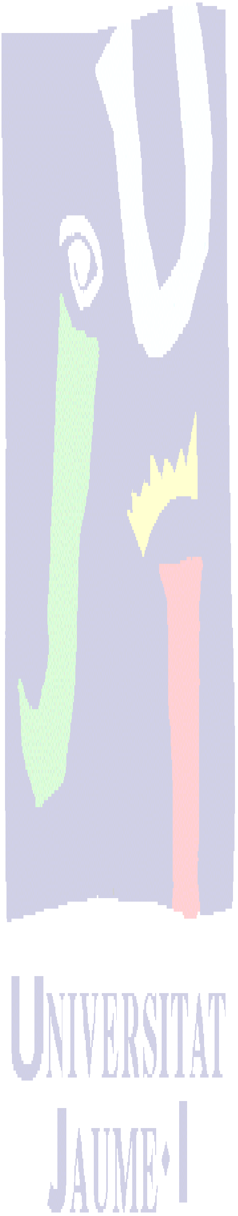
---

[1] A. Togni, T. Hayashi, *Ferrocenes: Homogeneous Catalysis-Organic Synthesis Materials-Science*, VCH Publishers, New York, NY (USA) **1995**.
[2] A. Togni, R. L. Halterman, *Metallocenes*, Wiley-VCH, Weinheim (Germany), **1998**.
[3] N. J. Long, *Metallocenes*, Blackwell Science, London, **1997**.
[4] J. Mata, S. Uriel, E. Peris, R. Llusar, S. Houbrechts, A. Persoons, *J. Organomet. Chem.* **1998**, *562*, 197.
[5] J. A. Mata, E. Falomir, R. Llusar, E. Peris, *J. Organomet. Chem.* **2000**, *616*, 80.



[6] J. A. Mata, S. Uriel, R. Llusar, E. Peris, *Organometallics* **2000**, *19*, 3797.
[7] I. S. Lee, Y. K. Chung, J. Mun, C. S. Yoon, *Organometallics* **2000**, *18*, 5080.
[8] T. J. J. Müller, *J. Organomet. Chem.* **1999**, *578*, 95.
[9] I. R. Whittall, A. M. McDonagh, M. G. Humphrey, M. Samoc, *Adv. Organomet. Chem. Vol 43*, Academic Press Inc, San Diego, **1999**, p. 349.
[10] I. R. Whittall, A. M. McDonagh, M. G. Humphrey, M. Samoc, *Adv. Organomet. Chem. Vol 42*, Academic Press Inc, San Diego, **1998**, p. 291.
[11] D. Braga, F. Grepioni, G. R. Desiraju, *Chem. Rev.* **1998**, *98*, 1375.
[12] A. Houlton, J. R. Miller, J. Silver, N. Jassim, M. J. Ahmet, T. L. Axon, D. Bloor, G. H. Cross, *Inorg. Chim. Acta* **1993**, *205*, 67.
[13] A. Hradsky, B. Bildstein, N. Schuler, H. Schottenberg, P. Jaitner, K.-H. Ongania, K. Wurst, J.-P. Launay, *Organometallics* **1997**, *16*, 392.
[14] P. A. Deck, M. J. Lane, J. L. Montgomery, C. Sebodnick, *Organometallics* **2000**, *19*, 1013.
[15] D. Naskar, S. K. Das, L. Giribabu, B. G. Maiya, S. Roy, *Organometallics* **2000**, *19*, 1464.
[16] T. J. J. Müller, A. Netz, M. Ansorge, E. Schmalzlin, C. Brauchle, K. Meerholz, *Organometallics* **1999**, *18*, 5066.
[17] S. Barlow, H. E. Bunting, C. Ringham, J. C. Green, G. U. Bublitz, S. G. Boxer, J. W. Perry, S. R. Marder, *J. Am. Chem. Soc.* **1999**, *121*, 3715.
[18] J. C. Calabrese, L.-T. Cheng, J. C. Green, S. R. Marder, W. Tam, *J. Am. Chem. Soc.* **1991**, *113*, 7227.
[19] H. E. Bunting, M. L. H. Green, S. R. Marder, M. E. Thompson, D. Bloor, P. V. Kolinsky, R. J. Jones, *Polyhedron* **1992**, *11*, 1489.
[20] J. Mata, E. Peris, I. Asselberghs, R. Van Boxel, A. Persoons, *New J. Chem.* **2001**, *25*, 299.
[21] H. Nock, H. Schottenberg, *J. Org. Chem.* **1993**, *58*, 7045.
[22] A. Houlton, N. Jasim, R. M. G. Rogerts, J. Silver, D. Cunningham, P. McArdle, T. Higgins, *J. Chem. Soc., Dalton Trans.* **1992**, 2235.
[23] V. Alain, A. Fort, M. Barzoukas, C.-T. Chen, M. Blanchard-Desce, S. R. Marder, J. W. Perry, *Inorg. Chim. Acta* **1996**, *242*, 43.
[24] D. R. Kanis, M. A. Ratner, T. J. Marks, *J. Am. Chem. Soc.* **1992**, *114*, 10338.
[25] I. R. Whittall, M. P. Cifuentes, M. J. Costigan, M. G. Humphrey, S. C. Goh, B. W. Skelton, A. H. White, *J. Organomet. Chem.* **1994**, *471*, 193.
[26] J. A. Bandy, H. E. Bunting, M.-H. Garcia, M. L. H. Green, S. R. Marder, M. E. Thompson, D. Bloor, P. V. Kolinsky, R. J. Jones, J. W. Perry, *Polyhedron* **1992**, *11*, 1429.
[27] M. L. H. Green, S. R. Marder, M. E. Thompson, J. A. Bandy, D. Bloor, P. V. Kolinsky, R. J. Jones, *Nature* **1987**, *26*, 360.
[28] M. L. H. Greeen, J. Qin, D. O'Hare, H. E. Bunting, M. E. Thompson, S. R. Marder, K. Chatakondu, *Pure Appl. Chem.* **1989**, *61*, 817.
[29] M. Sheikh-Bahae, A. A. Said, T. Wei, D. J. Hagan, E. W. van Stryland, *IEEE J. Quant. Electr.* **1990**, 760.
[30] C. S. Winter, S. N. Oliver, J. D. Rush, *Nonlinear Optical Effects in Organic Polymers*, Kluwer, Dordrecht, **1989**.
[31] C. S. Winter, S. N. Oliver, J. D. Rush, *Optics Commun.* **1998**, *69*, 45.
[32] C. S. Winter, S. N. Oliver, J. D. Rush, *Organic Materials for Nonlinear Optics*, Royal Society of Chemistry, London, **1989**.
[33] S. Ghosal, M. Samoc, P. N. Prasad, J. J. Tufariello, *J. Phys. Chem.* **1990**, *94*, 2847.
[34] I. R. Whittall, M. G. Humphrey, M. Samoc, J. Swiatkiewicz, B. Luther-Davies, *Organometallics* **1995**, *14*, 5493.
[35] A. M. McDonagh, M. Cifuentes, I. R. Whittall, M. G. Humphrey, M. Samoc, B. Luther-Davies, D. C. R. Hockless, *J. Organomet. Chem.* **1996**, *526*, 99.
[36] I. R. Whittall, M. P. Cifuentes, M. G. Humphrey, B. Luther-Davies, M. Samoc, S. Houbrechts, A. Persoons, G. A. Heath, D. Bogsányi, *Organometallics* **1997**, *16*, 2631.
[37] I. R. Whittall, M. G. Humphrey, M. Samoc, B. Luther-Davies, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 370.
[38] A. M. McDonagh, M. G. Humphrey, M. Samoc, B. Luther-Davies, S. Houbrechts, T. Wada, H. Sasabe, A. Persoons, *J. Am. Chem. Soc.* **1999**, *121*, 1405.
[39] A. M. McDonagh, M. G. Humphrey, M. Samoc, B. Luther-Davies, *Organometallics* **1999**, *18*, 5195.
[40] J. Vicente, M. T. Chicote, M. D. Abrisqueta, M. C. Ramirez de Arellano, P. G. Jones, M. G. Humphrey, M. P. Cifuentes, M. Samoc, B. Luther-Davies, *Organometallics* **2000**, *19*, 2968.
[41] W. H. Morrison, S. Krogsrud, D. N. Henrickson, *Inorg. Chem.* **1973**, *12*, 1998.
[42] K. R. J. Thomas, J. T. Lin, Y. S. Wen, *J. Organomet. Chem.* **1999**, *575*, 301.
[43] SAINT version 5.0, Bruker Analytical X-ray Systems, Madison, WI. G., **1998**.
[44] G. M. Sheldrick, University of Göttingen, **1996**.
[45] S. K. Kurtz, T. T. Perry, *J. Appl. Phys.* **1968**, *39*, 3798.

Received February 2, 2001
[I01069]



# Capítulo V

## BIFERROCENOS.
## INTERACCIÓN METAL-METAL

*La verdadera ciencia enseña, sobre todo,*
*a dudar y a ser ignorante.*

Ernest Rutherford (1871-1937)

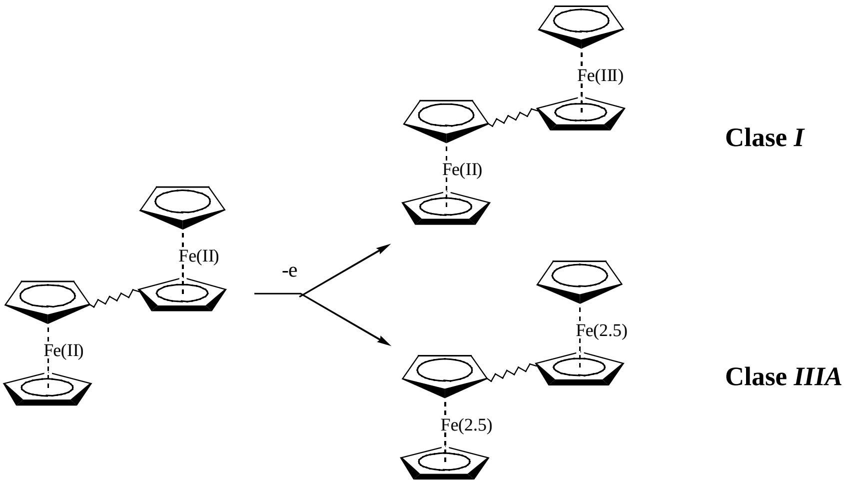
# 1. INTRODUCCIÓN

En los últimos años ha adquirido una gran importancia la síntesis y el desarrollo de metalocenos conectados a través de diferentes sistemas, debido a la posibilidad de deslocalización electrónica entre los centros metálicos. El interés principal de estos compuestos reside en la naturaleza de la interacción entre los centros metálicos. Estas interacciones pueden permitir la utilización de estos materiales en un gran número de aplicaciones tecnológicas. Una de estas aplicaciones es su uso como agentes dopantes en polímeros para obtener conductores monodimensionales. La obtención de poliferrocenos en donde se han oxidado sólo algunos ferrocenos, conduce a un polímero formado por compuestos de valencia mixta ($Fe^{II}/Fe^{III}$). La interacción electrónica entre ambos centros produce que, en algunos casos, el material sea un semiconductor. Si además se introducen metalocenos quirales, entonces se obtienen materiales quirales conductores.

Muchos biferrocenos muestran un fuerte comportamiento antiferromagnético, pero la utilización adecuada de ciertos ligandos, el diseño de diferentes grupos de unión entre los ferrocenos y la utilización de diferentes metales con distinto spin, puede conducir a interacciones ferrimagnéticas. Uno de los últimos ámbitos en los que se está estudiando estos compuestos es en el campo de la *ONL* de tercer orden.

## 1.1 Compuestos de valencia mixta.

Antes de adentrarnos un poco más en el estudio de la interacción entre metales, es conveniente definir el concepto de valencia mixta. Cuando oxidamos una molécula con dos o más centros metálicos se pueden producir dos situaciones extremas, como se muestra en el esquema 1.1. En primer lugar tenemos el caso en que ambos centros metálicos sean completamente diferentes. Esto es, que tengamos un catión con dos centros localizados en distintos estados de oxidación. Por ejemplo, si partimos de una molécula con dos centros $Fe^{II}$, al quitar un electrón tendríamos que uno de los átomos de hierro sería $Fe^{II}$ y el otro $Fe^{III}$. En este caso diremos que los dos centros metálicos no se observan o bien que la interacción entre los dos metales es nula. Otra situación que puede producirse es una completa deslocalización de la carga, en este caso tendríamos a los dos centros metálicos con un estado de oxidación $2.5^{+}$. Estas dos situaciones corresponden a las clases *I* y *IIIA* respectivamente, en la clasificación de las especies de valencia mixta de *Robin* y *Day*.[1] Los compuestos de la clase I no presentan interacción metal-metal, es decir sus propiedades son la suma de las propiedades individuales del centro oxidado y del centro sin oxidar. En cambio en los compuestos de clase *IIIA*, las propiedades son las correspondientes de un sistema cooperativo, como consecuencia de la deslocalización de la carga entre los centros metálicos. Entre estos dos extremos se encuentra toda una graduación de interacciónes metal-metal, denominados clase *II*.



***Esquema 1.1.***
*Clasificación de especies de valencia mixta, según Robin y Day*

## 1.2 Técnicas experimentales. Voltametría cíclica.

Existen un gran número de técnicas experimentales para evaluar la naturaleza de la interacción entre dos centros metálicos. Entre estas técnicas se encuentran, por ejemplo, la resonancia de espin electrónica (*EPR* o *ESR*), la espectroscopia *Mössbauer*, la voltametría cíclica, medidas magnéticas, espectroscopia electrónica y, más habitualmente, *RMN*, *IR* y cristalografía de rayos-*X*.

De entre todas las técnicas mencionadas anteriormente, la más utilizada es la voltametría cíclica, debido a las características que presenta. Es una técnica muy sencilla debido a que el equipamiento que se necesita es relativamente simple. Además, no es necesario aislar las especies oxidadas, ya que estas se generan en la superficie del electrodo en el mismo experimento. Otras técnicas requieren el aislamiento de las especies oxidadas, lo cual puede ser un inconveniente puesto que estas especies suelen ser relativamente inestables.

En una molécula con $n$ centros redox equivalentes que no interaccionan se puede demostrar que en un experimento redox, se debería observar una separación ($\Delta E$) igual a $(RT/F)ln2^n$ entre el primer y el último proceso redox, debido únicamente a la contribución electrostática.[2] Esto significa que para una molécula con dos centros redox, cabe esperar una separación de unos 36 $mV$. Sin embargo, la diferencia de 36 $mV$ es muy pequeña para poder observarse en experimentos rutinarios. Separaciones más grandes indican algún tipo de interacción electrónica entre los dos centros metálicos. Un aumento de la separación entre los picos implica un aumento de la constante de comproporción ($Kc$) para la reacción:

$$X + X^{2+} \overset{Kc}{\leftrightharpoons} 2X^{+}$$

El aumento de *Kc* indica un aumento en la estabilización de las especies de valencia mixta. Los factores que contribuyen a esta estabilización son tanto electrostáticos como electrónicos.

En metalocenos se ha observado que *ΔE* depende de la separación entre los dos centros metálicos y también del tipo de unión entre ambos. De este modo el polímero $[Fe(C_5H_3Me)_2(CH_2)_2]_n$ (*ΔE* ca. 60 *mV*) pertenece a la clase I porque esta formado por puentes muy largos y no conjugados, y el valor de *ΔE* presumiblemente esta dominado por factores electrostáticos. Sin embargo, el compuesto $Pn(FeCp^*)_2$ (*Pn* = pentaleno; dos ciclopentadienilos fusionados compartiendo un lado) presenta una gran interacción electrónica entre los centros metálicos y *ΔE* es de 1030 *mV*, perteneciendo de este modo a la clase IIIA.[3]

Es conveniente resaltar que es muy importante tener en cuenta el disolvente empleado a la hora de comparar resultados. Esto se debe a que la constante dieléctrica del disolvente empleado tiene un efecto importante en *ΔE*. Por ejemplo, para el compuesto $Pn(CoCp^*)_2$ se han encontrado separaciones de 900 *mV* y 710 *mV* en diclorometano y *THF* respectivamente.[3]

## 1.3 Constante de comproporción.

Aquellos compuestos que posean diferentes centros electroquímicamente activos, pueden presentar reacciones de transferencia de carga en diferentes etapas, tal y como se muestra en la siguiente ecuación:

$$A \xrightarrow{n_1 e^-, E_1^0} B \xrightarrow{n_2 e^-, E_2^0} C \qquad (1)$$

La relación de concentración de estas especies en el equilibrio se expresa mediante la constante de comproporción *Kc*, donde:

$$Kc = \frac{[B]^{n_1+n_2}}{[C]^{n_1}[A]^{n_2}} = \exp\left[\frac{(E_1^0 - E_2^0)\, n_1\, n_2\, F}{RT}\right] \qquad (2)$$

En donde *A*, *B* y *C* son las concentraciones de estas especies en el equilibrio, $n_i$ es el número de electrónes asociados a cada etapa, *F* es la constante de *Faraday* y $E_i^0$ el potencial estándar asociado al paso *i*.

El valor de la variación del potencial estándar ($\Delta E^0$) se puede calcular a partir de la variación del potencial de semionda ($\Delta E_{1/2}$) obtenido por métodos electroquímicos. La relación entre ambos es:

$$E^0 = E_{1/2} - \left(\frac{RT}{nF}\right) \ln \left(\frac{D_r}{D_o}\right)^{1/2} \left(\frac{f_o}{f_r}\right) \qquad (3)$$

En donde $D_i$ es el coeficiente de difusión de las especies oxidada y reducida y $f_i$ es el coeficiente de actividad de estas especies. En general se cumple que los coeficientes de difusión de la especie oxidada y reducida son similares, así que el segundo término de la ecuación *(**3**)* es prácticamente despreciable y $E^0 \simeq E_{1/2}$.

En nuestro caso hemos realizado el cálculo de la constante de comproporción en biferrocenos para la reacción:

$$Fc^{II}Fc^{II} + Fc^{III}Fc^{III} \overset{Kc}{\leftrightharpoons} 2Fc^{II}Fc^{III}$$

En los compuestos que hemos estudiado, se cumple que existen dos procesos redox encadenados monoelectrónicos, por lo que $n_i = 1$. Además, hemos considerado que los coeficientes de actividad son similares, por lo que la variación del potencial estándar es igual a la variación del potencial de semionda. A partir de estas consideraciones, de la ecuación (***2***) se obtiene:[4]

$$Kc = \exp\left[\frac{\Delta E_{1/2}}{25.69}\right] \qquad (T = 298\ K) \qquad \textit{(4)}$$

### 1.4 Antecedentes históricos.

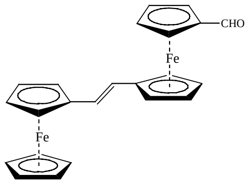
En la bibliografía podemos encontrar numerosos trabajos dedicados al estudio de diferentes tipos de bimetalocenos.[5] En nuestro trabajo, nos hemos centrado en el estudio de biferrocenos unidos a través de puentes insaturados.

Los sistemas con dos ferrocenos unidos a través de un puente olefínico presentan una mayor interacción metal-metal que sus análogos saturados. De este modo el compuesto $Fc\text{-}CH_2\text{-}CH_2\text{-}Fc$ muestra una única onda de oxidación/reducción, indicando que la interacción entre ambos centros metálicos es prácticamente nula, mientras que el análogo $Fc\text{-}CH{=}CH\text{-}Fc$ muestra dos ondas separadas una por 150 *mV*.[6] Las especies monooxidadas unidas a través de puentes olefínicos muestran absorciones en el infrarojo cercano, en cambio es muy difícil observar este tipo de banda en compuestos unidos a través de puentes saturados. Desde el punto de vista electroquímico los sistemas unidos a través de puentes acetileno conducen a los mismos tipos de interacciones electrónicas que los correspondientes puentes olefínicos, aunque, en general, la interacción metal-metal es de menor intensidad. En concreto, el compuesto $Fc\text{-}C{\equiv}C\text{-}Fc$ muestra dos ondas con una separación de 130 *mV* en diclorometano.[7]

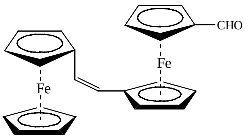
Uno de los factores más importantes que contribuyen a la interacción entre los diferentes centros metálicos es la distancia que hay entre ellos. Un estudio sistemático de diferentes biferrocenos del tipo $Fc\text{-}\{CH{=}CH\}_n\text{-}Fc$ en donde $n = 1 – 6$, demuestra que no existe interacción cuando $n > 3$ (distancia intermetálica ca. 11.5 *Å*).[6] La mayoría de los sistemas que presentan puentes olefinicos unidos a fenilos o heterociclos con más de tres eslabones no muestran ningún tipo de interacción. En compuestos de biferroceno unidos a través de puentes insaturados, la diferencia entre picos entre los procesos redox que tienen lugar suele estar en el intervalo de entre 100 y 200 *mV*.

## 1.5 Compuestos estudiados.

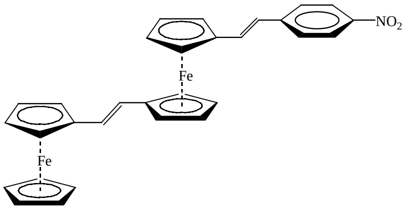
El siguiente esquema muestra los compuestos de biferroceno que se estudian en el presente capítulo, junto con la numeración utilizada, que coincide con la del trabajo V-5.1. Todos ellos son del tipo 1,1'-etilenbiferrocénico, es decir presentan dos fragmentos de ferroceno unidos por un puente etileno. Los biferrocenos empleados están funcionalizados con fragmentos: -aldehído, *p*-etenilnitrofenilo, y *p*-etenilpiridina. Además, también se obtuvieron los compuestos heterometálicos derivados de la coordinación de los ligandos piridina y nitrilo a fragmentos *M(CO)*$_5$ ( *M* = *Cr*, *Mo*, *W*).



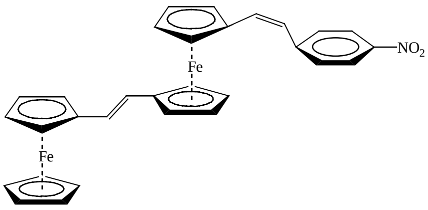
**1**-(E)



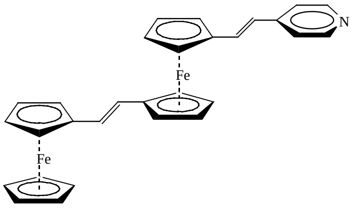
**1**-(Z)



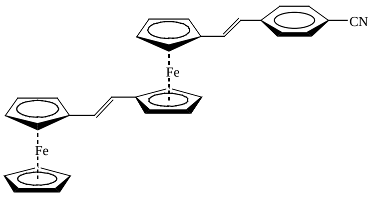
**2**-(E,E)



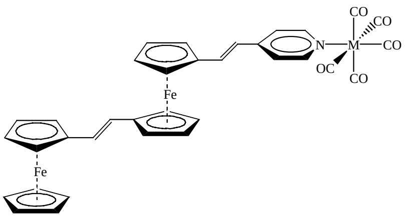
**2**-(E,Z)



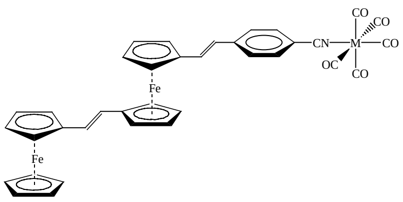
**3**



**4**



M = **3**-Cr, **3**-Mo, **3**-W

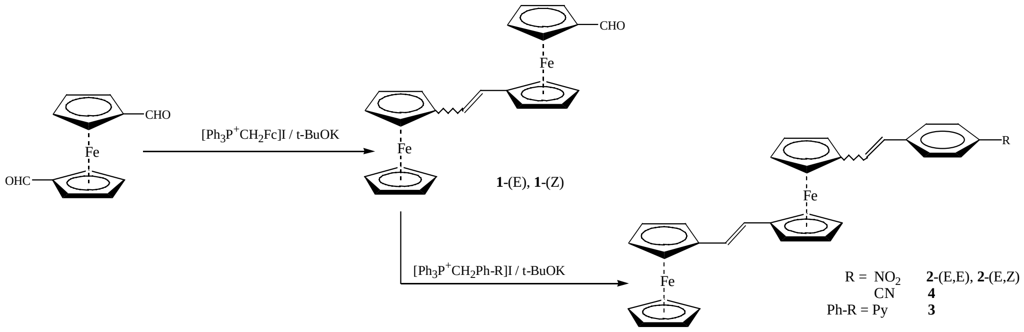


M = **4**-Cr, **4**-W

## 2. SÍNTESIS Y CARACTERIZACIÓN

### 2.1 *Síntesis.*

La síntesis de los biferrocenos se ha realizado utilizando la metodología de *Wittig*, como se muestra en el esquema 2.1. Los detalles experimentales de la síntesis de estos compuestos, se describen en el artículo V-5.1. Los compuestos terminados en nitrilo y piridina, han sido empleados como ligandos en la coordinación a fragmentos $M(CO)_5$ ($M$ = $Cr$, $Mo$, $W$). El procedimiento utilizado en la coordinación de estos fragmentos organometálicos, ha sido el mismo que se ha descrito en el capitulo IV para los derivados carbonílicos, es decir, se genera la vacante de coordinación del hexacarbonilo correspondiente por irradiación y, posteriormente, se adiciona el ligando ferrocénico correspondiente (compuestos **3** y **4**).



***Esquema 2.1***
*Procedimiento de síntesis utilizado en la obtención de los biferrocenos.*

La caracterización se ha realizado mediante las mismas técnicas descritas para el resto de compuestos y a las que nos hemos referido en capítulos anteriores. Una de las principales diferencias en este tipo de compuestos se observa en la espectroscopia *RMN* de $^1H$, ya que en la zona correspondiente a los protones del ferroceno aparece un gran número de señales como consecuencia de tener dos ferrocenos, mono- y bisustituidos, que no son equivalentes. En algunos casos aparecen señales solapadas, pero en la mayoría es posible discernir cada una de las señales, tal y como es el caso que se ilustra en la figura 2.1.

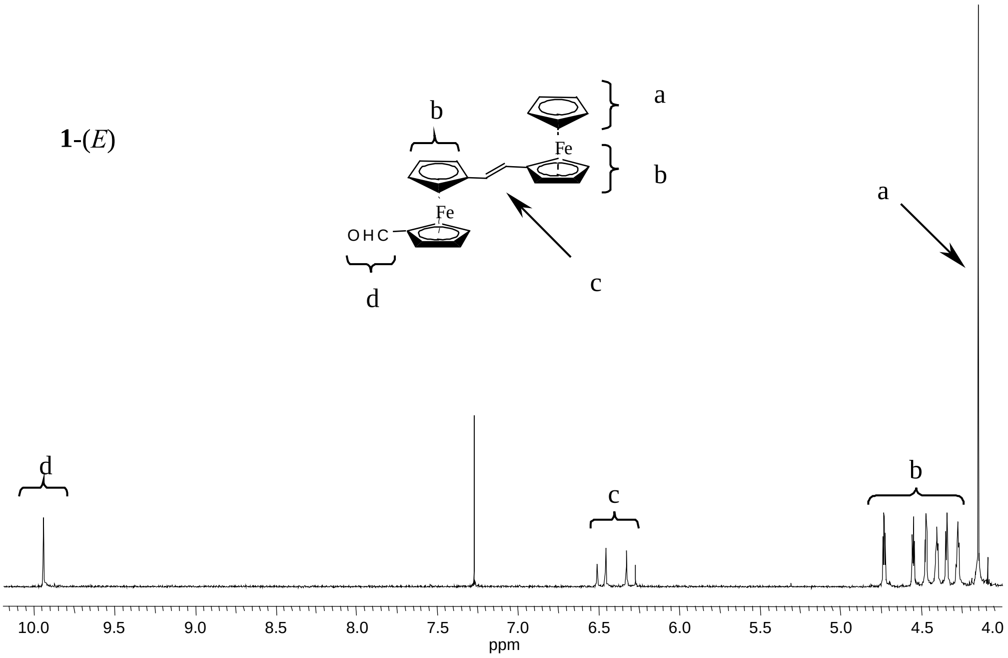


***Figura 2.1***
*Espectro RMN de $^1$H del compuesto (E)-Fc−=−Fc-CHO, **1**-(E).*

Los espectros de *IR* muestran la banda característica del *CO* en el caso de los aldehídos, mientras que en los compuestos heterobimetálicos se observan las tres bandas correspondientes al fragmento pentacarbonilo metálico. La asignación de estas bandas corresponde a los modos normales de vibración $A_1$, $B_2$ y *E*, típica de derivados carbonílicos con simetría *pseudo*-$C_{4v}$.[8]

## 2.2 Resultados cristalográficos.

La obtención de cristales de los compuestos **1**-(*E*), **3**-*Cr*, **3**-*Mo* y **3**-*W* se ha realizado evaporando lentamente a sequedad disoluciones de las muestras en diclorometano/hexano. Este método ha resultado muy eficaz a la hora de cristalizar los distintos compuestos derivados de ferroceno tratados en este trabajo.

En la parte experimental de la publicación que se adjunta al final del capítulo se recoge toda la información sobre las condiciones de medida y la toma de datos, y en el material suplementario en soporte informático, se presenta un resumen de los parámetros cristalográficos más relevantes referente a la resolución de las estructuras cristalinas, factores de agitación térmica, longitudes y ángulos de enlace.

En el caso concreto de nuestros biferrocenos hemos observado que todos ellos cristalizan en grupos espaciales centrosimétricos, *C2/c* para el compuesto **1**-(*E*) y *P-1* para los compuestos **3**-*Cr*, **3**-*Mo* y **3**-*W*. El compuesto **1**-(*E*) presenta un centro de inversión situado en el centro del puente olefínico. La unidad asimétrica consiste en un fragmento ferrocenilo, uno de los carbonos del etenilo y el grupo aldehído, estos dos últimos fragmentos con un factor de ocupación del 50% debido a desorden posicional. Este tipo de desorden es bastante habitual en derivados de ferroceno conectados a cadenas conjugadas de dobles enlaces. En la figura 2.2 se muestra la molécula completa del compuesto **1**-(*E*) en donde se han etiquetado los átomos correspondientes a la unidad asimétrica.

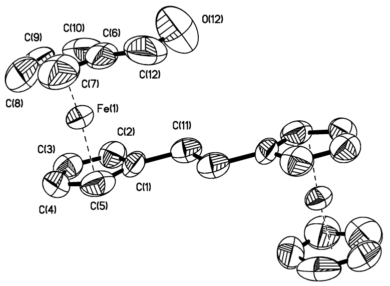


***Figura 2.2***

*Diagrama ORTEP del compuesto **1**-(E).*

Los compuestos **3**-*Cr*, **3**-*Mo* y **3**-*W* son isoestructurales, pertenecen al sistema cristalino triclínico y presentan dos moléculas completas en la unidad asimétrica. Tanto las dos moléculas independientes como la disposición relativa es prácticamente igual en los tres casos estudiados. En la figura 2.3 se muestra la unidad asimétrica correspondiente al compuesto **3**-*Cr*.

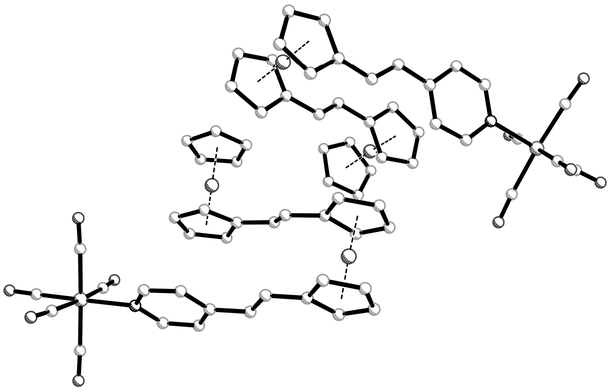
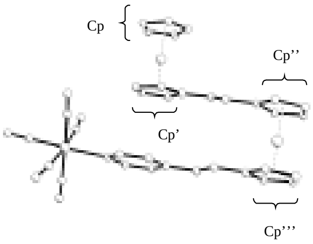


***Figura 2.3***

*Estructura del compuesto **3**-Cr. En la unidad asimétrica se encuentran dos moléculas completas, la disposición espacial es la que se muestra en la figura. Los ángulos y distancias de enlace son similares en ambas moléculas.*

En la tabla 2.1 se muestra un resumen de las distancias, ángulos de enlace y los ángulos entre los planos más importantes; en el artículo V-5.1 (Tabla 2) se encuentra detallada toda esta información. Las distancias y ángulos de enlace se encuentran en el intervalo esperado para este tipo de compuestos.

***Tabla 2.1***
*Distancias (Å), ángulos de enlace (°) y sistema de nomenclatura utilizado.*

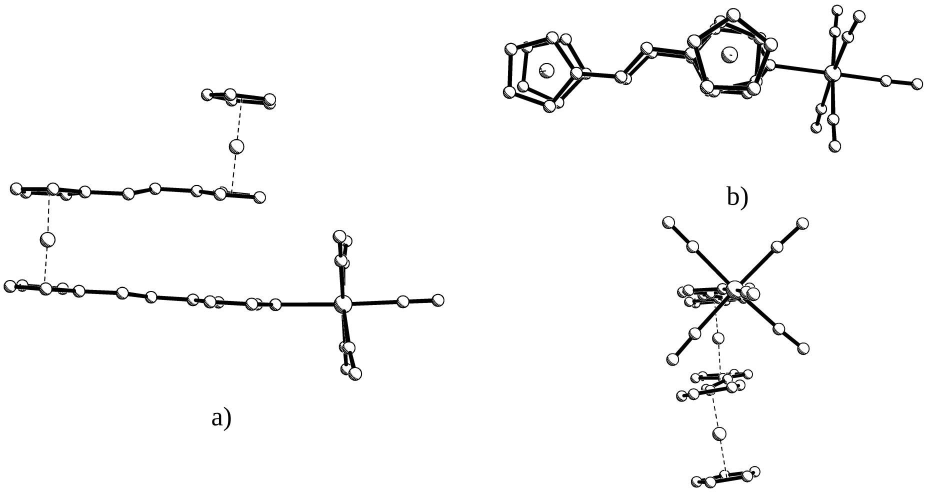


| Entorno Fe | **1**-(*E*) | **3**-*Cr* | **3**-*Mo* | **3**-*W* |
|---|---|---|---|---|
| Fe(1)-Cp (Cent.) | 1.64 | 1.64 | 1.66 | 1.66 |
| Fe(1)-Cp' (Cent.) | 1.65 | 1.65 | 1.65 | 1.65 |
| Fe(1) - Fe(2)(enlaces) | 8.49 | 8.30 | 8.33 | 8.31 |
| Fe(1) - Fe(2) (espacio) | 7.15 | 7.18 | 7.21 | 7.18 |
| Entorno M | | | | |
| M(1) - N(1) | --- | 2.159(4) | 2.288(4) | 2.271(5) |
| M – CO (min/max) | --- | 1.849-1.901 | 1.959-2.072 | 1.977-2.044 |
| Interacción-π | | | | |
| distancia (Cp' - Py) | --- | 3.78 | 3.69 | 3.76 |
| ángulo (Cp' - Py) | --- | 8.03(0.41) | 15.49(0.17) | 8.25(0.55) |
| Coplanaridad | | | | |
| Cp' - Cp" | 0 | 7.29(0.47) | 2.84(0.28) | 7.30(0.63) |
| Cp"' - Py | --- | 1.64(0.44) | 18.12(0.18) | 1.97(0.63) |

La orientación de los fragmentos $M(CO)_5$ respecto a la piridina forma unos ángulos diedros de 44.6º para el *Cr*, 66.1º para el *Mo,* y 44.7º para el *W*, como se ilustra en la figura 2.4c. La retrodonación $\pi$ del metal al orbital antienlazante de la piridina ($\pi$*) será máxima cuando estos ángulos sean de 0º o 90º. En nuestro caso, los fragmentos carbonílicos adoptan una disposición prácticamente cuasi-alternada (especialmente en el caso del *Cr* y del *W*, en donde el ángulo es muy cercano a la disposición alternada ideal de 45º) siendo mínima la retrodonación hacía la piridina y minimizando las repulsiones estéricas.

La influencia trans del *M* a los grupos *CO* se pone de manifiesto en las distancias de enlace *M-C trans* a la piridina (*Cr-C* = 1.84 *Å*, *Mo-C = 1.95 Å*, *W-C* = 1.97 *Å*), siendo significativamente más cortas que las distancias M-C *cis* a la piridina. (*Cr-C* = 1.90 *Å*, *Mo-C* = 2.05 *Å*, *W* = 2.02 *Å*). Estos resultados coinciden con los encontrados en la literatura por Sakanishi et al. en ligandos de piridina unidos a fragmentos carbonílicos.[9]

Los ángulos diedros formados entre los ciclopentadienilos de cada ferroceno varían entre 1.5º y 4.0º, como se observa en la mayoría de los ferrocenos. Los anillos ciclopentadienilo presentan una conformación *syn*. Como hemos observado en otros 1,1'-biferrocenos sustituidos, los sustituyentes adoptan la disposición más impedida estéricamente. En el caso de los compuestos **3**-*Cr*, **3**-*Mo* y **3**-*W* se podría pensar que se produce esta conformación *syn*, por la existencia de apilamiento *π* (ca. 3.7 *Å*) intramolecular. En cambio en el caso del compuesto **1**-(*E*) no existe la posibilidad de este tipo de interacción por lo que seguramente son los factores de empaquetamiento los que conducen a este tipo de conformación. En la figura 2.4 se muestran tres orientaciones diferentes de los compuestos **3**, en donde se observa la disposición *anti* de ambos ferrocenos, el apilamiento π y la conformación *syn* de los anillos ciclopentadienilo.



a)

b)

c)

***Figura 2.4***.

*Diferentes orientaciones correspondientes a los compuestos 3. a) M = Cr. Se observa la coplanaridad del sistema y el apilamiento π y disposición anti de ambos ferrocenos. b) M = Mo. Disposición syn de los anillos ciclopentadienilo. c) M = W. Disposición alternada del fragmento* $-W(CO)_5$.

# 3. PROPIEDADES ELECTROQUÍMICAS. CONSTANTE DE COMPROPORCIÓN

## *3.1 Introducción.*

Las técnicas electróquímicas han sido una de las herramientas más utilizadas en el estudio de las interacciónes metal-metal. La voltametría cíclica ha sido ampliamente utilizada en nuestro grupo de investigación para evaluar la influencia electrónica entre diferentes dadores y aceptores de electrones. Además, en nuestro caso, hemos utilizado esta técnica para investigar las interacciones metal-metal en los biferrocenos. De este modo, nos ha sido posible evaluar las propiedades redox de los centros metálicos, el grado de interacción, y el efecto producido por los ligandos.

En los capítulos anteriores hemos descrito los resultados electroquímicos de diferentes derivados de ferroceno, en donde se observa una onda reversible, asociada a un proceso monoelectrónico, en torno a los 500 *mV*. En los biferrocenos tratados en este capítulo se observa la aparición de dos ondas reversibles asociadas a dos procesos monoelectrónicos correspondientes a los ferrocenos, y en el caso de los biferrocenos coordinados a fragmentos carbonílicos se observa la presencia de tres ondas, como se muestra en la figura 3.1. Los procesos que tienen lugar se pueden esquematizar del siguiente modo:

a) Sistema *Fc-Fc:*

$$Fc\text{-}Fc \quad \leftrightarrow \quad [Fc\text{-}Fc]^{+} \quad \leftrightarrow \quad [Fc\text{-}Fc]^{2+}$$

b) Sistema $Fc\text{-}Fc\text{-}M(CO)_5$ ($M = Cr, Mo, W$):

$$Fc\text{-}Fc\text{-}M \quad \leftrightarrow \quad [Fc\text{-}Fc]^{+}\text{-}M \quad \leftrightarrow \quad [Fc\text{-}Fc]^{2+}\text{-}M \quad \leftrightarrow \quad [Fc\text{-}Fc\text{-}M]^{3+}$$

## *3.2 Discusión de resultados.*

En los voltagramas de la figura 3.1 se observa como los biferrocenos separados por un puente olefínico muestran la presencia de dos ondas asociadas a los ferrocenos. En principio podría pensarse que estas dos ondas se deben a la inequivalencia intrínseca de ambos ferrocenos, pero estudios preliminares de los fragmentos que componen el biferroceno muestran que los potenciales de semionda son muy diferentes a los de los fragmentos aislados, por lo que cabe esperar que se esté produciendo algún tipo de interacción entre ambos centros metálicos. Si no existiera ninguna interacción se observaría la aparición de una única onda reversible correspondiente a un proceso bielectrónico, o una onda mucho más ancha de lo esperado correspondiente a dos procesos monoelectrónicos muy similares.[10]

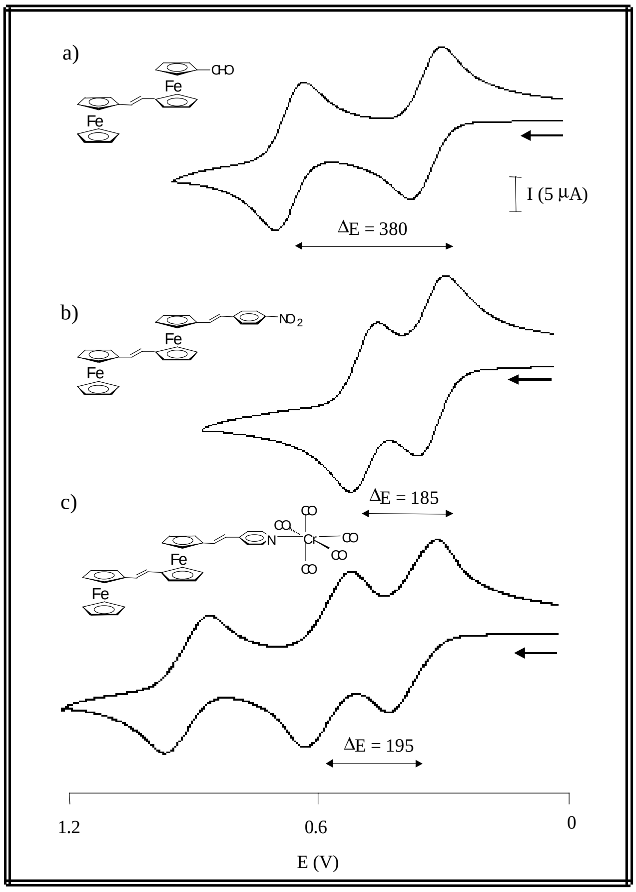


**Figura 3.1.**
*Voltagramas de los compuestos a)* ***1****-(E), b)* ***2****-(E,E) y c)* ***3****-Cr. Medidos a 100 mV/s en* $CH_2Cl_2$.

La interacción entre los dos centros redox activos conduce a una disminución del potencial de semionda de la primera oxidación, debido a un efecto de estabilización de la carga positiva por la deslocalización entre los dos centros metálicos. En la tabla 3.1 se resumen los potenciales de semionda atribuidos a los procesos descritos anteriormente. Se observa el desplazamiento catódico (40 – 90 *mV*) del primer proceso de oxidación respecto al ferroceno libre, lo que indica una mayor facilidad del complejo biferrocénico a ser oxidado.

***Tabla 3.1***

*Datos electroquímicos obtenidos mediante voltametría cíclica.*$^a$ *M = Cr, Mo, W.* $^b$ *Proceso irreversible, medido a 100 mV/s. Las medidas se han realizado en* $CH_2Cl_2$ *utilizando* $TBAPF_6$ *como sal de fondo.*

| *Compuesto* | $E_{1/2}(mV)\ (\Delta E_p(mV))$ *Ferrocenos* | | $E_{1/2}(mV)\ (\Delta E_p(mV))$ $M^a$ |
|---|---|---|---|
| Ferroceno | 445(105) | | --- |
| **1**-(*E*) | 405(90) | 785(85) | --- |
| **1**-(*Z*) | 400(110) | 760(75) | --- |
| **2**-(*E,E*) | 350(80) | 535(65) | --- |
| **2**-(*E,Z*) | 370(110) | 570(110) | --- |
| **3** | 370(145) | 570(140) | --- |
| **3**-*Cr* | 375(130) | 590(125) | 950(130) |
| **3**-*Mo* | 360(95) | 575(80) | 1115 $^b$ |
| **3**-*W* | 380(160) | 610(155) | 1240 $^b$ |
| **4** | 360(145) | 550(150) | --- |
| **4**-*Cr* | 360(135) | 555(110) | 975(125) |
| **4**-*W* | 360(95) | 540(85) | 1140 $^b$ |

Respecto a la segunda onda de oxidación, el potencial es más anódico que el del ferroceno, debido a la acción combinada de factores electrostáticos (se oxida una especie que ya es catiónica) y a la interacción electrónica entre los dos centros *Fc*.

La coordinación de los fragmentos neutros $M(CO)_5$ a los derivados de piridina y de nitrilo no produce ningún efecto significativo en los potenciales redox de los ferrocenos. La onda asociada a la oxidación de este fragmento solo es reversible para el *Cr*, mientras que en el caso del *Mo* y del *W* se obtienen ondas completamente irreversibles, tal y como habíamos observado en los sistemas tratados en el capítulo IV del tipo $Fc\text{---}M(CO)_5$. El potencial de semionda de este tercer proceso depende del metal considerado, siendo mayor en el caso del *W* respecto al *Mo* y *Cr*.

### *3.3 Cálculo de la constante de comproporción.*

El grado de separación entre los dos procesos redox asociados a las dos ondas correspondientes a los ferrocenos es una medida “cuasi-directa” del grado de interacción entre ambos centros metálicos. Es una medida cuasi-directa porque en nuestro caso los dos centros metálicos no son equivalentes, es decir, debemos considerar que la inequivalencia intrínseca entre ambos metales contribuye a la diferencia entre ambos procesos. Sin embargo, no hay duda de que existe interacción electrónica entre los dos ferrocenos, sobre todo si tenemos en cuenta el potencial de semionda de los fragmentos que constituyen el biferroceno, *Fc-CHO* y *Fc-CH=CH*$_2$, que poseen valores aproximados de $E_{1/2}$ = 460 *mV*.

A partir de la separación entre los dos procesos redox que se producen en los biferrocenos se han calculado los valores de *Kc* utilizando la ecuación (***4***), los resultados obtenidos se muestran en la tabla 3.2. Tal y como se observa en esta tabla, de los valores de *Kc* se deduce que estos compuestos pertenecen a la clase *II*, esto es compuestos de valencia mixta débilmente conectados.

***Tabla 3.2***
*Diferencia entre los dos procesos redox asociados a los ferrocenos y constante de comproporción.*

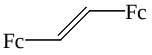
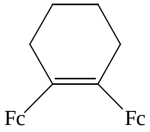
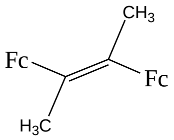
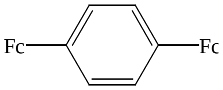
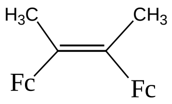
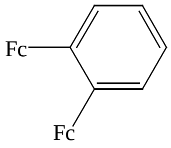
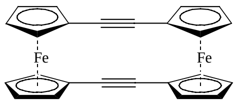
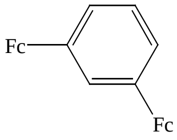
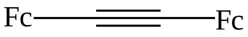
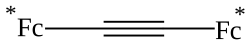
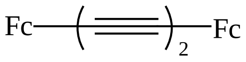
| Compuesto | ΔE(*mV*) Ferrocenos | Kc |
|---|---|---|
| **1**-(*E*) | 380 | $2.6 \times 10^6$ |
| **1**-(*Z*) | 355 | $1.0 \times 10^6$ |
| **2**-(*E,E*) | 185 | 1350 |
| **2**-(*E,Z*) | 195 | 1975 |
| **3** | 200 | 2400 |
| **3**-*Cr* | 215 | 4300 |
| **3**-*Mo* | 215 | 4300 |
| **3**-*W* | 230 | 7725 |
| **4** | 190 | 1625 |
| **4**-*Cr* | 195 | 1975 |
| **4**-*W* | 185 | 1350 |

En la tabla 3.3 se resumen los valores de separación de potenciales entre los dos procesos redox correspondientes a biferrocenos unidos a través de cadenas conjugadas, descritos en la bibliografía. En general, se observa que los biferrocenos muestran valores de *ΔE* en torno a 150 *mV*. En la tabla 3.3 se observa que el biferroceno unido a través de dos puentes acetileno presenta una diferencia entre picos (355 *mV*) muy superior a la mostrada por el resto de compuestos, seguramente debido a la rigidez del sistema, conservando la mínima distancia entre los hierros.

La principal característica observada en nuestros compuestos es la presencia de una interacción metal-metal muy fuerte para el compuesto **1**, tanto en el isómero *E* como en el *Z* (380 *mV* y 355 *mV*, respectivamente). Este resultado es el más elevado de los encontrados hasta la fecha para biferrocenos unidos a través de puentes insaturados. Si comparamos cualquier valor de los encontrados en la bibliografía con nuestros resultados se observa que la introducción del grupo aldehído conduce a un valor de *ΔE* de aproximadamente el doble que para el resto de compuestos. En cambio, este efecto no es tan importante cuando en lugar del aldehído, introducimos una cadena conjugada o un grupo alquilo. La estereoquímica del doble enlace no parece ser un efecto muy importante, aunque en nuestro caso el isómero *E*, presenta valores de *ΔE* ligeramente superiores a su análogo *Z*.

***Tabla 3.3***

*ΔE en biferrocenos unidos a través de enlaces de carbono insaturados, descritos en la bibliografía.*

| Compuesto | *ΔE*(*mV*) Ferrocenos (Disolvente) | Compuesto | *ΔE*(*mV*) Ferrocenos (Disolvente) |
|---|---|---|---|
|  | 170 ($CH_2Cl_2$)$^{6}$<br>120 ($CH_2Cl_2$)$^{11}$ |  | 170 (*MeCN*)$^{12}$ |
|  | 160 (*MeCN*)$^{12}$ |  | 105 ($CHCl_3$)$^{12}$ |
|  | 170 (*MeCN*)$^{12}$ |  | 130 (*MeCN*)$^{12}$ |
|  | 355 ($CH_2Cl_2$)$^{7}$ |  | 90 (*MeCN*)$^{12}$ |
|  | 130 ($CH_2Cl_2$)$^{7}$ | | |
|  | 160 ($CH_2Cl_2$)$^{13}$ | | |
|  | 100 ($CH_2Cl_2$)$^{7}$ | | |

## 4. REFERENCIAS.

(1) Robin, M.; Day, P. *Adv. Inorg. Chem.* **1967**, *10*, 247.

(2) Flanagan, J. B.; Margel, S.; Bard, A. J.; Anson, F. C. *J. Am. Chem. Soc.* **1978**, *100*, 4248.

(3) Manriquez, J. M.; Ward, M. D.; Reiff, W. M.; Calabrese, J. C.; Jones, N. L.; Carroll, P. J.; Bunel, E. E.; Miller, J. S. *J. Am. Chem. Soc.* **1995**, *117*, 6182.

(4) Richardson, D. E.; Taube, H. *Inorg. Chem.* **1981**, *20*, 1278.

(5) Barlow, S.; O'Hare, D. *Chem. Rev.* **1997**, *97*, 637.

(6) Ribou, A. C.; Launay, J. P.; Sachtleben, M. L.; Li, H.; Spangler, C. W. *Inorg. Chem.* **1996**, *35*, 3735.

(7) Levanda, C.; Bechgaard, K.; Cowan, D. O. *J. Org. Chem.* **1976**, *41*, 2700.

(8) Bratterman, P. S. *Metal Carbonyl Spectra*; Academic Press: New York, **1975**.

(9) Sakanishi, S.; Bardwell, D. A.; Couchman, S.; Jeffery, J. C.; McCleverty, J. A.; Ward, M. D. *J. Organomet. Chem.* **1997**, *528*, 35.

(10) Müller, T. J. J.; Netz, A.; Ansorge, M.; Schmalzlin, E.; Brauchle, C.; Meerholz, K. *Organomet.* **1999**, *18*, 506.

(11) Floris, B.; Tagliatesta, P. *J. Chem. Res.* **1993**, 42-43.

(12) Chen, Y. J.; Pan, D.-S.; Chiu, C.-F.; Su, J. X.; Ling, S. J.; Kwan, K. S. *Inorg. Chem.* **2000**, *39*, 953.

(13) Bunel, E. E.; Campos, P.; Ruz, J.; Valle, L.; Chadwick, I.; Santa Ana, M.; Gonzalez, G.; Manriquez, J. M. *Organomet.* **1988**, *7*, 474.

.

DALTON
FULL PAPER

# Syntheses, crystal structures and electrochemical studies of bi- and trimetallic conjugated ferrocene-based complexes

**José A. Mata and Eduardo Peris** *

*Dpto. de Química Inorgánica y Orgánica, Universitat Jaume I, E-12080 Castellón, Spain*

***Received 21st May 2001, Accepted 5th October 2001***
***First published as an Advance Article on the web 23rd November 2001***

New bisferrocenyl pyridine, nitrile and nitro terminated compounds have been obtained by Wittig reactions. The coordination capabilities of the nitrile and pyridine compounds have been proved by coordination to $M(CO)_5$ fragments, M being Cr, Mo or W. The electrochemical properties of the compounds have been studied by means of cyclic voltammetry, showing an effective electronic coupling between the two ferrocenyl fragments. The crystal structures of several of the described complexes are reported, showing that, in all cases, the *syn* conformation on the 1,1′ bis-substituted ferrocene is preferred over the *anti* one.

## Introduction

Much attention has been lately devoted to the chemistry of ferrocenyl complexes because ferrocene combines chemical versatility with high thermal stability. These properties, together with the exceptional electrochemical properties of ferrocene, make ferrocene-based complexes good candidates for the preparation of new materials with applications in organic synthesis, catalysis and materials science.[1,2] When two or more ferrocenyl fragments are connected to obtain compounds with linked ferrocenes, further interests are envisaged, since intermetallic electronic communication affords a wide range of new applications, and many studies have been made regarding intramolecular electron-exchange reactions.[3–9]

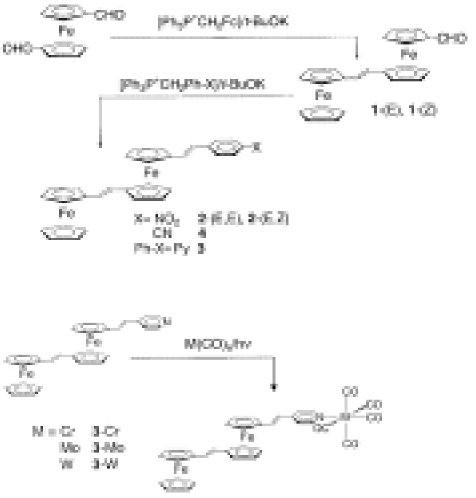
In the search of new materials with electronic communication between terminal subunits, we have focused our interest in the preparation of new conjugated ferrocenyl complexes with end capped nitro,[10] pyridine[11] and nitrile[12] groups. End-capping ferrocene with pyridine and nitrile allows the ferrocenyl subunit to link to different metallic fragments, affording interesting bimetallic complexes, in which the terminal metallic fragments are connected by a conjugated bridge. Some of the compounds so obtained showed high non linear optical responses,[10,13] which in most cases were envisaged from the molecular geometries and electronic properties of the compounds themselves.[11,12] In this sense, electrochemical studies, electronic spectroscopy and molecular structure determinations constitute the best tools to predict interesting physical properties of the compounds under study.

We now report, based on our previous findings, several efficient routes to the preparation of conjugated linked-bisferrocenyl conjugated compounds with end-capped nitro, nitrile and pyridine groups. These compounds are obtained by Wittig reactions, for which the corresponding bisferrocenyl-aldehydes have also been obtained. Coordination of Group 6 carbonyl fragments to the nitrile and pyridine ligands affords the preparation of trimetallic complexes. The crystal structures of several of these compounds have been determined and their electrochemistry has also been investigated.

## Results and discussion

### Synthesis and characterization of the compounds

Scheme 1 shows the general procedure for the synthesis of the bisferrocenyl complexes **1**–**4**. Since *E*-type isomers have shown higher efficiency for electronic coupling than the *Z*-type, we tried to optimize the preparation of the *E*-type isomers. In this sense, only the preparation of compounds **1**-(*E*) and **2**-(*E,E*) afforded a mixture of the corresponding *E*/*Z* isomers which could be easily separated. Furthermore, the *Z* isomers were quantitatively converted to the *E* homologues by treatment with $I_2$ in refluxing toluene.[12,14–16] The preparation of compounds **3** and **4** yielded the *E* isomers as the only isolable species.



Scheme 1

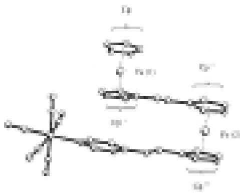
The coordination capabilities of the end-capped pyridine (**3**) and nitrile (**4**) bisferrocenyl complexes allowed us to obtain the trimetallic species **3**-M, and **4**-M (**3**, M = Cr, Mo, W; **4**, M = Cr, W), by reacting the ligands with (thf)$M(CO)_5$ which was photochemically generated *in situ*. The IR spectra of these heterometallic compounds are virtually identical, indicating the presence of a metal pentacarbonyl moiety, the bands being assigned to the two $A_1$, $B_2$ and E modes for the pseudo $C_{4v}$ metal center, by comparison with other monosubstituted metal carbonyl derivatives.[12,17]

DOI: 10.1039/b104433h

**Table 1** Crystallographic data

| Compound | **1**-(*E*) | **3**-Cr | **3**-Mo | **3**-W |
|---|---|---|---|---|
| Empirical formula | $C_{23}H_{20}Fe_2O$ | $C_{34}H_{25}Fe_2CrNO_5$ | $C_{34}H_{25}Fe_2MoNO_5$ | $C_{34}H_{25}Fe_2WNO_5$ |
| Formula weight/g mol$^{-1}$ | 424.09 | 691.25 | 735.19 | 823.10 |
| $T$/K | 293(2) | 293(2) | 293(2) | 293(2) |
| Wavelength/Å | 0.71073 | 0.71073 | 0.71073 | 0.71073 |
| Crystal system | Monoclinic | Triclinic | Triclinic | Triclinic |
| Space group | $C2/c$ | $P\bar{1}$ | $P\bar{1}$ | $P\bar{1}$ |
| $a$/Å | 22.861(3) | 10.4406(8) | 10.4088(11) | 10.4332(6) |
| $b$/Å | 7.5781(8) | 15.0730(12) | 15.1733(15) | 15.1577(8) |
| $c$/Å | 10.9377(12) | 20.1531(16) | 20.490(2) | 20.3793(11) |
| $\alpha$/° | 90 | 83.488(2) | 83.278(2) | 83.056(1) |
| $\beta$/° | 108.025(2) | 77.095(2) | 77.073(2) | 76.951(1) |
| $\gamma$/° | 90 | 84.630(2) | 85.000(2) | 84.614(1) |
| $V$/Å$^3$ | 1801.9(3) | 3063.8(4) | 3126.1(6) | 3109.2(3) |
| $Z$ | 4 | 4 | 4 | 4 |
| $D_c$/Mg m$^{-3}$ | 1.563 | 1.499 | 1.562 | 1.758 |
| $\mu$/mm$^{-1}$ | 1.618 | 1.325 | 1.352 | 4.653 |
| $F$(000) | 872 | 1408 | 1480 | 1608 |
| Crystal size/mm$^3$ | 0.40 × 0.25 × 0.12 | 0.19 × 0.19 × 0.12 | 0.30 × 0.16 × 0.12 | 0.23 × 0.13 × 0.05 |
| $\theta$ range/° | 1.87 to 24.71 | 1.04 to 23.25 | 1.02 to 30.51 | 1.03 to 26.37 |
| Index ranges | $-25 \le h \le 26$<br>$-8 \le k \le 8$<br>$-12 \le l \le 12$ | $-11 \le h \le 11$<br>$-16 \le k \le 16$<br>$-22 \le l \le 14$ | $-10 \le h \le 14$<br>$-21 \le k \le 21$<br>$-27 \le l \le 29$ | $-12 \le h \le 13$<br>$-17 \le k \le 18$<br>$-25 \le l \le 15$ |
| Reflections collected | 4813 | 15180 | 26545 | 19707 |
| Independent reflections | 1538 [$R_{int} = 0.0254$] | 8820[$R_{int} = 0.0466$] | 18642[$R_{int} = 0.0565$] | 12656[$R_{int} = 0.0.0441$] |
| Data/restraints/parameters | 1538/0/136 | 8820/0/775 | 18642/0/775 | 12656/0/775 |
| Goodness-of-fit on $F^2$ | 1.078 | 0.906 | 0.794 | 0.902 |
| Final $R$ indices [$I > 2\sigma(I)$] | $R1 = 0.0570$, $wR2 = 0.1575$ | $R1 = 0.0416$, $wR2 = 0.0835$ | $R1 = 0.0467$, $wR2 = 0.0819$ | $R1 = 0.0409$, $wR2 = 0.0928$ |
| $R$ indices (all data) | $R1 = 0.0728$, $wR2 = 0.1663$ | $R1 = 0.0929$, $wR2 = 0.1062$ | $R1 = 0.2101$, $wR2 = 0.1201$ | $R1 = 0.0761$, $wR2 = 0.1002$ |
| $\rho_{max}$, $\rho_{min}$/e Å$^{-3}$ | 1.048, −0.489 | 0.339, −0.295 | 0.426, −0.603 | 1.406, −1.406 |

**Table 2** Selected bond distances (Å) and angles (°)



| | **1**-(*E*) | **3**-Cr | **3**-Mo | **3**-W |
|---|---|---|---|---|
| Environment Fe | | | | |
| Fe(1)–Cp (cent.) | 1.64 | 1.64 | 1.66 | 1.66 |
| Fe(1)–Cp′ (cent.) | 1.65 | 1.65 | 1.65 | 1.65 |
| Fe(2)–Cp″ (cent.) | — | 1.64 | 1.66 | 1.64 |
| Fe(2)–Cp‴ (cent.) | — | 1.64 | 1.66 | 1.64 |
| Fe(1)–Fe(2) (bonds) | 8.49 | 8.30 | 8.33 | 8.31 |
| Fe(1)–Fe(2) (space) | 7.15 | 7.18 | 7.21 | 7.18 |
| Fe(1)–M(1) | — | 6.47 | 6.58 | 6.50 |
| Fe(2)–M(1) | — | 10.10 | 10.19 | 10.19 |
| Environment M | | | | |
| M(1)–N(1) | — | 2.159(4) | 2.288(4) | 2.271(5) |
| M–CO (min/max) | — | 1.849–1.901 | 1.959–2.072 | 1.977–2.044 |
| Tilt angles | | | | |
| Cp–Cp′ | 0.70(0.18) | 1.68(0.47) | 3.93(0.27) | 1.46(0.63) |
| Cp″–Cp‴ | — | 2.84(0.49) | 1.77(0.30) | 2.82(0.70) |
| π interaction | | | | |
| Distance (Cp′–Py) | — | 3.78 | 3.69 | 3.76 |
| Angle (Cp′–Py) | — | 8.03(0.41) | 15.49(0.17) | 8.25(0.55) |
| Coplanarity | | | | |
| Cp′–Cp″ | 0 | 7.29(0.47) | 2.84(0.28) | 7.30(0.63) |
| Cp‴–Py | — | 1.64(0.44) | 18.12(0.18) | 1.97(0.63) |

## Crystal structures

Crystals suitable for structure determination of compounds **1**-(*E*), **3**-Cr, **3**-Mo and **3**-W were grown from dichloromethane/hexane mixtures, by slow evaporation. A summary of the crystal data, data collection and processing parameters is given in Table 1. Selected bond distances and angles are displayed in Table 2. Figs. 1–4 display the ORTEP[29] diagrams of **1**-(*E*), **3**-Cr, **3**-Mo and **3**-W. It is noteworthy that the compounds **3**-Cr, **3**-Mo and **3**-W are almost isostructural, so different orientations of the three molecules have been chosen in order to facilitate their visualization. All the complexes crystallize in centrosymmetric space groups, $C2/c$ for compound **1**-(*E*) and $P\bar{1}$ for compounds **3**-Cr, **3**-Mo and **3**-W.

Compound **1**-(*E*) shows a center of inversion in the middle of the ethylene bridge. The asymmetric unit consists of a complete ferrocenyl fragment (100% occupancy), the ethenyl bridge (50% occupancy due to disorder) and the aldehyde group (50% occupancy). The other half of the molecule generated by the inversion center completes the molecule (Fig. 1).

For **3**-Cr, **3**-Mo and **3**-W, two independent molecules were found per asymmetric unit. As required by the presence of the center of symmetry the total number of molecules per unit cell is four. In all cases, there is a very similar geometrical arrangement in the two independent molecules. The iron distances to the Cp rings and the Cp(C–C) distances and angles lie in the expected range. In all the cases that we report in this paper, the complexes show a perfect eclipsed disposition of the Cp rings in all the ferrocene units, and a slightly tilting angle can be observed between the two Cp rings of every Fc unit (dihedral angles between 1.5 and 4.0°). As seen in some of the 1,1′-substituted bisferrocenyl complexes that we[18] and other authors[19,20] have reported so far, all these complexes adopt the sterically more hindered *syn* conformation, in a parallel disposition of the ancillary ligands in which intramolecular π-stacking may be having some effect. In the case of the complex **1**-(*E*), where π-stacking is not possible, the *syn* conformation is also observed, this indicating that packing effects may be having a more important effect in the steric disposition of the molecule in the crystal structure. In this sense, Lee *et al.* have reported a study in which the eclipsed/staggered conformation of 1,1′-bis(ethenyl-4-pyridine)ferrocene is controlled by cocrystallization in various solvents.[20] This effect, together with the different conformations that 1,1′-bisferrocenyl complexes may adopt upon oxidation,[21] make ferrocene behave as a 'hinge-like' compound, which can lead to interesting applications.

The orientation of the coordinated pyridyl rings with respect to the metal-carbonyl fragments is defined by the angles between the pyridyl plane and the plane defined by M (M = Cr, Mo, Cr) and three coplanar carbon atoms of the carbonyl ligands. In this regard, the pyridyl plane in **3**-Cr is at an angle of 44.6° to the Cr(1)–C(30)–C(33)–C(34) mean plane, this angle being 66.1 and 44.7° for **3**-Mo and **3**-W, respectively. M(dπ)–pyridine(π*) backbonding would be maximized when these angles are 0 or 90°. In our case, the carbonyl ligands adopt a quasi-staggered disposition with respect to the pyridine fragment (especially in the cases of **3**-Cr and **3**-W, where the angle is practically equal to the idealized staggered disposition, 45°), so minimizing the steric interactions. The expected *trans* influence

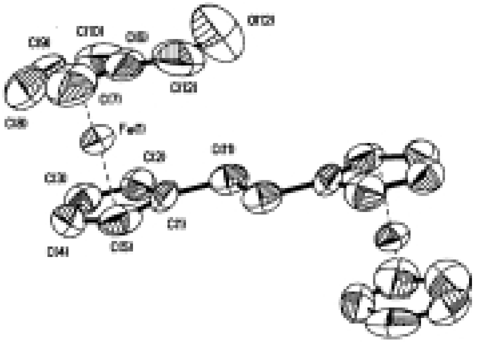


**Fig. 1** Molecular structure and atomic labeling scheme for **1**-(*E*), {(*E*)-($\eta^5$-$C_5H_5$)Fe($\eta^5$-$C_5H_4$)(CH=CH)($\eta^5$-$C_5H_4$)Fe($\eta^5$-$C_5H_4$CHO)}, with 50% anistropic displacement ellipsoids. Hydrogen atoms and disorder in the ethylene bridge and aldehyde have been omitted for clarity.

**Fig. 3** Molecular structure for compound **3**-Mo, {(*E,E*)-($\eta^5$-$C_5H_5$)-Fe($\eta^5$-$C_5H_4$)(CH=CH)($\eta^5$-$C_5H_4$)Fe($\eta^5$-$C_5H_4$)(CH=CH)PyMo(CO)$_5$}. Hydrogen atoms have been omitted for clarity.

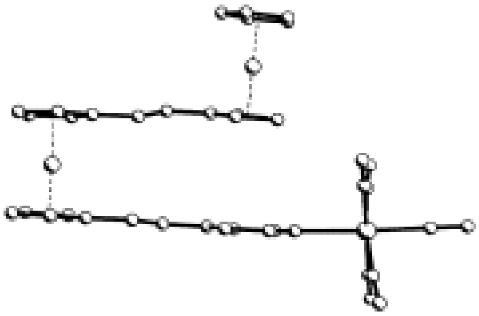


**Fig. 4** Molecular structure for compound **3**-W, {(*E,E*)-($\eta^5$-$C_5H_5$)-Fe($\eta^5$-$C_5H_4$)(CH=CH)($\eta^5$-$C_5H_4$)Fe($\eta^5$-$C_5H_4$)(CH=CH)PyW(CO)$_5$}. Hydrogen atoms have been omitted for clarity.

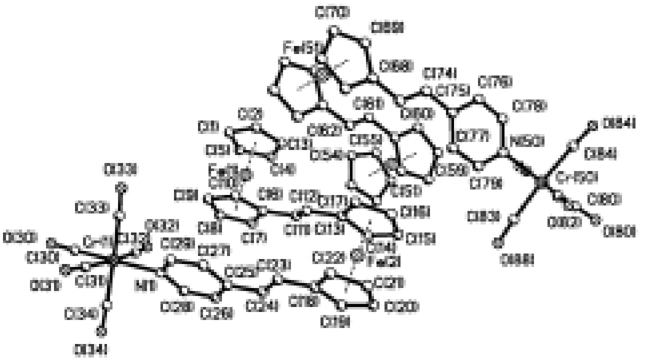


**Fig. 2** Molecular structure and atomic labeling scheme for **3**-Cr, {(*E,E*)-($\eta^5$-$C_5H_5$)Fe($\eta^5$-$C_5H_4$)(CH=CH)($\eta^5$-$C_5H_4$)Fe($\eta^5$-$C_5H_4$)(CH=CH)-PyCr(CO)$_5$}, with 50% displacement ellipsoids. The two molecules per asymmetric unit are shown. Hydrogen atoms have been omitted for clarity.

**Table 3** Electrochemical data for the diferrocenyl derivatives[a]

| Compound | $E_{1/2}$/mV ($\Delta E_p$/mV) Ferrocene-based | | $E_{1/2}$/mV ($\Delta E_p$/mV) $M^b$-based | $\Delta E = (E_{1/2})_2 - (E_{1/2})_1$(mV) Ferrocenes | $K_c$[d] |
|---|---|---|---|---|---|
| Ferrocene | 445(105) | | — | — | |
| **1**-(*E*) | 405(90) | 785(85) | — | 380 | $2.6 \times 10^6$ |
| **1**-(*Z*) | 400(110) | 760(75) | — | 355 | $1.0 \times 10^6$ |
| **2**-(*E,E*) | 350(80) | 535(65) | — | 185 | 1350 |
| **2**-(*E,Z*) | 370(110) | 570(110) | — | 195 | 1975 |
| **3** | 370(145) | 570(140) | — | 200 | 2400 |
| **3**-Cr | 375(130) | 590(125) | 950(130) | 215 | 4300 |
| **3**-Mo | 360(95) | 575(80) | 1115[c] | 215 | 4300 |
| **3**-W | 380(160) | 610(153) | 1240[c] | 230 | 7725 |
| **4** | 360(145) | 550(150) | — | 190 | 1625 |
| **4**-Cr | 360(135) | 555(110) | 975(125) | 195 | 1975 |
| **4**-W | 360(95) | 540(85) | 1140[c] | 185 | 1350 |

[a] Measured in $CH_2Cl_2$. [b] M = Cr, Mo, W. [c] Irreversible peak, measured at 100 mV $s^{-1}$. [d] $\Delta E_{1/2}$/mV = 59.15(log $K_c$) at 298 K.

is present, with the M–C bonds *trans* to the pyridine ligand (Cr, 1.84; Mo, 1.95; W, 1.97 Å) being significantly shorter than the other M–C bonds (Cr, 1.90; Mo, 2.05; W, 2.02 Å). These results are in good agreement with the features on the molecular structures reported by Sakanishi *et al.* for other related ferrocenyl–pyridyl ligands coordinated to $Cr(CO)_5$.[22]

## Cyclic voltammetry

Electrochemical techniques have been the most widely used tools to investigate metal–metal interactions in metallocene systems and also to evaluate the donor–acceptor electronic influence. In this work we have used cyclic voltammetry in order to evaluate the redox properties of the metal centers, the degree of interaction, and the effect of the acceptor moiety. Electrochemical data obtained for the compounds studied are summarized in Table 3.

Fig. 5 shows three voltammograms corresponding to compounds **1**-(*E*), **2**-(*E,E*) and **3**-Cr. As can be seen in Table 3, the redox bands corresponding to the two ferrocenyl fragments, are very little influenced by the nature of the ancillary ligands. Only in the case of the aldehyde complexes **1**-(*E*) and **1**-(*Z*), the half wave potential of the ferrocenyl moieties show a clear anodic shift compared to (*E*)–Fc–CH=CH–Fc, meaning some degree of electron transfer between the iron center and the electron-accepting aldehyde fragment. However, the halfwave potentials of the nitrile and pyridine derivatives with longer conjugated chains are similar to that shown for (*E*)-Fc–CH=CH–Fc indicating that the inclusion of the electron-accepting fragments (Py, CN), are somehow compensated by the delocalization of the charge along the longer conjugated system of the ligand, which makes oxidation easier.

Coordination of the neutral unit $M(CO)_5$ to the ferrocenyl nitrile and pyridine ligands does not have any significant effect on the redox potential of the ferrocene centers, compared to those of the uncoordinated ligands. The oxidation potential of the third step ascribed to the metal-carbonyl fragment depends on the metal present, this being higher for the W complexes compared to the Cr and Mo complexes. This band is only reversible in the case where $Cr(CO)_6$ was used. This result is consistent with those studies reported before where chromium and tungsten ferrocenyl derivatives show quasi-reversible and completely irreversible oxidation waves respectively.[12,13,15,23,24]

The degree of separation or resolution of the two waves in the homobimetallic compounds is a quasi-direct measure of the degree of interaction of these metals, although we have to take into account the intrinsic inequivalency of the two metal centers. The presence of two one-electron oxidations instead of one two-electron oxidation indicates a stabilization of the mixed valence species. The separation between the two oxidation potentials was employed to calculate the comproportionation constant, $K_c$, from eqns. (1) and (3).

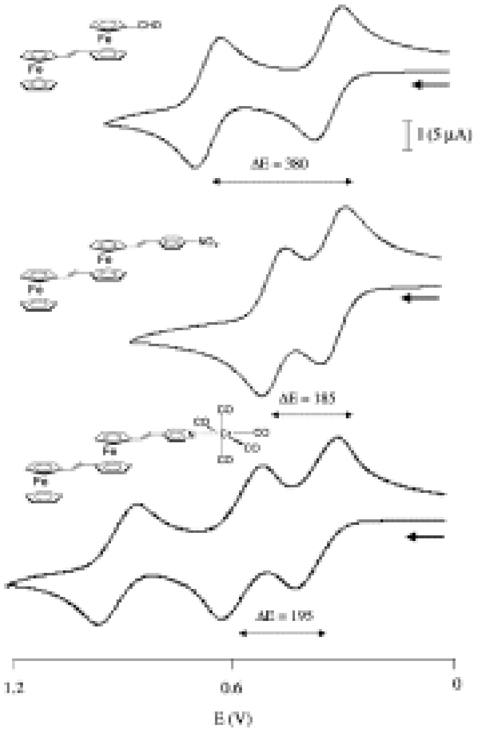


**Fig. 5** Cyclic voltammograms (scan rate 100 mV $s^{-1}$) of **1**-(*E*), **2**-(*E,E*) and **3**-Cr in 0.1M $[NBu^t_4]PF_6$-$CH_2Cl_2$.

$$(\mathrm{Fc^{II}, Fc^{II}}) + (\mathrm{Fc^{III}, Fc^{III}}) \xleftrightarrow{K} 2(\mathrm{Fc^{III}, Fc^{II}}) \qquad (1)$$

$$\Delta E = \Delta E_{1/2}(\mathrm{Fc^{III}, Fc^{III}}) - \Delta E_{1/2}(\mathrm{Fc^{III}, Fc^{II}}) \qquad (2)$$

$$\Delta E(\mathrm{mV}) = 59.15(\log K_c) \text{ at 298 K} \qquad (3)$$

This is a crude estimation of the interaction between the iron centers due to their geometrical inequivalence, but it gives us an approximate estimation of the electronic communication between the two metal centers. This approximation has also been used in some other examples in which the two metal centers were inequivalent, and even in cases in which the metals were different.[25] In any case, we are aware that the electronic communication between the redox centers must be less than that measured by the potential difference.

As can be seen in Table 3, $K_c$ values lie in the range of the weakly connected class II mixed-valence complexes. For all the compounds (except **1**-(*E*) and **1**-(*Z*)) $\Delta E$ values are quite similar, *ca.* 190 mV.

The most interesting feature of this interaction between our diferrocenyl derivatives is the strong coupling observed for compounds **1**-(*E*) ($\Delta E$ = 380 mV) and **1**-(Z) ($\Delta E$ = 355 mV), especially when we compare these values to the ones published before. For example in the case of (*E*)-Fc–CH=CH–Fc the coupling constant is *ca.* 150 mV.[26] The coupling in **1**-(*E*) is larger than that of (*E*)-Fc–CH=CH–Fc, even if we consider an intrinsic inequivalence of 60 mV, which is approximately the difference in the redox potentials of ferrocene (445 mV) and ferrocenealdehyde (500 mV).

## Experimental

All reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques. Solvents for synthesis and electrochemical measurements were dried and degassed by standard methods before use. Chromatographic work was performed on Silica gel 60 Å or Neutral Alumina columns.

NMR spectra were recorded on a Varian Innova 300 MHz and 500 MHz, using $CDCl_3$ as solvent unless otherwise stated. IR spectra were recorded on a Perkin-Elmer System 2000 FT-IR using NaCl pellets. Electronic absorption spectra were obtained on a UV-1603 Shimadzu spectrophotometer. Cyclic voltammetry experiments were performed with a Echochemie pgstat 20 electrochemical analyzer. All measurements were carried out at room temperature with a conventional three-electrode configuration consisting of platinum working and auxiliary electrodes and a Ag/AgCl reference electrode containing aqueous 3 M KCl. The solvents used in all experiments were $CH_2Cl_2$ or acetone, which were obtained in HPLC grade. The supporting electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate, synthesized by counter ion exchange of tetrabutylammonium bromide and $HPF_6$, recrystallized from ethanol and dried under vacuum. The $E_{1/2}$ values were determined as 1/2 ($E_{p,a} + E_{p,c}$), where $E_{p,a}$ and $E_{p,c}$ are the anodic and cathodic peak potentials, respectively. All potentials reported are not corrected for the junction potential. Ferrocenealdehyde was used as purchased (Aldrich), and 1,1′-ferrocenebiscarboxaldehyde was obtained according to the literature method.[27]

### Syntheses

**{(*E*)-($\eta^5$-$C_5H_5$)Fe($\eta^5$-$C_5H_4$)(CH=CH)($\eta^5$-$C_5H_4$)Fe($\eta^5$-$C_5H_4$)-CHO}, 1-(*E*) and {(*Z*)-($\eta^5$-$C_5H_5$)Fe($\eta^5$-$C_5H_4$)(CH=CH)($\eta^5$-$C_5H_4$)Fe($\eta^5$-$C_5H_4$)CHO}, 1-(*Z*).** To an ice-cold solution of (ferrocenylmethyl)triphenylphosphonium iodide (1 g, 1.7 mmol) in THF (75 ml) potassium *tert*-butoxide (213.2 mg, 1.9 mmol) was added and the resulting solution stirred for 20 min and then 40 min at room temperature. 1,1′-Ferrocenebiscarboxaldehyde (411.5 mg, 1.7 mmol) was added at 0 °C and the resulting solution stirred overnight at room temperature. After removing the solvent under reduced pressure, the product was extracted with $CH_2Cl_2/H_2O/NaHCO_3$ and dried over $MgSO_4$. The compounds were purified by column chromatography on silica gel using diethyl ether–hexane as eluent. Recrystallization of the first major fraction from $CH_2Cl_2$–hexane mixtures afforded pure compound **1**-(*E*). A second minor fraction containing **1**-(*Z*) was recrystallized by the same procedure. **1**-(*E*). Yield: 65%. $^1$H-NMR (300 MHz, $CDCl_3$): $\delta$ 9.94 (s, 1H, CHO); 6.48 (d, 1H, $^3J_{H-H}$ = 16.2 Hz, CH=CH); 6.31 (d, 1H, $^3J_{H-H}$ = 16.2 Hz, CH=CH); 4.74 (t, 2H, $^3J_{H-H}$ = 1.9 Hz, $C_5H_4$); 4.56 (t, 2H, $^3J_{H-H}$ = 1.9 Hz, $C_5H_4$); 4.48 (t, 2H, $^3J_{H-H}$ = 1.9 Hz, $C_5H_4$); 4.40 (t, 2H, $^3J_{H-H}$ = 1.8 Hz, $C_5H_4$); 4.35 (t, 2H, $^3J_{H-H}$ = 1.8 Hz, $C_5H_4$); 4.27 (t, 2H, $^3J_{H-H}$ = 1.7 Hz, $C_5H_4$); 4.15 (s, 5H, $C_5H_5$). $^{13}$C-NMR (300 MHz, $CDCl_3$): $\delta$ 193.9 (1C, CHO); 126.5, 121.9 (2C, CH=CH); 86.8, 83.3, 80.7 (3$C_q$, $C_5H_4$); 74.8, 70.9, 70.3, 69.5, 69.2, 67.8, 66.8 (17C, $C_5H_4$ and $C_5H_5$). IR (cm$^{-1}$): 1680 (s), 1411 (w), 1664 (s). Elemental anal. Calc. for compound **1**-(*E*), $C_{23}H_{20}Fe_2O$, $M$ = 424.11: C, 65.1; H, 4.75. Found: C, 65.2; H, 4.74%.

**1**-(*Z*). Yield <15%. $^1$H-NMR (300 MHz, $CDCl_3$): $\delta$ 9.86 (s, 1H, CHO); 6.24 (d, 1H, $^3J_{H-H}$ = 12.0 Hz, CH=CH); 6.00 (d, 1H, $^3J_{H-H}$ = 11.7 Hz, CH=CH); 4.70 (s, 2H, $C_5H_4$); 4.52 (s, 2H, $C_5H_4$); 4.42 (s, 2H, $C_5H_4$); 4.27 (s, 4H, $C_5H_4$); 4.18 (s, 2H, $C_5H_4$); 4.09 (s, 5H, $C_5H_5$). $^{13}$C-NMR (300 MHz, $CDCl_3$): $\delta$ 194.1 (1C, CHO); 127.7, 123.5 (2C, CH=CH); 85.4, 82.5, 80.4, (3$C_q$, $C_5H_4$); 75.1, 71.2, 70.3, 69.9, 69.8, 69.0, 67.2 (17C, $C_5H_4$ and $C_5H_5$). IR (cm$^{-1}$): 1679 (s), 1411 (w), 1663 (s). Elemental anal. Calc. for compound **1**-(*Z*), $C_{23}H_{20}Fe_2O$, $M$ = 424.11: C, 65.1; H, 4.75. Found: C, 65.2; H, 4.76%.

**{(*E,E*)-($\eta^5$-$C_5H_5$)Fe($\eta^5$-$C_5H_4$)(CH=CH)($\eta^5$-$C_5H_4$)Fe($\eta^5$-$C_5H_4$)-(CH=CH)Ph-$NO_2$}, 2-(*E,E*) and {(*E,Z*)-($\eta^5$-$C_5H_5$)Fe($\eta^5$-$C_5H_4$)-(CH=CH)($\eta^5$-$C_5H_4$)Fe($\eta^5$-$C_5H_4$)(CH=CH)Ph-$NO_2$}, 2-(*E,Z*).** These compounds were obtained following the general procedure described for compound **1**-(*E*), but the reaction was carried out overnight at 60 °C. [(*p*-nitrophenyl)methyl]-triphenylphosphonium iodide (813.1 mg, 1.7 mmol), and sodium hydride (dispersion in mineral oil 60%; 72.0 mg, 1.8 mmol) were mixed in THF at 0 °C for 45 min. Then the aldehyde **1**-(*E*) (721.0 mg, 1.7 mmol) was added, and the suspension was heated at 60 °C overnight. The two isomers were separated by column chromatography on silica gel using $CH_2Cl_2$–hexane (1 : 1) as eluent, the first major band containing **2**-(*E,E*) and the second (minor) **2**-(*E,Z*). Recrystallization from $CH_2Cl_2$–hexane mixtures afforded the pure compounds. Yield: 60%. **2**-(*E,E*). Yield: 60%. $^1$H-NMR (500 MHz, $CDCl_3$): $\delta$ 8.09 (2H, $^3J_{H-H}$ = 8.0 Hz, $C_6H_4$); 7.38 (2H, $^3J_{H-H}$ = 8.5 Hz, $C_6H_4$); 6.92 (d, 1H, $^3J_{H-H}$ = 16.0 Hz, CH=CH); 6.62 (d, 1H, $^3J_{H-H}$ = 15.5 Hz, CH=CH); 6.54 (d, 1H, $^3J_{H-H}$ = 16.0 Hz, CH=CH); 6.23 (d, 1H, $^3J_{H-H}$ = 16.0 Hz, CH=CH); 4.45 (s, 2H, $C_5H_4$); 4.37 (s, 2H, $C_5H_4$); 4.34 (s, 2H, $C_5H_4$); 4.24 (s, 2H, $C_5H_4$); 4.23 (s, 2H, $C_5H_4$); 4.18 (s, 2H, $C_5H_4$); 4.08 (s, 5H, $C_5H_5$). $^{13}$C-NMR (300 MHz, $CDCl_3$): $\delta$ 146.6, 144.9 (2$C_q$, $C_6H_4$); 133.1, 126.6, 125.9, 124.9, 124.6, 123.5 (8C, CH=CH and $C_6H_4$); 86.8, 85.3, 83.5 (3$C_q$, $C_5H_4$); 71.7, 70.5, 70.1, 69.6, 69.2, 68.2, 66.8 (17C, $C_5H_4$ and $C_5H_5$). Elemental anal. Calc. for compound **2**-(*E,E*), $C_{30}H_{25}Fe_2NO_2$, $M$ = 543.23: C, 66.3; H, 4.64; N, 2.58. Found: C, 66.4; H, 4.65; N, 2.57%.

**2**-(*E,Z*). Yield: <10%. $^1$H-NMR (500 MHz, $CDCl_3$): $\delta$ 8.10 (2H, $^3J_{H-H}$ = 7.9 Hz, $C_6H_4$); 7.46 (2H, $^3J_{H-H}$ = 8.5 Hz, $C_6H_4$); 6.46 (d, 1H, $^3J_{H-H}$ = 12.0 Hz, CH=CH); 6.42 (d, 1H, $^3J_{H-H}$ = 12.0 Hz, CH=CH); 6.36 (d, 1H, $^3J_{H-H}$ = 12.0 Hz, CH=CH); 6.22 (d, 1H, $^3J_{H-H}$ = 15.5 Hz, CH=CH); 4.43 (s, 2H, $C_5H_4$); 4.33 (s, 4H, $C_5H_4$); 4.21 (s, 4H, $C_5H_4$); 4.14 (s, 5H, $C_5H_5$); 4.12 (s, 2H, $C_5H_4$). $^{13}$C-NMR (300 MHz, $CDCl_3$): $\delta$ 146.6, 145.7 (2$C_q$, $C_6H_4$); 132.5, 129.9, 125.5, 125.4, 124.1, 123.1 (8C, CH=CH and $C_6H_4$); 86.2, 84.3, 81.5 (3$C_q$, $C_5H_4$); 71.5, 71.3, 70.8, 70.3, 69.8, 68.3, 66.9 (17C, $C_5H_4$ and $C_5H_5$). Elemental anal. Calc. for compound **2**-(*E,Z*), $C_{30}H_{25}Fe_2NO_2$, $M$ = 543.23: C, 66.3; H, 4.64; N, 2.58. Found: C, 66.3; H, 4.63; N, 2.59%.

**{(*E,E*)-($\eta^5$-$C_5H_5$)Fe($\eta^5$-$C_5H_4$)(CH=CH)($\eta^5$-$C_5H_4$)Fe($\eta^5$-$C_5H_4$)-(CH=CH)Py} 3.** This compound was obtained following the general procedure described for compound **2**-(*E,E*), using (4-pyridylmethyl)triphenylphosphonium chloride (389.5 mg, 1.0 mmol), potassium *tert*-butoxide (123.4 mg, 1.1 mmol) and the aldehyde **1**-(*E*) (424.1 mg, 1.0 mmol). The compound was purified by column chromatography on silica gel using $CH_2Cl_2$–Acetone (4 : 1) as eluent. Recrystallization from $CH_2Cl_2$–hexane mixtures afforded pure compound **3**. Yield: 57%. $^1$H-NMR (300 MHz, $CD_2Cl_2$): $\delta$ 8.43 (2H, $^3J_{H-H}$ = 4.9 Hz, $C_5H_4N$); 7.20 (2H, $^3J_{H-H}$ = 4.8 Hz, $C_5H_4N$); 7.45 (d, 1H, $^3J_{H-H}$ = 15.3 Hz, CH=CH); 6.55 (d, 1H, $^{3}J_{H-H}$ = 15.6 Hz, CH=CH); 6.38 (d, 1H, $^{3}J_{H-H}$ = 15.3 Hz, CH=CH); 6.27 (d, 1H, $^{3}J_{H-H}$ = 15.3 Hz, CH=CH); 4.45 (s, 2H, $C_5H_4$); 4.37 (s, 2H, $C_5H_4$); 4.32 (s, 2H, $C_5H_4$); 4.29 (s, 2H, $C_5H_4$); 4.23 (s, 2H $C_5H_4$); 4.21 (s, 2H, $C_5H_4$); 4.09 (s, 5H, $C_5H_5$). $^{13}$C-NMR (500 MHz, $CDCl_3$): $\delta$ 150.8, 133.3, 125.6, 123.9, 123.2, 121.6 (8C, CH=CH and $C_5H_4N$); 146.0 (1$C_q$, $C_5H_4N$); 86.4, 84.7, 82.9 (3$C_q$, $C_5H_4$); 71.7, 70.5, 69.8, 69.5, 69.3 (17C, $C_5H_4$ and $C_5H_5$). Elemental anal. Calc. for compound **3**, $C_{29}H_{25}Fe_2N$, *M* = 499.22: C, 69.8; H, 5.05; N, 2.81. Found: C, 69.6; H, 5.09; N, 2.80%.

**{(*E,E*)-(η$^5$-$C_5H_5$)Fe(η$^5$-$C_5H_4$)(CH=CH)(η$^5$-$C_5H_4$)Fe(η$^5$-$C_5H_4$)-(CH=CH)PyCr$(CO)_5$} 3-Cr.** Chromium hexacarbonyl (330.1 mg, 1.5 mmol) was dissolved in THF (30 ml) and the resulting solution was irradiated using a Hg lamp for 1 h. Compound **3** (499.2 mg, 1 mmol) was added to the yellow solution formed upon irradiation in order to obtain compound **3**-Cr. The reaction mixture was stirred for another 30 min, filtered to remove the solid, and the solvent was removed under reduced pressure. Purification by column chromatography on neutral alumina with $CH_2Cl_2$–Hexane (3 : 1) afforded the pure compound **3**-Cr. Yield: 60%. $^{1}$H-NMR (500 MHz, $CDCl_3$): $\delta$ 8.24 (2H, $^{3}J_{H-H}$ = 5.3 Hz, $C_5H_4N$); 6.92 (2H, $^{3}J_{H-H}$ = 5.3 Hz, $C_5H_4N$); 6.87 (d, 1H, $^{3}J_{H-H}$ = 15.9 Hz, CH=CH); 6.35 (d, 1H, $^{3}J_{H-H}$ = 16.0 Hz, CH=CH); 6.25 (d, 1H, $^{3}J_{H-H}$ = 16.0 Hz, CH=CH); 6.05 (d, 1H, $^{3}J_{H-H}$ = 15.7 Hz, CH=CH); 4.47 (s, 2H, $C_5H_4$) 4.39; (s, 2H, $C_5H_4$); 4.37 (s, 2H, $C_5H_4$); 4.27 (s, 2H, $C_5H_4$); 4.24 (s, 2H, $C_5H_4$); 4.19 (s, 2H, $C_5H_4$); 4.10 (s, 5H, $C_5H_5$). $^{13}$C-NMR (500 MHz, $CDCl_3$): $\delta$ 221.5, 215.3 (5C, CO); 146.8, 135.6, 126.0, 122.7, 122.1, 121.4 (8C, CH=CH and $C_5H_4N$); 155.8 (1$C_q$, $C_5H_4N$); 86.8, 84.5, 82.3 (3$C_q$, $C_5H_4$); 71.8, 70.3, 69.9, 69.5, 69.3, 68.1, 66.8 (17C, $C_5H_4$ and $C_5H_5$). IR (cm$^{-1}$): 2061 (s), 1980 (s), 1908 (vs). Elemental anal. Calc. for compound **3**-Cr, $C_{34}H_{25}Fe_2NO_5Cr$, *M* = 691.27: C, 59.1; H, 3.65; N, 2.03. Found: C, 59.0; H, 3.66; N, 2.03%.

**{(*E,E*)-(η$^5$-$C_5H_5$)Fe(η$^5$-$C_5H_4$)(CH=CH)(η$^5$-$C_5H_4$)Fe(η$^5$-$C_5H_4$)-(CH=CH)PyMo$(CO)_5$} 3-Mo.** This compound was obtained using the general procedure described for **3**-Cr but using molybdenum hexacarbonyl (396.0 mg, 1.5 mmol) instead of chromium hexacarbonyl. Yield 45%. $^{1}$H-NMR (300 MHz, $CDCl_3$): $\delta$ 8.28 (2H, $^{3}J_{H-H}$ = 6.6 Hz, $C_5H_4N$); 6.94 (2H, $^{3}J_{H-H}$ = 6.6 Hz, $C_5H_4N$); 6.88 (d, 1H, $^{3}J_{H-H}$ = 16.2 Hz, CH=CH); 6.37 (d, 1H, $^{3}J_{H-H}$ = 16.2 Hz, CH=CH); 6.29 (d, 1H, $^{3}J_{H-H}$ = 16.2 Hz, CH=CH); 6.10 (d, 1H, $^{3}J_{H-H}$ = 15.9 Hz, CH=CH); 4.47 (t, 2H, $^{3}J_{H-H}$ = 1.8 Hz, $C_5H_4$); 4.39 (t, 2H, $^{3}J_{H-H}$ = 1.8 Hz, $C_5H_4$); 4.37 (t, 2H, $^{3}J_{H-H}$ = 1.8 Hz, $C_5H_4$); 4.23 (t, 2H, $^{3}J_{H-H}$ = 1.8 Hz, $C_5H_4$); 4.20 (t, 2H, $^{3}J_{H-H}$ = 1.8 Hz, $C_5H_4$); 4.17 (t, 2H, $^{3}J_{H-H}$ = 1.8 Hz, $C_5H_4$); 4.07 (s, 5H, $C_5H_5$). $^{13}$C-NMR (500 MHz, $CDCl_3$): $\delta$ 214.9, 205.4 (5C, CO); 155.5, 136.0, 126.4, 122.9, 122.5, 121.8 (8C, CH=CH and $C_5H_4N$); 147.1 (1$C_q$, $C_5H_4N$); 87.2, 84.9, 82.6 (3$C_q$, $C_5H_4$); 72.3, 70.7, 70.3, 69.9, 69.7, 68.5, 67.2 (17C, $C_5H_4$ and $C_5H_5$). IR (cm$^{-1}$): 2070 (s), 1970 (s), 1904 (vs). Elemental anal. Calc. for compound **3**-Mo, $C_{34}H_{25}Fe_2NO_5Mo$, *M* = 735.21: C, 55.5; H, 3.43; N, 1.91. Found: C, 55.6; H, 3.42; N, 1.91%.

**{(*E,E*)-(η$^5$-$C_5H_5$)Fe(η$^5$-$C_5H_4$)(CH=CH)(η$^5$-$C_5H_4$)Fe(η$^5$-$C_5H_4$)-(CH=CH)PyW$(CO)_5$} 3-W.** This compound was obtained using the general procedure described for **3**-Cr but using tungsten hexacarbonyl (527.9 mg, 1.5 mmol) instead of chromium hexacarbonyl. Yield 65%. $^{1}$H-NMR (300 MHz, $CDCl_3$): $\delta$ 8.43 (2H, $^{3}J_{H-H}$ = 4.0 Hz, $C_5H_4N$); 6.93 (2H, $^{3}J_{H-H}$ = 4.5 Hz, $C_5H_4N$); 6.90 (d, 1H, $^{3}J_{H-H}$ = 16.2 Hz, CH=CH); 6.36 (d, 1H, $^{3}J_{H-H}$ = 16.0 Hz, CH=CH); 6.29 (d, 1H, $^{3}J_{H-H}$ = 15.5 Hz, CH=CH); 6.08 (d, 1H, $^{3}J_{H-H}$ = 15.5 Hz, CH=CH); 4.47 (s, 2H, $C_5H_4$); 4.39 (s, 2H, $C_5H_4$); 4.37 (s, 2H, $C_5H_4$); 4.22 (s, 2H, $C_5H_4$); 4.20 (s, 2H, $C_5H_4$); 4.18 (s, 2H, $C_5H_4$); 4.07 (s, 5H, $C_5H_5$). $^{13}$C-NMR (500 MHz, $CDCl_3$): $\delta$ 203.0, 199.4 (5C, CO); 156.2, 136.0, 126.0, 122.6, 122.1, 121.9 (8C, CH=CH and $C_5H_4N$); 146.6, (1$C_q$, $C_5H_4N$); 86.8, 84.8, 82.2 (3$C_q$, $C_5H_4$); 71.9, 70.4, 69.9, 69.6, 69.3, 68.0, 66.7 (17C, $C_5H_4$ and $C_5H_5$). IR (cm$^{-1}$): 2069 (s), 1969 (s), 1898 (vs). Elemental anal. Calc. for compound **3**-W, $C_{34}H_{25}Fe_2NO_5W$, *M* = 823.12: C, 49.6; H, 3.06; N, 1.70. Found: C, 49.5; H, 3.02; N, 1.71%.

**{(E,E)-(η$^5$-$C_5H_5$)Fe(η$^5$-$C_5H_4$)(CH=CH)(η$^5$-$C_5H_4$)Fe(η$^5$-$C_5H_4$)-(CH=CH)PhCN} 4.** This compound was obtained following the general procedure described for compound **2**-(E,E), using [(*p*-nitrilephenyl)methyl]triphenylphosphonium iodide (500 mg, 1.1 mmol), potassium *tert*-butoxide (135 mg, 1.2 mmol) and the aldehyde **1**-(*E*) (460 mg, 1.1 mmol). The compound was purified by column chromatography on silica gel using $CH_2Cl_2$–hexane (4 : 6) as eluent. Recrystallization from $CH_2Cl_2$–hexane mixtures afforded pure compound **4**. Yield: 57%. $^{1}$H-NMR (300 MHz, $CD_2Cl_2$): $\delta$ 7.52 (2H, $^{3}J_{H-H}$ = 8.4 Hz, $C_6H_4$); 7.38 (2H, $^{3}J_{H-H}$ = 8.1 Hz, $C_6H_4$); 6.91 (d, 1H, $^{3}J_{H-H}$ = 16.2 Hz, CH=CH); 6.61 (d, 1H, $^{3}J_{H-H}$ = 16.2 Hz, CH=CH); 6.37 (d, 1H, $^{3}J_{H-H}$ = 16.2 Hz, CH=CH); 6.25 (d, 1H, $^{3}J_{H-H}$ = 16.2 Hz, CH=CH); 4.45 (t, 2H, $^{3}J_{H-H}$ = 1.8 Hz, $C_5H_4$); 4.37 (t, 2H, $^{3}J_{H-H}$ = 1.8 Hz, $C_5H_4$); 4.31 (t, 2H, $^{3}J_{H-H}$ = 1.9 Hz, $C_5H_4$); 4.24 (t, 2H, $^{3}J_{H-H}$ = 1.8 Hz, $C_5H_4$); 4.23 (t, 2H, $^{3}J_{H-H}$ = 1.8 Hz, $C_5H_4$); 4.19 (t, 2H, $^{3}J_{H-H}$ = 1.8 Hz, $C_5H_4$); 4.08 (s, 5H, $C_5H_5$). $^{13}$C-NMR (500 MHz, $CDCl_3$): $\delta$ 142.9, 120.1 (2$C_q$, $C_6H_4$); 133.1, 131.8, 126.8, 125.9, 125.1, 123.7 (8C, CH=CH and $C_6H_4$); 110.0 (1$C_q$, CN); 86.7, 85.5, 83.8 (3$C_q$, $C_5H_4$); 71.6, 70.6, 70.1, 69.7, 69.1, 68.1, 66.8 (17C, $C_5H_4$ and $C_5H_5$). IR (cm$^{-1}$): 2222 (s), 1598 (s). Elemental anal. Calc. for compound **4**, $C_{31}H_{25}Fe_2N$, *M* = 523.24: C, 71.2; H, 4.82; N, 2.68. Found: C, 71.1; H, 4.82; N, 2.68%.

**{(*E,E*)-(η$^5$-$C_5H_5$)Fe(η$^5$-$C_5H_4$)(CH=CH)(η$^5$-$C_5H_4$)Fe(η$^5$-$C_5H_4$)-(CH=CH)PhCNCr$(CO)_5$} 4-Cr.** This compound was obtained using the general procedure described for **3**-Cr but using chromium hexacarbonyl (396 mg, 1.8 mmol) and compound **4** (523 mg, 1.0 mmol). Yield 65%. $^{1}$H-NMR (300 MHz, $CDCl_3$): $\delta$ 7.51 (2H, $^{3}J_{H-H}$ = 8.0 Hz, $C_6H_4$); 7.38 (2H, $^{3}J_{H-H}$ = 7.9 Hz, $C_6H_4$); 6.90 (d, 1H, $^{3}J_{H-H}$ = 16.0 Hz, CH=CH); 6.53 (d, !H, $^{3}J_{H-H}$ = 16.0 Hz, CH=CH); 6.30 (d, 1H, $^{3}J_{H-H}$ = 16.0 Hz, CH=CH); 6.15 (d, 1H, $^{3}J_{H-H}$ = 16.0 Hz, CH=CH); 4.40 (s, 2H, $C_5H_4$); 4.36 (s, 2H, $C_5H_4$); 4.35 (s, 2H, $C_5H_4$); 4.22 (s, 4H, $C_5H_4$); 4.20 (s, 2H, $C_5H_4$); 4.08 (s, 5H, $C_5H_5$). $^{13}$C-NMR (300 MHz, $CDCl_3$): $\delta$ 219.8, 214.5 (5C, CO); 143.7, 123.1 (2$C_q$, $C_6H_4$); 133.2, 133.0, 126.7, 126.5, 125.5, 124.4 (8C, CH=CH and $C_6H_4$); 108.2 (1$C_q$, CN); 86.4, 84.6, 83.0 (3$C_q$, $C_5H_4$); 71.7, 70.6, 69.9, 69.4, 69.2, 68.2, 66.9 (17C, $C_5H_4$ and $C_5H_5$). IR (cm$^{-1}$): 2072 (s), 1989 (s), 1929 (vs), 1901 (sh). Elemental anal. Calc. for compound **4**-Cr, $C_{36}H_{25}Fe_2NCrO_5$, *M* = 715.29: C, 60.5; H, 3.52; N, 1.96. Found: C, 60.4; H, 3.55; N, 1.97%.

**{(*E,E*)-(η$^5$-$C_5H_5$)Fe(η$^5$-$C_5H_4$)(CH=CH)(η$^5$-$C_5H_4$)Fe(η$^5$-$C_5H_4$)-(CH=CH)PhCNW$(CO)_5$} 4-W.** This compound was obtained using the general procedure described for **3**-Cr but using tungsten hexacarbonyl (633 mg, 1.8 mmol) and compound **4** (523 mg, 1.0 mmol). Yield 70%. $^{1}$H-NMR (500 MHz, $CDCl_3$): $\delta$ 7.51 (2H, $^{3}J_{H-H}$ = 8.0 Hz, $C_6H_4$); 7.39 (2H, $^{3}J_{H-H}$ = 7.9 Hz, $C_6H_4$); 6.93 (d, 1H, $^{3}J_{H-H}$ = 16.0 Hz, CH=CH); 6.58 (d, 1H, $^{3}J_{H-H}$ = 16.0 Hz, CH=CH); 6.47 (d, 1H, $^{3}J_{H-H}$ = 16.0 Hz, CH=CH); 6.24 (d, 1H, $^{3}J_{H-H}$ = 15.5 Hz, CH=CH); 4.44 (s, 2H, $C_5H_4$); 4.38 (s, 2H, $C_5H_4$); 4.35 (s, 2H, $C_5H_4$); 4.24 (s, 4H, $C_5H_4$); 4.22 (s, 2H, $C_5H_4$); 4.10 (s, 5H, $C_5H_5$). $^{13}$C-NMR (300 MHz, $CDCl_3$): $\delta$ 196.8, 191.2 (5C, CO); 144.1, 123.0 (2$C_q$, $C_6H_4$); 133.6, 133.3, 126.8, 125.6, 124.3, 123.0 (8C, CH=CH and $C_6H_4$); 107.2 (1$C_q$, CN); 86.5, 84.6, 82.9 (3$C_q$, $C_5H_4$); 71.8, 70.5, 69.9, 69.4, 69.2, 68.2, 66.9 (17C, $C_5H_4$ and $C_5H_5$). IR (cm$^{-1}$): 2068 (s), 1925 (vs), 1891 (sh). Elemental anal. Calc. for compound **4**-W, $C_{36}H_{25}Fe_2NWO_5$, *M* = 847.14: C, 51.0; H, 2.97; N, 1.65. Found: C, 51.1; H, 2.98; N, 1.65.

### X-Ray diffraction studies

Single crystals were grown by slow diffusion of hexane into

$CH_2Cl_2$ solutions and mounted on a glass fiber in a random orientation. Data collection was performed at room temperature on a Siemens Smart CCD diffractometer using graphite monochromated Mo-$K_\alpha$ radiation ($\lambda = 0.71073$ Å) with a nominal crystal to detector distance of 4.0 cm. An hemisphere of data was collected based on three $\omega$-scans runs (starting $\omega = -28°$) at values $\phi = 0$, 90 and 180° with the detector at $2\theta = 28°$. At each of these runs, frames (606, 435 and 230 respectively) were collected at 0.3° intervals and 40 s per frame for compound **1**-(*E*), 60 s for compound **3**-Cr, 30 s for compound **3**-Mo and 20 s for compound **3**-W. Space group assignments are based on systematic absences, E statistics and successful refinement of the structures. Structures were solved by direct methods with the aid of successful difference Fourier maps and were refined using the SHELXTL 5.1 software package.[28] All non-hydrogen were refined anisotropically. Hydrogen atoms were assigned to ideal positions and refined using a riding model. Details of the data collection and cell dimensions are given in Table 1 and structure refinement. The diffraction frames were integrated using the SAINT[30] package and corrected for absorption with SADABS.[31]

CCDC reference numbers 164936–164939.

See http://www.rsc.org/suppdata/dt/b1/b104433h/ for crystallographic data in CIF or other electronic format.

## Acknowledgements

We thank the DGESIC (PB98–1044) and BANCAIXA (P1B98–07) for financial support. We would also like to thank the Generalitat Valenciana for a fellowship (J. A. M.). We are very thankful to Dr Rosa Llusar for her useful advice on the determination of the crystal structure of **1**-(*E*.

## References

1 A. Togni and T. Hayashi, *Ferrocenes*; VCH, Weinheim, Germany, 1995.
2 N. J. Long, *Metallocenes*; 1st edn., Blackwell Science Ltd., London, 1997.
3 S. Barlow and D. O'Hare, *Chem. Rev.*, 1997, **97**, 637.
4 M. Kurosawa, T. Nankawa, T. Matsuda, K. Kubo, M. Kurihara and H. Nishihara, *Inorg. Chem.*, 1999, **38**, 5113.
5 T. Horikoshi, K. Kubo and H. Nishihara, *J. Chem. Soc., Dalton Trans.*, 1999, 3355.
6 T.-Y. Dong, P.-H. Ho, X.-Q. Lai, Z.-W. Lin and K.-J. Lin, *Organometallics*, 2000, **19**, 1096.
7 Y. J. Chen, D.-S. Pan, C.-F. Chiu, J.-X. Su, S. J. Ling and K. S. Kwan, *Inorg. Chem.*, 2000, **39**, 953.
8 T. Y. Dong, C. K. Chang, C. H. Cheng and K. J. Lin, *Organometallics*, 1999, **18**, 1911.
9 N. J. Long, A. J. Martin, R. Vilar, A. J. P. White, D. J. Williams and M. Younus, *Organometallics*, 1999, **18**, 4261.
10 J. A. Mata, E. Peris, I. Asselberghs, R. van Boxel and A. Persoons, *New J. Chem.*, 2001, **25**, 299.
11 J. A. Mata, S. Uriel, R. Llusar and E. Peris, *Organometallics*, 2000, **19**, 3797.
12 J. A. Mata, E. Falomir, R. Llusar and E. Peris, *J. Organomet. Chem.*, 2000, **616**, 80.
13 J. A. Mata, S. Uriel, E. Peris, R. Llusar, S. Houbrechts and A. Persoons, *J. Organomet. Chem.*, 1998, **562**, 197.
14 G. G. A. Balavoine, J. C. Daran, G. Iftime, P. G. Lacroix, E. Manoury, J. A. Delaire, I. Maltey-Fanton, K. Nakatani and S. Di Bella, *Organometallics*, 1999, **18**, 21.
15 M. Bhadbhade, A. Das, J. C. Jeffery, J. A. McCleverty, J. A. N. Badiola and M. D. Ward, *J. Chem. Soc., Dalton Trans.*, 1995, 2769.
16 H. E. Bunting, M. L. H. Green, S. R. Marder, M. E. Thompson, D. Bloor, P. V. Kolinsky and R. J. Jones, *Polyhedron*, 1992, **11**, 1489.
17 E. Peris, J. A. Mata and V. Moliner, *J. Chem. Soc., Dalton Trans.*, 1999, 3893.
18 J. A. Mata, E. V. Peris, R. Llusar, S. Uriel, M. P. Cifuentes, M. G. Humphrey, M. Samoc and B. Luther-Davies, *Eur. J. Inorg. Chem.*, 2001, **8**, 2113.
19 A. Togni, M. Hobi, G. Rihs, G. Rist, A. Albinati, P. Zanello, D. Zech and H. Keller, *Organometallics*, 1994, **13**, 1224.
20 I. S. Lee, Y. K. Chung, J. Mun and C. S. Yoon, *Organometallics*, 1999, **18**, 5080.
21 A. Peruga, J. A. Mata, D. Sainz and E. Peris, *J. Organomet. Chem.*, 2001.
22 S. Sakanishi, D. A. Bardwell, S. Couchman, J. C. Jeffery, J. A. McCleverty and M. D. Ward, *J. Organomet. Chem.*, 1997, **528**, 35.
23 L. K. Yeung, J. E. Kim, Y. K. Chung, P. H. Rieger and D. A. Sweigart, *Organometallics*, 1996, **15**, 3891.
24 I. P. Gubin and V. S. Khabdkarova, *J. Organomet. Chem.*, 1970, **22**, 449.
25 J. Y. Chen, C.-H. Kao, S. J. Lin, C.-C. Tai and K. S. Kwan, *Inorg. Chem.*, 2000, **39**, 189.
26 A.-C. Ribou, J. P. Launay, M. L. Sachtleben, H. Li and C. W. Spangler, *Inorg. Chem.*, 1996, **35**, 3735.
27 G. G. A. Balavoine, G. Doisneau and T. Fillebeenkhan, *J. Organomet. Chem.*, 1991, **412**, 381.
28 SHELXTL 5.1, Bruker AXS, Madison, WI, 1999.
29 C. K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.
30 SAINT, v. 5.0, Bruker Analytical X-Ray Systems, Madison, WI, 1998.
31 G. M. Sheldrick, SADABS, Empirical Absorption Program, University of Göttingen, Germany, 1996.

# Capítulo VI

## DENDRÍMEROS

*Nunca me he encontrado con alguien tan ignorante*
*del que no pudiera aprender algo.*

Johannes Kepler (1571-1630)

VI-5.1 A. Peruga, J. A. Mata, D. Sainz**,** E. Peris. “Facile synthesis of bidimensional ferrocenyl-based branched oligomers by Palladium catalyzed coupling reactions.” *J. Organomet. Chem. 637-639 (***2001***) 191.*

VI-5.2 J. Palomero, J. A. Mata, F. González, E. Peris. “Facile Synthesis of First Generation Ferrocene Dendrimers by a Convergent Approach Using Ditopic Conjugated Dendrons.”*New J. Chem. 3 (***2002***) 291.*

VI-5.3 J. A. Mata, J. Palomero, E. Peris. “Pd-Mediated synthesis of linked conjugated tri- and penta-ferrocenyl complexes.” *J. Organomet. Chem (Enviado* **2002***).*

VI-5.4 E. Peris, J. Loch, J. A. Mata, R.H. Crabtree. “A Pd Complex of a Tridentate Pincer CNC Bis-carbene Ligand as a Robust Homogenous Heck Catalyst.” *Chem. Comm. 2 (***2001***) 201.*

# 1. INTRODUCCIÓN

## 1.1 Introducción.

Los dendrímeros son macromoléculas hiperramificadas, que están construidas a partir de un core central multifuncional, y se expanden hacia la periferia aumentando la densidad de fragmentos repetitivos a medida que aumenta el número de generaciones. Su estructura confiere a este tipo de compuestos unas propiedades físicas y químicas características.[1] El diseño y la síntesis de estas macromoléculas ha experimentando un gran crecimiento en las últimas décadas en diversos campos de la química, como pueden ser la química orgánica, inorgánica, supramolecular y polímeros. Los primeros trabajos de dendrímeros de *Vögtle*, *Denkewalter, Newkome* y *Tomalia*, se centraron en la obtención de dendrímeros puramente orgánicos, y más recientemente inorgánicos, siendo el principal objetivo la síntesis de compuestos con elevados pesos moleculares y con el mayor número de generaciones posible.[2] En los últimos años esta tendencia ha cambiado y las investigaciones se centran más en la modificación de las propiedades de los dendrímeros mediante la introducción de determinados grupos funcionales, tanto en la periferia como en su interior.

Recientemente, la introducción de metales como grupos funcionales ha atraído la atención de muchos grupos de investigación.[3] El interés en el desarrollo de estos materiales se basa en la capacidad de obtener mediante la introducción de metales, materiales altamente ordenados con propiedades magnéticas, electrónicas y ópticas de interés tecnológico.

En concreto, la introducción de fragmentos organometálicos en la periferia o en el core de los dendrímeros, ha supuesto un nuevo camino para el diseño y la síntesis de nuevas macromoléculas organometálicas nanoestructuradas, con nuevas topologías y con la nuclearidad deseada. Este tipo de compuestos se denomina metalodendrímeros. Hay que destacar que la combinación del doble carácter $\sigma$ y $\pi$ del enlace metal-carbono, la flexibilidad de coordinación y la variedad de estados de oxidación de los metales de transición, tienen una influencia muy importante en la reactividad del dendrímero. De este modo, la elección del core y los dendrones adecuados nos va a permitir diseñar macromoléculas organometálicas con el número de centros metálicos y en las posiciones deseadas para que estos dendrímeros posean unas propiedades determinadas, como por ejemplo, catalizadores con un número determinado de centros activos, sensores moleculares y fotocatalizadores.

Actualmente son numerosos los trabajos que describen la obtención y propiedades de metalodendrímeros en los que el fragmento metálico es ferroceno.[4] En algunos puede observarse que existe comunicación electrónica entre los centros metálicos, lo que provoca una gran movilidad electrónica y una serie de propiedades muy interesantes. En otros, sin embargo, no se observa ningún tipo de comunicación electrónica entre los centros metálicos, que son electrónicamente independientes. También hay trabajos en los que el ferroceno no es el único centro metálico del dendrímero, ya que pueden haber fragmentos organometálicos de otros metales que dan lugar a dendrímeros heterometálicos. Gráficamente podemos representar la estructura de los dendrímeros como se muestra en la figura 1.1.

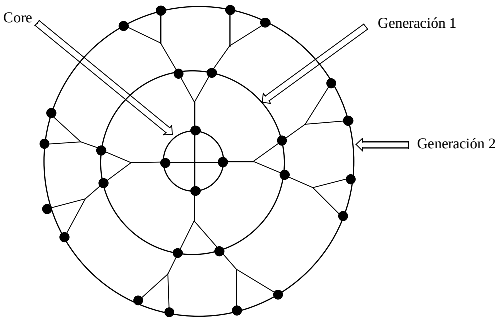


***Figura 1.1***
*Estructura de un dendrímero*

Puede observarse que hay una unidad central de la cual emanan todas las ramas, a esta unidad se la denomina core, y las diferentes ramas se llaman dendrones. Cada dendrón contiene centros de ramificación en los que puede continuar creciendo la molécula. Cada capa construida sobre las viejas ramas se denomina generación, y se numeran desde el centro hacía la periferia con los números 0 (core), 1, 2, 4, etc.

El número de monómeros contenidos en un dendrímero aumenta de forma exponencial a medida que aumenta el número de generaciones, conforme va creciendo el tamaño del dendrímero, los grupos terminales se disponen más cercanos entre sí, aunque eventualmente el crecimiento excesivo de los dendrones puede provocar una congestión superficial, que impide que el dendrímero siga creciendo. La generación a la cual se produce esta congestión se denomina '*starburst limit'* o límite estérico.

## 1.2 Rutas sintéticas.

Existen dos estrategias generales de síntesis de dendrímeros: la estrategia divergente y la estrategia convergente. Cada una de ellas tiene sus ventajas y sus inconvenientes como se discute a continuación.

**Estrategia divergente.** Se trata de la alternativa más general. Los dendrímeros se sintetizan desde el core central hacia la periferia creando una estructura altamente ramificada. El core representa la generación cero, que posee uno o más centros reactivos, sobre los cuales van a unirse covalentemente una nueva generación de monómeros dando lugar a la primera generación del dendrímero, y así sucesivamente. La adición repetitiva de bloques similares (o diferentes) vía protección-desprotección de grupos funcionales, origina nuevas generaciones de dendrímeros. Es importante tener en cuenta que cada serie de reacciones nos conduce a una nueva generación, que debe completarse antes de comenzar la construcción de la generación siguiente, ya que pueden aparecer defectos en la estructura del dendrímero. En la figura 1.2 se esquematiza la formación de un dendrímero a través de la ruta divergente.

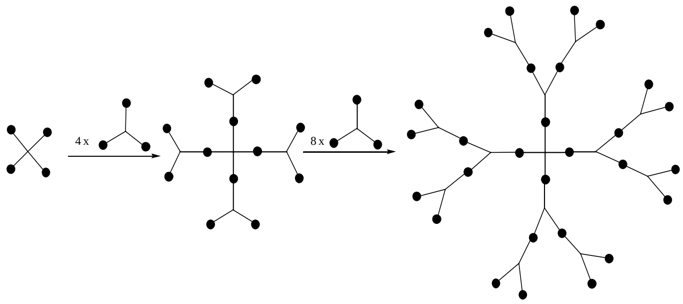


***Figura 1.2***
*Ruta divergente en la formación de dendrímeros.*

La principal ventaja de este método es que permite un crecimiento rápido del dendrímero, ya que al pasar de una generación a otra la masa molecular se ve altamente incrementada. Ahora bien, también presenta inconvenientes, ya que a medida que el dendrímero crece en tamaño, el número de grupos terminales que participa en la reacción es mayor y pueden haber etapas en las que el crecimiento sea incompleto, aumentando el número de defectos en la estructura del dendrímero. De este inconveniente deriva la dificultad de conocer exactamente la extensión en la transformación de una generación a la siguiente, lo que nos puede originar mezclas de generaciones que son prácticamente imposibles de purificar y de caracterizar.

**Estrategia convergente.** Se trata de la alternativa inversa a la estrategia divergente. La síntesis comienza construyendo los dendrones que van a surgir de la periferia del dendrímero. Las unidades monoméricas se van enlazando entre sí con más unidades monoméricas, hasta que finalmente se genera una porción de la estructura de la molécula que contiene un grupo reactivo en un extremo. El paso final de la síntesis consiste en la reacción de un número determinado de porciones estructurales con un core multifuncional. En la figura 1.3 se muestra el esquema de esta ruta sintética.

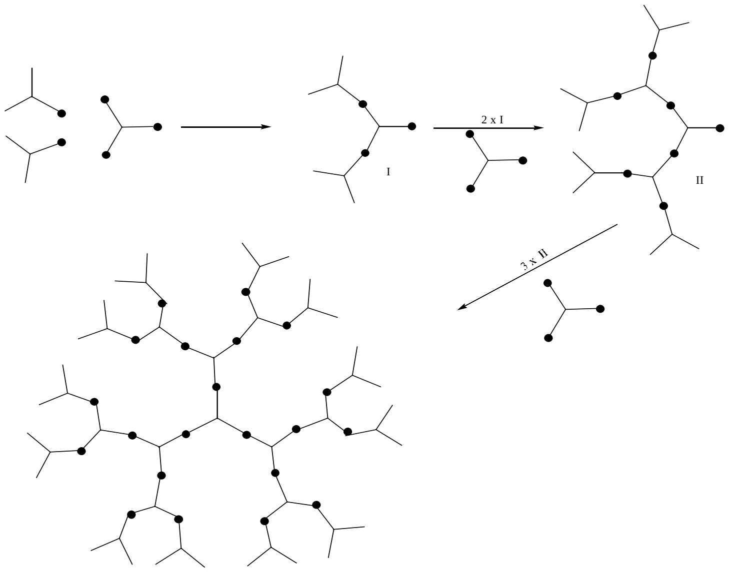


***Figura 1.3***
*Ruta convergente en la formación de dendrímeros.*

La ventaja de este método es que en la formación de las sucesivas generaciones, se ve involucrado un pequeño número de moléculas; ésto contrasta con la estrategia divergente ya que en ésta para pasar de una generación a otra es necesaria la participación de gran número de moléculas. Así pues, puede evitarse la utilización de grandes excesos de reactivos y la aparición de fases impuras, sin necesidad de sacrificar los altos rendimientos.

La principal desventaja de la estrategia convergente es que tras cada ciclo reactivo no se observa un aumento importante en la masa molecular del dendrímero, en contraposición con la estrategia divergente. Además, el número de etapas reactivas en la estrategia convergente no se ve reducido significativamente en comparación con el número de etapas en la estrategia divergente.[5]

Actualmente el método más utilizado en la síntesis de dendrímeros es el divergente, aprovechando su elevado '*starburst limit'* en el que se produce la congestión estérica, ya que los dendrones no reaccionan directamente con el core, siendo las especies monoméricas las que van reaccionando con las diversas generaciones.

## 1.3 Propiedades electroquímicas de metalodendrímeros con ferroceno.

Cuando los centros metálicos se encuentran en la periferia del dendrímero o pertenecen a la estructura del dendrón, se genera un metalodendrímero altamente simétrico en el que los centros metálicos pueden o no interaccionar entre sí, en función de la distancia que los separe y de la naturaleza de la unión entre ellos.

En los últimos años, se ha obtenido gran cantidad de metalodendrímeros que contienen ferroceno en su periferia, las principales aplicaciones de estos compuestos se basan en su uso como sistemas catalíticos multielectrónicos para catálisis homogénea, sensores aniónicos, y modificadores de la superficie de electrodos. En la mayoría de los casos, al estudiar las propiedades electroquímicas de estos compuestos, se observa que las unidades de ferroceno que se encuentran en la periferia del dendrímero son independientes entre sí, y por lo tanto únicamente se detecta una onda redox en los experimentos de voltametría cíclica.

También han sido sintetizados metalodendrímeros en los que los centros metálicos constituyen el core del dendrímero.[6] Una de las características más importantes de estos sistemas, es la presencia de centros redox activos en el core y en la periferia del dendrímero, que son electroquímicamente diferentes.

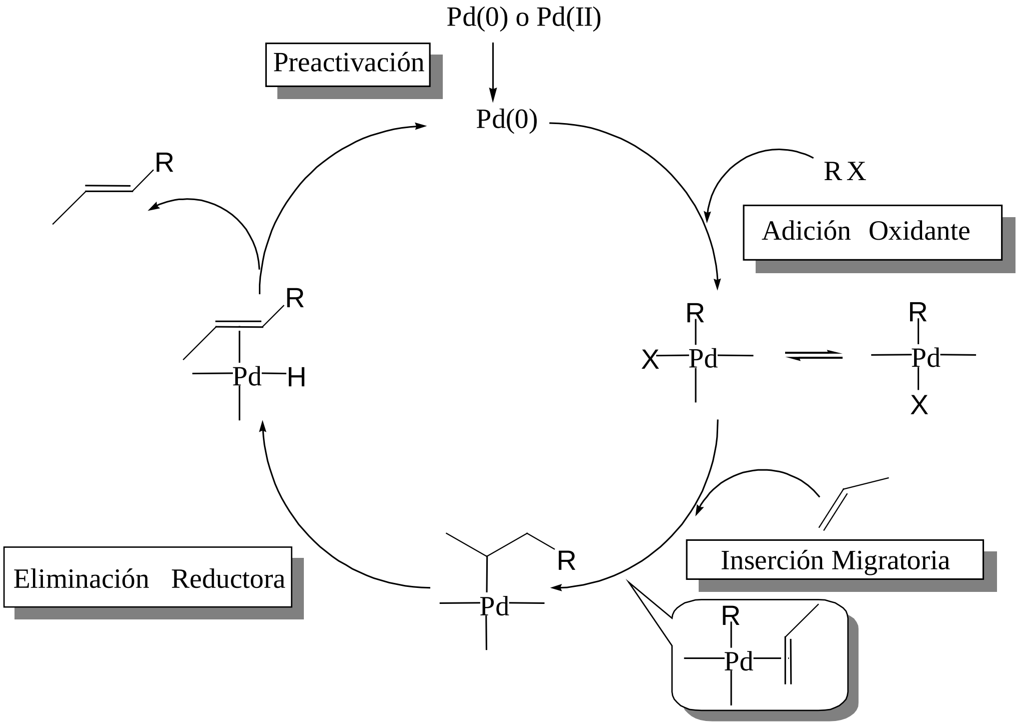
En la búsqueda de nuevos materiales con comunicación electrónica entre las subunidades terminales, en el capítulo IV de esta memoria se describen ferrocenos funcionalizados con grupos nitro, piridina o nitrilo. Aquéllos funcionalizados con grupos piridina y nitrilo permiten que el complejo pueda unirse a diferentes fragmentos metálicos, lo que nos a permitido obtener complejos bimetálicos de gran interés. Algunos de los compuestos obtenidos presentan elevadas respuestas de óptica no lineal, debido a su geometría molecular y a sus propiedades electrónicas. Recientemente, hemos obtenido compuestos biferrocénicos con elevadas constantes de comproporción, cuya coordinación a ciertos fragmentos organometálicos nos ha permitido sintetizar compuestos trimetálicos, como se describe en el capítulo V.

Las propiedades electrónicas de los centros rédox de un metalodendrímero pueden verse modificadas por la presencia de otras especies añadidas a la disolución, lo que abre un camino hacia el reconocimiento molecular, y hacia otras aplicaciones muy interesantes. Concretamente, los metalodendrímeros formados por un core orgánico, y por dendrones que contienen ferroceno pueden utilizarse como sensores aniónicos. La adición de especies aniónicas a una disolución de estos compuestos puede provocar un desplazamiento catódico de la onda, o incluso puede aparecer una nueva onda. Este efecto se reduce a medida que disminuye el número de moléculas de ferroceno en el dendrímero, y se denomina “efecto dendrímero”, que puede definirse como la habilidad que presenta un dendrímero para llevar a cabo el reconocimiento de aniones.

## 1.4 Reacción de *Heck*.

Los metalodendrímeros estudiados en este trabajo se han obtenido a través de reacciones de *Heck*, utilizando como sustratos bromoarilos y olefinas terminales.[7]

El mecanismo propuesto para la reacción de *Heck* consiste en primer lugar en una preactivación del catalizador, obteniéndose la especie de *Pd(0)*. Dentro del ciclo catálico en sí, en primer lugar se produce una adición oxidante por parte del bromoarilo, volviendo a tener un especie de *Pd(II)*. Luego se produce la inserción *syn* de la olefina terminal y se produce una rotación interna que permite la eliminación reductora. Después de la eliminación reductora se obtiene el producto del ciclo catalítico y se regenera el catalizador con ayuda de la base empleada.

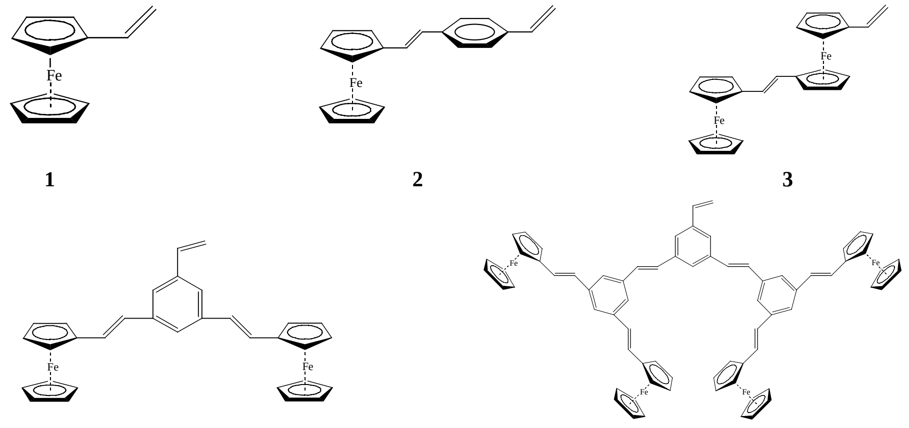


**Esquema 1.1**
*Ciclo catalítico de la reacción de Heck.*

# 2. SINTESIS Y CARACTERIZACIÓN

## 2.1 Síntesis de los precursores y dendrones utilizados.

La formación de enlaces C-C para la síntesis de precursores y dendrones se ha basado en reacciones de acoplamiento de *Wittig*. Este procedimiento nos ha permitido acceder a un gran número de precursores de un modo sencillo a partir de los aldehídos correspondientes y de yoduro de metiltrifenilfosfonio. En la figura 2.1 se muestran los compuestos obtenidos utilizando este procedimiento junta a la numeración utilizada en este apartado.

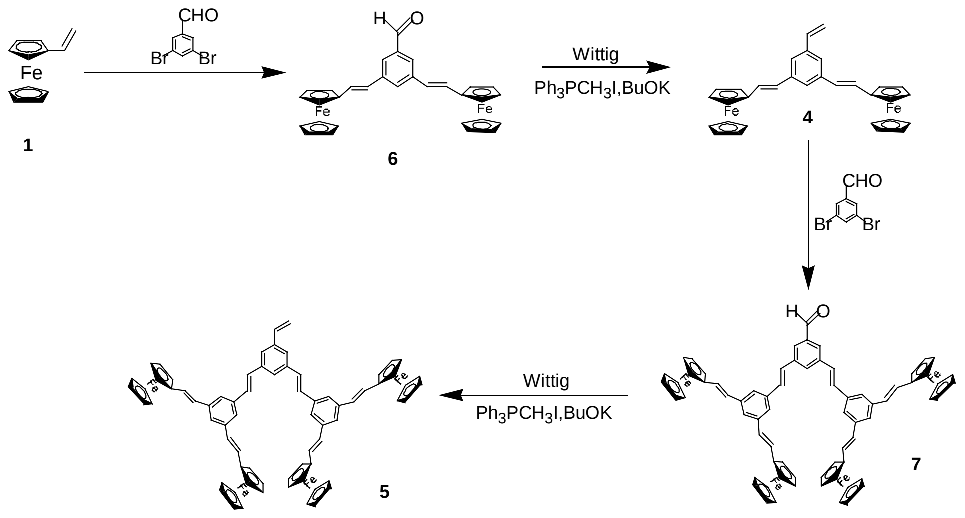


**1** **2** **3**

**4** **5**

***Figura 2.1***
*Dendrones obtenidos a partir de los aldehídos, mediante el acoplamiento de Wittig con el yoduro de metil-trifenilfosfonio.*

En la síntesis de los dendrones de generaciones superiores hemos combinado reacciones de *Wittig* con reacciones de acoplamiento carbono-carbono de *Heck*. En el esquema de reacción 2.1 se muestra la ruta sintética utilizada para la obtención de los dendrones **4** y **5**.



***Esquema 2.1***
*Procedimiento de síntesis de los dendrones.*

La purificación y caracterización de los productos obtenidos se ha realizado siguiendo la misma metodología descrita en los capítulos anteriores. El *RMN* de $^{1}H$ resulta de gran utilidad no solo para la caracterización de los productos finales, sino también para seguir el avance de la reacción. En la figura 2.2 se muestra el espectro *RMN* de $^{1}H$ del dendrón **4** en donde hay que destacar las señales características de los protones terminales de la olefina, que aparecen en la zona del espectro entre 5 y 6 *ppm* (*Hb* y *Hc*), y el protón interior (*Ha*) que aparece solapado con el sistema AB formado por las otras olefinas en torno a 6.7 *ppm*. La importancia de estas señales reside en que van a ser las más afectadas a medida que se vaya produciendo el acoplamiento con el haloarilo correspondiente. De hecho, las señales de los protones terminales van a desaparecer, mientras que la señal del protón *Ha* pasará de ser un doblete de dobletes a un doblete, permitiéndonos, de este modo, realizar un seguimiento espectroscópico del avance de la reacción.

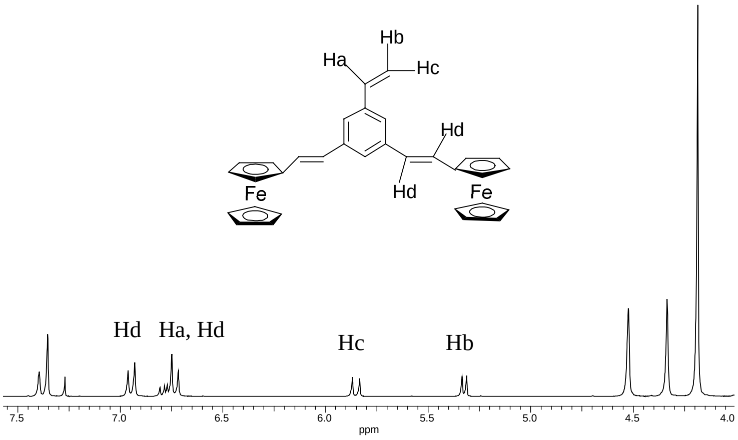


***Figura 2.2***

*Espectro RMN de $^{1}$H del dendrón **4**, asignación de las señales correspondientes al puente etileno y a la olefina terminal. Las señales en torno a 4.5 ppm corresponden a los protones de los ferrocenos.*

En general es difícil obtener monocristales de dendrímeros, debido a la fluxionalidad que presentan. Nuestros dendrímeros poseen una cierta rigidez debido al sistema hiperconjugado, sin embargo, no hemos conseguido obtener ningún monocristal. No obstante, hemos podido determinar la estructura cristalográfica de algunos dendrones, lo que nos permite extrapolar sus características estructurales a los dendrímeros. En concreto, en la figura 2.3 se muestra la estructura cristalográfica del aldehído **6**, que es isoestructural con la del dendrón **4**, también resuelta e incluida en el material suplementario. Ambas estructuras muestran un ordenamiento espacial análogo. Las principales características de esta estructura son la disposición relativa de los dos ferrocenos de forma *syn* y la coplanaridad entre el fenilo central y los ciclopentadienilos de los dos ferrocenos, lo que es una consecuencia de la conjugación a través de todo el sistema.

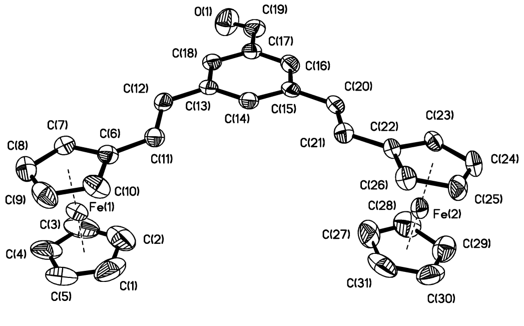
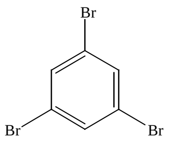


***Figura 2.3***

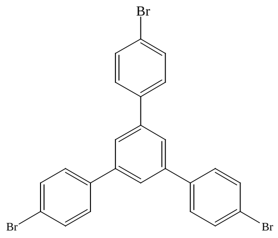
*Estructura cristalográfica del aldehído precursor del dendrón **4**.*

## 2.2 Síntesis de los cores.

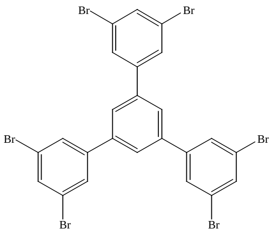
Los cores sintetizados en este trabajo pueden clasificarse en dos grupos: los cores completamente orgánicos y aquellos que poseen ferroceno. El hecho de introducir un ferroceno en el core del dendrímero nos permite preparar macromoléculas con ferrocenos electroquímicamente diferentes. En la figura 2.4 se muestran los distintos cores utilizados.



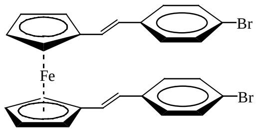
**8**



**9**



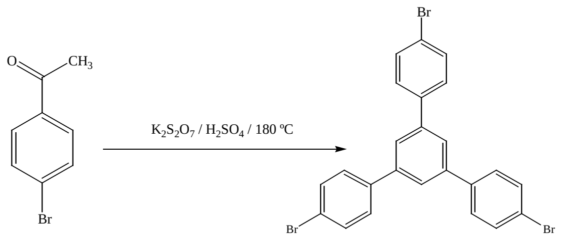
**10**



**11**

***Figura 2.4***
*Cores utilizados en la síntesis de los dendrímeros*

El core más sencillo utilizado ha sido el compuesto comercial 1,3,5-tribromobenzeno (**8**), y aunque los compuestos obtenidos van a ser de bajo peso molecular, nos ha servido como modelo para la obtención de dendrímeros de mayores generaciones cuya síntesis y caracterización es mucho más complicada. El resto de los cores orgánicos se han obtenido por ciclodeshidratación de las cetonas correspondientes en presencia de $K_2S_2O_7$ y $H_2SO_4$ tal y como se muestra en el esquema 2.2.[8]



***Esquema 2.2***
*Procedimiento de síntesis de los cores orgánicos.*

Como core organometálico hemos utilizado el compuesto **11**, que consiste en un ferroceno 1,1'-bisustituido con dos ligandos 4-vinil-bromobenceno. La síntesis y caracterización de este compuesto se ha realizado mediante la metodología de *Wittig* descrita en capítulos anteriores. Una de las características más importantes de este core reside en la disposición *syn* de los sustituyentes, de mayor congestión estérica, tal y como se observa en el diagrama ORTEP de la figura 2.5. Esta disposición nos indica que este rotámero esta estabilizado por el apilamiento $\pi$ del sistema conjugado, y es un efecto a tener en cuenta a la hora de diseñar y explicar algunas de las propiedades de los dendrímeros que de él se derivan.

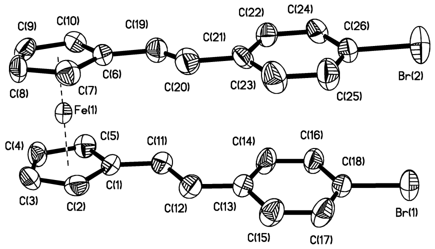


***Figura 2.5***
*Estructura cristalográfica del core organometálico **11**.*

## 2.3 Catalizadores utilizados.

Los catalizadores que hemos utilizado para realizar las reacciones de *Heck* son los representados en la figura 2.6. El catalizador ***i*** es un dímero ciclometalado de paladio (*II*) unido a través de puentes cloruro,[9] mientras que el catalizador ***ii*** es un carbeno con un ligando pinza de Arduengo de paladio (*II*).[10]

Aunque estos catalizadores son muy diferentes desde el punto de vista químico presentan algunas características comunes que los diferencian de los sistemas tradicionales. Estos catalizadores son estables al aire, a la humedad y soportan temperaturas elevadas. Se pueden utilizar a temperaturas de entre 130 *ºC* – 140 *ºC* durante muchas horas sin disminuir la actividad y sin descomposición del catalizador. En concreto el catalizador ***ii*** combina la estabilidad de los ligandos carbeno-heterocíclicos con la elevada estabilización entrópica conferida por los ligandos de tipo pinza. Este catalizador ha demostrado su eficacia a temperaturas superiores a los 180 *ºC* en acoplamientos *C-C* de *Heck*. Ambos catalizadores son mucho más estables que el sistema tradicional $Pd(OAc)_2$/fosfina y por lo tanto resultan más convenientes para nuestras síntesis.

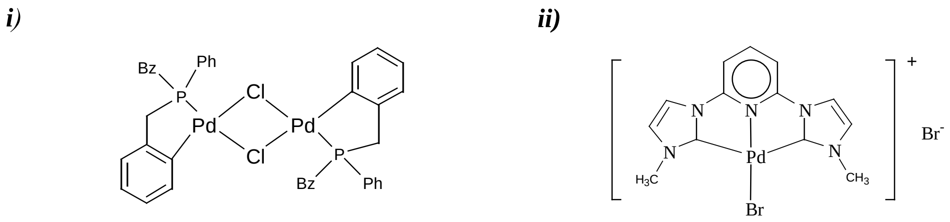
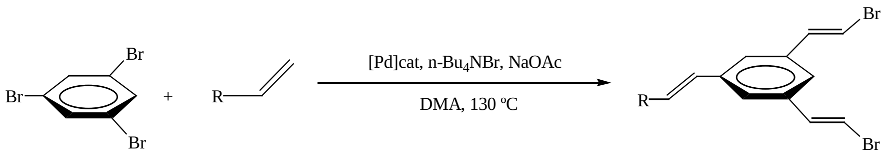


***Figura 2.6***
*Catalizadores utilizados en las reacciones de Heck. i) dímero ciclometalado y ii) carbeno con ligando pinza de Arduengo.*

## 2.4 Síntesis y caracterización de los dendrímeros.

La síntesis de los dendrímeros se ha realizado mediante reacciones de *Heck* a partir de haloarilos y olefinas terminales, utilizando las condiciones generales que se describen en el esquema 2.3. En nuestro caso, los haloarilos siempre han formado parte del core, mientras que las olefinas terminales pertenecen a los dendrones, tal y como se describe en los apartados 2.1 y 2.2 del presente capítulo.

Las condiciones generales de reacción requieren la presencia de una base que facilite la regeneración del catalizador al finalizar el proceso catalítico, en nuestro caso acetato sódico. Los disolventes empleados han sido *DMF* y *DMA* muy utilizados en reacciones de *Heck*. El bromuro de tetrabutilamonio se ha utilizado para facilitar la preactivación del catalizador.



***Esquema 2.3.***
*Esquema general de reacción utilizado en la obtención de los dendrímeros.*

Las reacciones de catálisis se han seguido por espectroscopia *RMN* de $^{1}H$ realizando pequeñas microextracciones del crudo de la reacción. En la figura 2.7 se muestra el avance de la reacción en uno de los casos estudiados, concretamente en la síntesis del compuesto **19**, obtenido a partir del core organometálico **11** y de vinilferroceno **1**. En esta figura puede verse como las señales correspondientes a los protones geminales de la olefina terminal van desapareciendo a medida que transcurre la reacción. Estas señales son muy características, ya que aparecen en una zona del espectro bastante limpia, sólo enmascarada algunas veces por el diclorometano utilizado en la extracción.

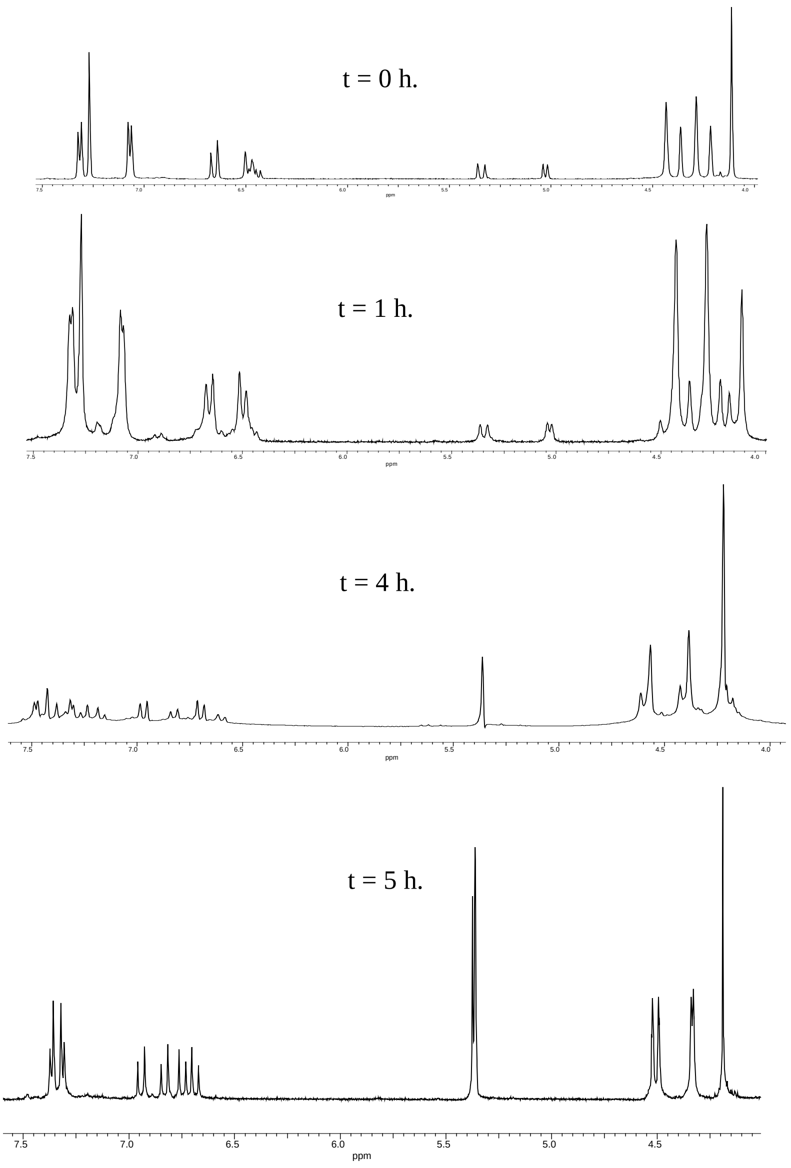
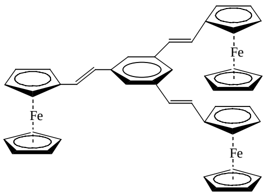


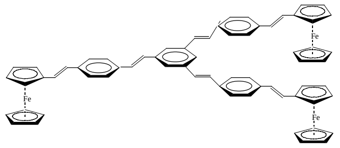
***Figura 2.7***
*Seguimiento espectroscópico de la síntesis del compuesto* ***19***.

La purificación de los dendrímeros se ha realizado por columna de gradientes utilizando gel de sílice como soporte. Este procedimiento nos ha permitido purificar los dendrímeros y separar parte de los sustratos que no han reaccionado. En general se observa en todos los casos que el primer producto en eluir siempre es el dendrón que contiene la olefina terminal.

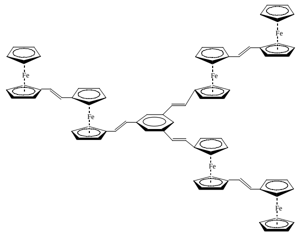
Los dendrímeros obtenidos se muestran en la figura 2.8, con la numeración utilizada. Además de la espectroscopia *RMN* de $^{1}H$, también se emplearon otras técnicas tan útiles en la caracterización de los dendrímeros como es la espectroscopia de masas *FAB* (*FABMS*), en donde se han observado los picos moleculares y las fragmentaciones más características.



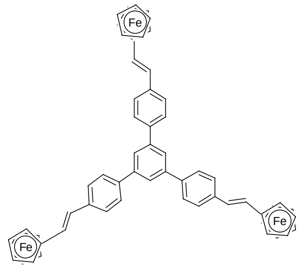
**12**



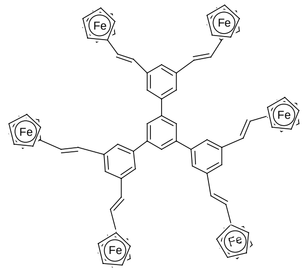
**13**



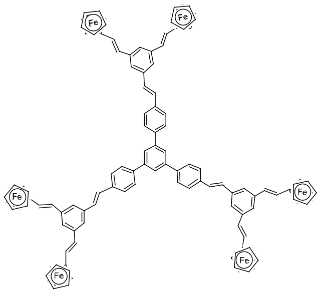
**14**



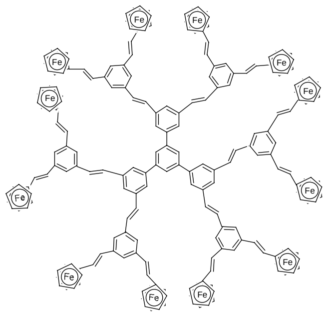
**15**



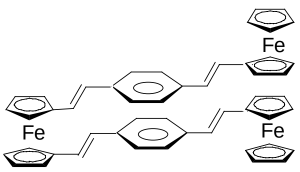
**16**



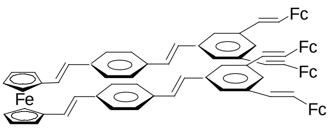
**17**



**18**



**19**



**20**

***Figura 2.8***
*Dendrímeros sintetizados.*

# 3. RESULTADOS Y DISCUSIÓN. PROPIEDADES ELECTROQUÍMICAS

## 3.1 Metalodendrímeros con core orgánico.

La síntesis de los “*minidendrímeros*” **12**, **13** y **14** (Figura 2.8) nos ha servido de introducción en el campo de investigación de los dendrímeros y de modelo para la síntesis y estudio de sistemas más complicados. El compuesto **12** está descrito en la bibliografía, aunque la utilización de la metodogía de *Wittig*[11] conduce a mezclas de los isómeros (*E,Z*), mientras que Köning et al.[12] utilizan el acoplamiento de *Heck* para la obtención del isómero *E* puro, aunque con bajo rendimiento y tras varios días de reacción a 80 ºC. En nuestro caso la utilización de los catalizadores descritos anteriormente, nos ha permitido trabajar a temperaturas superiores, consiguiendo de este modo mejorar el procedimiento de síntesis, obteniendo mayores rendimientos, menor tiempo de reacción y mayor estereoselectividad.

Desde el punto de vista electroquímico los tres “*minidendrímos*” muestran el pico reversible asociado al par ferroceno/ferricinio. En el caso de los compuestos **12** y **13** se observa una única onda asociada a tres electrones correspondiente a cada uno de los ferrocenos. Los tres ferrocenos se oxidan al mismo potencial, lo que indica que es un sistema en el que no existe interacción entre los centros metálicos. En el caso del compuesto **14** se observan dos ondas de igual intensidad, asociadas cada una de ellas a un proceso en el que intervienen tres electrones. En este caso sí que existe una interacción entre los centros metálicos, aunque esta interacción es la que se genera en cada uno de los biferrocenos, es decir no existe interacción electrónica entre las diferentes ramas del minidendrímero.

Todos los compuestos muestran un potencial de semionda inferior al del ferroceno, indicando que se oxidan con más facilidad; una observación atribuible a la estabilización de la carga positiva generada debido a la mayor conjugación del sistema. En la tabla 3.1 se muestran los resultados de los potenciales de semionda de los compuestos **1** - **4** y **12** - **18**.

***Tabla 3.1***

*Resultados electroquímicos en diclorometano/TBAPF$_6$.*

| *Compuesto* | $E_{1/2}$(mV) ($\Delta E_p$(mV))<br>$[Fc\text{-}(Fc)]^+$ | $E_{1/2}$(mV) ($\Delta E_p$(mV))<br>$[Fc\text{-}Fc]^{2+}$ |
|---|---|---|
| **Ferroceno** | 445(100) | --- |
| **1** | 460(120) | --- |
| **2** | 425(100) | --- |
| **3** | 355(150) | 530(120) |
| **4** | 415(90) | --- |
| **12** | 410(110) | --- |
| **13** | 400(160) | --- |
| **14** | 320(100) | 520(120) |
| **15** | 415(100) | --- |
| **16** | 385(125) | --- |
| **17** | 375(65) | --- |
| **18** | 415(60) | --- |

La rotación de los ciclopentadienilos en los derivados 1,1'-bisustituidos hace que estos compuestos puedan comportarse como compuestos “bisagra”. Como hemos visto en el capítulo III, los sistemas 1,1'-bisustituidos presentan estructuras bastante alejadas de la conformación *anti*, respecto a los sustituyentes. En el compuesto **14** no podemos obviar algún efecto similar. De este modo cabe esperar que en la forma neutra la disposición del dendrímero sea bastante cerrada mientras que cuando se oxidan los ferrocenos la estructura tiende a abrirse lo máximo posible para minimizar las repulsiones electrostáticas, tal y como se muestra en la figura 3.1. Este efecto, que se enmarca dentro de lo que hoy se conoce como ‘molecular *switch*’, puede tener importantes repercusiones en el futuro, ya que nos permite modular el tamaño de la molécula con solo modificar las condiciones redox del sistema.

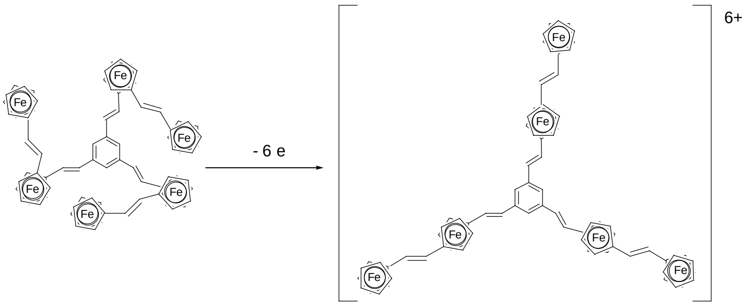
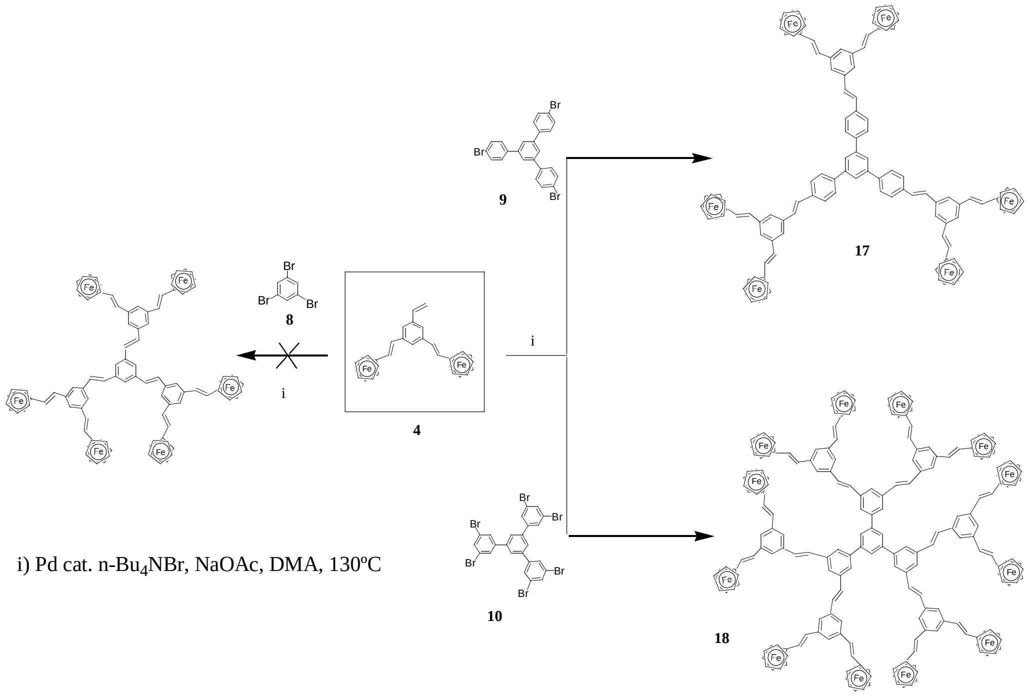


***Figura 3.1***

*Comportamiento tipo “bisagra” del compuesto* ***14***.

Con el fin de obtener dendrímeros de mayor tamaño, nuestra primera estrategia ha sido la modificación de los dendrones sintetizados. En el esquema 3.1 se muestran las diferentes rutas sintéticas investigadas. De este modo hemos obtenido el dendrón **4** que mediante un acoplamiento de *Heck* con el 1,3,5-tribromobezeno nos conduciría a la obtención de un dendrímero con seis ferrocenos en la periferia. La coordinación del dendrón **4** a 1,3,5-tribromobezeno presenta impedimentos estéricos derivados de la coplanaridad impuesta por el sistema conjugado y únicamente hemos observado que se produce una coordinación parcial; este hecho muestra que el límite estérico o ‘starburst’ del dendrímero bidimensional se alcanza ya en la primera generación, como se muestra en el esquema 3.1.



i) Pd cat. n-Bu$_4$NBr, NaOAc, DMA, 130ºC

***Esquema 3.1***
*Estrategia de síntesis de los dendrímeros.*

Este hecho nos impulsó al diseño de cores que disminuyeran la congestión estérica respecto del 1,3,5-tribromobenceno. De este modo se obtuvieron los dendrónes **9** y **10** cuya principal característica es la mayor separación de los bromos y la posibilidad de pérdida de la coplanaridad, por rotación de los enlaces C-C que unen a los fenilos, pero manteniéndose en cada una de las ramas del dendrímero.[8]

En general todos estos dendrímeros presentan un potencial de semionda inferior al del ferroceno, como se muestra en la tabla 3.1. A modo de ejemplo en la figura 3.2 se muestra el voltagrama del metalodendrímero **18**. Esta disminución del $E_{1/2}$ se debe a una gran deslocalización de la densidad electrónica y a la capacidad dadora de cada uno de los ferrocenos. Los compuestos **15**, **16** ,**17** y **18** muestran la presencia de un único proceso redox asociado a la oxidación simultánea de 3, 6, 6 y 12 ferrocenos, respectivamente. Como también se ha observado en otros dendrímeros funcionalizados con ferrocenos, el comportamiento redox de estos compuestos está marcado por cambios importantes en la solubilidad a medida que aumentamos el número de ferrocenos oxidados.[13] Los voltagramas de estos dendrímeros muestran un pico anódico que tiene una forma difusional y un pico catódico puntiagudo y de mucha mayor intensidad, que indica que parte del dendrímero se está depositando en la superficie del electrodo.

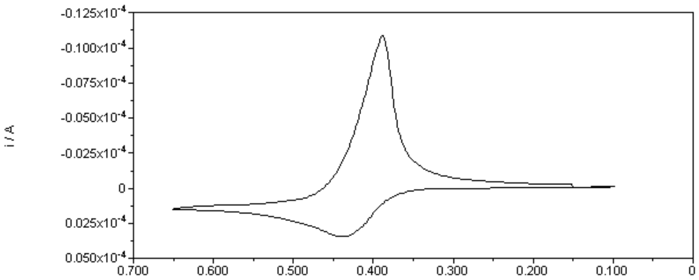


***Figura 3.2***
*Voltagrama del dendrímero* ***18****. La semionda de reducción es mucho más intensa que la correspondiente semionda de oxidación debido a que parte del dendrímero se deposita en la superficie del electródo.*

## 3.2 Metalodendrímeros con core organometálico.

La importancia de estos sistemas reside en las propiedades estructurales y electroquímicas del ferroceno. En primer lugar desde el punto de vista estructural los derivados de ferroceno 1,1'-bisustituidos presentan una gran variedad de rotámeros en disolución, si bien es cierto que en estado sólido la conformación más estable es la *syn*. En segundo lugar las propiedades electroquímicas de los dos tipos de ferrocenos van a gobernar la naturaleza de la estructura del dendrímero.

El estudio de las propiedades de dendrímeros cuyo core esta formado por ferrocenos es un campo muy novedoso e interesante. La importancia de estos sistemas reside en la obtención de nuevos materiales, con propiedades redox poco habituales y por la similitud de estos sistemas con la actividad catalítica de las proteínas. En general se observa que se produce una disminución en la reversibilidad electroquímica de la onda asociada al ferroceno en dendrímeros donde éste está actuando como core, debido a que las ramificaciones producen un impedimento estérico que dificulta la transferencia electrónica entre el centro redox y la superficie del electrodo.[14]

Nuestros sistemas presentan dos tipos de ferrocenos. El ferroceno bisustituido que actúa como core y los ferrocenos monosustituidos que se encuentran en la periferia. Debido a la presencia de dos tipos de ferrocenos los voltagramas muestran dos procesos redox diferentes: El que se produce a potenciales menores es de mayor intensidad (el doble en el compuesto **19** y el cuadruple en el **20**) y corresponde a la oxidación de los ferrocenos terminales y el que aparece a potenciales más elevados, corresponde a la oxidación del ferroceno perteneciente al core.

Los valores de los potenciales de semionda nos indican que los ferrocenos terminales son más fáciles de oxidar que el ferroceno. En cambio, cuando nos fijamos en los ferrocenos que actúan como core, el potencial de semionda es menor en el caso del core (compuesto **11**), pero es mucho mayor que el de ferroceno en el caso de los metalodendrímeros **19** y **20** que presentan valores de $E_{1/2}$ de 725 *mV* y 800 *mV* respectivamente. Este hecho se debe a que en la oxidación de los dos últimos compuestos, la molécula que queremos oxidar ya está cargada positivamente ($2^+$ o $4^+$), lo que dificulta mucho la segunda oxidación del compuesto.

***Tabla 3.2***
*Resultados electroquímicos*

| *Compuesto* | $E_{1/2}$ *(mV) (ΔEp (mV))* *Fe-based (terminal/core)* |
|---|---|
| Ferroceno | 445 (105) |
| 9 | 435 (130) |
| 17 | 425 (100) / 725 (105) |
| 18 | 400 (85) / 800 (80) |

Una de las ventajas de los dendrímeros con dos tipos de ferrocenos, es la posibilidad de obtener compuestos de valencia mixta *Fe(II)* y *Fe(III)*. Con esta finalidad se ha realizado la oxidación del compuesto **11** con hexafluorofosfato de ferricinio, para obtener el compuesto **11-PF$_6$** de *Fe(III)* que se muestra en la figura 3.4. La estructura del compuestos muestra la perdida de la coplanaridad del sistema entre los anillos *Cp* del ferroceno y los fenilos, respecto al compuesto sin oxidar, aunque la disposición de los sustituyentes sigue siendo *syn*. En los compuestos **19** y **20** es difícil pensar que pueda mantenerse esta disposición *syn*, ya que la repulsión electrostática de los dos *Fe(III)* de los ferrocenos periféricos, conduciría a un rotámero que minimizase estas repulsiones.

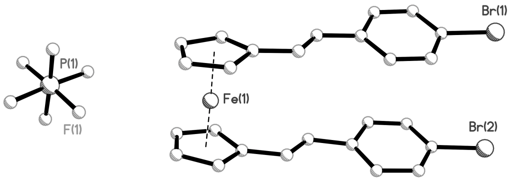


***Figura 3.4***
*Estructura cristalográfica del compuesto **11-PF$_6$**.*

Los últimos experimentos realizados en nuestro laboratorio sobre oxidaciones en este tipo de compuestos, muestran que es posible la oxidación de los ferrocenos de la periferia únicamente o incluso de los tres ferrocenos con la utilización adecuada de un oxidante más o menos fuerte. Nuestros esfuerzos se están centrando ahora en el estudio de los sistemas obtenidos, en su posible oxidación y caracterización estructural.

## 4. REFERENCIAS

(1) Newkome, G. R.; Moorefield, C. N.; Vötgle, F. *Dendritic molecules: Concepts, Synthesis, Perspectives.*; VCH: Weinheim, **1996**.

(2) Zeng, F. W.; Zimmerman, S. C. *Chem. Rev.* **1997**, *97*, 1681.

(3) Cuadrado, I.; Morán, M.; Losada, J.; Casado, C. M.; Pascual, C.; Alonso, B.; Lobete, F. *Advances in Dendritic Macromolecules*; Newkome G.R.: Greenwich, 1996; Vol. 3.

(4) Casado, C. M.; Cuadrado, I.; Moran, M.; Alonso, B.; Garcia, B.; Gonzalez, B.; Losada, J. *Coord. Chem. Rev.* **1999**, *186*, 53.

(5) Stoddart, F. J.; Welton, T. *Polyhedron* **1999**, *18*, 3575.

(6) Venturi, M.; Serroni, S.; Juris, A.; Campagna, S.; Balzani, V. In *Dendrimers*; Springer-Verlag Berlin: Berlin 33, 1998; Vol. 197, p 193-228.

(7) Beletskaya, I. P.; Cheprakov, A. V. *Chem. Rev.* **2000**, *100*, 3009.

(8) Miller, T. M.; Neenan, T. X.; Zayas, R.; Bair, H. E. *J. Am. Chem. Soc.* **1992**, *114*, 1018.

(9) Castella, M.; Calahorra, F.; Sainz, D.; Velasco, D. *Org. Letters* **2001**, *3*, 541.

(10) Peris, E.; Loch, J. A.; Mata, J.; Crabtree, R. H. *Chem. Comm.* **2001**, 201.

(11) Briel, O.; Fehn, A.; Beck, W. *J. Organomet. Chem.* **1999**, *578*, 247.

(12) König, B.; Zieg, H.; Bubenitschek, P.; Jones, P. G. *Chem. Ber.* **1994**, *127*, 1811.

(13) Cuadrado, I.; Moran, M.; Casado, C. M.; Alonso, B.; Lobete, F.; Garcia, B.; Ibisate, M.; Losada, J. *Organomet.* **1996**, *15*, 5278.

(14) Stone, D. L.; Smith, D. K.; McGrail, P. T. *J. Am. Chem. Soc.* **2002**, *124*, 856.

Journal of Organometallic Chemistry 637–639 (2001) 191–197

www.elsevier.com/locate/jorganchem

# Facile synthesis of bidimensional ferrocenyl-based branched oligomers by palladium-catalyzed coupling reactions

Arantxa Peruga [a], José A. Mata [a], Daniel Sainz [b], Eduardo Peris [a,*]

[a] *Departamento de Química Inorgánica y Orgánica, Universitat Jaume I, E-12080 Castellón, Spain*
[b] *Departamento de Química Inorgánica, Universitat de Barcelona, Barcelona, Spain*

Received 21 December 2000; received in revised form 14 February 2001; accepted 17 February 2001

## Abstract

New ferrocenyl-based star-shaped complexes have been obtained by palladium-catalyzed reactions. The synthetic method reported shows an advantage over the traditional Wittig reaction for the synthesis of olefinated compounds, both in yields and in selectivity towards the all-*E* isomers. The electrochemistry of the compounds has been studied. The crystal structure of *E*-ferrocenyl-4-(vinylphenyl)vinylene, one of the starting complexes to the star-shaped compounds, has been determined by means of single crystal X-ray diffraction. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Ferrocenes; Metal-containing dendrimers; Star-shaped complexes; Electrochemistry

## 1. Introduction

Metal-containing long-chained conjugated systems have emerged as an important category of materials. The impetus for developing these materials is based on the premise that conjugated chains containing metals are expected to posses properties significantly different from those of conventional organic conjugated oligomers. Examples of these properties include: electrical conductivity, magnetic behavior, thermal stability, nonlinear optical (NLO) effects, and even superconductivity. Because of the special electronic and chemical properties of ferrocene, many efforts have been directed towards the incorporation of a ferrocene moiety into a polymer [1–19], in order to investigate novel properties such as those mentioned above. Besides, the preparation of ferrocenyl conjugated systems offers the possibility of electronic communication between terminal subunits, this being of particular interest in terms of modulating the electronic properties of the material.

Since the mid-1980s, interest in highly branched molecular architectures has emerged to become an intriguing area of research of scientists worldwide. The term *dendrimer* has been used to define a new type of highly branched regular three-dimensonal monodisperse macromolecules with a branch occurring at each monomer unit. The introduction of metal atoms into the structure of the dendrimer has allowed the generation of a new type of molecules called *metallodendrimers* [1,20–24]. Metallodendrimers are supramolecular species with interesting physical, optical, electrochemical, photochemical, biological and catalytic properties, promoted by the existence of redox centers into the molecule structure. Many approaches have been used to introduce the metal centers into the dendrimer structure, but still we can see that the lack of systematic preparation procedures remains a bottleneck in the study of this new type of materials. The synthesis of low molecular weight organometallic dendrimers (or minidendrimers) [25–28], via single-step procedures, provides a series of precursors to higher molecular weight metallodendrimers with interesting and potentially exciting cross-linked metal-conjugated networks.

We have used ferrocenyl-based conjugated ligands in order to obtain bimetallic and heterometallic push–pull complexes [29–32], and have found interesting redox and spectroscopic properties that have been related to high nonlinear optical responses [29–32]. We now report, based on our previous findings, a facile synthetic

---

* Corresponding author. Tel.: +34-964-728-243; fax: +34-964-728-214.
*E-mail address:* eperis@qio.uji.es (E. Peris).

0022-328X/01/$ - see front matter © 2001 Elsevier Science B.V. All rights reserved.
PII: S0022-328X(01)00903-2

route to bidimensional ferrocenyl-based star-shaped complexes, with interesting physical properties. The compounds that we report in the present work can be considered as the germ for new types of conjugated metallodendrimers.

## 2. Results and discussion

### 2.1. Syntheses of the star-shaped compounds

In our previous works [29–32], we reported the synthetic procedures of several ferrocene-containing phenylene–vinylene oligomers by means of Wittig or Horner–Emmons–Wadsworth (HEW) methods. In fact, these two methods for olefin formation have been widely used in vinylene-containing organometallic species [3,33–38]. Although in most of the cases, these procedures afforded moderate to good yields in the desired products, the low stereoselectivity to the all-*E* isomers and the complicated work-ups, prompted us to look for better procedures in the synthesis of vinylene-containing ferrocenyl derivatives.

Small mononuclear and easily accessible metallocenes bearing reactive functional groups for condensation or cross-coupling reactions allow the application of well-established organic synthetic procedures. Palladium-mediated olefin formation via Heck reaction has been widely used in organic chemistry for the synthesis of *E*-olefins. Some ferrocenyl–olefin-containing complexes have been recently obtained by palladium-catalyzed procedures, showing high stereoselectivities to the *E* configuration and high yields [39–42]. Besides, the continuous search for more active and selective Pd catalysts has widely increased the number of olefins and halides that can be coupled by this procedure.

In the search of such mononuclear ferrocenyl fragments with reactive functional groups, we have considered complexes **1**–**3** as good candidates for Heck coupling reactions to 1,3,5-tribromobenzene, in order to obtain tri-branched conjugated complexes. Compounds **2** and **3** can be readily obtained by olefination of the corresponding aldehydes $CpFe(\eta^5\text{-}C_5H_4)$-*E*-(CH=CH)–4-($C_6H_4CHO$) and $CpFe(\eta^5\text{-}C_5H_4)$-*E*-(CH=CH)–($\eta^5\text{-}C_5H_4$)–Fe–($\eta^5\text{-}C_5H_4$)–CHO by the Wittig procedure using $[Ph_3P^+CH_3]I^-$.

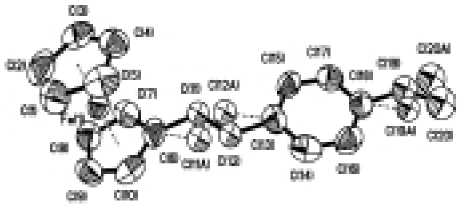
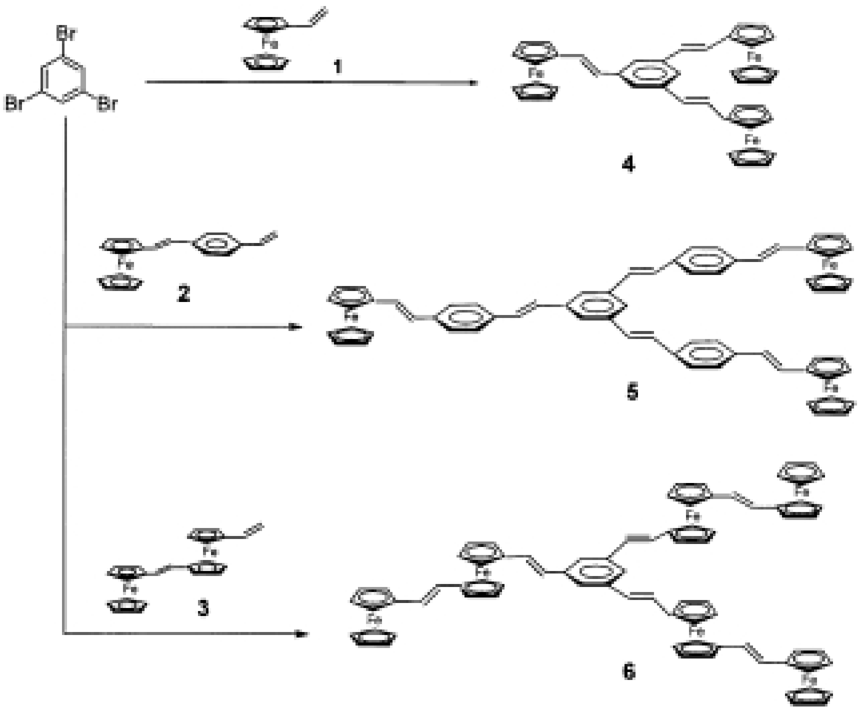


Fig. 1. Molecular structure and atomic labeling scheme for compound **2**, (*E*)-($\eta^5\text{-}C_5H_5$)Fe($\eta^5\text{-}C_5H_4$)–CH=CH–$C_6H_4$–CH=$CH_2$, with 50% anisotropic displacement ellipsoids. Hydrogen atoms are omitted for clarity. Distances: Fe(1)–C(20) (through space) = 10.65 Å, Fe(1)–C(20A) (through space) = 10.61 Å, and Fe(1)–C(20) (through bonds) = 13.34 Å, Fe(1)–C(20A) (through bonds) = 13.39 Å. Planes: Cp–Cp(Subs.) = 0.87(0.33)°, Cp(Subs.)–Ph = 14.86(0.24)°.

The structure of **2** (Fig. 1) was determined by using single crystal X-ray diffraction method. Bond distances and angles are in the usual range. The two Cp rings are almost perfectly parallel. Like other ferrocenyl-containing conjugated molecules, **2** exhibits a rigid-rod and almost perfect planar geometry, with a Fe–C(20) distance of 10.6 Å (through space) and 13.3 Å (through bonds). As shown in Fig. 1, compound **2** presents a disorder in a 7:3 ratio with regard to the orientation of the *trans* olefinic moieties. This kind of disorder has been previously observed in similar molecules [30,43,44].

For the synthesis of the star-shaped complexes by the Heck method, we decided to use the Pd compound *syn*-di(μ-chloro)-bis[*o*-(benzylphenylphosphyno)benzyl] dipalladium(II) as the catalyst, since it has shown to have an extremely good activity in C–Br activation [45]. Compounds **1**–**3** readily react with 1,3,5-tribromobenzene to give compounds **4**–**6**, respectively, in high yields, as shown in Scheme 1. The reaction conditions and the catalytic activity of the system are summarized in Table 1. Despite the fact that TON numbers may not seem to be very high, we have to consider that in all the cases the coupling is made between rather large fragments, and that the addition of each individual ferrocenyl fragment to the arene may cause its deactivation towards the subsequent Heck coupling, as a consequence of its electron-donating character. The three reactions are stereoselective to the all-*E* isomers. Although we were unsuccessful to get single crystals of any of these three compounds, we presume that compounds **4** and **5** must have a fully expanded and coplanar structure, as can be inferred from the structure shown by **2** and other related complexes [26]. In this regard, taking into account the head-to-tail distance of **2**, we estimate an approximate radius for **5** of 14 Å. Compound **4** has already been described in two previous papers [36,42]. In the most recent one [36], **4** was obtained by means of the Wittig reaction procedure, from 1,3,5-tris[(triphenylphosphonio)methyl]benzene tribromide and ferrocenecarboxaldehyde, but the product obtained was a mixture of *E* and *Z* isomers that could not be separated. In the other paper [42], König et al. obtained **4** in the all-*E* form, by means of a Pd-catalyzed reaction similar to ours, but the yields were significantly lower and the reaction time longer (two days), probably due to the fact that thermal stability of the catalyst that we used allowed us to raise the temperature to 130 °C and thus considerably reduce the reaction time to just a few hours.



Scheme 1.

### 2.2. Electrochemical studies

The electrochemical data obtained for the compounds studied are summarized in Table 2. All the complexes display the chemically reversible ferrocene/ferricinium couple in $CH_2Cl_2$. The peak-to-peak separations are, however, significantly greater than the ideal value of 60 mV $s^{-1}$ for a fully reversible one-electron process. This may be due to a combination of uncompensated solution resistance and slightly slow electron-transfer kinetics. The oxidation of the ferrocenyl centers is facilitated compared to that of free ferrocene, meaning that some degree of electron delocalization is occurring along the conjugated systems, this stabilizing the positive charge of the cationic oxidized species. Lower potentials are observed for those systems with higher electron delocalization abilities, **4**–**6.** Compounds **4** and **5** show a reversible three-electron wave, therefore, the three iron centers in each compound are essentially non-interacting. A similar effect is observed for the compound 1,3,5-tris(ferrocenylethynyl)benzene [26], for which the redox potential is considerably higher (490 mV) compared to the related ethenyl compound, **4** (410 mV). This difference may be explained by the more effective conjugation and stabilization of the oxidized species in the ethenyl complex.

Compounds **3** and **6** show two peaks corresponding to two reversible three-electron oxidations. In the cases where the two redox centers are equivalent, the peak difference is a direct measure of the communication between the two redox centers. In our case, the difference in the two potentials is a combination of their communication and their intrinsic inequivalence, so the measure of electronic communication in **3** and **6** must be less than that measured by the potential difference.

As it has been previously reported for similar compounds, the redox behavior of compounds **4**–**6** is marked by changes in solubility with the change in the oxidation state of the ferrocene units [46]. The intensity of the cathodic peak is slightly higher and sharper than the anodic one, which indicates the precipitation onto the electrode surface.

The rotation of the two Cp rings in 1,1′-bis-substituted ferrocenyl complexes makes them behave as 'hinge-like' complexes. 1,1′-Bis-substituted ferrocenyl compounds typically show structures far from the *anti*

¶

Table 1
Reaction conditions and catalytic activity for the synthesis of compounds **4–6** (reactions carried out at 130 °C in DMF)

| Compound | Catalyst (%) | Time (h) | TON | Yield (%) |
|---|---|---|---|---|
| **4** | 3.4 | 9 | 81 | 90 |
| **5** | 12.5 | 8 | 20 | 82 |
| **6** | 16.7 | 8 | 15 | 78 |

Table 2
Cyclic voltammetric data for the ferrocenyl derivatives in $CH_2Cl_2$

| Compound | $E_{1/2}$ (mV) ($\Delta E_p$ (mV)) | |
|---|---|---|
| | [Fe(II)/Fe(III)] | [Fe′(II)/Fe′(III)] |
| Ferrocene | 445 (105) | – |
| **1** | 460 (200) | – |
| **2** | 425 (100) | – |
| Fc–=–Fc–CHO | 405 (90) | 785 (85) |
| **3** | 355 (150) | 530 (120) |
| **4** | 410 (170) | – |
| **5** | 400 (160) | – |
| **6** | 320 (100) | 520 (90) |

conformation with respect to the two ancillary ligands. This fact may be explained by the stabilization produced by an intramolecular π-stacking of the conjugated ancillary ligands (in the examples in which a *syn* conformation is observed), or to a better packing of the compressed geometry in the solid state. In compound **6**, we cannot discard that some of this effect also occurs or, in any case, that the compound is not showing a perfect *anti* configuration in its neutral form. Once it is fully oxidized, it must show a structural rearrangement to a fully expanded form in which the electrostatic repulsion between all the six iron centers is minimized (Scheme 2). This behavior makes **6** a good candidate to a size tunable complex, in which the radius of the star-shaped compound can be electrochemically switched.

## 3. Conclusions

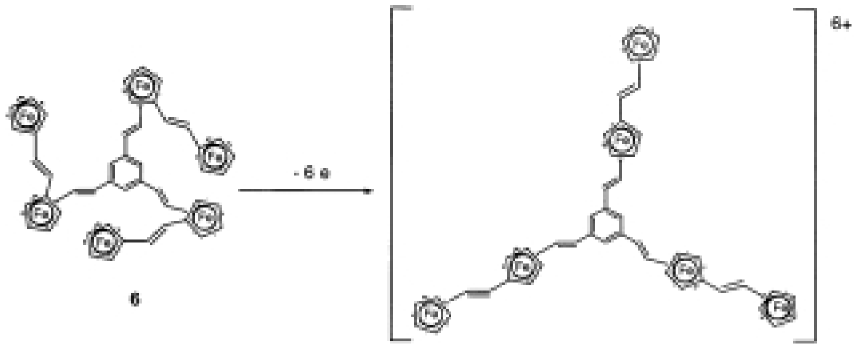
By means of palladium-catalyzed reactions we have designed an effective method for the synthesis of several star-shaped ferrocenyl containing compounds. The method shows clear advantages over the traditional Wittig method for the synthesis of olefinated complexes, both in yields and in selectivities on the all-*E* isomers. The electrochemical studies do not show any significant interactions between the iron centers of different branches of the complexes, although there is an important electronic coupling in those complexes in which the ferrocene units are separated by a vinylene unit.

## 4. Experimental

### 4.1. General details

All reactions were carried out under a $N_2$ atmosphere using standard Schlenk techniques. Solvents for synthesis and electrochemical measurements were dried and deoxygenated by standard methods before use. Chromatographic work was performed on silica gel 60 Å.

NMR spectra were recorded on Varian Innova 300 and 500 MHz spectrometers, using $CDCl_3$ as solvent unless otherwise stated. IR spectra were recorded on a Perkin–Elmer System 2000 FT-IR using NaCl pellets. Electronic absorption spectra were obtained on a UV-1603 Shimadzu spectrophotometer. Elemental analyses were performed on an EA 1108 CHNS-O Carlo Erba instrument. Cyclic voltammetry experiments were performed with an Echochemie pgstat 20 electrochemical



Scheme 2.

analyzer. All measurements were carried out at room temperature (r.t.) with a conventional three-electrode configuration consisting of platinum working and auxiliary electrodes and a Ag | AgCl reference electrode containing aqueous 3 M KCl. The solvent used in all experiments was $CH_2Cl_2$, which was obtained in HPLC grade and used as received. The supporting electrolyte was 0.1 M tetra-*n*-butylammonium hexafluorophosphate, synthesized by reaction of tetra-*n*-butylammonium bromide and $HPF_6$, recrystallized from EtOH and dried under vacuum. $E_{1/2}$ values were determined as $(E_{pa} + E_{pc})/2$, where $E_{pa}$ and $E_{pc}$ are the anodic and cathodic peak potentials, respectively. All reported potentials are not corrected for the junction potential.

### *4.2. Synthesis of (E)-(η⁵-$C_5H_5$)Fe(η⁵-$C_5H_4$)–CH=CH–$C_6H_4$–CH=$CH_2$* (**2**)

To a solution of methyltriphenylphosphonium iodide (1.4 g, 3.4 mmol) in THF (100 ml) was added potassium *tert*-butoxide (500 mg, 4.4 mmol) at 0 °C and the resulting suspension was allowed to warm to r.t. After 30 min, the yellow suspension indicated that the ylide was completely formed. CpFe($\eta^5$-$C_5H_4$)-*E*-(CH=CH)–4-($C_6H_4CHO$) (900 mg, 2.8 mmol), was then added at 0 °C and the solution was stirred for ca. 15 h at r.t. After removing the solvent under reduced pressure, the product was separated with a $CH_2Cl_2$–$H_2O$–$NaHCO_3$ mixture and the $CH_2Cl_2$ extract dried over $MgSO_4$. Purification by column chromatography on silica gel using hexane–$CH_2Cl_2$ (1:1) as eluent afforded pure **2** in 60% yield.

$^1$H-NMR (300 MHz, $CDCl_3$): $\delta$ 7.40 (s, 4H, $C_6H_4$); 6.89 (d, 1H, $^3J_{H-H} = 16.5$ Hz, CH=CH); 6.77–6.66 (m, 2H, CH=CH, CH=$CH_2$); 5.76 (d, 1H, $^3J_{H-H} = 17.7$ Hz, CH=$CH_2$); 5.25 (d, 1H, $^3J_{H-H} = 10.5$ Hz, CH=$CH_2$); 4.48 (s, 2H, $C_5H_4$); 4.31 (s, 2H, $C_5H_4$); 4.15 (s, 5H, $C_5H_5$). $^{13}$C-NMR (500 MHz, $CDCl_3$): $\delta$ 138.2, 136.8 (2Cq, $C_6H_4$); 127.2, 126.6 (4C, $C_6H_4$); 137.3, 127.7, 126.6 (3C, CH=CH, CH=); 113.9 (1C, =$CH_2$); 84.1 (1Cq, $C_5H_4$); 69.9 (5C, $C_5H_5$), 69.8 (2C, $C_5H_4$), 67.6 (2C, $C_5H_4$). Anal. Found: C, 76.68; H, 5.75. Calc. for compound **2**-(*E*), $C_{20}H_{18}Fe$ (MW 314.21 g mol$^{-1}$): C, 76.50; H, 5.77%.

### *4.3. Synthesis of (E)-(η⁵-$C_5H_5$)Fe(η⁵-$C_5H_4$)–CH=CH–(η⁵-$C_5H_4$)Fe(η⁵-$C_5H_4$)–CH=$CH_2$* (**3**)

To a solution of methyltriphenylphosphonium iodide (769 mg, 1.9 mmol) in THF (100 ml) was added potassium *tert*-butoxide (320 mg, 2.8 mmol) at 0 °C and the resulting suspension was allowed to warm to r.t. After 30 min, the yellow suspension indicated that the ylide was completely formed. CpFe($\eta^5$-$C_5H_4$)-*E*-(CH=CH)–($\eta^5$-$C_5H_4$)–Fe–($\eta^5$-$C_5H_4$)–CHO (600 mg, 1.4 mmol) was then added at 0 °C and the solution was stirred for ca. 15 h at r.t. After removing the solvent under reduced pressure, the product was separated with a $CH_2Cl_2$–$H_2O$–$NaHCO_3$ mixture, and the $CH_2Cl_2$ extract dried over $MgSO_4$. Purification by column chromatography on silica gel using hexane–$CH_2Cl_2$ (6:4) as eluent afforded pure **3** in 40% yield.

$^1$H-NMR (500 MHz, $CDCl_3$): $\delta$ 6.47–6.35 (m, 3H, CH=CH, CH=$CH_2$); 5.35 (dd, 1H, $^3J_{H-H} = 17.5$ Hz, $^2J_{H-H} = 1.5$ Hz, CH=$CH_2$); 5.08 (dd, 1H, $^3J_{H-H} = 10.5$ Hz, $^2J = 1.5$ Hz, CH=$CH_2$); 4.38 (t, 2H, $^3J_{H-H} = 1.5$ Hz, $C_5H_4$); 4.28–4.29 (m, 4H, $C_5H_4$); 4.24 (t, 2H, $^3J_{H-H} = 1.5$ Hz, $C_5H_4$); 4.19–4.17 (m, 4H, $C_5H_4$); 4.14 (s, 5H, $C_5H_5$). $^{13}$C-NMR (300 MHz, $CDCl_3$): $\delta$ 135.0, 124.8, 124.1 (3C, CH=CH, CH=); 112.0 (1C, =$CH_2$); 85.7, 85.3, 84.9 (3Cq, $C_5H_4$); 70.7, 70.6, 69.9, 69.3, 68.6, 68.1, 66.9 (17C, $C_5H_4$, $C_5H_5$). Anal. Found: C, 68.41; H, 5.24. Calc. for compound **3**-*E*, $C_{24}H_{22}Fe_2$ (MW 422.13 g mol$^{-1}$): C, 68.30; H, 5.25%.

### *4.4. Synthesis of (E)-{(η⁵-$C_5H_5$)Fe(η⁵-$C_5H_4$)–CH=CH}$_3$–$C_6H_3$* (**4**)

A mixture of 2.3 mmol (500 mg) of CpFe($\eta^5$-$C_5H_4$)–(CH=$CH_2$), 0.6 mmol of (184 mg) 1,3,5-tribromobenzene, 2.6 mmol (210 mg) of sodium acetate anhydrous, 0.2 mmol (50 mg) of tetrabutylammonium bromide, and 0.02 mmol (20 mg) of *syn*-di(μ-chloro)-bis[*o*-(benzylphenylphosphyno)benzyl]dipalladium(II) in DMF (15 ml) was heated at 130 °C for 16 h. After removing the solvent under reduced pressure, the product was separated with a $CH_2Cl_2$–$H_2O$–$NaHCO_3$ mixture, and the $CH_2Cl_2$ extract dried over $MgSO_4$. Purification by column chromatography on silica gel using $CH_2Cl_2$–acetone (10:1) as eluent afforded pure **4** in 90% yield.

### *4.5. Syntheses of (E,E)-{(η⁵-$C_5H_5$)Fe(η⁵-$C_5H_4$)–CH=CH–($C_6H_4$)–CH=CH}$_3$–$C_6H_3$* (**5**) *and (E,E)-{(η⁵-$C_5H_5$)Fe(η⁵-$C_5H_4$)–CH=CH–(η⁵-$C_5H_4$)Fe(η⁵-$C_5H_4$)–CH=CH}$_3$–$C_6H_3$* (**6**)

These compounds were obtained following the general procedure described for compound **4**, using compound **2** (0.6 mmol, 200 mg) or **3** (0.5 mmol, 200 mg) instead of **1**. Purification by column chromatography on silica gel using hexane–$CH_2Cl_2$ (1:1) as eluent afforded pure compounds **5** (yield 82%) and **6** (yield 78%).

$^1$H-NMR for compound **5** (500 MHz, $CDCl_3$): $\delta$ 7.59 (s, 3H, $C_6H_3$); 7.54 (d, 6H, $^3J_{H-H} = 8.0$ Hz, $C_6H_4$); 7.46 (d, 6H, $^3J_{H-H} = 8.0$ Hz, $C_6H_4$); 7.22 (d, 3H, $J_{H-H} = 16.5$ Hz, CH=CH); 7.17 (d, 3H, $J_{H-H} = 16.5$ Hz, CH=CH); 6.95 (d, 3H, $J_{H-H} = 16.0$ Hz, CH=CH); 6.73 (d, 3H, $J_{H-H} = 16.0$ Hz, CH=CH); 4.51 (s, 6H, $C_5H_4$); 4.33 (s, 6H, $C_5H_4$); 4.17 (s, 15H, $C_5H_5$). $^{13}$C-NMR (500 MHz, $CDCl_3$): $\delta$ 138.9, 138.2, 136.5 (9Cq, $C_6H_4$, $C_6H_3$); 129.7,

Table 3
Crystal data and structure refinement parameters for compound **2**

| | |
|---|---|
| Empirical formula | $C_{20}H_{18}Fe$ |
| Formula weight | 314.19 |
| Temperature (K) | 293(2) |
| Wavelength (Å) | 0.71073 |
| Crystal system | Monoclinic |
| Space group | $P2_1$ |
| Unit cell dimensions | |
| $a$ (Å) | 6.2555(5) |
| $b$ (Å) | 7.8041(6) |
| $c$ (Å) | 15.5956(12) |
| $\alpha$ (°) | 90 |
| $\beta$ (°) | 90.590(2) |
| $\gamma$ (°) | 90 |
| $V$ (Å$^3$) | 761.31(10) |
| $Z$ | 2 |
| $D_{calc}$ (g m$^{-3}$) | 1.371 |
| Absorption coeffficient (mm$^{-1}$) | 0.980 |
| $F$(000) | 328 |
| Crystal size (mm) | $0.35 \times 0.16 \times 0.12$ |
| $\theta$ range for data collection (°) | 1.31–30.52 |
| Index ranges | $-8 \leq h \leq 8$, $-8 \leq k \leq 11$, $-22 \leq l \leq 22$ |
| Reflections collected | 6431 |
| Independent reflections | 3679 [$R_{int} = 0.0224$] |
| Data/restraints/parameters | 3679/1/188 |
| Final $R$ indices [$I > 2\sigma(I)$] | $R_1 = 0.0394$, $wR_2 = 0.1034$ |
| $R$ indices (all data) | $R_1 = 0.0712$, $wR_2 = 0.1149$ |
| Goodness-of-fit-on $F^2$ | 0.655 |
| Largest difference peak and hole (e Å$^{-3}$) | 0.421 and −0.194 |

128.5, 127.9, 127.6, 126.8, 126.4, 124.5 (27C, CH=CH, $C_6H_4$, $C_6H_3$); 84.3 (3Cq, $C_5H_5$); 70.0, 69.9, 67.7 (27C, $C_5H_4$, $C_5H_5$). Anal. Found: C, 78.18; H, 5.37. Calc. for compound **5**-($E$,$E$), $C_{66}H_{54}Fe_3$ (MW 1014.70 g mol$^{-1}$): C, 78.10; H, 5.36%.

$^1$H-NMR for compound **6** (300 MHz, $CDCl_3$): $\delta$ 7.32 (s, 3H, $C_6H_3$); 6.90 (d, 3H, $^3J_{H-H} = 16.5$ Hz, CH=CH); 6.70 (d, 3H, $^3J_{H-H} = 16.2$ Hz, CH=CH); 6.41–6.39 (m, 6H, CH=CH); 4.43–4.09 (m, 51H, $C_5H_5$, $C_5H_4$). $^{13}$C-NMR (300 MHz, $CDCl_3$): $\delta$ 138.9, 127.1, 126.9, 124.9, 123.7, 122.5 (18C, CH=CH, $C_6H_3$); 85.8, 84.8, 84.6 (9Cq, $C_5H_4$); 70.9, 70.5, 69.9, 69.4, 68.9, 68.3, 67.0 (51C, $C_5H_4$, $C_5H_5$). Anal. Found: C, 70.12; H, 4.98. Calc. for compound **6**-($E$,$E$), $C_{78}H_{66}Fe_6$ (MW 1338.46 g mol$^{-1}$): C, 70.00; H, 4.97%.

### 4.6. *X-ray diffraction studies*

Single crystals of **2** were grown by slow diffusion of hexane into concentrated $CH_2Cl_2$ solutions and mounted on a glass fiber in a random orientation. Data collection was performed at r.t. on a Siemens Smart CCD diffractometer using graphite monochromated Mo–K$_\alpha$ radiation ($\lambda = 0.71073$ Å) with a nominal crystal to detector distance of 4.0 cm. A hemisphere of data was colleted based on three $\omega$-scan runs (starting $\omega = -28°$) at values $\phi = 0$, 90 and 180° with the detector at $2\theta = 28°$. At each of these runs, frames (606, 435 and 230, respectively) were collected at 0.3° intervals and 40 s per frame. Space group assignment was based on systematic absences, $E$ statistics and successful refinement of the structures. The structure was solved by direct methods with the aid of successive difference Fourier maps and were refined using the SHELXTL 5.1 software package. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned to ideal positions and refined using a riding model. Details of the data collection, cell dimensions and structure refinement are given in Table 3. The diffraction frames were integrated using the SAINT package and corrected for absorption with SADABS [47].

## 5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 154164 for compound **2**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

## Acknowledgements

We thank the DGESIC (PB98-1044 and PB97-0407-C05-04) and BANCAIXA (P1B98-07) for financial support. We would also like to thank the Generalitat Valenciana for a fellowship (J.A.M.).

## References

[1] C.M. Casado, I. Cuadrado, M. Moran, B. Alonso, B. Garcia, B. Gonzalez, J. Losada, Coord. Chem. Rev. 186 (1999) 53.
[2] H. Schottenberger, K. Wurst, M.R. Buchmeiser, J. Organomet. Chem. 584 (1999) 301.
[3] T.J.J. Müller, J. Organomet. Chem. 578 (1999) 95.
[4] N.W. Duffy, B.H. Robinson, J. Simpson, J. Organomet. Chem. 573 (1999) 36.
[5] T.A. Okamura, K. Sakauye, N. Ueyama, A. Nakamura, Inorg. Chem. 37 (1998) 6731.
[6] H.K. Sharma, K.H. Pannell, I. Ledoux, J. Zyss, A. Ceccanti, P. Zanello, Organometallics 19 (2000) 770.
[7] M. Herberhold, O. Nuyken, T. Pohlmann, J. Organomet. Chem. 501 (1995) 13.
[8] K.H. Pannell, V.V. Dementiev, H. Li, F. Cervanteslee, M.T. Nguyen, A.F. Diaz, Organometallics 13 (1994) 3644.
[9] S.L. Ingham, M.S. Khan, J. Lewis, N.J. Long, P.R. Raithby, J. Organomet. Chem. 470 (1994) 153.
[10] M. Moran, C.M. Casado, I. Cuadrado, J. Losada, Organometallics 12 (1993) 4327.

[11] H. Plenio, J. Hermann, J. Leukel, Eur. J. Inorg. Chem. (1998) 2063.

[12] G. Wilbert, S. Traud, R. Zentel, Macromol. Chem. Phys. 198 (1997) 3769.

[13] G.G.A. Balavoine, J.C. Daran, G. Iftime, P.G. Lacroix, E. Manoury, J.A. Delaire, I. Maltey-Fanton, K. Nakatani, S. Di Bella, Organometallics 18 (1999) 21.

[14] M.J. MacLachlan, J. Zheng, A.J. Lough, I. Manners, Organometallics 18 (1999) 1337.

[15] R. Rulkens, A.J. Lough, I. Manners, S.R. Lovelace, C. Grant, W.E. Geiger, J. Am. Chem. Soc. 118 (1996) 12683.

[16] B. Garcia, C.M. Casado, I. Cuadrado, B. Alonso, M. Moran, J. Losada, Organometallics 18 (1999) 2349.

[17] C.M. Casado, I. Cuadrado, W. Moran, B. Alonso, M. Barranco, J. Losada, Appl. Organomet. Chem. 13 (1999) 245.

[18] C.F. Shu, H.M. Shen, J. Mater. Chem. 7 (1997) 47.

[19] M. Grosche, E. Herdtweck, F. Peters, M. Wagner, Organometallics 18 (1999) 4669.

[20] M. Venturi, S. Serroni, A. Juris, S. Campagna, V. Balzani, Dendrimers, vol. 197, Springer-Verlag, Berlin, 1998 (p. 193).

[21] D. Astruc, Acc. Chem. Res. 33 (2000) 287.

[22] I. Cuadrado, M. Moran, C.M. Casado, B. Alonso, J. Losada, Coord. Chem. Rev. 195 (1999) 395.

[23] G.R. Newkome, E.F. He, C.N. Moorefield, Chem. Rev. 99 (1999) 1689.

[24] F.J. Stoddart, T. Welton, Polyhedron 18 (1999) 3575.

[25] T.J.J. Müller, H.J. Lindner, Chem. Ber. 129 (1996) 607.

[26] H. Fink, N.J. Long, A.J. Martin, G. Opromolla, A.J.P. White, D.J. Williams, P. Zanello, Organometallics 16 (1997) 2646.

[27] U.H.F. Bunz, V. Enkelmann, Organometallics 13 (1994) 3823.

[28] M. Altmann, U.H.F. Bunz, Angew. Chem. Int. Ed. Engl. 34 (1995) 569.

[29] J.A. Mata, E. Peris, I. Asselberghs, R. van Boxel, A. Persoons, New J. Chem. 25 (2001) 299.

[30] J.A. Mata, S. Uriel, R. Llusar, E. Peris, Organometallics 19 (2000) 3797.

[31] J.A. Mata, E. Falomir, R. Llusar, E. Peris, J. Organomet. Chem. 616 (2000) 80.

[32] J.A. Mata, S. Uriel, E. Peris, R. Llusar, S. Houbrechts, A. Persoons, J. Organomet. Chem. 562 (1998) 197.

[33] T. Farrell, T. Meyer-Friedrichsen, J. Heck, A.R. Manning, Organometallics 19 (2000) 3410.

[34] K.N. Jayaprakash, P.C. Ray, I. Matsuoka, M.M. Bhadbhade, V.G. Puranik, P.K. Das, H. Nishihara, A. Sarkar, Organometallics 18 (1999) 3851.

[35] P. Molina, A. Tarraga, J.L. Lopez, J.C. Martinez, J. Organomet. Chem. 584 (1999) 147.

[36] O. Briel, A. Fehn, W. Beck, J. Organomet. Chem. 578 (1999) 247.

[37] P. Molina, A. Pastor, M.J. Vilaplana, M.D. Velasco, M.C.R. de Arellano, Organometallics 16 (1997) 5836.

[38] J.G. Rodriguez, M. Gayo, I. Fonseca, J. Organomet. Chem. 534 (1997) 35.

[39] M. Bochmann, J.J. Lu, R.D. Cannon, J. Organomet. Chem. 518 (1996) 97.

[40] D. Naskar, S.K. Das, L. Giribabu, B.G. Maiya, S. Roy, Organometallics 19 (2000) 1464.

[41] K.-Y. Kay, Y.G. Baek, D. Won Han, S. Yong Yeu, Synthesis (1997) 35.

[42] B. König, H. Zieg, P. Bubenitschek, P.G. Jones, Chem. Ber. 127 (1994) 1811.

[43] S. Sakanishi, D.A. Bardwell, S. Couchman, J.C. Jeffery, J.A. McCleverty, M.D. Ward, J. Organomet. Chem. 528 (1997) 35.

[44] A. Hradsky, B. Bildstein, N. Schuler, H. Schottenberg, P. Jaitner, K.-H. Ongania, K. Wurst, J.-P. Launay, Organometallics 16 (1997) 392.

[45] M. Castella, F. López Calahorra, D. Sainz, D. Velasco, Org. Lett. 13 (2001) 541.

[46] I. Cuadrado, M. Moran, C.M. Casado, B. Alonso, F. Lobete, B. Garcia, M. Ibisate, J. Losada, Organometallics 15 (1996) 5278.

[47] M. Sheldrick, SADABS: Empirical Absorption Program, University of Göttingen, Göttingen, Germany, 1996.

# Facile synthesis of first generation ferrocene dendrimers by a convergent approach using ditopic conjugated dendrons†

**Juan Palomero, José A. Mata, Florenci González and Eduardo Peris***

*Dpto. de Química Inorgánica y Orgánica, Universitat Jaume I, E-12080 Castellón, Spain*

***Received (in Strasbourg, France) 3rd September 2001, Accepted 29th October 2001***
***First published as an Advance Article on the web***

A facile synthesis of new conjugated ferrocenyl-based dendrimers is reported and the compounds obtained have been fully characterized. The synthetic method consists of a two-step procedure, which combines olefination by the Wittig procedure and Pd-mediated C–C coupling, leading to high yields of first generation dendrimers with 3, 6 and 12 peripheral ferrocene units. The crystal structure of the conjugated ditopic ferrocenyl dendron and its aldehyde precursor are also described.

Since Vögtle and coworkers obtained the first acyclic branched polyamines,[1] dendrimer chemistry has attracted the interest of a large number of chemists, who mainly pursued new synthetic routes to the production of high molecular weight compounds with as many generations as possible. More recently, the interest in dendrimer chemistry turned to the modification of the properties of dendritic compounds by either the introduction of internal or peripheral functionalities, as this can provide access to materials with potentially useful magnetic, electronic, photo-optical or catalytical properties. The introduction of metal atoms into the structure of the dendrimer has allowed the generation of a new type of molecules called *metallodendrimers*.[2–7] The inclusion of redox centers into the dendrimer widens the structural diversity and the properties of these materials. Many approaches have been used to introduce the metal centers into the dendrimer structure, but still we can see that the lack of systematic preparation procedures constitutes the bottleneck of the study of this new type of materials.

Among all the metallodendrimers obtained until now, those containing ferrocene seem to have attracted special attention,[4,8–31] undoubtedly because ferrocene combines chemical versatility with high thermal and redox stability. In our previous works, we have used ferrocenyl-based conjugated ligands in order to obtain bimetallic and heterometallic push-pull complexes,[32–35] and found interesting redox and spectroscopic properties that have been related to high non linear optical responses.[32,35] In all the cases that we studied, the connecting bridges between the redox centers were oligophenylenevinylene-based, which have recently demonstrated high efficiency electronic communication capabilities.[36] Our results prompted us to design facile methods for the preparation of phenylene-vinylene dendrimers, in order to study the effect of an extended, conjugated coplanar system in the structure of a metallodendrimer. In our first approach, we reported a high efficiency method for the preparation of bidimensional conjugated ferrocenyl minidendrimers.[29] Based on our experience, we now report the convergent synthesis of dendrimers with up to 12 peripheral ferrocenyl units. The electrochemical properties of these new materials, as well as the crystal structures of the conjugated ditopic ferrocenyl dendron and its aldehyde precursor, are also described.

## Results and discussion

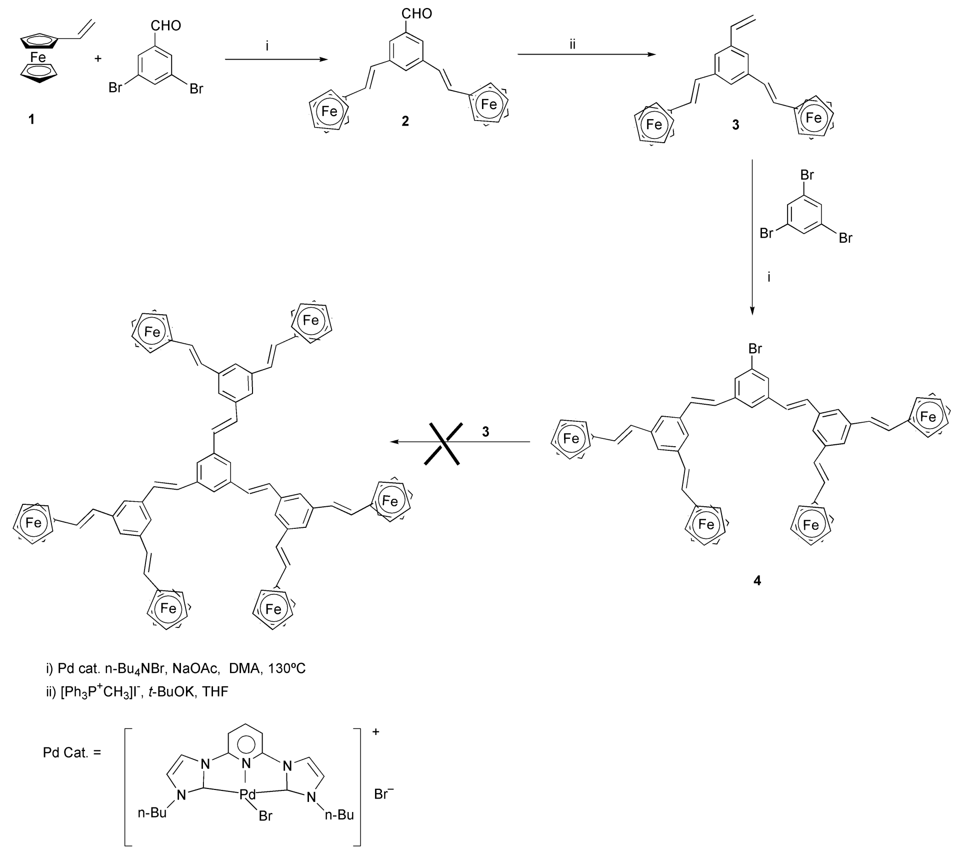
Small mononuclear and easily accessible metallocenes bearing reactive functional groups for condensation or cross-coupling reactions allow the application of well-established organic synthetic procedures. Palladium-mediated olefin formation *via* the Heck reaction has been widely used in organic chemistry for the synthesis of *E*-olefins. Some ferrocenyl olefin-containing complexes have been recently obtained by palladium-catalyzed procedures, showing high stereoselectivities to the *E* configuration and high yields.[37–40] The continuous search for more active and selective Pd catalysts has widely increased the number of olefins and halides that can be coupled by this procedure. Taking this into account, we decided to approach a new synthetic route to ferrocene-containing dendrimers, combining our experience in the Wittig olefination with the well-established Heck C–C coupling.

Our first objective was to obtain a dendron having two identical ferrocene units, connected by a conjugated bridge. We envisaged that **3** (Scheme 1) might allow electronic communication between the ferrocene units by virtue of the conjugated bridge. The preparation of **3** implies commercial and easily accessible compounds such as vinylferrocene (**1**) and 3,5-dibromobenzaldehyde. The palladium-mediated coupling of these two compounds yields the bisferrocene aldehyde **2** in high yield (72%) in just 12 h at 130 °C in DMA. Due to the high temperature used, we decided to utilize the thermally stable imidazolyl pincer Pd catalyst shown in Scheme 1, related to the one recently described by us with methyl instead of *n*-butyl terminal groups.[41] This catalyst showed a higher activity than its methyl analog. The preparation and catalytical properties of this new catalyst will be published in detail elsewhere. Olefination of **2** by the Wittig procedure using triphenylmethylphosphonium iodide afforded the bisferrocenyl dendron **3** in high yield (65%). Both compounds, **2** and **3**, were fully characterized by conventional spectroscopic methods and gave satisfactory elemental analysis. Both reactions yielded stereospecifically the *E* isomers, showing no significant amounts of side-products, so the purification procedures were rather simple.

Compounds **2** and **3** gave single crystals suitable for X-ray diffraction, so their crystal structures could be determined. Fig. 1 shows the ORTEP diagrams of **3** in two different perspectives. Both compounds crystallize in the centrosymmetric space group $P2_1/c$ and the molecular structures display a very

---

† Electronic supplementary information (ESI) available: molecular structure of **2**. See http://www.rsc.org/suppdata/nj/b1/b108142j/



i) Pd cat. n-Bu$_4$NBr, NaOAc, DMA, 130ºC
ii) [Ph$_3$P$^+$CH$_3$]I$^-$, *t*-BuOK, THF

**Scheme 1**

similar atomic arrangement (the molecular structure of **2** can be found in the electronic suplementary information). The most remarkable feature of these two structures is that they show an almost coplanar structure between the Cp, vinylene and phenylene units, as can be seen in Fig. 1(b), confirming that the conjugation extends along the whole structure. As seen for most neutral ferrocenyl complexes, the Cp rings adopt a quasi-eclipsed conformation. Table 1 shows the most significant bond distances, angles and planes of **2** and **3**.

In an extension of our previously reported work on the preparation of ferrocenyl minidendrimers using 1,3,5-tribromobenzene,[29] we tried to use this compound as a core for our newly prepared dendron **3**. The reaction of a three-fold excess of **3** with 1,3,5-tribromobenzene, yielded unambiguously the tetraferrocenyl complex **4** (Scheme 1), whose structure was confirmed by means of FABMS. Higher excesses of **3** in the reaction procedure, higher amounts of catalyst or the use of higher temperatures did not afford the three-fold coupled dendrimer. We believe that the reason for this failure is the coplanarity imposed by the extended conjugated system; this clearly shows that the steric or 'starburst' limit of this two-dimensional dendrimer is already achieved in the first generation.

Since we believed that steric reasons were the only ones to blame for the failure in the synthesis of our hexaferrocenyl dendrimer, we decided to use compounds **5-Br$_3$** and **6-Br$_6$** as new cores. With these two compounds the steric strain is largely released because (*i*) the bromine atoms have a larger through-space separation than in 1,3,5-tribromobenzene and (*ii*) the less effective conjugation between the phenylene connections affords a lower C–C rotation barrier that can break the coplanarity of the whole molecule, while the coplanarity of each individual branch should be maintained. Compound **6-Br$_6$** was obtained by Miller *et al.*[42] and was satisfactorily used in the preparation of a series of monodisperse organic dendrimers. By a similar method to that leading to **6-Br$_6$**, we obtained **5-Br$_3$** in very high yield (*ca.* 80%) starting from commercially available 4-bromoacetophenone.

In order to test the C–C Heck coupling on these two new compounds, we started by coupling vinylferrocene, **1**, to **5-Br$_3$** and **6-Br$_6$**. These reactions afforded **7-Fc$_3$** and **8-Fc$_6$** in high yields (Scheme 2). The reactions could be followed *in situ* by extracting small amounts of the reaction mixture and making micro-extractions in CH$_2$Cl$_2$–H$_2$O. The solvent of the organic fraction was removed and the crude solid redissolved in CDCl$_3$ and introduced in an NMR tube. By this simple method we could monitor the reaction progress by $^1$H NMR, by simply checking the disappearance of the signals due to the terminal olefin of complex **1**. After 14 h the reactions were completed according to the complete consumption of **1**. The compounds so obtained, **7-Fc$_3$** and **8-Fc$_6$**, were fully characterized by

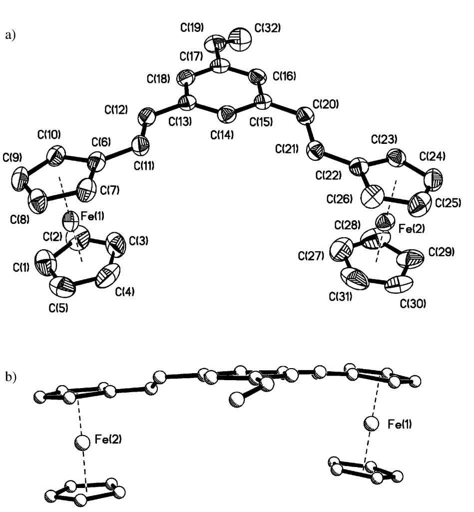


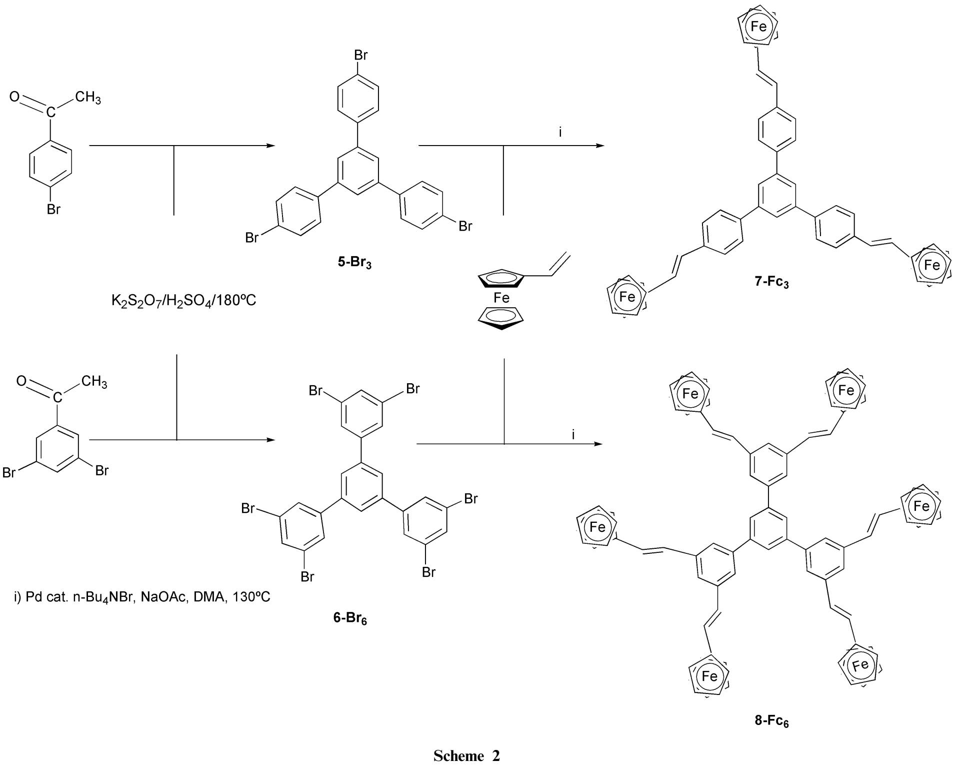
**Fig. 1** (a) Ortep diagram of compound **3** showing the atom numbering scheme. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. (b) Molecular diagram showing the coplanarity of compound **3**.

**Table 1** Selected bond distances (Å), angles and planes (deg.) for compounds **2** and **3**

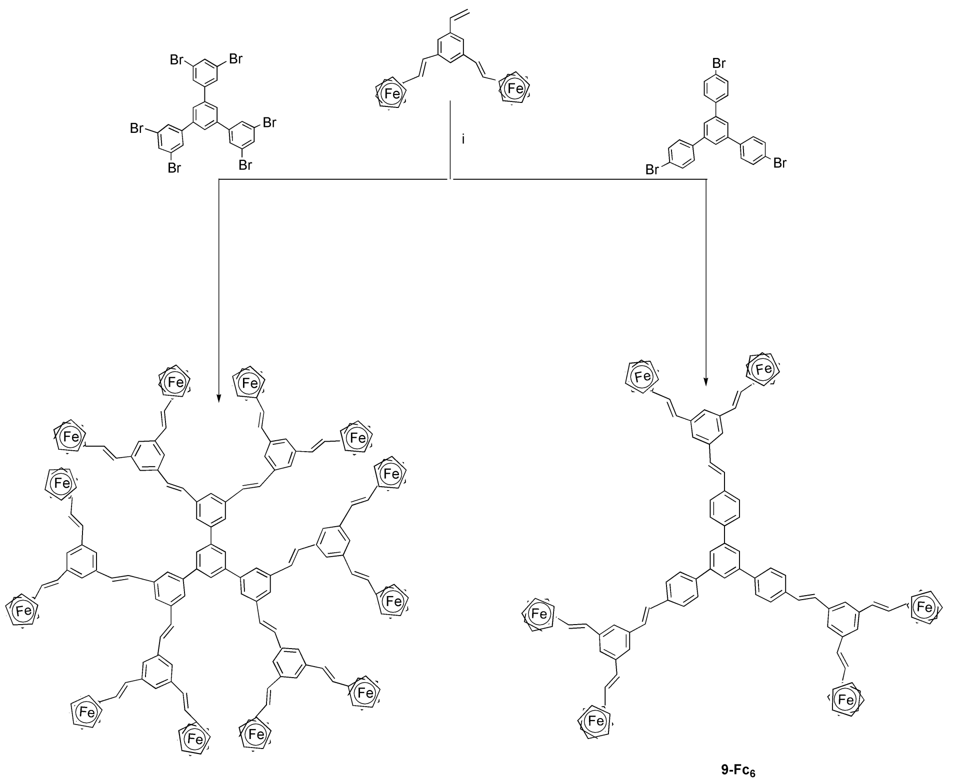
| | **2** | **3** |
|---|---|---|
| Fe(1)–Cp (subst) | 1.643 | 1.649 |
| Fe(1)–Cp | 1.652 | 1.644 |
| Fe(2)–Cp (subst) | 1.653 | 1.646 |
| Fe(2)–Cp | 1.649 | 1.651 |
| C(19)–O(1) | 1.188(5) | — |
| C(19)–C(32) | — | 1.291(4) |
| Fe(1)···Fe(2) | 9.82 | 9.72 |
| C(6)–C(11)–C(12)–C(13) | −178.9(4) | −176.8(3) |
| C(15)–C(20)–C(21)–C(22) | 178.5(4) | −178.8(3) |
| Planes | | |
| Ph–[C(6),C(7),C(8),C(9),C(10)] | 4.0 | 10.2 |
| Ph–[C(22),C(23),C(24),C(25),C(26)] | 7.4 | 4.2 |

conventional methods. The $^1$H NMR spectra showed the typical pattern of monosubstituted ferrocenyl compounds, this confirming the equivalence of all the ferrocene units.

The reaction of **5-Br$_3$** and **6-Br$_6$** with **3** afforded the first generation dendrimers **9-Fc$_6$** and **10-Fc$_{12}$**, respectively (Scheme 3). As mentioned above, the reactions could be easily followed by $^1$H NMR by the same method described, monitoring the disappearance of the signals due to the terminal olefin of **3**. The products were purified by column chromatography and no significant side-products were isolated. Although the $^1$H and $^{13}$C NMR spectra of **9-Fc$_6$** and **10-Fc$_{12}$** were very clean, the assignment of the signals could not be easily made due to the overlapping of the peaks corresponding



**Scheme 2**



10-Fc$_{12}$

9-Fc$_6$

i) Pd cat. n-Bu$_4$NBr, NaOAc, DMA, 130ºC

**Scheme 3**

to the olefin and aromatic hydrogens. However, the $^3J_{H\text{-}H}$ couplings of the olefin hydrogen atoms were in all cases very close to 16 Hz, this unambiguously confirming the all-*E* configuration of the complexes. The $^1$H NMR spectra also showed the pattern of monosubstituted ferrocenyl compounds, this confirming the equivalence of the peripheral ferrocene units.

The structures of the dendrimers **9-Fc$_6$** and **10-Fc$_{12}$** were corroborated by fast atom bombardment (FAB) mass spectrometry, which showed the molecular ions at $m/z$ 1871 and 3440, respectively.

The electrochemical data obtained for the compounds studied are summarized in Table 2. All the complexes display the chemically reversible ferrocene/ferricinium couple in $CH_2Cl_2$.

The presence of the aldehyde in compound **2** leads to a higher redox potential (445 mV) compared to that of the vinyl-functionalized dendron **3** (415 mV), due to the electron-accepting capabilities of the aldehyde.

In general, all the dendrimer-type complexes show lower potentials than that shown for ferrocene (445 mV), probably due to their higher electron delocalization. In addition, a cooperative electron-donating behavior of each ferrocenyl unit may also be contributing to this redox potential lowering. Compounds **7-Fc$_3$**, **8-Fc$_6$**, **9-Fc$_6$** and **10-Fc$_{12}$** show a unique reversible electron wave, this corresponding to the simultaneous oxidation of 3, 6, 6 and 12 ferrocene units, respectively. This result indicates that the ferrocenyl centers in each compound are essentially non-interacting. However, this result may also be interpreted as a consequence of fast heterogeneous electron-transfer kinetics. It has been suggested that one of the reasons for this observation may be due to the fast rotation of

**Table 2** Cyclic voltammetric data[a]

| Compound | $E_{1/2}$/mV ($\Delta E_p$/mV) Fe-based |
|---|---|
| Ferrocene | 445 (105) |
| **1** | 460 (100) |
| **2** | 445 (150) |
| **3** | 415 (90) |
| **7-Fc$_3$** | 415 (100) |
| **8-Fc$_6$** | 385 (125) |
| **9-Fc$_6$** | 375 (65) |
| **10-Fc$_{12}$** | 415 (57) |

[a] All compounds were studied in $CH_2Cl_2$ between 0 and 1.25 V.

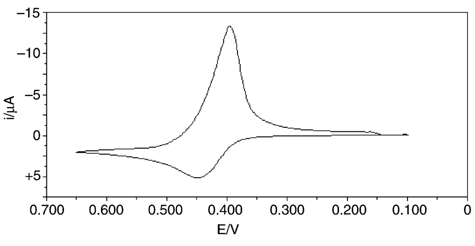


**Fig. 2** Cyclic voltammogram of compound **10-Fc$_{12}$**.

the dendrimer compared to the electrochemical timescale, so that all redox centers come close to the electrode within this timescale.[13] A similar effect was observed for the compound 1,3,5-tris(ferrocenylethenyl)benzene.[29]

As it has been previously reported for other ferrocenyl dendrimers,[43] the redox behavior of the compounds **7-Fc$_3$**, **8-Fc$_6$**, **9-Fc$_6$** and **10-Fc$_{12}$** is marked by changes in solubility with the change in the oxidation state of the ferrocene units. Whereas the anodic wave has a typical diffusional shape, a sharp cathodic stripping peak is observed (Fig. 2), which indicates the precipitation of the dendrimers onto the electrode upon oxidation.

## Conclusions

We have obtained a bisferrocenyl ethenyl-terminated compound, which has been satisfactorily used as a dendron in the preparation of a series of ferrocenyl-based dendrimers, which, according to the crystal structure of the conjugated dendron, must show three planar branches, the coplanarity only being disrupted at the central core. The new bromo-functionalized tetraphenyl cores have shown to be very convenient starting materials. We have established that Pd-mediated C–C double bond formation is an effective method for the synthesis of conjugated ferrocenyl dendrimers. The extension of this synthetic methodology to the construction of higher generation dendrimers is currently in progress in our laboratory.

## Experimental

### General details

NMR spectra were recorded on Varian Innova 300 MHz and 500 MHz spectrometers, using $CDCl_3$ as solvent unless otherwise stated. IR spectra were recorded on a Perkin Elmer System 2000 FT-IR using NaCl pellets. Electronic absorption spectra were obtained on a Shimazdzu UV-1603 spectrophotometer. Cyclic voltammetry experiments were performed with an Echochemie pgstat 20 electrochemical analyzer. All measurements were carried out at room temperature with a conventional three-electrode configuration consisting of platinum working and auxiliary electrodes and an Ag/AgCl reference electrode containing aqueous 3 M KCl. The supporting electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate. All potential data reported are uncorrected for the junction potential. Mass spectra were run in the fast atom bombardment mode (FABMS, *m*-nitrobenzyl alcohol matrix) on a VG AutoSpec mass spectrometer. Vinylferrocene, **1**, was used as purchased (Aldrich) or synthesized by Wittig olefination of the ferrocenecarboxaldehyde, using $[Ph_3P^+CH_3]I^-$ and *t*-BuOK. Compound **6-Br$_6$** was obtained according to literature methods.[42] *N*,*N*-Dimethylacetamide (DMA) was anhydrous, 99.8% pure.

### Synthesis of cores

**Compound 2.** A mixture (440 mg, 2.1 mmol) of $CpFe(\eta^5$-$C_5H_4)$–$(CH{=}CH_2)$, **1**, 3, 5-dibromobenzaldehyde (264 mg, 1.0 mmol), anhydrous sodium acetate (213 mg, 2.6 mmol), tetrabutylammonium bromide (20 mg, 0.06 mmol) and palladium pincer catalyst (20 mg, 0.03 mmol) in DMA (15 mL) was heated at 130 °C for 12 h. After removing the solvent under reduced pressure, the product was extracted with a $CH_2Cl_2$–$H_2O$–$NaHCO_3$ mixture and the organic phase was dried over $MgSO_4$. Purification was carried out by column chromatography on silica gel, washing with hexane to remove unreacted vinylferrocene **1** and using hexane–$CH_2Cl_2$ (1 : 1) as eluent to afford pure compound **2**. Yield: 72%. $^1$H-NMR (300 MHz, $CDCl_3$): $\delta$ 10.07 (s, 1H, CHO); 7.82 (s, 2H, $C_6H_3$); 7.67 (s, 1H, $C_6H_3$); 7.05 (d, 2H, $^3J_{H\text{-}H} = 16.2$ Hz, CH=CH); 6.75 (d, 2H, $^3J_{H\text{-}H} = 16.2$, CH=CH); 4.52 (s, 4H, $C_5H_4$); 4.35 (s, 4H, $C_5H_4$); 4.18 (s, 10H, $C_5H_5$). $^{13}$C-NMR (500 MHz, $CDCl_3$): $\delta$ 67.8, 70.0 (18C, $C_5H_4$ and $C_5H_5$); 83.3 (2Cq, $C_5H_4$); 125.1, 125.4, 129.7, 129.9 (7C, CH=CH and $C_6H_4$); 137.9, 139.9 (3Cq, $C_6H_4$); 193.2 (1C, CHO). Anal. calcd for compound **2**, $C_{31}H_{26}Fe_2O$, $M_w = 526.24$: C, 70.8; H, 4.98; found: C, 70.9; H, 4.99. FABMS: *m*/*z* 526 ($M^+$).

**Compound 3.** To an ice-cold solution of $[Ph_3P^+CH_3]I^-$ (324 mg, 0.8 mmol) in THF (50 ml), potassium *tert*-butoxide (112 mg, 1.0 mmol) was added and the resulting solution stirred for 30 min. at 0 °C and 30 min. at room temperature. The aldehyde **2** (421 mg, 0.8 mmol) was added at 0 °C and the resulting solution stirred overnight at room temperature. After removing the solvent under reduced pressure, the product was extracted with $CH_2Cl_2$–$H_2O$–$NaHCO_3$ and dried over $MgSO_4$. The title compound was purified by column chromatography on silica gel using hexane–$CH_2Cl_2$ (7 : 3) as eluent. Recrystallization from $CH_2Cl_2$–hexane afforded pure compound **3**. Yield: 65%. $^1$H-NMR (500 MHz, $CDCl_3$): $\delta$ 7.40 (s, 1H, $C_6H_3$); 7.36 (s, 2H, $C_6H_3$); 6.48 (d, 2H, $^3J_{H\text{-}H} = 16.0$ Hz, CH=CH); 6.76–6.71 (m, 3H, CH=CH, $CH{=}CH_2$); 5.85 (d, 1H, $^3J_{H\text{-}H} = 17.5$ Hz, $CH{=}CH_2$); 5.32 (d, 1H, $^3J_{H\text{-}H} = 11.0$ Hz, $CH{=}CH_2$); 4.53 (s, 4H, $C_5H_4$); 4.36 (s, 4H, $C_5H_4$); 4.19 (s, 10H, $C_5H_5$). $^{13}$C-NMR (500 MHz, $CDCl_3$): $\delta$ 67.7, 69.8, 70.0 (18C, $C_5H_4$ and $C_5H_5$); 84.2 (2Cq, $C_5H_4$); 114.8, 122.9, 123.5, 126.6, 128.0, 139.0 (9C, CH=CH, $CH{=}CH_2$ and $C_6H_4$); 137.5, 138.9 (3Cq, $C_6H_4$). Anal. calcd for compound **3**, $C_{32}H_{28}Fe_2$, $M_w = 524.27$: C, 73.3; H, 5.38; found: C, 73.5; H, 5.39. FABMS: *m*/*z* 524 ($M^+$).

**Compound 5-Br$_3$.** 4-Bromoacetophenone (20 g, 100.5 mmol), 1 mL of $H_2SO_4$(c) and $K_2S_2O_7$ (30 g, 118 mmol) were heated at 180 °C for 14 h. The resulting crude solid was cooled to room temperature and refluxed in 100 mL of EtOH for 1 h. The solution was filtered and the resulting solid was refluxed in 100 mL of $H_2O$, yielding a pale-yellow solid that was filtered, dried under vacuum and recrystallized in $CHCl_3$. Yield 80%. $^1$H-NMR (500 MHz, $CDCl_3$): $\delta$ 7.72 (s, 3H, $C_6H_3$); 7.63 (d, 6H, $^3J_{H\text{-}H} = 8.5$ Hz, $C_6H_4$); 7.55 (d, 6H, $^3J_{H\text{-}H} = 8.5$ Hz, $C_6H_4$). $^{13}$C-NMR (300 MHz, $CDCl_3$): $\delta$ 122.4 (3Cq, $C_6H_4$–Br); 125.2 (3C, $C_6H_3$); 129.1 (6C, $C_6H_3$), 132.3 (3Cq, $C_6H_4$); 139.9 (3Cq, $C_6H_4$); 141.8 (3Cq, $C_6H_4$).

### General procedure for the synthesis of G1 dendrimers

A mixture of the olefin (**1** or **3**), the tri- or hexabromide core (**5-Br$_3$** or **6-Br$_6$**), anhydrous sodium acetate (NaOAc), tetrabutylammonium bromide (TBABr), and the pincer palladium catalyst in DMA (15 mL) was heated at 130 °C for 15 to 20 h. After removing the solvent under reduced pressure, the product was extracted with a $CH_2Cl_2$–$H_2O$–$NaHCO_3$ mixture and the organic phase was dried over $MgSO_4$. Purification was carried out by column chromatography on silica gel and the product recrystallized from $CH_2Cl_2$–hexane.

**Compound 7-Fc$_3$.** Olefin **1** (400 mg, 1.89 mmol), core **5-Br$_3$** (342 mg, 0.63 mmol), NaOAc (233 mg, 2.8 mmol), TBABr (20 mg, 0.06 mmol), DMA (15 mL), and palladium pincer catalyst (20 mg, 0.03 mmol) were used. Eluent used in the purification by column chromatography was hexane–$CH_2Cl_2$ (1 : 9). Yield 72%. $^1$H-NMR (500 MHz, $CDCl_3$): $\delta$ 7.82 (s, 3H, $C_6H_3$); 7.70 (d, 6H, $^3J_{H\text{-}H} = 7.5$ Hz, $C_6H_4$); 7.57 (d, 6H, $^3J_{H\text{-}H} = 7.5$ Hz, $C_6H_4$); 6.97 (d, 3H, $^3J_{H\text{-}H} = 16.5$ Hz, CH=CH); 6.77 (d, 3H, $^3J_{H\text{-}H} = 16.5$, CH=CH); 4.53 (s, 6H, $C_5H_4$); 4.34 (s, 6H, $C_5H_4$); 4.19 (s, 15H, $C_5H_5$). $^{13}$C-NMR (300 MHz, $CDCl_3$): $\delta$ 67.7, 69.7, 70.1 (27C, $C_5H_4$ and $C_5H_5$); 84.3 (3Cq, $C_5H_4$); 125.2, 126.2, 127.0, 128.0, 128.2 (21C, CH=CH, $C_6H_4$ and $C_6H_3$); 137.9, 140.1, 142.7 (9Cq, $C_6H_4$, $C_6H_3$). Anal. calcd for compound **7-Fc$_3$**, $C_{60}H_{48}Fe_3$, $M_w = 936.58$: C, 76.9; H, 5.17; found: C, 76.8; H, 5.16. FABMS: $m/z$ 935 ($M^+$).

**Compound 8-Fc$_6$.** Olefin **1** (500 mg, 2.36 mmol), core **6-Br$_6$** (306 mg, 0.40 mmol), NaOAc (295 mg, 3.6 mmol), TBABr (20 mg, 0.06 mmol), DMA (15 mL) and palladium pincer catalyst (20 mg, 0.03 mmol) were used. Eluent used in the purification by column chromatography was hexane–$CH_2Cl_2$ (7 : 3). Yield 68%. $^1$H-NMR (300 MHz, $CDCl_3$): $\delta$ 7.45–7.30 (m, 12H, $C_6H_3$); 6.88 (d, 6H, $^3J_{H\text{-}H} = 16.2$ Hz, CH=CH); 6.70 (d, 6H, $^3J_{H\text{-}H} = 16.2$, CH=CH); 4.49 (s, 12H, $C_5H_4$); 4.31 (s, 12H, $C_5H_4$); 4.16 (s, 30H, $C_5H_5$). $^{13}$C-NMR (300 MHz, $CDCl_3$): $\delta$ 67.7, 70.0, 70.2 (54C, $C_5H_4$ and $C_5H_5$); 84.6 (6Cq, $C_5H_4$); 126.42, 126.8, 127.4, 129.2, 129.5 (24C, CH=CH and $C_6H_4$); 132.6, 133.5, 138.4 (12Cq, $C_6H_4$). Anal. calcd for compound **8-Fc$_6$**, $C_{96}H_{78}Fe_6$, $M_w = 1566.76$: C, 73.6; H, 5.02; found: C, 73.5; H, 5.03. FABMS: $m/z$ 1567 ($M^+$).

**Compound 9-Fc$_6$.** Olefin **3** (400 mg, 0.76 mmol), core **5-Br$_3$** (138 mg, 0.25 mmol), NaOAc (98 mg, 1.2 mmol), TBABr (20 mg, 0.06 mmol), DMA (15 mL) and palladium pincer catalyst (20 mg, 0.03 mmol) were used. Eluent used in the purification by column chromatography was hexane–$CH_2Cl_2$ (5 : 6). Yield 62%. $^1$H-NMR (300 MHz, $CD_2Cl_2$): $\delta$ 7.95 (s, 3H, $C_6H_3$); 7.84 (d, 6H, $^3J_{H\text{-}H} = 8.0$ Hz, $C_6H_4$); 7.75 (d, 6H, $^3J_{H\text{-}H} = 8.1$ Hz, $C_6H_4$); 7.37 (d, 3H, $^3J_{H\text{-}H} = 16.0$ Hz, CH=CH); 7.21 (d, 3H, $^3J_{H\text{-}H} = 16.0$, CH=CH); 7.05 (d, 6H, $^3J_{H\text{-}H} = 15.9$ Hz, CH=CH); 6.80 (d, 6H, $^3J_{H\text{-}H} = 16.2$, CH=CH); 4.55 (t, $^3J_{H\text{-}H} = 1.8$ Hz, 12H, $C_5H_4$); 4.34 (t, $^3J_{H\text{-}H} = 1.8$ Hz, 12H, $C_5H_4$); 4.20 (s, 30H, $C_5H_5$). $^{13}$C-NMR (300 MHz, $CDCl_3$): $\delta$ 67.0, 69.3, 69.5 (54C, $C_5H_4$ and $C_5H_5$); 83.5 (6Cq, $C_5H_4$); 122.5, 122.7, 124.7, 125.8, 127.0, 127.4, 127.5, 128.3, 128.8 (42C, CH=CH and $C_6H_4$); 136.6, 137.7, 138.4, 140.1, 141.8 (18Cq, $C_6H_4$). Anal. calcd for compound **9-Fc$_6$**, $C_{120}H_{96}Fe_6$, $M_w = 1873.16$: C, 76.9; H, 5.17; found: C, 77.0; H, 5.19. FABMS: $m/z$ 1871 ($M^+$).

**Compound 10-Fc$_{12}$.** Olefin **3** (600 mg, 1.14 mmol), core **6-Br$_6$** (148 mg, 0.19 mmol), NaOAc (140 mg, 1.7 mmol), TBABr (20 mg, 0.06 mmol), DMA (15 mL) and palladium pincer catalyst (20 mg, 0.03 mmol) were used. Eluent used in the purification by column chromatography was hexane–$CH_2Cl_2$ (3 : 7). Yield 55%. $^1$H-NMR (300 MHz, $CD_2Cl_2$): $\delta$ 8.23, 8.16, 8.03, 7.97, 7.89 (s, 30H, $C_6H_3$); 7.45 (m, 12H, CH=CH); 7.02 (d, 12H, $^3J_{H\text{-}H} = 16.2$ Hz, CH=CH); 6.77 (d, 12H, $^3J_{H\text{-}H} = 15.9$ Hz, CH=CH); 4.50 (s, 24H, $C_5H_4$); 4.30 (s, 24H, $C_5H_4$); 4.16 (s, 60H, $C_5H_5$). $^{13}$C-NMR (300 MHz, $CD_2Cl_2$): $\delta$ 67.7, 69.9 (108C, $C_5H_4$ and $C_5H_5$); 83.9 (12Cq, $C_5H_4$); 143.0, 142.8, 139.6, 138.4, 130.2, 129.0, 128.3, 126.1, 125.3, 123.3, 123.0 (96C, CH=CH and $C_6H_3$). Anal. calcd for compound **10-Fc$_{12}$**, $C_{216}H_{174}Fe_{12}$, $M_w = 3439.92$: C, 75.4; H, 5.10; found: C, 75.5; H, 5.13. FABMS: $m/z$ 3440 ($M^+$).

**Table 3** Selected crystallographic data for **2** and **3**

| | **2** | **3** |
|---|---|---|
| Empirical formula | $C_{31}H_{26}Fe_2O$ | $C_{32}H_{28}Fe_2$ |
| FW/g mol$^{-1}$ | 526.22 | 524.24 |
| $T$/K | 293(2) | 293(2) |
| $\lambda$/Å | 0.71073 | 0.71073 |
| Crystal System | Monoclinic | Monoclinic |
| Space group | $P2_1/c$ | $P2_1/c$ |
| $a$/Å | 18.624(3) | 19.198(2) |
| $b$/Å | 11.2643(17) | 11.1627(12) |
| $c$/Å | 11.6667(16) | 11.5538(12) |
| $\alpha$/deg. | 90 | 90 |
| $\beta$/deg. | 106.174(3) | 102.890(2) |
| $\gamma$/deg. | 90 | 90 |
| $U$/Å$^3$ | 2350.6(6) | 2413.6(4) |
| $Z$ | 4 | 4 |
| $\mu$/mm$^{-1}$ | 1.257 | 1.221 |
| Collect. Reflect. | 12 559 | 14 849 |
| Indep. Reflect. | 3994 | 4926 |
| $R_{int}$ | 0.0512 | 0.0367 |
| $R_1$ [$I > 2\sigma(I)$] $R_1$ [$I > 2\sigma(I)$] | 0.0479 | 0.0333 |
| $wR_2$ [$I > 2\sigma(I)$] $wR_2$ [$I > 2\sigma(I)$] | 0.1135 | 0.0763 |
| $R_1$ (all data) | 0.0758 | 0.0565 |
| $wR_2$ (all data) | 0.1226 | 0.0939 |

### X-Ray diffraction studies

Single crystals were grown by slow evaporation of hexane–$CH_2Cl_2$ mixtures and mounted on a glass fiber in a random orientation. Data collection was performed at room temperature on a Siemens Smart CCD diffractometer using graphite monocromated Mo-K$\alpha$ radiation ($\lambda = 0.71073$ Å) with a nominal crystal-to-detector distance of 4.0 cm. A hemisphere of data was colleted based on three $\omega$-scan runs (starting $\omega = -28°$) at values of $\phi = 0°$, 90° and 180° with the detector at $2\theta = 28°$. In each of these runs, frames (606, 435 and 230 respectively) were collected at 0.3° intervals and for 40 s per frame for compound **2** and 30 s per frame for compound **3**. Space group assignments are based on systematic absences, $E$ statistics and successful refinement of the structures. Structures were solved by direct methods with the aid of successive difference Fourier maps and were refined using the SHELXTL 5.1 software package.[44a] All non-hydrogen were refined anisotropically. Hydrogen atoms were assigned to ideal positions and refined using a riding model. Details of the data collection and cell dimensions are given in Table 3. The diffraction frames were integrated using the SAINT package[44b] and corrected for absorption with SADABS.[44c]

CCDC reference numbers 178989 and 178990. See http://www.rsc.org/suppdata/nj/b1/b108142j/ for crystallographic data in CIF or other electronic format.

## Acknowledgements

We thank the CICYT (PB98-1044) and BANCAIXA (P1B98-07) for financial support and the Generalitat Valenciana for a fellowship (J. Mata). We would also like to thank Prof. Francisco Estevan (Universitat de Valencia) for performing the FAB mass spectra.

## References

1 E. Buhleier, W. Wehner and F. Vötgle, *Synthesis*, 1978, 155.
2 G. R. Newkome, E. F. He and C. N. Moorefield, *Chem. Rev.*, 1999, **99**, 1689.
3 I. Cuadrado, M. Moran, C. M. Casado, B. Alonso and J. Losada, *Coord. Chem. Rev.*, 1999, **195**, 395.
4 C. M. Casado, I. Cuadrado, M. Moran, B. Alonso, B. Garcia, B. Gonzalez and J. Losada, *Coord. Chem. Rev.*, 1999, **186**, 53.
5 D. Astruc, *Acc. Chem. Res.*, 2000, **33**, 287.

6 L. Lindoy, *Coord. Chem. Rev.*, 1998, **174**, 327.

7 V. Balzani, S. Campagna, G. Denti, A. Juris, S. Serroni and M. Venturi, *Acc. Chem. Res.*, 1998, **31**, 26.

8 J. Ruiz, E. Alonso, J. C. Blais and D. Astruc, *J. Organomet. Chem.*, 1999, **582**, 139.

9 O. Briel, A. Fehn and W. Beck, *J. Organomet. Chem.*, 1999, **578**, 247.

10 D. Vos, A. Salmon, H. G. Stammler, B. Neumann and P. Jutzi, *Organometallics*, 2000, **19**, 3874.

11 C. Valério, F. Moulines, J. Ruiz, J. C. Blais and D. Astruc, *J. Org. Chem.*, 2000, **65**, 1996.

12 C. M. Cardona, T. D. McCarley and A. E. Kaifer, *J. Org. Chem.*, 2000, **65**, 1857.

13 S. Nlate, J. Ruiz, J. C. Blais and D. Astruc, *Chem. Commun.*, 2000, 417.

14 K. W. Poon, Y. Yan, X. Y. Li and D. K. P. Ng, *Organometallics*, 1999, **18**, 3528.

15 B. Garcia, C. M. Casado, I. Cuadrado, B. Alonso, M. Moran and J. Losada, *Organometallics*, 1999, **18**, 2349.

16 C. M. Casado, I. Cuadrado, W. Moran, B. Alonso, M. Barranco and J. Losada, *Appl. Organomet. Chem.*, 1999, **13**, 245.

17 C. M. Casado, I. Cuadrado, B. Alonso, M. Moran and J. Losada, *J. Electroanal. Chem.*, 1999, **463**, 87.

18 C. Cardona and A. E. Kaifer, *Abstr. Pap. Am. Chem. Soc.*, 1998, **216**, 030.

19 C. M. Cardona and A. E. Kaifer, *J. Am. Chem. Soc.*, 1998, **120**, 4023.

20 H. Tokuhisa, M. Q. Zhao, L. A. Baker, V. T. Phan, D. L. Dermody, M. E. Garcia, R. F. Peez, R. M. Crooks and T. M. Mayer, *J. Am. Chem. Soc.*, 1998, **120**, 4492.

21 C. F. Shu and H. M. Shen, *J. Mater. Chem.*, 1997, **7**, 47.

22 A. Miedaner, C. J. Curtis, R. M. Barkley and D. L. Dubois, *Inorg. Chem.*, 1994, **33**, 5482.

23 G. E. Oosterom, R. J. van Haaren, J. N. H. Reek, P. C. J. Kamer and P. W. N. M. van Leeuwen, *Chem. Commun.*, 1999, 1119.

24 C. M. Cardona and A. E. Kaifer, *J. Am. Chem. Soc.*, 1998, **120**, 4023.

25 C. Valério, J.-L. Fillaut, J. Ruiz, J. Guittard, J.-C. Blais and D. Astruc, *J. Am. Chem. Soc.*, 1997, **119**, 2588.

26 P. Jutzi, C. Batz, B. Neumann and H.-G. Stammler, *Angew. Chem., Int. Ed.*, 1996, **35**, 2118.

27 B. Alonso, I. Cuadrado, M. Morán and J. Losada, *J. Chem. Soc., Chem. Commun.*, 1994, 2575.

28 J.-L. Fillaut and D. Astruc, *J. Chem. Soc., Chem. Commun.*, 1993, 1320.

29 A. Peruga, J. A. Mata, D. Sainz and E. Peris, *J. Organomet. Chem.*, 2001, **637**, 194.

30 S. Sengupta and S. K. Sandhukhan, *Organometallics*, 2001, **20**, 1889.

31 S. Sengupta and S. K. Sadhukan, *Tetrahedron Lett.*, 2001, **42**, 3659.

32 J. A. Mata, E. Peris, I. Asselberghs, R. van Boxel and A. Persoons, *New J. Chem.*, 2001, **25**, 299.

33 J. A. Mata, S. Uriel, R. Llusar and E. Peris, *Organometallics*, 2000, **19**, 3797.

34 J. A. Mata, E. Falomir, R. Llusar and E. Peris, *J. Organomet. Chem.*, 2000, **616**, 80.

35 J. A. Mata, S. Uriel, E. Peris, R. Llusar, S. Houbrechts and A. Persoons, *J. Organomet. Chem.*, 1998, **562**, 197.

36 H. D. Sikes, J. F. Smalley, S. P. Dudek, A. R. Cook, M. D. Newton, C. E. D. Chidsey and S. W. Feldberg, *Science*, 2001, **291**, 1519.

37 M. Bochmann, J. J. Lu and R. D. Cannon, *J. Organomet. Chem.*, 1996, **518**, 97.

38 D. Naskar, S. K. Das, L. Giribabu, B. G. Maiya and S. Roy, *Organometallics*, 2000, **19**, 1464.

39 K.-Y. Kay, Y. G. Baek, D. Won Han and S. Yong Yeu, *Synthesis*, 1997, 35.

40 B. König, H. Zieg, P. Bubenitschek and P. G. Jones, *Chem. Ber.*, 1994, **127**, 1811.

41 The preparation of **1** is similar to that described for the methylated homolog reported in E. Peris, J. Loch, J. A. Mata and R. H. Crabtree, *Chem. Commun.*, 2001, 201. Synthesis of **1**: Pd(AcO)$_2$ (200 mg, 0.9 mmol) and [2,6-bis(*N*-*n*-butyl)imidazolyumpyridine] dibromide (365 mg, 0.9 mmol) were heated at 90 °C in DMSO for 12 h. The resulting solution was then heated at 170 °C for 2 h, after which the solvent was removed and the crude solid was recrystallized in $CH_2Cl_2$–MeCN. The complete characterization and crystal structure of **1** will be published in a manuscript in preparation.

42 T. M. Miller, T. X. Neenan, R. Zayas and H. E. Bair, *J. Am. Chem. Soc.*, 1992, **114**, 1018.

43 I. Cuadrado, M. Moran, C. M. Casado, B. Alonso, F. Lobete, B. Garcia, M. Ibisate and J. Losada, *Organometallics*, 1996, **15**, 5278.

44 (*a*) G. M. Sheldrick, SHELXTL, version 5.03, Bruker, AXS, Madison, WI, 1998; (*b*) SAINT 5.0, Bruker Analytical X-Ray Systems, Madison, WI, 1996; (*c*) G. M. Sheldrick, SADABS Empirical Absorption Program, University of Göttingen, Germany, 1996.

# Pd-Mediated synthesis of linked conjugated tri- and penta-ferrocenyl complexes.

**José A. Mata, Juan Palomero and Eduardo Peris***

*Dpto. de Química Inorgánica y Orgánica, Universitat Jaume I. E-12080 Castellón. (Spain)*

## Abstract

A facile synthesis of new conjugated oligo-ferrocenyl compounds is described. The synthetic method consists of a two step procedure, which combines olefination by the Wittig procedure and Pd-mediated C-C coupling, leading to high yields of a tri- and penta- ferrocenyl complexes. The crystal structures of the 1,1'-bissubstituted ferrocenyl precursors is described. The electrochemical analysis of the compounds obtained, reveal that the peripheral ferrocenyl units display an equivalent redox behavior, with a large separation of the peak corresponding to the central ferrocenyl unit.

*Keywords*: Ferrocene, electrochemistry, crystal structure, Palladium-catalyzed.

## 1. Introduction

One of the richest areas of metallocene chemistry has been that of linked metallocenes.[1] Much of the interest in these species is concerned with the interaction between metal centers. When two or more ferrocenyl fragments are connected to obtain compounds with linked ferrocenes, many interests are envisaged, since intermetallic electronic communication affords a wide range of new applications. Many studies have been made during the last decade, regarding intramolecular electron-exchange reactions.[1-7]

In the search of new materials with electronic communication between terminal subunits, we have focused our interest in the preparation of new conjugated ferrocenyl complexes with end capped nitro,[8] pyridine[9] and nitrile[10] groups. End-capping ferrocene with pyridine and nitrile, allows the ferrocenyl subunit to link to different metallic fragments, affording interesting bimetallic complexes, in which the terminal metallic fragments are connected by a conjugated bridge. Some of the compounds so obtained, showed high non linear optical responses,[8, 11] which in most cases were envisaged from their molecular geometries and the electronic properties of the compounds themselves.[9, 10] More recently, we obtained a series of nitrile-terminated bisferrocenyl compounds with high comproportionation constants, which we coordinated to group 6 metal carbonyl fragments, affording several trimetallic complexes whose crystal structures were determined.[12]

In the search for new synthetic methods of ferrocenyl conjugated compounds, we have also designed a series of Palladium catalyzed reactions directed towards the synthesis of conjugated dendritic compounds.[13, 14] The synthetic methodology employed in this work, has now been applied to the synthesis of new linked conjugated tri- and penta-ferrocenyl complexes whose properties are described.

## 2. Results and discussion

In our previous works, we mainly focused our attention on the electronic communication along phenylene-ethenyl bridges. This studies were based on the structure-properties relationships provided by electrochemical, electronic and crystal structure determinations. This conjugated connection, has recently demonstrated high efficient electronic communication capabilities.[15] In the search of new polyferrocenyl complexes, we considered that 1,1'-(phenylene-ethenyl)bissubstituted ferrocenes could provide a new family of complexes with interesting structural and electronic properties. In this sense, we synthesized (*E*,*E*)-1,1' bis[p-bromophenyl-ethenyl]-ferrocene, **1-(*E,E*)** as the core for the new polyferrocenyl compounds. The synthesis of **1-(*E,E*)** was based on the conventional Wittig olefination method from 1,1'-biscarboxaldehyde-ferrocene-(Scheme 1). Since Wittig olefinations are not often very stereoselective, a mixture of the (*E*,*E*), (*E*,*Z*) and (*Z*,*Z*) isomers was obtained, being the (*E*,*E*) form the major one. The isomers are readily separated by column chromatography, but a simple isomerization reaction with $I_2$ in refluxing toluene, yields **1-(*E,E*)** in an almost quantitative form.[8, 16]

The crystal structures of the compounds **1-(*E,E*)** and **1-(*E,Z*)** were determined by means of X-ray diffractommetry. Figures 1 and 2 show the ORTEP diagrams of **1-(*E,E*)** and **1-(*E,Z*)** respectively. Table 1 shows the selected bond distances and angles of these compounds. Both compounds crystallize in the centrosymmetric space groups $P2_1/c$. The most remarkable feature of **1-(*E,E*)** is that it shows an almost coplanar structure between the Cp, vinylene and phenylene units, as can be seen in Figure 1, confirming that the conjugation is extended along all the structure. As seen for most neutral ferrocenyl complexes, the Cp rings adopt an eclipsed conformation, with the two ancillary ligands in a *syn* conformation. Many approaches have been made in order to rationalize the conformational properties of 1,1'-bissubstituted ferrocenes but still there is not a clear explanation for the conformational disposition of this type of complexes. We first thought that an intramolecular π–stacking could be having some effect in the stabilization of the *syn* disposition,[9] but the structure of **1-(*E,Z*)** were intramolecular π-stacking is not possible, is also showing a *syn* conformation, so packing effects may be having a dominant role. In order to check whether electronic modifications on **1-(*E,E*)** may be having any effect in its conformational structure, we oxidized this compound with ferrocenium hexafluorophosphate, yielding [**1-(*E,E*)**]$PF_6$ whose molecular structure was determined by single crystal X-ray diffraction (Figure 3). As can be seen by comparing the crystal structures of compounds **1-(*E,E*)** and [**1-(*E,E*)**]$PF_6$ (Table 1), one electron oxidation leads to an increase of the distance Fe-C (Cp rings) and a decrease of the coplanarity of the two ancillary ligands. No other significant differences are observed.

As mentioned before, we used **1-(*E,E*)** as the core for the synthesis of several oligo-ferrocenyl complexes. The palladium catalyzed reaction of **1-(*E,E*)** with vivnylferrocene afforded the trisferrocenyl complex **2** in very high yield (72%) in just 5 hours at 130ºC in DMA. Due to the high temperature used, we decided to utilize the thermally-stable imidazolyl pincer Pd catalyst shown in Scheme 2, related to the one recently described by us with methyl instead of n-butyl terminal groups.[17] This catalyst showed a higher activity than its methyl analogue. The preparation and catalytical properties of this new catalyst will be published in detail elsewhere. The reaction could be followed in situ by extracting little amounts of the reaction mixture and making micro-extractions in $CH_2Cl_2/H_2O$. The solvent of the organic fraction was removed and the crude solid redissolved in $CDCl_3$ and introduced in an NMR tube. By this simple method we could monitor the reaction progress by $^1H$ NMR, by simply checking the disappearance of the signals due to the terminal olefin of vinylferrocene, and taking the Cp signals of all the ferrocenyl complexes as internal reference (26H). Figure 4 plots the evolution of the reaction according to the analysis of the $^1H$-RMN spectra recorded by this method.

Following the same procedure, we reacted the bisferrocenyl complex **3**[14] with **1-(*E,E*)** and obtained the pentaferrocenyl complex **4** (Scheme 2) in high yield (62%). Compounds **2** and **4** were fully characterized by the conventional methods. The $^1H$ NMR spectra showed the typical pattern of monosubstituted and bissubstituted ferrocenyl compounds in a 2:1 (**2**) and 4:1 (**4**) ratio, this confirming the equivalence of all the terminal ferrocenyl units. Attempts to grow single crystals suitable for X-ray diffraction failed for these two compounds. The structure of the biferrocenyl-vinylene complex **3** was reported in one of our previous papers,[14] showing perfect coplanarity between the Cp, ethenyl and phenylene units. For this reason, we consider that it is highly expectable that the structure of **4** also shows a high degree of coplanarity. If we also consider the ability 1,1'-bissubstituted ferrocenyl complexes to display syn conformations, we believe that a fluxional equilibrium of all the possible rotamers must be present in solution of compounds **2** and **4.**

The electrochemical data obtained for the compounds studied are summarized in Table 2. All the complexes display the chemically reversible ferrocene/ferricinium couple in $CH_2Cl_2$. The peak to peak separations are, however, significantly greater than the ideal value of 60 mV/s for a fully reversible one electron process. This may be due to a combination of uncompensated solution resistance and slightly slow electron-transfer kinetics.

The presence of the bromine in compounds **1-(*E,E*)**, **1-(*E,Z*)** and **1-(*Z,Z*)** results in an decrease of the redox potential compared to compound the related nitro, and nitrile groups that we have reported before,[16] this confirming the lower electronaccepting ability of bromine compared to $NO_2$ and CN. The complex with a higher degree of (*E*) stereochemistry (i.e. *E,E* >*E,Z*>*Z,Z*) possess a lower halfwave potential than the ones with higher degree of (*Z*) contribution [halfwave potential **1-(*E,E*)** < **1-(*E,Z*)** < **1-(*Z,Z*)**]. This is in good agreement with the higher stabilization of the positive charge corresponding to the more effective conjugation of the (*E*) isomers, and indicates a higher degree of charge transfer from the metal center to the polyene backbone.[9, 10, 18]

The tri- and penta-ferrocenyl complexes **2** and **4** display two reversible peaks corresponding to the central ferrocene and the equivalent terminal ferrocenyl units (Table 2). The lower potential wave corresponds to a two-electron oxidation process in compound **2** and four-electron in the case of compound **4** this implying that the oxidation of the terminal units occurs at a lower potential than the central bis-substituted ferrocene. It has been published[1] that in a molecule with $n$ noninteracting equivalent redox centers, it can be shown that, in an electrochemical experiment, one should observe a separation, $\Delta E$, of $(RT/F)\ln 2^n$ between the first and the last redox events within the equivalent redox centers. This would imply that, in our case, compound **2**, with two non interacting redox centers, should display a peak separation of 36 mV for the two terminal ferrocenyl units. In the case of compound **4**, the peak separation of the four non interacting peripheral units would be of 72 mV. Both numbers are rather small separations to be resolvable in routine electrochemical experiments. When we study the peak separation between the peripheral and the central ferroceneyl units, we observe that this is rather large for both compounds **2** (300 mV) and **4** (400 mV). The presence of two one-electron oxidation instead of one two-electron oxidation, indicates a stabilization of the mixed valence species. In any case, we are aware that the electronic communication between the redox centers must be less than that measured by the potential difference due to the geometrical inequivalence of the iron centers implied in the redox processes.

The half-wave peak separations in **2** and **4** prompted us to obtain the mixed-valence complexes $\mathbf{2}^{2+}$ and $\mathbf{4}^{4+}$ by oxidizing **2** and **4** with an excess of ferrocinium-hexafluorophosfate as oxidant. The resulting products were analyzed by electrospray mass spectroscopy showing major peaks corresponding to the dicationic species for **2** and tetracationic for **4**. **2** and **4** were oxidized to the $\mathbf{2}^{3+}$ and $\mathbf{4}^{5+}$ species by using a stronger oxidant such as $NOBF_4$. $\mathbf{2}^{2+}$ and $\mathbf{2}^{3+}$ were analyzed by electrospray mass spectroscopy, but the species derived from **4** could not be analyzed by this method due to the low solubility of the tetracationic ($\mathbf{4}^{4+}$) and pentacationic ($\mathbf{4}^{5+}$) species obtained in all solvents that we tried. Although we failed in our attempts to grow crystals of the oxidized derivatives of **2** and **4**, we strongly believe that the compounds must display interesting structural features, such as a fully expanded *anti* conformation in order to avoid electrostatic repulsions of the peripheral cationic centers.

## 3. Experimental Section

NMR spectra were recorded on a Varian Innova 300 MHz and 500 MHz spectrometers, using $CDCl_3$ or $CD_2Cl_2$ as solvent unless otherwise stated. IR spectra were recorded on a Perkin Elmer System 2000 FT-IR using NaCl pellets. Electronic absorption spectra were obtained on a UV-1603 Shimazdzu spectrophotometer. Cyclic voltammetry experiments were performed with a Echochemie pgstat 20 electrochemical analyzer. All measurements were carried out at room temperature with a conventional three-electrode configuration consisting of platinum working and auxiliary electrodes and a Ag/AgCl reference electrode containing aqueous 3 M KCl. The supporting electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate. All potential data reported are not corrected for the junction potential. FAB Mass spectra were run by the fast atom bombardment mode (FABMS, *m*-nitrobenzyl alcohol matrix) on a VG AutoSpec mass spectrometer. Electrospray mass spectra were recorded using a Micromass Quattro LC instrument, using $CH_3CH_2OH$ as the mobile phase solvent. The samples were added to give a mobile phase of approximate concentration 0.1 mM. Vinylferrocene, was used as purchased (Aldrich) or syntesized by Wittig olefination of the ferrocenecarboxaldehyde, using $[Ph_3P^+CH_3]I^-$ and t-BuOK. Bisferrocenyl complex **3** was obtained according to literature methods.[14] DMA, N,N-Dimethylacetamide, anydrous, 99.8%.

### 3.1 Synthesis of Compound 1-(E,E), 1-(E,Z), 1-(Z,Z)

To an ice-cold solution of [(*p*-bromophenyl)methyl]triphenylphosphonium bromide (5.87 g, 11.5 mmol) in THF (50 ml), sodium hydride (458 mg, 11.5 mmol) was added and the resulting solution stirred for 30 min. at 0 ºC and 30 min. at room temperature. The 1,1'-biscarboxaldehyde-ferrocene (925 mg, 38 mmol) was added and the resulting solution stirred overnight at room temperature. After removing the solvent under reduced pressure, the product was extracted with $CH_2Cl_2/H_2O/NaHCO_3$ and dried over $MgSO_4$. Purification by column chromatography on silica gel using hexane/$CH_2Cl_2$ (4:1) as eluent afforded pure compounds **1-(Z,Z)**, **1-(E,Z)** and **1-(E,E)**. All compounds were recrystallizated from $CH_2Cl_2$/hexane mixture and characterized. All fractions were dissolved in toluene with traces of $I_2$. The mixture was refluxed for 20 minutes, after which the solvent was eliminated by reduced presure. The crude product was flash-chromatographed, yielding pure **1-(E,E)** compound. Yield: 65%.

*Compound **1-(Z,Z)***

$^1$H-RMN (300 MHz, $CDCl_3$): $\delta$ (ppm) 7.39 (d, 4H, $^3J_{H-H}$ = 8.1 Hz, $C_6H_4$); 7.17 (d, 4H, $^3J_{H-H}$ = 8.4 Hz, $C_6H_4$); 6.36 (d, 2H, $^3J_{H-H}$ = 12.0 Hz, CH=CH); 6.21 (d, 2H, $^3J_{H-H}$ = 12.0 Hz, CH=CH); 4.12 (s, 4H, $C_5H_4$); 4.08 (s, 4H, $C_5H_4$).

$^{13}$C-RMN (300 MHz, $CDCl_3$): $\delta$ (ppm) 137.5, (2 Cq, $C_6H_4$-CH=CH); 131.7, 131.0, 128.9, 126.7 (12C, CH=CH,$C_6H_4$); 120.9 (2 Cq, $C_6H_4$-Br); 82.5 (2 Cq, $C_5H_4$); 71.0 (4C, $C_5H_4$); 68.9 (4C, $C_5H_4$).

*Compound **1-(E,Z)***

$^1$H-RMN (300 MHz, $CDCl_3$): $\delta$ (ppm) 7.48 (d, 4H, $^3J_{H-H}$ = 8.0 Hz, $C_6H_4$); 7.36 (d, 4H, $^3J_{H-H}$ = 8.5 Hz, $C_6H_4$); 6.78 (d, 1H, $^3J_{H-H}$ = 15.5 Hz, CH=CH); 6.59 (d, 2H, $^3J_{H-H}$ = 16.0 Hz, CH=CH); 6.30 (d, 1H, $^3J_{H-H}$ = 11.5 Hz, CH=CH); 6.24 (d, 1H, $^3J_{H-H}$ = 12.0 Hz,

CH=CH); 4.38 (s, 2H, $C_5H_4$); 4.24 (s, 2H, $C_5H_4$); 4.16 (s, 2H, $C_5H_4$); 4.14 (s, 2H, $C_5H_4$).
$^{13}$C-RMN (500 MHz, $CDCl_3$): δ (ppm) 137.5, (2 Cq, $C_6H_4$-CH=CH); 131.9, 130.9, 127.9, 125.9 (12C, $C_6H_4$, CH=CH); 121.1 (2 Cq, $C_6H_4$-Br); 84.6 (2 Cq, $C_5H_4$); 71.2 (4C, $C_5H_4$); 69.0 (4C, $C_5H_4$).

*Compound **1-(E,E)***
$^1$H-RMN (300 MHz, $CDCl_3$): δ (ppm) 7.30 (d, 4H, $^3J_{H-H}$ = 6.6 Hz, $C_6H_4$); 7.28 (d, 4H, $^3J_{H-H}$ = 7.8 Hz, $C_6H_4$); 6.63 (d, 2H, $^3J_{H-H}$ = 15.9 Hz, CH=CH); 6.42 (d, 2H, $^3J_{H-H}$ = 15.9 Hz, CH=CH); 4.47 (s, 4H, $C_5H_4$); 4.32 (s, 4H, $C_5H_4$).
$^{13}$C-RMN (300 MHz, $CDCl_3$): δ (ppm) 137.0, (2 Cq, $C_6H_4$-CH=CH); 132.1, 127.7, 127.1, 126.1 (12C, CH=CH, $C_6H_4$); 120.9 (2 Cq, $C_6H_4$-Br); 85.2 (2 Cq, $C_5H_4$); 70.9 (4C, $C_5H_4$); 68.7 (4C, $C_5H_4$).

Elemental Anal. Calc. for compound **1-*(E,E)***, $C_{26}H_{20}FeBr_2$, Mw=548.1: C, 57.0; H, 3.86. Found: C, 56.9; H, 3.89. FABMS, *m/z* 548 ($M^+$).

### 3.2 Synthesis of Compound [1-(E,E)]$PF_6$

To a solution of **1-(E,E)** (100 mg, 0.18 mmol) in $N_2$-purged dry MeCN, was added ferrocenium hexafluorophosphate (59.6 mg, 0.18 mmol) and the mixture was sonicated in an ultrasound bath for 15 min. After evaporation of the solvent the residue was washed several times with ether until the filtrate was colorless. The solid was dried yielding pure **[1-(E,E)]$PF_6$**. Crystals suitable for X-ray diffraction analysis were grown from a solution of MeOH/$CH_2Cl_2$. This compound was characterized by means of single crystal X-ray studies.

### 3.3 Synthesis of Compound 2

A mixture (315 mg, 1.5 mmol) of vinylferrocene, (400 mg, 0.73 mmol) of **1-(E,E)**, (200 mg, 2.4 mmol) of sodium acetate anhydrous, (40 mg, 0.2 mmol) of tetrabutylammonium bromide and Pd catalyst (20 mg, 0.02 mmol) in DMA (12 mL) was heated at 130ºC for 5 h. After removing the solvent under reduced pressure, the product was extracted with a $CH_2Cl_2/H_2O$ mixture, and the organic phase was dried over $MgSO_4$. Purification was made by column chromatography on silica gel, washing with hexane to remove unreacted vinylferrocene and using hexane/$CH_2Cl_2$ (1:3) as eluent to afford compound **2**, that was recrystallizated from $CH_2Cl_2$/hexane mixtures to obtain pure compound **2**. Yield: 72%.

$^1$H-NMR (300 MHz, $CDCl_3$): δ (ppm) 7.36 (d, 4H, $^3J_{H-H}$ = 8.0 Hz, $C_6H_4$); 7.31 (d, 4H, $^3J_{H-H}$ = 8.0 Hz, $C_6H_4$); 6.94 (d, 2H, $^3J_{H-H}$ = 16.5 Hz, CH=CH); 6.83 (d, 2H, $^3J_{H-H}$ = 16.0 Hz, CH=CH); 6.75 (d, 2H, $^3J_{H-H}$ = 16.5 Hz, CH=CH); 6.68 (d, 2H, $^3J_{H-H}$ = 16.0 Hz, CH=CH); 4.52 (s, 4H, $C_5H_4$); 4.49 (s, 4H, $C_5H_4$); 4.34 (s, 4H, $C_5H_4$); 4.33 (s, 4H, $C_5H_4$); 3.90 (s, 10H, $C_5H_5$).
$^{13}$C-RMN (500 MHz, $CD_2Cl_2$): δ (ppm) 136.8, 136.6 (4Cq, $C_6H_4$); 126.8, 126.5, 126.3, 126.2, 126.0, 125.9 (16C, CH=CH, $C_6H_4$); 84.7, 83.8 (4Cq, $C_5H_4$); 70.3, 69.5, 69.3, 68.3 (16C, $C_5H_4$); 67.1 (10C, $C_5H_5$).
Elemental Anal. Calc. for compound **2**, $C_{50}H_{42}Fe_3$, Mw=810.42: C, 74.10; H, 5.22. Found: C, 74.5; H, 5.19. FABMS, *m/z* 810 ($M^+$).

### 3.4 Synthesis of Compound 2[($PF_6$)]$_2$.

a) To a solution of **2** (50 mg, 0.06 mmol) in $CH_2Cl_2$, $NOBF_4$ (14.4 mg, 0.12 mmol) was added and the resulting solution stirred for 2 hours. The mixture was filtrated, obtaining a black solid of **2[($PF_6$)]$_2$** (Yield, 72%).
b) To a solution of **2** (50 mg, 0.06 mmol) in $N_2$-purged dry MeCN was added ferrocenium hexafluorophosphate (41 mg, 0.12 mmol) and mixture was sonicated in an ultrasound cleaning bath for 15 min. After evaporation of the solvent the residue was washed several times with ether until the filtrate was colorless, and was then dried yielding pure **2[($PF_6$)]$_2$** (Yield, 81%) Electrospray MS, cone 45V, *m/z* 405 ($M^{2+}$).

### 3.5 Synthesis of Compound 2[($BF_4$)]$_3$.

To a solution of **2** (50 mg, 0.06 mmol) in $CH_2Cl_2$, $NOBF_4$ (28.8 mg, 0.24 mmol) was added and the resulting solution stirred for 2 hours. The mixture was filtrated, obtaining a black solid of **2[($BF_4$)]$_3$**. (Yield, 80%) Electrospray MS, cone 45V, *m/z* 270 ($M^{3+}$).

### 3.6 Synthesis of Compound 4.

A mixture (200 mg, 0.4 mmol) of bisferrocenyl complex **3**, (105 mg, 0.2 mmol) of **1-(E,E)**, (40 mg, 0.6 mmol) of sodium acetate anhydrous, (40 mg, 0.2 mmol) of tetrabutylammonium bromide and pincer Pd catalyst (20 mg, 0.02 mmol) in DMA (12 mL) was heated at 130ºC for 5 h. After removing the solvent under reduced pressure, the product was extracted with a $CH_2Cl_2/H_2O$ mixture, and the organic phase was dried over $MgSO_4$. Purification was made by column chromatography on silica gel, washing with hexane/$CH_2Cl_2$ (2:1) to remove unreacted compound **3** and using hexane/$CH_2Cl_2$ (1:3) as eluent to afford compound **4**, that was recrystallized from $CH_2Cl_2$/hexane mixtures to obtain pure compound **4**. Yield: 62%.

$^1$H-RMN (500 MHz, $CD_2Cl_2$): δ (ppm) 7.48 (d, 4H, $^3J_{H-H}$ = 7.5 Hz, $C_6H_4$); 7.43 (s, 4H, $C_6H_3$); 7.38 (s, 2H, $C_6H_3$); 7.31 (d, 4H, $^3J_{H-H}$ = 7.5 Hz, $C_6H_4$); 7.25 (d, 2H, $^3J_{H-H}$ = 16.5 Hz, CH=CH); 7.17 (d, 2H, $^3J_{H-H}$ = 16.0 Hz, CH=CH); 6.97 (d, 4H, $^3J_{H-H}$ = 16.5 Hz, CH=CH); 6.82 (d, 2H, $^3J_{H-H}$ = 16.5 Hz, CH=CH); 6.70 (d, 4H, $^3J_{H-H}$ = 16.0 Hz, CH=CH); 6.60 (d, 2H, $^3J_{H-H}$ = 16.5 Hz, CH=CH); 4.61 (s, 4H, $C_5H_4$); 4.57 (s, 8H, $C_5H_4$); 4.43 (s, 4H, $C_5H_4$); 4.38 (s, 8H, $C_5H_4$); 4.22 (s, 20H, $C_5H_5$).
$^{13}$C-RMN (500 MHz, $CD_2Cl_2$): δ (ppm) 140.3, 138.7, 130.2, 129.2, 128.3, 128.0, 127.6, 126.9, 126.4, 126.1, 124.4, 122.7, 121.6 (10Cq, 30C, CH=CH, $C_6H_2$, $C_6H_3$); 85.6, 71.3, 69.8, 68.9 (6Cq, 44C, $C_5H_4$, $C_5H_5$).

Elemental Anal. Calc. for compound **4**, $C_{90}H_{72}Fe_5$, Mw=1434.8: C, 75.3; H, 5.20. Found: C, 75.7; H, 5.15. FABMS, *m/z* 1435 ($M^+$).

### 3.7 X-Ray Diffraction Studies.

Single crystals of compounds **1-(E,E)**, **1-(E,Z)** and **1-(E,E)PF$_6$** were grown by slow diffusion of hexane into concentrated $CH_2Cl_2$ solutions and mounted on a glass fiber in a random orientation. Data collection was performed at room temperature on a Siemens Smart CCD diffractometer using graphite monochromated Mo-K$\alpha$ radiation ($\lambda$=0.71073 Å) with a nominal crystal to detector distance of 4.0 cm. An hemisphere of data was colleted based on three $\omega$-scans runs (starting $\omega = -28^o$) at values $\phi=0^\circ$, $90^\circ$ and $180^\circ$ with the detector at $2\theta = 28^\circ$ At each of these runs, frames (606, 435 and 230, respectively) were collected at $0.3^\circ$ intervals and 40 s per frame for compounds **1-(E,E)** and **1-(E,Z)**, and 20 s per frame for compound **1-(E,E)PF$_6$**. Space group assignment was based on systematic absences, E statistics and successful refinement of the structures. The structure was solved by direct methods with the aid of successive difference Fourier maps and were refined using the SHELXTL 5.1 software package.[19] All non-hydrogen were refined anisotropically. Hydrogen atoms were assigned to ideal positions and refined using a riding model. Details of the data collection, cell dimensions and structure refinement are given in Table 3. The diffraction frames were integrated using the SAINT package and corrected for absorption with SADABS.[20, 21]

### 4. Supplementary Data

Crystallographic data have been deposited with the CCDC (123 Union Road, Cambridge, CB2 1EZ, UK) and are available on request quoting the deposition numbers 171141 for compound **1-(E,E)**, 171142 for compound **1-(E,Z)** and 171143 for compound **1-(E,E)PF$_6$**.

### Acknowledgements

We thank the DGESIC (PB98-1044) and BANCAIXA (P1B98-07) for financial support. We would also like to thank the Generalitat Valenciana for a fellowship (J. Mata).

### References

[1] S. Barlow and D. O'Hare, Chem. Rev. 97 (1997) 637.
[2] M. Kurosawa, T. Nankawa, T. Matsuda, K. Kubo, M. Kurihara and H. Nishihara, Inorg. Chem. 38 (1999) 5113.
[3] T. Horikoshi, K. Kubo and H. Nishihara, J. Chem. Soc.-Dalton Trans. (1999) 3355.
[4] T.-Y. Dong, P.-H. Ho, X.-Q. Lai, Z.-W. Lin and K.-J. Lin, Organometallics 19 (2000) 1096.
[5] Y. J. Chen, D.-S. Pan, C.-F. Chiu, J.-X. Su, S. J. Ling and K. S. Kwan, Inorg. Chem. 39 (2000) 953.
[6] T. Y. Dong, C. K. Chang, C. H. Cheng and K. J. Lin, Organometallics 18 (1999) 1911.
[7] N. J. Long, A. J. Martin, R. Vilar, A. J. P. White, D. J. Williams and M. Younus, Organometallics 18 (1999) 4261.
[8] J. A. Mata, E. Peris, I. Asselberghs, R. Van Boxel and A. Persoons, New. J. Chem. 25 (2001) 299.
[9] J. A. Mata, S. Uriel, R. Llusar and E. Peris, Organometallics 19 (2000) 3797.
[10] J. A. Mata, E. Falomir, R. Llusar and E. Peris, J. Organomet. Chem. 616 (2000) 80.
[11] J. Mata, S. Uriel, E. Peris, R. Llusar, S. Houbrechts and A. Persoons, J. Organomet. Chem. 562 (1998) 197.
[12] J. A. Mata and E. Peris, J. Chem. Soc.-Dalton Trans. (2001) 3634.
[13] A. Peruga, J. A. Mata, D. Sainz and E. Peris, J. Organomet. Chem. 637 (2001) 191.
[14] J. Palomero, J. A. Mata and E. Peris, New J. Chem. (2001) (Accepted).
[15] H. D. Sikes, J. F. Smalley, S. P. Dudek, A. R. Cook, M. D. Newton, C. E. D. Chidsey and S. W. Feldberg, Science 291 (2001) 1519.
[16] J. A. Mata, E. Peris, R. Llusar, S. Uriel, M. P. Cifuentes, M. G. Humphrey, M. Samoc and B. Luther-Davies, Eur. J. Inorg. Chem. (2001) 2113.
[17] E. Peris, J. A. Loch, J. Mata and R. H. Crabtree, Chem. Commun. (2001) 201.
[18] D. Naskar, S. K. Das, L. Giribabu, B. G. Maiya and S. Roy, Organometallics 19 (2000) 1464.
[19] G. M. Sheldrick, SHELXTL, version 5.1, Bruker AXS, Inc, Madison, WI 1997.
[20] SAINT, Bruker Analytical X-ray System, version 5.0, Madison, WI 1998.
[21] G. M. Sheldrick, SADABS empirical absorption program, University of Göttingen, Göttingen 1996.

**Figure Captions**

**Figure 1:** Molecular structure and atomic labeling scheme for **1-(E,E)**, with 50% anisotropic displacement ellipsoids. Hydrogen atoms have been omitted for clarity.

**Figure 2:** Molecular structure and atomic labeling scheme for **1-(E,Z)**, with 50% anisotropic displacement ellipsoids. Hydrogen atoms have been omitted for clarity.

**Figure 3:** Molecular structure and atomic labeling scheme for **1-(E,E)PF$_6$**, with 50% anisotropic displacement ellipsoids. Hydrogen atoms have been omitted for clarity.

**Figure 4:** Evolution of the Heck coupling to the compound **2** at 130 ºC in DMA.

**Table 1.** Selected Bond Distances (Å) and Angles (deg.) for compounds **1-(E,E)**, **1-(E,Z)** and **1-(E,E)PF$_6$**.

| | **1-(E,E)** | **1-(E,Z)** | **1-(E,E)PF$_6$** |
|---|---|---|---|
| Fe(1)-Cp [C(1)...C(5)] | 2.049(12) | 2.058(14) | 2.08(4) |
| Fe(1)-Cp [C(6)...C(10)] | 2.049(13) | 2.04(2) | 2.08(4) |
| C(11)-C(12) | 1.307(6) | 1.319(14) | 1.309(15) |
| C(18)-Br(1) | 1.909(4) | 1.917(9) | 1.881(14) |
| C(26)-Br(2) | 1.904(4) | 1.906(10) | 1.883(12) |
| Ph-Ph (cent.) | 3.93 | --- | 3.88 |
| C(1)-C(11)-C(12) | 126.4(4) | 126.2(10) | 125.0(12) |
| C(11)-C(12)-C(13) | 126.9(4) | 127.2(10) | 126.1(13) |
| C(6)-C(19)-C(20) | 126.2(5) | 134.3(9) | 126.7(14) |
| C(19)-C(20)-C(21) | 127.3(5) | 132.9(10) | 124.8(15) |
| Planes | | | |
| Cp-Cp | 2.1 | 1.4 | 6.7 |
| Cp [C(1)...C(5)] - Ph [C(13)...C(18)] | 7.0 | 10.6 | 17.2 |
| Cp [C(6)...C(10)] - Ph [C(21)..C(26)] | 6.9 | 39.8 | 14.1 |
| Ph - Ph | 4.3 | 42.9 | 3.3 |

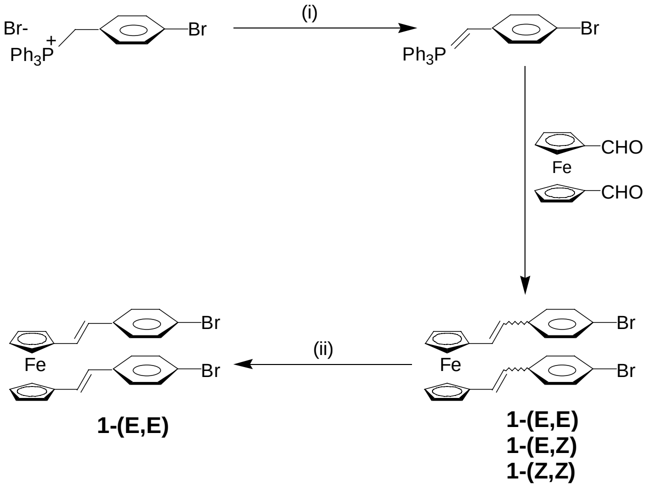
**Table 2:** Cyclic voltammetric data.[a]

| Compound | $E_{1/2}$ (mV) (ΔEp (mV))<br>Fe-based (terminal) | $E_{1/2}$ (mV) (ΔEp (mV))<br>Fe-based (central) |
|---|---|---|
| Ferrocene | 445 (105) | --- |
| **1-(E,E)** | 435 (130) | --- |
| **1-(E,Z)** | 480 (95) | --- |
| **1-(Z,Z)** | 505 (110) | --- |
| **2** | 425 (100) | 725 (105) |
| **3** | 415 (90) | --- |
| **4** | 400 (85) | 800 (80) |

[a] All compounds were measured in $CH_2Cl_2$ between 0 V and 1.25 V.

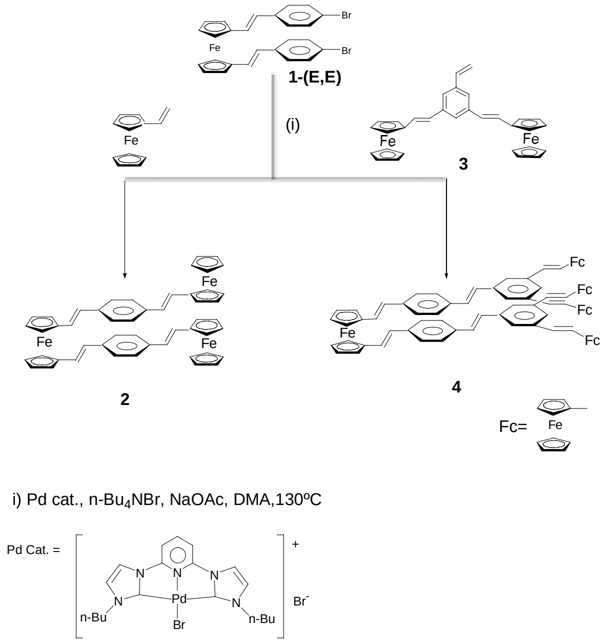
**Table 3** Crystallographic Data.

| Compound | **1-(E,E)** | **1-(E,Z)** | **1-(E,E)$PF_6$** |
|---|---|---|---|
| Empirical formula | $C_{26}H_{20}FeBr_2$ | $C_{26}H_{20}FeBr_2$ | $C_{27}H_{22}FeBr_2Cl_2PF_6$ |
| Formula Weight (g.mol$^{-1}$) | 548.09 | 548.09 | 777.99 |
| Temperature (K) | 293(2) | 293(2) | 293(2) |
| Wavelength (Å) | 0.71073 | 0.71073 | 0.71073 |
| Crystal System | Monoclinic | Monoclinic | Triclinic |
| Space group | $P2_1/c$ | $P2_1/c$ | P-1 |
| a (Å) | 6.2534(6) | 6.3542(13) | 10.2909(9) |
| b (Å) | 14.1477(13) | 23.123(5) | 12.2832(11) |
| c (Å) | 24.016(2) | 14.704(3) | 13.7003(13) |
| α (deg.) | 90 | 90 | 115.345(2) |
| β (deg.) | 94.046(2) | 102.165(2) | 106.462(2) |
| γ (deg.) | 90 | 90 | 90.559(2) |
| Volume (Å$^3$) | 2119.4(3) | 2111.9(7) | 1483.7(2) |
| Z | 4 | 4 | 2 |
| Density (calc. Mg.m$^{-3}$) | 1.718 | 1.724 | 1.741 |
| Absorption Coef. (mm$^{-1}$) | 4.492 | 4.508 | 3.490 |
| F(000) | 1088 | 1088 | 766 |
| Crystal Size (mm$^3$) | 0.5 x 0.2 x 0.1 | 1.1 x 0.3 x 0.2 | 0.32 x 0.24 x 0.14 |
| θ range (deg.) | 1.67 to 24.71 | 1.67 to 24.71 | 1.73 to 19.78 |
| Index Ranges | -7<=h<=7<br>-15<=k<=16<br>-25<=l<=28 | -7<=h<=7<br>-27<=k<=23<br>-17<=l<=12 | -9<=h<=7<br>-11<=k<=11<br>-11<=l<=13 |
| Reflections Collected | 11589 | 11369 | 4968 |
| Independent Reflections | 3623[R(int.) = 0.0421] | 3593[R(int.) = 0.0623] | 2672[R(int.) = 0.032] |
| Data/Restrains/Parameters | 3623 / 0 / 262 | 3593 / 0 / 262 | 2672 / 0 / 352 |
| Goodness-of-fit-on $F^2$ | 0.983 | 1.092 | 1.049 |
| Final R indices [I>2σ(I)] | R1=0.0374, wR2=0.0822 | R1=0.0685, wR2=0.2051 | R1=0.0641, wR2=0.1641 |
| R indices (all data) | R1=0.0687, wR2=0.0907 | R1=0.0870, wR2=0.2105 | R1=0.0936, wR2=0.1845 |
| ρ max, ρ min (e Å$^{-3}$) | 0.786, -0.738 | 0.630, -0.779 | 0.638, -0.496 |



i) NaH, THF
ii) $I_2$, toluene, reflux

Scheme I



i) Pd cat., n-$Bu_4$NBr, NaOAc, DMA,130ºC

Scheme II

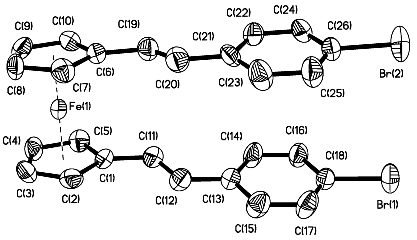


Figure 1

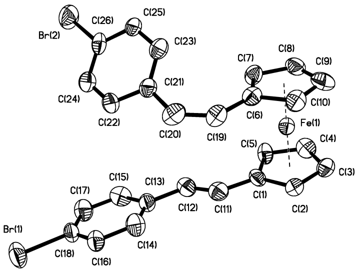


Figure 2

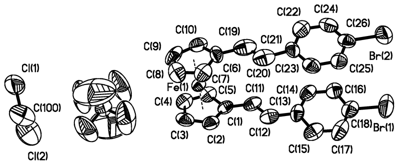
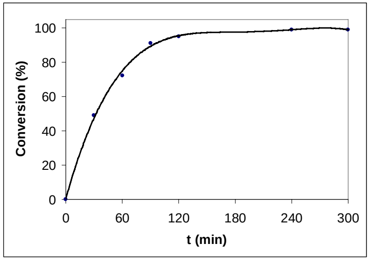


Figure 3



Figuire 4

ChemComm

# A Pd complex of a tridentate pincer CNC bis-carbene ligand as a robust homogenous Heck catalyst†

**Eduardo Peris,*[a] Jennifer A. Loch,[b] José Mata,[a] and Robert H. Crabtree*[b]**

[a] *Dpto. de Química Inorgánica y Orgánica, Universitat Jaume I, 12080 Castellón, Spain. E-mail: eperis@vents.uji.es*

[b] *Department of Chemistry, Yale University, P.O. Box 208107, New Haven, CT 06520-8107, USA. E-mail: robert.crabtree@yale.edu*

***Received (in Irvine, CA, USA) 2nd October 2000, Accepted 6th December 2000***
***First published as an Advance Article on the web***

**The bis-carbene precursor, 1, gives a thermally very robust Pd(II) catalyst for Heck coupling that maintains activity even in boiling diethylacetamide (bp 184 °C) in air.**

One common and significant limitation of some homogeneous catalysts is their relatively rapid deactivation, particularly when high temperatures or harsh conditions are needed; this is often the case for cross-coupling reactions and alkane functionalization.[1] The facility of P–C bond cleavage reactions has been implicated in catalyst deactivation of phosphine complexes.[2] For example, the deactivation of the $[IrH_2(tfa)(P\{C_6H_4F\}_3)_2]$ catalyst in alkane dehydrogenation was shown to correlate with the appearance of $C_6H_5F$, the product of P–aryl hydrogenolysis.[3]

The recent discovery of imidazole-based carbenes[4] and of their effectiveness as ligands[5] offers an opportunity to develop phosphine-free homogeneous catalysis. These carbenes are not only excellent ligands for late transition metals but are also able to promote a variety of catalytic reactions, including C–C[6] and C–N[7] coupling and olefin metathesis.[8] The thermal stability of carbene complexes is often high and they lack sensitive bonds that might be cleaved in any deactivation process. Since thermal stability of phosphine complexes can be improved by incorporation into a chelating ligand, as in the well known 'pincer' phosphines,[9] the same strategy might be useful in enhancing stability in the carbene case. Several authors have recently reported thermally stable palladium complexes active for the Heck reaction either with carbene or with pincer phosphines of both mono- and multi-dentate types as ligands.[6*b,d,e,i,j*,10]

We now report that the known carbene precursor,[11] **1**, readily formed by an improved synthesis (95% yield), reacts with $Pd(OAc)_2$ to give a carbene complex, **2**, as shown in Scheme 1 (ESI†). The thermal stability of the product is emphasized by the fact that the final stage of the synthesis of **2** takes place at 160 °C.

Fig. 1 shows the structure and metric parameters of the resulting complex from an X-ray structure determination.‡ The molecule is flat with a ligand bite angle of 79°. Otherwise, the metric parameters are similar to those previously found for related complexes.[6*b,d*] The Pd–C distance (2.038(6) Å) indicates that the bond is essentially single with very little back donation, as expected for this strongly Fischer-type carbene. This Pd–C distance is somewhat longer than in most prior cases,[6*b,d*] probably because the two high *trans*-effect carbene ligands are mutually *trans*.

Scheme 1

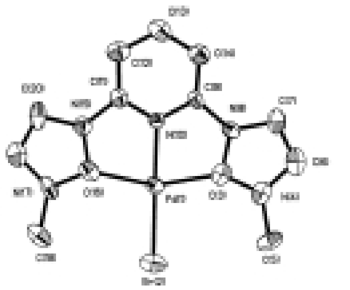
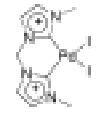


**Fig. 1** ORTEP diagram of complex **2** showing the atom numbering scheme. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Pd(1)–N(10) 1.979(4), Pd(1)–C(3) 2.033(6), Pd(1)–C(16) 2.044(6), Pd(1)–Br(2) 2.4099(7); N(10)–Pd(1)–C(3) 78.9(2), N(10)–Pd(1)–C(16) 79.6(2), C(3)–Pd(1)–C(16) 158.5(2), N(10)–Pd(1)–Br(2) 179.03(13), C(3)–Pd(1)–Br(2) 100.29(16), C(16)–Pd(1)–Br(2) 101.18(16). Thermal ellipsoids are drawn at 50% probability.

The stability that ligand **1** imparts to complex **2** is apparent from comparison with other Heck catalysts containing chelating ligands. Catalysts **3**[6*d,e*] and **4**[12] are very active for the Heck reaction when used under nitrogen at 140 °C. Complex **3**, however, is reported[6*e*] to decompose in dimethylacetamide (DMA, bp 165 °C) above 70 °C. Our own work shows that in refluxing DMA in air, complex **3** begins to deposit Pd black after 8 h and complex **4** deposits Pd black after 17 h, while our complex, **2**, is unchanged ( > 24 h). Other Pd pincer complexes, of PCP and SCS types, are also known as Heck catalysts.[10]



3

4

The new complex **2** shows catalytic activity under argon for a standard Heck reaction between PhI and styrene (Table 1, entry 1) in refluxing diethylacetamide (DEA, bp 184 °C) in the presence of NaOAc as base.§ We find that with 0.2 mol% catalyst, good yields and turnover frequencies are found. Complex **2** shows comparable activity to the Heck catalysts, **3** and **4**, at least for PhI (Table 1, entries 1–3). Bromobenzene and styrene can also be converted to *trans*-stilbene in essentially quantitative yield in the presence of 5 mol% catalyst, NaOAc, and refluxing DMA, within 1 h (Table 2, entry 1). Surprisingly, but not uniquely,[10*b,c,e*] the catalyst retains activity even under air (Table 2, entry 2). Iodobenzene and styrene can also be converted to *trans*-stilbene in near quantitative yield in the presence of 5 mol% **2**, NaOAc, and refluxing DMA in a reflux

---

† Electronic supplementary information (ESI) available: synthesis details and NMR data. See http://www.rsc.org/suppdata/cc/b0/b008038l/

DOI: 10.1039/b008038l

**Table 1** Comparison of yields for catalysts **2**–**4** for the reaction of PhI with styrene in refluxing DEA to form *trans*-stilbene (under Ar with 0.2 mol% catalyst and NaOAc)[a]

| Entry | Catalyst | 0.5 h | 1 h | 1.5 h | 2 h | 4 h |
|---|---|---|---|---|---|---|
| 1[b] | **2** | 48, 494 | 58, 298 | 67, 230 | 73, 188 | 85, 109 |
| 2 | **3** | 36, 370 | 48, 247 | 62, 213 | 72, 185 | 84, 108 |
| 3 | **4** | 50, 514 | 61, 314 | 67, 230 | 75, 193 | 90, 116 |

[a] Reported as: yield (%), TOF [mol product/(mol Pd × h)]. Yield determined by $^1$H NMR based on amount of product *vs.* amount of starting material remaining. [b] Average of two runs.

**Table 2** Heck reaction between aryl halides and styrene to form *trans*-stilbene. All reactions carried out in refluxing DMA with NaOAc as base

| Entry (air/Ar) | Aryl halide | **2** (mol %) | Reaction time/h | Stilbene yield (%)[a] | TOF [mol prod./(mol Pd)(h)] |
|---|---|---|---|---|---|
| 1 (Ar) | PhBr | 5 | 1 | > 99 | 20 |
| 2 (air) | PhBr | 5 | 1 | > 99 | 20 |
| 3 (air) | PhI | 5 | 1 | > 99 | 20 |
| 4 (air) | PhI | 1 | 1 | 89 | 89 |
| 5 (air) | PhI | 0.0001 | 20 | 33 | 16.500 |
| 6 (Ar)[b] | *p*-(CHO)$C_6H_4Cl$ | 5 | 20 | 75 | 15 |

[a] Yield determined by $^1$H NMR based on amount of product *vs.* amount of starting material remaining. [b] In the presence of *n*-$Bu_4NBr$ (20 mol% *vs.* Pd).

apparatus open to the air (Table 2, entry 3). A yield of 89% can still be obtained in only 1 h if 1 mol% of **2** is used (Table 2, entry 4). To see if the TOF could be improved at low loading, we find that as little as $10^{-4}$ mol% of **2** still gives a TOF of 16.500 after 20 h under air (Table 2, entry 5). Aryl chlorides react more slowly (Table 2, entry 6). Other alkenes react satisfactorily—for example, *n*-butyl acrylate and PhI give the Heck product in 99% yield after 1 h in refluxing DMA with 1 mol% catalyst.

In view of recent studies that find evidence that the active species can be metallic palladium,[13] we checked **2**–**4** for heterogeneity by the Hg drop test.[14] Heck catalysis with **2**–**4** was unaffected by the presence of Hg, and no induction period is observed for **2**, so a homogeneous active species is likely.

On the standard model of the Heck reaction, with $[Pd(0)\{PR_3\}_2]$ as the key intermediate, a pincer carbene might seem to be a poor choice, even if the carbene is an acceptable replacement for the tertiary phosphine of the standard system. On the Amatore–Jutand model,[15] however, $[Pd(0)(OAc)\{PR_3\}_2]^-$ is the key intermediate. Our work supports this model if the pyridine part of the pincer ligand is considered as replacing the OAc group. It is true that $[Pd(0)XL_2]^-$ would normally be expected to adopt a trigonal geometry, but the presumed intermediate Pd(0) form of the metal being d$^{10}$, there should be no strong penalty to adopt the pincer geometry. Eisenstein and Clot[16] are currently looking at such mechanistic issues in detail.

The results are of interest not so much as an advance in Heck catalysis—other catalysts can be better[6,10]—but as an indication that chelating carbenes can provide ligand systems that give high catalytic activity with excellent stability, even in air. This approach should be widely applicable to the development of non-phosphine late metal homogeneous catalysis.

We thank US DOE (J. A. L.) and NSF (R. H. C.) for funding and Matthew Torres for some preliminary observations.

## Notes and references

‡ *Crystal data for* **2**: $C_{11}H_7Br_2N_5Pd{\cdot}H_2O$, monoclinic, space group $P2(1)/n$, $a$ = 8.7782(4), $b$ = 14.3181(6), $c$ = 13.5684(6) Å, $\alpha$ = 90, $\beta$ = 107.1600(10), $\gamma$ = 90°, $Z$ = 4, $D$ = 2.011 g cm$^{-3}$, $\mu$ = 6.044 mm$^{-1}$, 5300 measured reflections, 1467 [$R$(int) = 0.0310] independent reflections, $R$ = 0.0225 [$F > 2\sigma(F)$]. Crystals were grown by diffusion of $CH_2Cl_2$ into a DMSO solution. Data collection: Siemens Smart CCD diffractometer ($\lambda$ = 0.71073 Å). The structure was solved by direct methods and was refined using the SHELXTL 5.1 software package. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned to ideal positions and refined using a riding model. CCDC 182/1880. See http://www.rsc.org/suppdata/cc/b0/b008038l for crystallographic files in .cif format. The diffraction frames were integrated using the SAINT[17] package and corrected for absorption with SADABS.[18]

§ *General Heck procedure*: NaOAc (360 mg, 4.4 mmol) and the catalyst were placed in a 3-necked flask fitted with a reflux condenser and degassed. Aryl halide (4 mmol), styrene (640 µL, 5.6 mmol), and solvent (DMA or DEA, 5 mL), were added under Ar or air. The reaction vessel was placed into an oil bath preheated to the desired temperature. Aliquots (200 µL) were removed after fixed times and added to 10 mL $CH_2Cl_2$. The organic layer was extracted five times with 10 mL portions of water and dried with $MgSO_4$. The mixture was then filtered and the $CH_2Cl_2$ removed *in vacuo*. The residue was dissolved in $CDCl_3$ or $CD_2Cl_2$ and analyzed by $^1$H NMR (400 MHz).

1 R. H. Crabtree, *The Organometallic Chemistry of the Transition Metals*, 3rd edn., Wiley, New York, 2001.

2 P. Garrou, *Chem. Rev.*, 1981, **81**, 229.

3 M. J. Burk and R. H. Crabtree, *J. Am. Chem. Soc.*, 1987, **109**, 8025.

4 A. J. Arduengo, III, R. L. Harlow and M. Kline, *J. Am. Chem. Soc.*, 1991, **113**, 361; A. J. Arduengo, III, *Acc. Chem. Res.*, 1999, **32**, 913.

5 K. Öfele, W. A. Herrmann, D. Mihalios, M. Elison, E. Herdtweck, W. Scherer and J. Mink, *J. Organomet. Chem.*, 1993, **459**, 177.

6 (*a*) V. P. W. Böhm, C. W. K. Gstottmayr, T. Weskamp and W. A. Herrmann, *J. Organomet. Chem.*, 2000, **595**, 186; (*b*) J. Schwarz, V. P. W. Böhm, M. G. Gardiner, M. Grosche, W. A. Herrmann, W. Hieringer and G. Raudaschl-Sieber, *Chem. Eur. J.*, 2000, **6**, 1773; (*c*) T. Weskamp, V. P. W. Böhm and W. A. Herrmann, *J. Organomet. Chem.*, 1999, **585**, 348; (*d*) W. A. Herrmann, C.-P. Reisinger and M. Spiegler, *J. Organomet. Chem.*, 1998, **557**, 93; (*e*) W. A. Herrmann, M. Elison, J. Fischer, C. Köcher and G. R. J. Artus, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2371; (*f*) C. Zhang and M. L. Trudell, *Tetrahedron Lett.*, 2000, **41**, 595; (*g*) C. Zhang, J. Huang, M. L. Trudell and S. P. Nolan, *J. Org. Chem.*, 1999, **64**, 3804; (*h*) J. Huang and S. P. Nolan, *J. Am. Chem. Soc.*, 1999, **121**, 9889; (*i*) D. S. McGuiness and K. J. Cavell, *Organometallics*, 2000, **19**, 741; (*j*) D. S. McGuiness, K. J. Cavell, B. W. Skelton and A. H. White, *Organometallics*, 1999, **18**, 1596.

7 S. R. Stauffer, S. Lee, J. P. Stambuli, S. I. Hauck and J. F. Hartwig, *Org. Lett.*, 2000, **2**, 1423; J. Huang, G. Grasa and S. P. Nolan, *Org. Lett.*, 1999, **1**, 1307.

8 C. W. Bielawski and R. H. Grubbs, *Angew. Chem., Int. Ed.*, 2000, **39**, 2903; M. Scholl, S. Ding, C. W. Lee and R. H. Grubbs, *Org. Lett.*, 1999, **1**, 953; T. Weskamp, F. J. Kohl, W. Hieringer, D. Gleigh and W. A. Herrmann, *Angew. Chem., Int. Ed.*, 1999, **38**, 2416; U. Frenzel, T. Weskamp, F. J. Kohl, W. C. Schattenman, O. Nuyken and W. A. Herrmann, *J. Organomet. Chem.*, 1999, **586**, 263; J. Huang, E. D. Stevens, S. P. Nolan and J. L. Petersen, *J. Am. Chem. Soc.*, 1999, **121**, 2674; J. K. Huang, H. J. Schanz, E. D. Stevens and S. P. Nolan, *Organometallics*, 1999, **18**, 5375; S. B. Garber, J. S. Kingsbury, B. L. Gray and A. H. Hoveyda, *J. Am. Chem. Soc.*, 2000, **122**, 8168.

9 C. M. Jensen, *Chem. Commun.*, 1999, 2443; C. J. Moulton and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1976, 1020.

10 (*a*) D. Morales-Morales, R. Redón, C. Yung and C. M. Jensen, *Chem. Commun.*, 2000, 1619; (*b*) D. Morales-Morales, C. Grause, K. Kasaoka, R. Redón, R. E. Cramer and C. M. Jensen, *Inorg. Chim. Acta*, 2000, **300**–**302**, 958; (*c*) M. Ohff, A. Ohff, M. E. van der Boom and D. Milstein, *J. Am. Chem. Soc.*, 1997, **119**, 11687; (*d*) I. P. Beletskaya, A. V. Chuchurjukin, H. P. Dijkstra, G. P. M. van Klink and G. van Koten, *Tetrahedron Lett.*, 2000, **41**, 1075; (*e*) D. E. Bergbreiter, P. L. Osburn and Y. S. Liu, *J. Am. Chem. Soc.*, 1999, **121**, 9531.

11 J. C. C. Chen and I. J. B. Lin, *J. Chem. Soc., Dalton Trans.*, 2000, 839.

12 W. A. Herrmann, C. Brossmer, C.-P. Reisinger, T. H. Riermeier, K. Öfele and M. Beller, *Chem. Eur. J.*, 1997, **3**, 1357.

13 M. Nowotny, U. Hanefeld, H. van Koningsveld and T. Maschmeyer, *Chem Commun.*, 2000, 1877; M. T. Reetz and E. Westermann, *Angew. Chem., Int. Ed.*, 2000, **39**, 165.

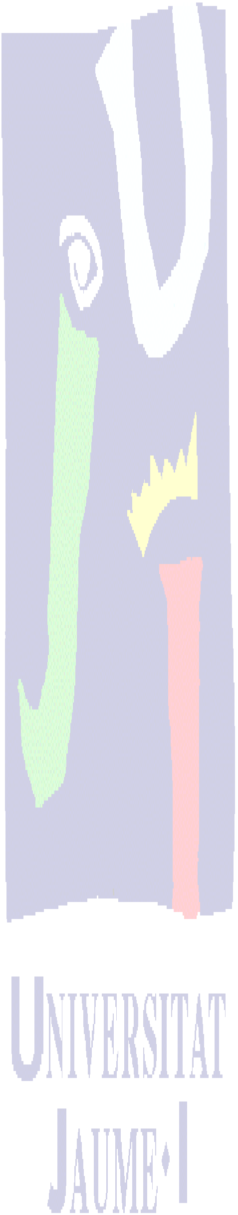
14 D. R. Anton and R. H. Crabtree, *Organometallics*, 1983, **2**, 855; P. Foley, R. DiCosimo and G. M. Whitesides, *J. Am. Chem. Soc.*, 1980, **102**, 6713.

15 C. Amatore and A. Jutand, *Acc. Chem. Res.*, 2000, **33**, 314.

16 O. Eisenstein and E. Clot, personal communication, 2000.

17 SAINT, version 5.0, Bruker Analytical X-ray Systems, Madison, WI.

18 G. M. Sheldrick, SADABS empirical absorption program, University of Göttingen, 1996.



# Capítulo VII

## CONCLUSIONES

*La frase más excitante que se puede oir en ciencia,*
*la que anuncia nuevos descubrimientos,*
*no es “’¡Eureka!”, sino ‘Es extraño…’*

Stephen W. Hawking.

## CONCLUSIONES.

Transcurridos cincuenta años desde el descubrimiento del ferroceno, todavía son muchos los hallazgos y estudios que se realizan en torno a esta molécula. Esta tesis doctoral es una pequeña contribución al desarrollo de la química del ferroceno y las conclusiones generales que hemos alcanzado son:

***1.-*** Las reacciones de acoplamiento carbono-carbono de *Wittig*, *Horner-Emmons-Wadsword* (*HEW*) y *Heck* constituyen una metodología sencilla y eficaz para la obtención de ferrocenos funcionalizados con sistemas conjugados.

***2.-*** La determinación estructural mediante difracción de rayos-*X* en monocristal, nos ha permitido relacionar la estructura molecular con el grado de conjugación de estos sistemas.

***3.-*** La respuesta *ONL* de los cromóforos ferrocénicos investigados es elevada, con valores comparables a los más altos descritos en compuestos organometálicos. Las tendencias generales observadas son:

- Aumento de $\beta$ con el aumento de la cadena conjugada.
- Aumento de la respuesta *ONL* en los sistemas heterobimetálicos.
- Mayores valores de $\beta$ para los isómeros *E*.
- Influencia del contraión sobre la respuesta *ONL*.

***4.-*** Las interacciones débiles, como los enlaces de hidrógeno, producen una transferencia electrónica a larga distancia que se trasmite a través del sistema conjugado. La magnitud de esta interacción ha sido evaluada a partir de la variación de la frecuencia de vibración de los grupos carbonilo.

***5.-*** La comunicación electrónica en sistemas biferrocénicos ha sido analizada mediante técnicas electroquímicas. Los elevados valores de la constante de comproporción, *Kc*, indican la presencia de fuertes interacciones metal-metal.

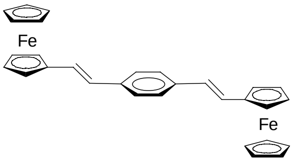
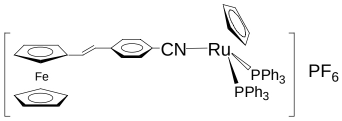
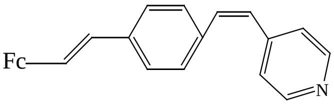
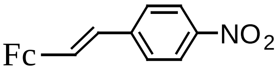
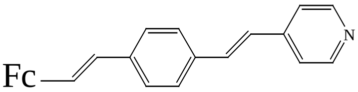
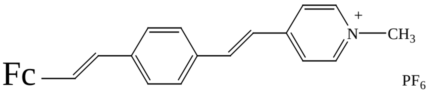
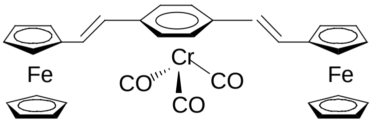
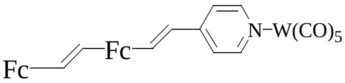
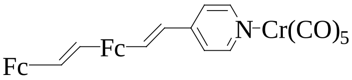
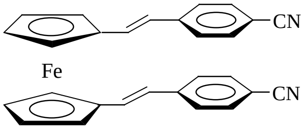
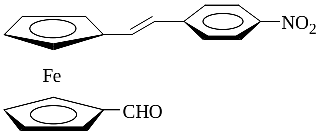
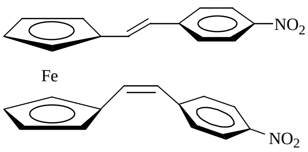
***6.-*** La síntesis de metalodendrímeros hiperconjugados funcionalizados con ferroceno se ha efectuado mediante reacciones de *Heck* utilizando catalizadores termoestables.

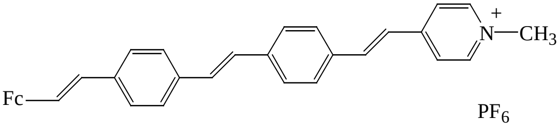
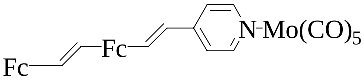
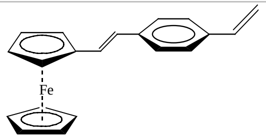
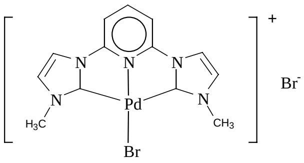
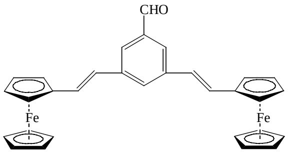
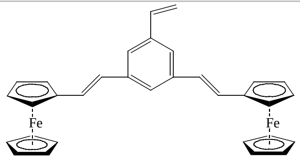
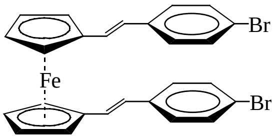
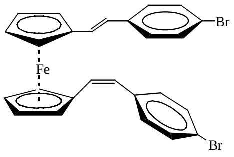
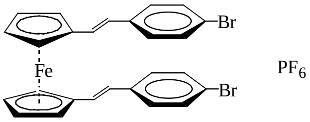
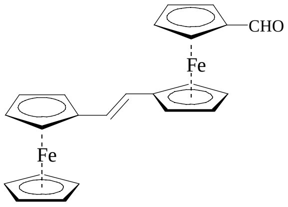
# Tesis Doctoral

## *Estudio de las Propiedades Electrónicas y Ópticas de Ferrocenos Funcionalizados con Sistemas Conjugados.*

Jose A. Mata Martínez

### ***MATERIAL SUPLEMENTARIO***

|  | Identificación | Estructura | Página |
|---|---|---|---|
| 1 | Str29 |  | 208 |
| 2 | Str32 |  | 218 |
| 3 | Str53 |  | 236 |
| 4 | Str54 |  | 243 |
| 5 | Str55 |  | 252 |
| 6 | Str57 |  | 259 |
| 7 | Str67 |  | 267 |
| 8 | Str75 |  | 291 |
| 9 | Str76 |  | 321 |
| 10 | Str94 |  | 347 |
| 11 | Str99 |  | 359 |
| 12 | Str100 |  | 372 |

| | | | |
|---|---|---|---|
| 13 | Str62 |  | 384 |
| 14 | Str105 |  | 397 |
| 15 | Str129 |  | 427 |
| 16 | Str132 |  | 440 |
| 17 | Str157 |  | 447 |
| 18 | Str161 |  | 462 |
| 19 | Str162 |  | 476 |
| 20 | Str174 |  | 487 |
| 21 | Str193 |  | 497 |
| 22 | Str196 |  | 511 |

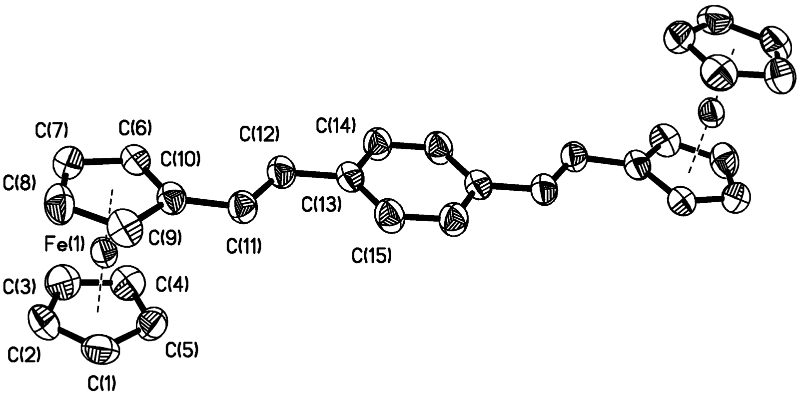

C(7)
C(6)
C(10)
C(12)
C(14)
C(8)
C(13)
Fe(1)
C(9)
C(11)
C(15)
C(3)
C(4)
C(2)
C(5)
C(1)

**Table 1**. Crystal data and structure refinement for str29m.

| | | |
|---|---|---|
| Identification code | str29m | |
| Empirical formula | C30 H26 Fe2 | |
| Formula weight | 498.21 | |
| Temperature | 293(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | P2(1)/c | |
| Unit cell dimensions | a = 12.7324(4) Å | $\alpha$= 90°. |
| | b = 7.7128(2) Å | $\beta$= 98.5460(10)°. |
| | c = 11.6266(5) Å | $\gamma$ = 90°. |
| Volume | 1129.08(7) Å$^3$ | |
| Z | 2 | |
| Density (calculated) | 1.465 Mg/m$^3$ | |
| Absorption coefficient | 1.300 mm$^{-1}$ | |
| F(000) | 516 | |
| Crystal size | 0.95 x 0.32 x 0.16 mm$^3$ | |
| Theta range for data collection | 1.62 to 30.85°. | |
| Index ranges | -18<=h<=17, -11<=k<=11, -16<=l<=16 | |
| Reflections collected | 12797 | |
| Independent reflections | 3395 [R(int) = 0.0439] | |
| Completeness to theta = 30.85° | 95.6 % | |
| Refinement method | Full-matrix least-squares on F$^2$ | |
| Data / restraints / parameters | 3395 / 0 / 145 | |
| Goodness-of-fit on F$^2$ | 0.919 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0328, wR2 = 0.0669 | |
| R indices (all data) | R1 = 0.0748, wR2 = 0.0760 | |
| Largest diff. peak and hole | 0.303 and -0.229 e.Å$^{-3}$ | |

**Table 2**. Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters (Å$^2$x $10^3$) for str29m. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| Fe(1) | 1863(1) | 1607(1) | 4070(1) | 40(1) |
| C(1) | 396(2) | 2086(3) | 3156(2) | 58(1) |
| C(2) | 484(2) | 2837(3) | 4274(2) | 62(1) |
| C(3) | 1320(2) | 4033(3) | 4383(2) | 61(1) |
| C(4) | 1764(2) | 4024(3) | 3345(2) | 56(1) |
| C(5) | 1188(2) | 2817(3) | 2584(2) | 55(1) |
| C(6) | 3439(1) | 1002(3) | 4522(2) | 47(1) |
| C(7) | 2898(2) | 787(3) | 5489(2) | 53(1) |
| C(8) | 2085(2) | -427(3) | 5194(2) | 55(1) |
| C(9) | 2110(2) | -991(3) | 4032(2) | 50(1) |
| C(10) | 2964(1) | -111(2) | 3615(2) | 42(1) |
| C(11) | 3295(1) | -322(2) | 2470(2) | 43(1) |
| C(12) | 4196(2) | 276(2) | 2184(2) | 45(1) |
| C(13) | 4595(1) | 97(2) | 1068(2) | 41(1) |
| C(14) | 5488(2) | 1020(3) | 878(2) | 48(1) |
| C(15) | 4115(2) | -938(3) | 162(2) | 48(1) |

**Table 3**. Bond lengths [Å] and angles [°] for str29m.

| | |
|---|---|
| Fe(1)-C(9) | 2.030(2) |
| Fe(1)-C(8) | 2.034(2) |
| Fe(1)-C(5) | 2.038(2) |
| Fe(1)-C(2) | 2.040(2) |
| Fe(1)-C(1) | 2.040(2) |
| Fe(1)-C(4) | 2.042(2) |
| Fe(1)-C(3) | 2.046(2) |
| Fe(1)-C(6) | 2.0515(18) |
| Fe(1)-C(7) | 2.053(2) |
| Fe(1)-C(10) | 2.0545(17) |
| C(1)-C(5) | 1.405(3) |
| C(1)-C(2) | 1.412(3) |
| C(2)-C(3) | 1.400(3) |
| C(3)-C(4) | 1.407(3) |
| C(4)-C(5) | 1.412(3) |
| C(6)-C(7) | 1.413(2) |
| C(6)-C(10) | 1.423(3) |
| C(7)-C(8) | 1.400(3) |
| C(8)-C(9) | 1.423(3) |
| C(9)-C(10) | 1.426(2) |
| C(10)-C(11) | 1.464(2) |
| C(11)-C(12) | 1.323(2) |
| C(12)-C(13) | 1.469(2) |
| C(13)-C(14) | 1.387(2) |
| C(13)-C(15) | 1.389(3) |
| C(14)-C(15)#1 | 1.380(2) |
| C(15)-C(14)#1 | 1.380(2) |
| C(9)-Fe(1)-C(8) | 41.01(7) |
| C(9)-Fe(1)-C(5) | 118.76(8) |
| C(8)-Fe(1)-C(5) | 153.99(9) |
| C(9)-Fe(1)-C(2) | 126.93(9) |
| C(8)-Fe(1)-C(2) | 108.94(9) |
| C(5)-Fe(1)-C(2) | 67.89(9) |
| C(9)-Fe(1)-C(1) | 107.51(9) |
| C(8)-Fe(1)-C(1) | 120.26(9) |
| C(5)-Fe(1)-C(1) | 40.31(8) |
| C(2)-Fe(1)-C(1) | 40.49(8) |
| C(9)-Fe(1)-C(4) | 153.18(8) |
| C(8)-Fe(1)-C(4) | 164.42(9) |
| C(5)-Fe(1)-C(4) | 40.50(8) |
| C(2)-Fe(1)-C(4) | 67.79(9) |
| C(1)-Fe(1)-C(4) | 67.92(9) |
| C(9)-Fe(1)-C(3) | 164.65(9) |
| C(8)-Fe(1)-C(3) | 127.56(9) |
| C(5)-Fe(1)-C(3) | 67.72(9) |
| C(2)-Fe(1)-C(3) | 40.08(9) |
| C(1)-Fe(1)-C(3) | 67.66(9) |
| C(4)-Fe(1)-C(3) | 40.25(9) |
| C(9)-Fe(1)-C(6) | 68.40(8) |
| C(8)-Fe(1)-C(6) | 67.83(8) |
| C(5)-Fe(1)-C(6) | 126.45(8) |
| C(2)-Fe(1)-C(6) | 154.44(8) |
| C(1)-Fe(1)-C(6) | 163.60(8) |
| C(4)-Fe(1)-C(6) | 108.11(9) |
| C(3)-Fe(1)-C(6) | 120.37(9) |
| C(9)-Fe(1)-C(7) | 68.30(9) |
| C(8)-Fe(1)-C(7) | 40.08(8) |
| C(5)-Fe(1)-C(7) | 164.13(9) |
| C(2)-Fe(1)-C(7) | 120.74(8) |
| C(1)-Fe(1)-C(7) | 154.61(9) |
| C(4)-Fe(1)-C(7) | 127.26(9) |
| C(3)-Fe(1)-C(7) | 109.39(9) |
| C(6)-Fe(1)-C(7) | 40.28(7) |
| C(9)-Fe(1)-C(10) | 40.86(7) |
| C(8)-Fe(1)-C(10) | 68.46(7) |
| C(5)-Fe(1)-C(10) | 107.15(8) |
| C(2)-Fe(1)-C(10) | 164.09(8) |
| C(1)-Fe(1)-C(10) | 126.10(8) |
| C(4)-Fe(1)-C(10) | 119.00(8) |
| C(3)-Fe(1)-C(10) | 153.76(9) |
| C(6)-Fe(1)-C(10) | 40.56(7) |
| C(7)-Fe(1)-C(10) | 68.11(8) |

| | |
|---|---|
| C(5)-C(1)-C(2) | 107.86(19) |
| C(5)-C(1)-Fe(1) | 69.76(11) |
| C(2)-C(1)-Fe(1) | 69.74(12) |
| C(3)-C(2)-C(1) | 108.00(19) |
| C(3)-C(2)-Fe(1) | 70.20(12) |
| C(1)-C(2)-Fe(1) | 69.77(11) |
| C(2)-C(3)-C(4) | 108.39(19) |
| C(2)-C(3)-Fe(1) | 69.72(12) |
| C(4)-C(3)-Fe(1) | 69.71(12) |
| C(3)-C(4)-C(5) | 107.67(19) |
| C(3)-C(4)-Fe(1) | 70.03(12) |
| C(5)-C(4)-Fe(1) | 69.60(12) |
| C(1)-C(5)-C(4) | 108.07(18) |
| C(1)-C(5)-Fe(1) | 69.93(12) |
| C(4)-C(5)-Fe(1) | 69.90(12) |
| C(7)-C(6)-C(10) | 108.36(18) |
| C(7)-C(6)-Fe(1) | 69.90(11) |
| C(10)-C(6)-Fe(1) | 69.83(10) |
| C(8)-C(7)-C(6) | 108.24(18) |
| C(8)-C(7)-Fe(1) | 69.24(12) |
| C(6)-C(7)-Fe(1) | 69.83(11) |
| C(7)-C(8)-C(9) | 108.49(18) |
| C(7)-C(8)-Fe(1) | 70.68(12) |
| C(9)-C(8)-Fe(1) | 69.35(11) |
| C(8)-C(9)-C(10) | 107.63(18) |
| C(8)-C(9)-Fe(1) | 69.65(12) |
| C(10)-C(9)-Fe(1) | 70.50(11) |
| C(6)-C(10)-C(9) | 107.26(16) |
| C(6)-C(10)-C(11) | 126.30(17) |
| C(9)-C(10)-C(11) | 126.44(17) |
| C(6)-C(10)-Fe(1) | 69.60(10) |
| C(9)-C(10)-Fe(1) | 68.64(10) |
| C(11)-C(10)-Fe(1) | 127.30(13) |
| C(12)-C(11)-C(10) | 124.59(18) |
| C(11)-C(12)-C(13) | 128.02(18) |
| C(14)-C(13)-C(15) | 116.99(16) |
| C(14)-C(13)-C(12) | 119.46(17) |
| C(15)-C(13)-C(12) | 123.54(17) |
| C(15)#1-C(14)-C(13) | 122.12(17) |
| C(14)#1-C(15)-C(13) | 120.89(18) |

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y,-z

**Table 4**. Anisotropic displacement parameters (Å$^2$x 10$^3$) for str29m. The anisotropic displacement factor exponent takes the form: $-2\pi^2$[ $h^2$ $a^{*2}U^{11}$ + ... + 2 h k a* b* $U^{12}$ ]

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| Fe(1) | 38(1) | 43(1) | 39(1) | -4(1) | 12(1) | 0(1) |
| C(1) | 41(1) | 65(1) | 64(1) | -5(1) | -2(1) | 1(1) |
| C(2) | 47(1) | 79(2) | 64(1) | -3(1) | 20(1) | 14(1) |
| C(3) | 66(2) | 55(1) | 62(1) | -16(1) | 6(1) | 15(1) |
| C(4) | 61(1) | 45(1) | 63(1) | 8(1) | 11(1) | 4(1) |
| C(5) | 60(1) | 61(1) | 42(1) | 1(1) | 6(1) | 12(1) |
| C(6) | 39(1) | 58(1) | 45(1) | -4(1) | 9(1) | 3(1) |
| C(7) | 52(1) | 68(1) | 40(1) | -1(1) | 8(1) | 7(1) |
| C(8) | 65(1) | 56(1) | 49(1) | 10(1) | 26(1) | 6(1) |
| C(9) | 53(1) | 39(1) | 60(1) | 1(1) | 15(1) | -2(1) |
| C(10) | 44(1) | 40(1) | 43(1) | 1(1) | 12(1) | 5(1) |
| C(11) | 46(1) | 43(1) | 42(1) | -5(1) | 10(1) | 4(1) |
| C(12) | 46(1) | 47(1) | 44(1) | -8(1) | 11(1) | 3(1) |
| C(13) | 40(1) | 41(1) | 43(1) | -2(1) | 11(1) | 5(1) |
| C(14) | 46(1) | 54(1) | 47(1) | -13(1) | 11(1) | -7(1) |
| C(15) | 42(1) | 53(1) | 52(1) | -10(1) | 16(1) | -8(1) |

**Table 5**. Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters ($Å^2$x 10 $^3$) for str29m.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1) | -98 | 1256 | 2852 | 69 |
| H(2) | 61 | 2582 | 4838 | 74 |
| H(3) | 1544 | 4717 | 5032 | 74 |
| H(4) | 2334 | 4692 | 3189 | 68 |
| H(5) | 1311 | 2553 | 1835 | 65 |
| H(6) | 4009 | 1744 | 4484 | 57 |
| H(7) | 3055 | 1355 | 6200 | 64 |
| H(8) | 1609 | -802 | 5675 | 66 |
| H(9) | 1653 | -1790 | 3620 | 60 |
| H(11) | 2842 | -918 | 1905 | 52 |
| H(12) | 4629 | 885 | 2761 | 54 |
| H(14) | 5830 | 1718 | 1471 | 58 |
| H(15) | 3517 | -1585 | 258 | 58 |

**Table 6**. Torsion angles [°] for str29m.

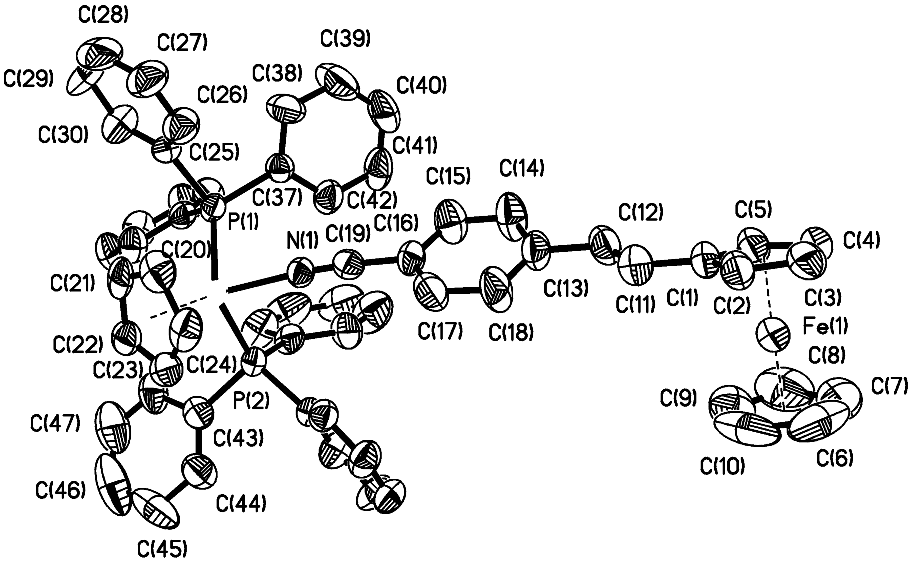
| | |
|---|---|
| C(9)-Fe(1)-C(1)-C(5) | -114.09(13) |
| C(8)-Fe(1)-C(1)-C(5) | -157.03(12) |
| C(2)-Fe(1)-C(1)-C(5) | 118.98(19) |
| C(4)-Fe(1)-C(1)-C(5) | 37.78(13) |
| C(3)-Fe(1)-C(1)-C(5) | 81.42(14) |
| C(6)-Fe(1)-C(1)-C(5) | -41.2(4) |
| C(7)-Fe(1)-C(1)-C(5) | 169.78(18) |
| C(10)-Fe(1)-C(1)-C(5) | -72.80(15) |
| C(9)-Fe(1)-C(1)-C(2) | 126.93(14) |
| C(8)-Fe(1)-C(1)-C(2) | 83.99(15) |
| C(5)-Fe(1)-C(1)-C(2) | -118.98(19) |
| C(4)-Fe(1)-C(1)-C(2) | -81.20(15) |
| C(3)-Fe(1)-C(1)-C(2) | -37.56(13) |
| C(6)-Fe(1)-C(1)-C(2) | -160.2(3) |
| C(7)-Fe(1)-C(1)-C(2) | 50.8(3) |
| C(10)-Fe(1)-C(1)-C(2) | 168.22(12) |
| C(5)-C(1)-C(2)-C(3) | 0.5(2) |
| Fe(1)-C(1)-C(2)-C(3) | 60.04(15) |
| C(5)-C(1)-C(2)-Fe(1) | -59.58(14) |
| C(9)-Fe(1)-C(2)-C(3) | 168.64(12) |
| C(8)-Fe(1)-C(2)-C(3) | 126.38(13) |
| C(5)-Fe(1)-C(2)-C(3) | -81.22(14) |
| C(1)-Fe(1)-C(2)-C(3) | -118.87(19) |
| C(4)-Fe(1)-C(2)-C(3) | -37.33(13) |
| C(6)-Fe(1)-C(2)-C(3) | 48.3(3) |
| C(7)-Fe(1)-C(2)-C(3) | 83.87(15) |
| C(10)-Fe(1)-C(2)-C(3) | -155.9(3) |
| C(9)-Fe(1)-C(2)-C(1) | -72.49(16) |
| C(8)-Fe(1)-C(2)-C(1) | -114.75(14) |
| C(5)-Fe(1)-C(2)-C(1) | 37.65(13) |
| C(4)-Fe(1)-C(2)-C(1) | 81.54(14) |
| C(3)-Fe(1)-C(2)-C(1) | 118.87(19) |
| C(6)-Fe(1)-C(2)-C(1) | 167.21(18) |
| C(7)-Fe(1)-C(2)-C(1) | -157.26(13) |
| C(10)-Fe(1)-C(2)-C(1) | -37.0(4) |
| C(1)-C(2)-C(3)-C(4) | -0.6(2) |
| Fe(1)-C(2)-C(3)-C(4) | 59.18(15) |
| C(1)-C(2)-C(3)-Fe(1) | -59.77(15) |
| C(9)-Fe(1)-C(3)-C(2) | -36.5(4) |
| C(8)-Fe(1)-C(3)-C(2) | -73.86(16) |
| C(5)-Fe(1)-C(3)-C(2) | 81.67(14) |
| C(1)-Fe(1)-C(3)-C(2) | 37.93(13) |
| C(4)-Fe(1)-C(3)-C(2) | 119.67(19) |
| C(6)-Fe(1)-C(3)-C(2) | -158.06(12) |
| C(7)-Fe(1)-C(3)-C(2) | -115.05(13) |
| C(10)-Fe(1)-C(3)-C(2) | 165.32(16) |
| C(9)-Fe(1)-C(3)-C(4) | -156.2(3) |
| C(8)-Fe(1)-C(3)-C(4) | 166.47(13) |
| C(5)-Fe(1)-C(3)-C(4) | -38.01(13) |
| C(2)-Fe(1)-C(3)-C(4) | -119.67(19) |
| C(1)-Fe(1)-C(3)-C(4) | -81.74(14) |
| C(6)-Fe(1)-C(3)-C(4) | 82.27(14) |
| C(7)-Fe(1)-C(3)-C(4) | 125.28(13) |
| C(10)-Fe(1)-C(3)-C(4) | 45.7(2) |
| C(2)-C(3)-C(4)-C(5) | 0.5(2) |
| Fe(1)-C(3)-C(4)-C(5) | 59.67(14) |
| C(2)-C(3)-C(4)-Fe(1) | -59.19(15) |
| C(9)-Fe(1)-C(4)-C(3) | 166.29(17) |
| C(8)-Fe(1)-C(4)-C(3) | -43.7(4) |
| C(5)-Fe(1)-C(4)-C(3) | 118.67(18) |
| C(2)-Fe(1)-C(4)-C(3) | 37.18(13) |
| C(1)-Fe(1)-C(4)-C(3) | 81.05(14) |
| C(6)-Fe(1)-C(4)-C(3) | -115.91(13) |
| C(7)-Fe(1)-C(4)-C(3) | -75.35(15) |
| C(10)-Fe(1)-C(4)-C(3) | -158.81(12) |
| C(9)-Fe(1)-C(4)-C(5) | 47.6(2) |
| C(8)-Fe(1)-C(4)-C(5) | -162.3(3) |
| C(2)-Fe(1)-C(4)-C(5) | -81.49(13) |
| C(1)-Fe(1)-C(4)-C(5) | -37.62(12) |
| C(3)-Fe(1)-C(4)-C(5) | -118.67(18) |
| C(6)-Fe(1)-C(4)-C(5) | 125.43(12) |
| C(7)-Fe(1)-C(4)-C(5) | 165.98(11) |
| C(10)-Fe(1)-C(4)-C(5) | 82.53(14) |

| | | | |
|---|---|---|---|
| C(2)-C(1)-C(5)-C(4) | -0.2(2) | C(10)-C(6)-C(7)-C(8) | -0.7(2) |
| Fe(1)-C(1)-C(5)-C(4) | -59.73(14) | Fe(1)-C(6)-C(7)-C(8) | 58.76(15) |
| C(2)-C(1)-C(5)-Fe(1) | 59.57(15) | C(10)-C(6)-C(7)-Fe(1) | -59.45(13) |
| C(3)-C(4)-C(5)-C(1) | -0.2(2) | C(9)-Fe(1)-C(7)-C(8) | -37.96(12) |
| Fe(1)-C(4)-C(5)-C(1) | 59.75(14) | C(5)-Fe(1)-C(7)-C(8) | -157.6(3) |
| C(3)-C(4)-C(5)-Fe(1) | -59.94(14) | C(2)-Fe(1)-C(7)-C(8) | 83.09(14) |
| C(9)-Fe(1)-C(5)-C(1) | 83.31(14) | C(1)-Fe(1)-C(7)-C(8) | 47.3(3) |
| C(8)-Fe(1)-C(5)-C(1) | 50.2(2) | C(4)-Fe(1)-C(7)-C(8) | 167.34(12) |
| C(2)-Fe(1)-C(5)-C(1) | -37.81(13) | C(3)-Fe(1)-C(7)-C(8) | 125.83(13) |
| C(4)-Fe(1)-C(5)-C(1) | -119.04(18) | C(6)-Fe(1)-C(7)-C(8) | -119.73(18) |
| C(3)-Fe(1)-C(5)-C(1) | -81.26(14) | C(10)-Fe(1)-C(7)-C(8) | -82.12(12) |
| C(6)-Fe(1)-C(5)-C(1) | 166.62(12) | C(9)-Fe(1)-C(7)-C(6) | 81.77(13) |
| C(7)-Fe(1)-C(5)-C(1) | -163.8(3) | C(8)-Fe(1)-C(7)-C(6) | 119.73(18) |
| C(10)-Fe(1)-C(5)-C(1) | 126.13(13) | C(5)-Fe(1)-C(7)-C(6) | -37.8(4) |
| C(9)-Fe(1)-C(5)-C(4) | -157.65(12) | C(2)-Fe(1)-C(7)-C(6) | -157.18(13) |
| C(8)-Fe(1)-C(5)-C(4) | 169.28(17) | C(1)-Fe(1)-C(7)-C(6) | 166.99(18) |
| C(2)-Fe(1)-C(5)-C(4) | 81.23(13) | C(4)-Fe(1)-C(7)-C(6) | -72.93(15) |
| C(1)-Fe(1)-C(5)-C(4) | 119.04(18) | C(3)-Fe(1)-C(7)-C(6) | -114.44(14) |
| C(3)-Fe(1)-C(5)-C(4) | 37.79(13) | C(10)-Fe(1)-C(7)-C(6) | 37.61(12) |
| C(6)-Fe(1)-C(5)-C(4) | -74.34(15) | C(6)-C(7)-C(8)-C(9) | 0.1(2) |
| C(7)-Fe(1)-C(5)-C(4) | -44.8(3) | Fe(1)-C(7)-C(8)-C(9) | 59.24(14) |
| C(10)-Fe(1)-C(5)-C(4) | -114.83(13) | C(6)-C(7)-C(8)-Fe(1) | -59.12(14) |
| C(9)-Fe(1)-C(6)-C(7) | -81.49(14) | C(9)-Fe(1)-C(8)-C(7) | 119.43(17) |
| C(8)-Fe(1)-C(6)-C(7) | -37.14(13) | C(5)-Fe(1)-C(8)-C(7) | 166.22(16) |
| C(5)-Fe(1)-C(6)-C(7) | 167.96(13) | C(2)-Fe(1)-C(8)-C(7) | -115.57(12) |
| C(2)-Fe(1)-C(6)-C(7) | 50.6(3) | C(1)-Fe(1)-C(8)-C(7) | -158.62(12) |
| C(1)-Fe(1)-C(6)-C(7) | -160.0(3) | C(4)-Fe(1)-C(8)-C(7) | -40.5(4) |
| C(4)-Fe(1)-C(6)-C(7) | 126.82(13) | C(3)-Fe(1)-C(8)-C(7) | -74.73(15) |
| C(3)-Fe(1)-C(6)-C(7) | 84.47(15) | C(6)-Fe(1)-C(8)-C(7) | 37.31(11) |
| C(10)-Fe(1)-C(6)-C(7) | -119.46(17) | C(10)-Fe(1)-C(8)-C(7) | 81.17(12) |
| C(9)-Fe(1)-C(6)-C(10) | 37.97(11) | C(5)-Fe(1)-C(8)-C(9) | 46.8(2) |
| C(8)-Fe(1)-C(6)-C(10) | 82.32(12) | C(2)-Fe(1)-C(8)-C(9) | 125.00(13) |
| C(5)-Fe(1)-C(6)-C(10) | -72.58(14) | C(1)-Fe(1)-C(8)-C(9) | 81.95(14) |
| C(2)-Fe(1)-C(6)-C(10) | 170.04(18) | C(4)-Fe(1)-C(8)-C(9) | -159.9(3) |
| C(1)-Fe(1)-C(6)-C(10) | -40.6(3) | C(3)-Fe(1)-C(8)-C(9) | 165.83(12) |
| C(4)-Fe(1)-C(6)-C(10) | -113.72(12) | C(6)-Fe(1)-C(8)-C(9) | -82.12(13) |
| C(3)-Fe(1)-C(6)-C(10) | -156.07(12) | C(7)-Fe(1)-C(8)-C(9) | -119.43(17) |
| C(7)-Fe(1)-C(6)-C(10) | 119.46(17) | C(10)-Fe(1)-C(8)-C(9) | -38.26(11) |

| | |
|---|---|
| C(7)-C(8)-C(9)-C(10) | 0.5(2) |
| Fe(1)-C(8)-C(9)-C(10) | 60.55(13) |
| C(7)-C(8)-C(9)-Fe(1) | -60.07(15) |
| C(5)-Fe(1)-C(9)-C(8) | -158.62(12) |
| C(2)-Fe(1)-C(9)-C(8) | -75.77(15) |
| C(1)-Fe(1)-C(9)-C(8) | -116.26(13) |
| C(4)-Fe(1)-C(9)-C(8) | 168.20(17) |
| C(3)-Fe(1)-C(9)-C(8) | -47.1(4) |
| C(6)-Fe(1)-C(9)-C(8) | 80.61(13) |
| C(7)-Fe(1)-C(9)-C(8) | 37.12(12) |
| C(10)-Fe(1)-C(9)-C(8) | 118.31(17) |
| C(8)-Fe(1)-C(9)-C(10) | -118.31(17) |
| C(5)-Fe(1)-C(9)-C(10) | 83.08(13) |
| C(2)-Fe(1)-C(9)-C(10) | 165.92(11) |
| C(1)-Fe(1)-C(9)-C(10) | 125.43(12) |
| C(4)-Fe(1)-C(9)-C(10) | 49.9(2) |
| C(3)-Fe(1)-C(9)-C(10) | -165.4(3) |
| C(6)-Fe(1)-C(9)-C(10) | -37.70(11) |
| C(7)-Fe(1)-C(9)-C(10) | -81.18(12) |
| C(7)-C(6)-C(10)-C(9) | 1.0(2) |
| Fe(1)-C(6)-C(10)-C(9) | -58.51(13) |
| C(7)-C(6)-C(10)-C(11) | -178.56(17) |
| Fe(1)-C(6)-C(10)-C(11) | 121.95(18) |
| C(7)-C(6)-C(10)-Fe(1) | 59.49(14) |
| C(8)-C(9)-C(10)-C(6) | -0.9(2) |
| Fe(1)-C(9)-C(10)-C(6) | 59.11(13) |
| C(8)-C(9)-C(10)-C(11) | 178.64(18) |
| Fe(1)-C(9)-C(10)-C(11) | -121.34(18) |
| C(8)-C(9)-C(10)-Fe(1) | -60.01(14) |
| C(9)-Fe(1)-C(10)-C(6) | -119.03(16) |
| C(8)-Fe(1)-C(10)-C(6) | -80.64(12) |
| C(5)-Fe(1)-C(10)-C(6) | 126.57(12) |
| C(2)-Fe(1)-C(10)-C(6) | -164.2(3) |
| C(1)-Fe(1)-C(10)-C(6) | 166.87(12) |
| C(4)-Fe(1)-C(10)-C(6) | 84.21(13) |
| C(3)-Fe(1)-C(10)-C(6) | 52.3(2) |
| C(7)-Fe(1)-C(10)-C(6) | -37.35(12) |
| C(8)-Fe(1)-C(10)-C(9) | 38.39(11) |
| C(5)-Fe(1)-C(10)-C(9) | -114.40(12) |
| C(2)-Fe(1)-C(10)-C(9) | -45.2(3) |
| C(1)-Fe(1)-C(10)-C(9) | -74.10(14) |
| C(4)-Fe(1)-C(10)-C(9) | -156.76(11) |
| C(3)-Fe(1)-C(10)-C(9) | 171.35(17) |
| C(6)-Fe(1)-C(10)-C(9) | 119.03(16) |
| C(7)-Fe(1)-C(10)-C(9) | 81.68(12) |
| C(9)-Fe(1)-C(10)-C(11) | 120.3(2) |
| C(8)-Fe(1)-C(10)-C(11) | 158.65(19) |
| C(5)-Fe(1)-C(10)-C(11) | 5.85(18) |
| C(2)-Fe(1)-C(10)-C(11) | 75.1(3) |
| C(1)-Fe(1)-C(10)-C(11) | 46.2(2) |
| C(4)-Fe(1)-C(10)-C(11) | -36.5(2) |
| C(3)-Fe(1)-C(10)-C(11) | -68.4(3) |
| C(6)-Fe(1)-C(10)-C(11) | -120.7(2) |
| C(7)-Fe(1)-C(10)-C(11) | -158.06(19) |
| C(6)-C(10)-C(11)-C(12) | 11.9(3) |
| C(9)-C(10)-C(11)-C(12) | -167.53(19) |
| Fe(1)-C(10)-C(11)-C(12) | 102.9(2) |
| C(10)-C(11)-C(12)-C(13) | 178.88(17) |
| C(11)-C(12)-C(13)-C(14) | 171.0(2) |
| C(11)-C(12)-C(13)-C(15) | -7.8(3) |
| C(15)-C(13)-C(14)-C(15)#1 | 0.5(3) |
| C(12)-C(13)-C(14)-C(15)#1 | -178.39(18) |
| C(14)-C(13)-C(15)-C(14)#1 | -0.5(3) |
| C(12)-C(13)-C(15)-C(14)#1 | 178.34(18) |

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y,-z


C(28)
C(27)
C(39)
C(29)
C(38)
C(40)
C(26)
C(30)
C(25)
C(41)
C(15)
C(14)
C(37)
C(42)
C(12)
C(5)
P(1)
C(16)
C(4)
N(1)
C(19)
C(20)
C(13)
C(21)
C(11)
C(1)
C(2)
C(3)
C(17)
C(18)
Fe(1)
C(22)
C(8)
C(23)
C(24)
C(7)
C(9)
P(2)
C(47)
C(43)
C(10)
C(6)
C(46)
C(44)
C(45)

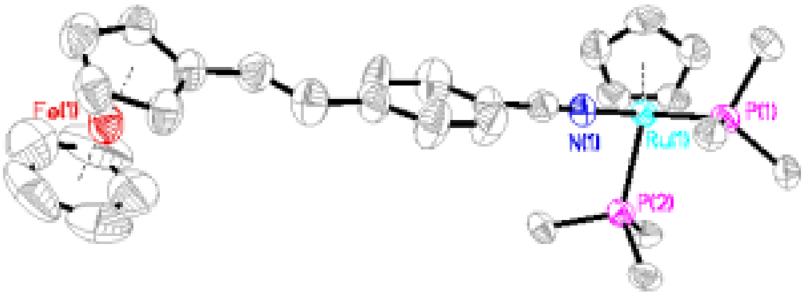

Fe(1)
N(1)
Ru(1)
P(1)
P(2)

**Table 1**. Crystal data and structure refinement for str32m.

| | | |
|---|---|---|
| Identification code | str32m | |
| Empirical formula | C60 H50 B Cl0 F4 Fe N O0 P2 Ru | |
| Formula weight | 1090.68 | |
| Temperature | 293(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | P2(1)/n | |
| Unit cell dimensions | a = 11.3280(7) Å | $\alpha$= 90°. |
| | b = 29.5349(17) Å | $\beta$= 95.778(2)°. |
| | c = 16.7223(9) Å | $\gamma$ = 90°. |
| Volume | 5566.4(6) Å$^3$ | |
| Z | 4 | |
| Density (calculated) | 1.301 Mg/m$^3$ | |
| Absorption coefficient | 0.640 mm$^{-1}$ | |
| F(000) | 2232 | |
| Crystal size | 0.32 x 0.18 x 0.05 mm$^3$ | |
| Theta range for data collection | 1.38 to 23.28°. | |
| Index ranges | -12<=h<=12, -32<=k<=21, -18<=l<=18 | |
| Reflections collected | 27054 | |
| Independent reflections | 8026 [R(int) = 0.0872] | |
| Completeness to theta = 23.28° | 99.9 % | |
| Absorption correction | Bruker SADABS | |
| Max. and min. transmission | 0.970265 and 0.822843 | |
| Refinement method | Full-matrix least-squares on F$^2$ | |
| Data / restraints / parameters | 8026 / 0 / 598 | |
| Goodness-of-fit on F$^2$ | 1.195 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0785, wR2 = 0.2264 | |
| R indices (all data) | R1 = 0.1370, wR2 = 0.2572 | |
| Largest diff. peak and hole | 1.660 and -0.859 e.Å$^{-3}$ | |

**Table 2**. Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters (Å$^2$x $10^3$) for str32m. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| Ru(1) | 23707(1) | -6727(1) | -14662(1) | 38(1) |
| Fe(1) | 17652(2) | -5348(1) | -20792(1) | 59(1) |
| P(1) | 22494(2) | -6704(1) | -13604(1) | 41(1) |
| C(1) | 17916(10) | -5119(4) | -19626(6) | 55(3) |
| N(1) | 22379(7) | -6442(3) | -15397(5) | 44(2) |
| B(1) | 14928(9) | -5881(3) | -17510(6) | 400(30) |
| F(1) | 14288(15) | -5715(6) | -17022(10) | 369(12) |
| P(2) | 23264(2) | -7440(1) | -15244(1) | 42(1) |
| C(2) | 18224(10) | -4782(4) | -20161(6) | 58(3) |
| F(2) | 14321(12) | -6085(5) | -18127(8) | 228(6) |
| C(3) | 17234(12) | -4682(4) | -20683(7) | 70(3) |
| F(3) | 15466(14) | -5556(5) | -17824(9) | 265(8) |
| C(4) | 16291(11) | -4950(4) | -20497(6) | 67(3) |
| F(4) | 15646(13) | -6164(5) | -17232(9) | 247(7) |
| C(5) | 16730(10) | -5233(4) | -19836(6) | 60(3) |
| C(6) | 18120(30) | -5461(7) | -21909(11) | 124(7) |
| C(7) | 17090(20) | -5668(9) | -21828(15) | 136(9) |
| C(8) | 17210(20) | -5983(6) | -21154(15) | 121(6) |
| C(9) | 18370(20) | -5966(6) | -20884(11) | 107(5) |
| C(10) | 18946(14) | -5665(9) | -21311(18) | 127(8) |
| C(11) | 18740(11) | -5305(4) | -18990(7) | 62(3) |
| C(12) | 18479(10) | -5547(4) | -18382(7) | 67(3) |
| C(13) | 19343(11) | -5728(4) | -17727(7) | 64(3) |
| C(14) | 18915(11) | -5901(4) | -17028(7) | 78(4) |
| C(15) | 19698(11) | -6074(4) | -16423(7) | 70(3) |
| C(16) | 20897(10) | -6080(3) | -16484(6) | 49(3) |
| C(17) | 21347(11) | -5903(4) | -17150(7) | 72(3) |
| C(18) | 20548(11) | -5738(5) | -17792(7) | 80(4) |
| C(19) | 21720(9) | -6273(3) | -15859(6) | 48(3) |
| C(20) | 24952(10) | -6147(4) | -14419(8) | 66(3) |
| C(21) | 25237(9) | -6497(4) | -13857(7) | 59(3) |
| C(22) | 25560(9) | -6889(4) | -14272(7) | 55(3) |
| C(23) | 25480(9) | -6776(4) | -15081(7) | 58(3) |

| | | | | |
|---|---|---|---|---|
| C(24) | 25117(10) | -6325(5) | -15169(7) | 65(3) |
| C(25) | 22950(9) | -6249(4) | -12899(6) | 48(3) |
| C(26) | 22939(10) | -5801(4) | -13196(7) | 66(3) |
| C(27) | 23238(12) | -5450(5) | -12704(9) | 79(4) |
| C(28) | 23528(12) | -5524(5) | -11900(11) | 100(5) |
| C(29) | 23512(13) | -5949(5) | -11574(8) | 90(5) |
| C(30) | 23237(11) | -6325(4) | -12086(7) | 71(3) |
| C(31) | 22515(9) | -7199(3) | -12958(5) | 45(3) |
| C(32) | 21487(10) | -7400(4) | -12726(6) | 58(3) |
| C(33) | 21574(12) | -7787(4) | -12252(7) | 76(4) |
| C(34) | 22616(12) | -7968(4) | -12002(7) | 71(3) |
| C(35) | 23656(11) | -7783(4) | -12219(7) | 71(3) |
| C(36) | 23591(10) | -7398(4) | -12698(6) | 59(3) |
| C(37) | 20923(9) | -6581(3) | -13818(6) | 46(3) |
| C(38) | 20324(11) | -6261(5) | -13422(9) | 90(4) |
| C(39) | 19142(12) | -6172(5) | -13624(11) | 107(5) |
| C(40) | 18517(11) | -6382(5) | -14228(9) | 81(4) |
| C(41) | 19057(10) | -6723(5) | -14606(7) | 76(4) |
| C(42) | 20252(10) | -6811(4) | -14423(6) | 63(3) |
| C(43) | 24499(9) | -7845(3) | -15037(7) | 55(3) |
| C(44) | 25174(11) | -7987(4) | -15639(8) | 72(3) |
| C(45) | 26117(13) | -8308(5) | -15445(13) | 115(6) |
| C(46) | 26363(15) | -8451(6) | -14655(16) | 123(7) |
| C(47) | 25717(15) | -8285(5) | -14076(12) | 100(5) |
| C(48) | 24808(11) | -8005(4) | -14257(7) | 74(4) |
| C(49) | 23099(9) | -7435(4) | -16345(6) | 48(3) |
| C(50) | 23363(9) | -7049(4) | -16777(6) | 50(3) |
| C(51) | 23309(10) | -7067(4) | -17606(6) | 63(3) |
| C(52) | 22993(11) | -7462(5) | -18000(7) | 76(4) |
| C(53) | 22746(11) | -7850(5) | -17599(7) | 76(4) |
| C(54) | 22773(10) | -7834(4) | -16766(6) | 65(3) |
| C(55) | 21934(9) | -7773(4) | -15050(6) | 53(3) |
| C(56) | 20887(10) | -7713(4) | -15541(8) | 73(4) |
| C(57) | 19863(14) | -7926(6) | -15405(10) | 102(5) |
| C(58) | 19888(15) | -8214(7) | -14763(12) | 117(7) |
| C(59) | 20918(17) | -8295(5) | -14275(9) | 106(6) |
| C(60) | 21945(12) | -8068(4) | -14409(7) | 77(4) |

**Table 3**. Bond lengths [Å] and angles [°] for str32m.

| | |
|---|---|
| Ru(1)-N(1) | 2.027(8) |
| Ru(1)-C(22) | 2.187(11) |
| Ru(1)-C(21) | 2.193(10) |
| Ru(1)-C(23) | 2.197(11) |
| Ru(1)-C(24) | 2.225(10) |
| Ru(1)-C(20) | 2.229(10) |
| Ru(1)-P(1) | 2.348(3) |
| Ru(1)-P(2) | 2.352(3) |
| Fe(1)-C(10) | 2.010(15) |
| Fe(1)-C(9) | 2.010(15) |
| Fe(1)-C(6) | 2.018(15) |
| Fe(1)-C(8) | 2.018(16) |
| Fe(1)-C(7) | 2.020(15) |
| Fe(1)-C(5) | 2.024(11) |
| Fe(1)-C(3) | 2.035(12) |
| Fe(1)-C(4) | 2.039(11) |
| Fe(1)-C(2) | 2.045(11) |
| Fe(1)-C(1) | 2.057(10) |
| P(1)-C(31) | 1.816(10) |
| P(1)-C(37) | 1.817(10) |
| P(1)-C(25) | 1.828(10) |
| C(1)-C(5) | 1.395(15) |
| C(1)-C(2) | 1.405(15) |
| C(1)-C(11) | 1.450(14) |
| N(1)-C(19) | 1.134(11) |
| B(1)-F(4) | 1.226(9) |
| B(1)-F(1) | 1.246(9) |
| B(1)-F(3) | 1.277(9) |
| B(1)-F(2) | 1.325(10) |
| P(2)-C(49) | 1.833(9) |
| P(2)-C(43) | 1.847(11) |
| P(2)-C(55) | 1.855(10) |
| C(2)-C(3) | 1.382(15) |
| C(3)-C(4) | 1.388(17) |
| C(4)-C(5) | 1.435(14) |
| C(6)-C(7) | 1.34(3) |
| C(6)-C(10) | 1.43(3) |
| C(7)-C(8) | 1.46(3) |
| C(8)-C(9) | 1.35(2) |
| C(9)-C(10) | 1.35(2) |
| C(11)-C(12) | 1.302(14) |
| C(12)-C(13) | 1.491(15) |
| C(13)-C(18) | 1.380(16) |
| C(13)-C(14) | 1.407(16) |
| C(14)-C(15) | 1.375(15) |
| C(15)-C(16) | 1.372(14) |
| C(16)-C(17) | 1.373(15) |
| C(16)-C(19) | 1.447(14) |
| C(17)-C(18) | 1.419(15) |
| C(20)-C(24) | 1.391(15) |
| C(20)-C(21) | 1.413(15) |
| C(21)-C(22) | 1.415(15) |
| C(22)-C(23) | 1.386(14) |
| C(23)-C(24) | 1.398(15) |
| C(25)-C(30) | 1.384(14) |
| C(25)-C(26) | 1.413(14) |
| C(26)-C(27) | 1.344(15) |
| C(27)-C(28) | 1.37(2) |
| C(28)-C(29) | 1.37(2) |
| C(29)-C(30) | 1.417(16) |
| C(31)-C(36) | 1.383(14) |
| C(31)-C(32) | 1.397(14) |
| C(32)-C(33) | 1.389(15) |
| C(33)-C(34) | 1.324(16) |
| C(34)-C(35) | 1.379(16) |
| C(35)-C(36) | 1.388(14) |
| C(37)-C(38) | 1.372(14) |
| C(37)-C(42) | 1.382(14) |
| C(38)-C(39) | 1.373(17) |
| C(39)-C(40) | 1.328(18) |
| C(40)-C(41) | 1.365(17) |
| C(41)-C(42) | 1.382(16) |
| C(43)-C(44) | 1.390(15) |

| | |
|---|---|
| C(43)-C(48) | 1.398(15) |
| C(44)-C(45) | 1.441(19) |
| C(45)-C(46) | 1.39(2) |
| C(46)-C(47) | 1.36(2) |
| C(47)-C(48) | 1.331(18) |
| C(49)-C(50) | 1.397(14) |
| C(49)-C(54) | 1.402(14) |
| C(50)-C(51) | 1.382(14) |
| C(51)-C(52) | 1.371(16) |
| C(52)-C(53) | 1.372(17) |
| C(53)-C(54) | 1.392(15) |
| C(55)-C(60) | 1.381(15) |
| C(55)-C(56) | 1.384(15) |
| C(56)-C(57) | 1.359(17) |
| C(57)-C(58) | 1.37(2) |
| C(58)-C(59) | 1.37(2) |
| C(59)-C(60) | 1.380(18) |
| N(1)-Ru(1)-C(22) | 154.6(4) |
| N(1)-Ru(1)-C(21) | 137.5(4) |
| C(22)-Ru(1)-C(21) | 37.7(4) |
| N(1)-Ru(1)-C(23) | 118.8(4) |
| C(22)-Ru(1)-C(23) | 36.9(4) |
| C(21)-Ru(1)-C(23) | 61.7(4) |
| N(1)-Ru(1)-C(24) | 93.8(4) |
| C(22)-Ru(1)-C(24) | 61.7(4) |
| C(21)-Ru(1)-C(24) | 61.1(4) |
| C(23)-Ru(1)-C(24) | 36.9(4) |
| N(1)-Ru(1)-C(20) | 102.1(4) |
| C(22)-Ru(1)-C(20) | 62.8(4) |
| C(21)-Ru(1)-C(20) | 37.3(4) |
| C(23)-Ru(1)-C(20) | 61.8(4) |
| C(24)-Ru(1)-C(20) | 36.4(4) |
| N(1)-Ru(1)-P(1) | 89.4(2) |
| C(22)-Ru(1)-P(1) | 113.5(3) |
| C(21)-Ru(1)-P(1) | 90.8(3) |
| C(23)-Ru(1)-P(1) | 149.9(3) |
| C(24)-Ru(1)-P(1) | 140.3(4) |
| C(20)-Ru(1)-P(1) | 104.3(3) |
| N(1)-Ru(1)-P(2) | 90.3(2) |
| C(22)-Ru(1)-P(2) | 95.0(3) |
| C(21)-Ru(1)-P(2) | 130.8(3) |
| C(23)-Ru(1)-P(2) | 88.4(3) |
| C(24)-Ru(1)-P(2) | 116.8(4) |
| C(20)-Ru(1)-P(2) | 150.2(3) |
| P(1)-Ru(1)-P(2) | 102.72(9) |
| C(10)-Fe(1)-C(9) | 39.2(7) |
| C(10)-Fe(1)-C(6) | 41.7(8) |
| C(9)-Fe(1)-C(6) | 68.5(8) |
| C(10)-Fe(1)-C(8) | 66.8(7) |
| C(9)-Fe(1)-C(8) | 39.0(7) |
| C(6)-Fe(1)-C(8) | 69.4(8) |
| C(10)-Fe(1)-C(7) | 65.9(7) |
| C(9)-Fe(1)-C(7) | 66.7(7) |
| C(6)-Fe(1)-C(7) | 38.6(8) |
| C(8)-Fe(1)-C(7) | 42.3(8) |
| C(10)-Fe(1)-C(5) | 151.2(11) |
| C(9)-Fe(1)-C(5) | 117.2(7) |
| C(6)-Fe(1)-C(5) | 164.1(11) |
| C(8)-Fe(1)-C(5) | 105.1(7) |
| C(7)-Fe(1)-C(5) | 127.7(10) |
| C(10)-Fe(1)-C(3) | 132.6(9) |
| C(9)-Fe(1)-C(3) | 169.7(9) |
| C(6)-Fe(1)-C(3) | 109.1(7) |
| C(8)-Fe(1)-C(3) | 150.7(9) |
| C(7)-Fe(1)-C(3) | 118.2(8) |
| C(5)-Fe(1)-C(3) | 67.9(5) |
| C(10)-Fe(1)-C(4) | 167.4(11) |
| C(9)-Fe(1)-C(4) | 149.7(9) |
| C(6)-Fe(1)-C(4) | 126.4(9) |
| C(8)-Fe(1)-C(4) | 116.0(8) |
| C(7)-Fe(1)-C(4) | 107.3(6) |
| C(5)-Fe(1)-C(4) | 41.4(4) |
| C(3)-Fe(1)-C(4) | 39.8(5) |
| C(10)-Fe(1)-C(2) | 113.4(6) |
| C(9)-Fe(1)-C(2) | 132.2(7) |
| C(6)-Fe(1)-C(2) | 120.9(8) |

| | |
|---|---|
| C(8)-Fe(1)-C(2) | 165.8(9) |
| C(7)-Fe(1)-C(2) | 151.8(11) |
| C(5)-Fe(1)-C(2) | 67.5(5) |
| C(3)-Fe(1)-C(2) | 39.6(4) |
| C(4)-Fe(1)-C(2) | 67.2(5) |
| C(10)-Fe(1)-C(1) | 121.4(8) |
| C(9)-Fe(1)-C(1) | 110.5(6) |
| C(6)-Fe(1)-C(1) | 154.8(10) |
| C(8)-Fe(1)-C(1) | 126.7(8) |
| C(7)-Fe(1)-C(1) | 165.9(11) |
| C(5)-Fe(1)-C(1) | 40.0(4) |
| C(3)-Fe(1)-C(1) | 67.1(4) |
| C(4)-Fe(1)-C(1) | 67.8(4) |
| C(2)-Fe(1)-C(1) | 40.1(4) |
| C(31)-P(1)-C(37) | 103.5(5) |
| C(31)-P(1)-C(25) | 102.9(5) |
| C(37)-P(1)-C(25) | 100.8(5) |
| C(31)-P(1)-Ru(1) | 116.8(3) |
| C(37)-P(1)-Ru(1) | 119.5(3) |
| C(25)-P(1)-Ru(1) | 111.0(3) |
| C(5)-C(1)-C(2) | 107.8(9) |
| C(5)-C(1)-C(11) | 128.7(11) |
| C(2)-C(1)-C(11) | 123.5(11) |
| C(5)-C(1)-Fe(1) | 68.8(6) |
| C(2)-C(1)-Fe(1) | 69.5(6) |
| C(11)-C(1)-Fe(1) | 126.3(8) |
| C(19)-N(1)-Ru(1) | 173.1(8) |
| F(4)-B(1)-F(1) | 115.3 |
| F(4)-B(1)-F(3) | 110.0 |
| F(1)-B(1)-F(3) | 108.0 |
| F(4)-B(1)-F(2) | 105.0 |
| F(1)-B(1)-F(2) | 113.5 |
| F(3)-B(1)-F(2) | 104.7 |
| C(49)-P(2)-C(43) | 101.1(5) |
| C(49)-P(2)-C(55) | 100.2(5) |
| C(43)-P(2)-C(55) | 103.7(5) |
| C(49)-P(2)-Ru(1) | 113.9(4) |
| C(43)-P(2)-Ru(1) | 112.1(3) |
| C(55)-P(2)-Ru(1) | 123.1(3) |
| C(3)-C(2)-C(1) | 108.4(11) |
| C(3)-C(2)-Fe(1) | 69.8(7) |
| C(1)-C(2)-Fe(1) | 70.4(6) |
| C(2)-C(3)-C(4) | 109.3(11) |
| C(2)-C(3)-Fe(1) | 70.6(7) |
| C(4)-C(3)-Fe(1) | 70.2(7) |
| C(3)-C(4)-C(5) | 106.9(11) |
| C(3)-C(4)-Fe(1) | 69.9(7) |
| C(5)-C(4)-Fe(1) | 68.8(6) |
| C(1)-C(5)-C(4) | 107.6(11) |
| C(1)-C(5)-Fe(1) | 71.3(6) |
| C(4)-C(5)-Fe(1) | 69.9(6) |
| C(7)-C(6)-C(10) | 104.6(19) |
| C(7)-C(6)-Fe(1) | 70.7(11) |
| C(10)-C(6)-Fe(1) | 68.8(9) |
| C(6)-C(7)-C(8) | 110.8(18) |
| C(6)-C(7)-Fe(1) | 70.6(10) |
| C(8)-C(7)-Fe(1) | 68.8(9) |
| C(9)-C(8)-C(7) | 104.4(18) |
| C(9)-C(8)-Fe(1) | 70.2(10) |
| C(7)-C(8)-Fe(1) | 68.9(9) |
| C(8)-C(9)-C(10) | 110.8(18) |
| C(8)-C(9)-Fe(1) | 70.8(10) |
| C(10)-C(9)-Fe(1) | 70.4(9) |
| C(9)-C(10)-C(6) | 109.1(17) |
| C(9)-C(10)-Fe(1) | 70.4(10) |
| C(6)-C(10)-Fe(1) | 69.5(9) |
| C(12)-C(11)-C(1) | 127.0(12) |
| C(11)-C(12)-C(13) | 125.9(12) |
| C(18)-C(13)-C(14) | 118.8(10) |
| C(18)-C(13)-C(12) | 122.1(11) |
| C(14)-C(13)-C(12) | 119.0(11) |
| C(15)-C(14)-C(13) | 119.7(11) |
| C(16)-C(15)-C(14) | 121.4(11) |
| C(17)-C(16)-C(15) | 120.4(10) |
| C(17)-C(16)-C(19) | 118.2(10) |
| C(15)-C(16)-C(19) | 121.4(9) |

| | |
|---|---|
| C(16)-C(17)-C(18) | 118.9(11) |
| C(13)-C(18)-C(17) | 120.7(11) |
| N(1)-C(19)-C(16) | 176.3(11) |
| C(24)-C(20)-C(21) | 106.3(11) |
| C(24)-C(20)-Ru(1) | 71.6(6) |
| C(21)-C(20)-Ru(1) | 70.0(6) |
| C(20)-C(21)-C(22) | 108.9(10) |
| C(20)-C(21)-Ru(1) | 72.8(6) |
| C(22)-C(21)-Ru(1) | 71.0(6) |
| C(23)-C(22)-C(21) | 106.8(10) |
| C(23)-C(22)-Ru(1) | 71.9(6) |
| C(21)-C(22)-Ru(1) | 71.3(6) |
| C(22)-C(23)-C(24) | 108.7(10) |
| C(22)-C(23)-Ru(1) | 71.2(6) |
| C(24)-C(23)-Ru(1) | 72.7(6) |
| C(20)-C(24)-C(23) | 109.3(11) |
| C(20)-C(24)-Ru(1) | 72.0(6) |
| C(23)-C(24)-Ru(1) | 70.5(6) |
| C(30)-C(25)-C(26) | 119.3(10) |
| C(30)-C(25)-P(1) | 122.5(9) |
| C(26)-C(25)-P(1) | 118.1(8) |
| C(27)-C(26)-C(25) | 120.9(11) |
| C(26)-C(27)-C(28) | 120.0(13) |
| C(27)-C(28)-C(29) | 121.6(12) |
| C(28)-C(29)-C(30) | 119.3(12) |
| C(25)-C(30)-C(29) | 118.8(12) |
| C(36)-C(31)-C(32) | 117.6(10) |
| C(36)-C(31)-P(1) | 119.2(8) |
| C(32)-C(31)-P(1) | 123.1(8) |
| C(33)-C(32)-C(31) | 119.7(11) |
| C(34)-C(33)-C(32) | 121.4(12) |
| C(33)-C(34)-C(35) | 121.0(12) |
| C(34)-C(35)-C(36) | 118.6(11) |
| C(31)-C(36)-C(35) | 121.5(11) |
| C(38)-C(37)-C(42) | 115.5(10) |
| C(38)-C(37)-P(1) | 124.4(8) |
| C(42)-C(37)-P(1) | 120.1(8) |
| C(37)-C(38)-C(39) | 122.0(12) |
| C(40)-C(39)-C(38) | 122.0(14) |
| C(39)-C(40)-C(41) | 117.9(13) |
| C(40)-C(41)-C(42) | 120.8(12) |
| C(41)-C(42)-C(37) | 121.6(12) |
| C(44)-C(43)-C(48) | 117.9(11) |
| C(44)-C(43)-P(2) | 121.5(9) |
| C(48)-C(43)-P(2) | 120.6(9) |
| C(43)-C(44)-C(45) | 119.0(13) |
| C(46)-C(45)-C(44) | 119.2(16) |
| C(47)-C(46)-C(45) | 119.7(17) |
| C(48)-C(47)-C(46) | 121.3(17) |
| C(47)-C(48)-C(43) | 122.6(14) |
| C(50)-C(49)-C(54) | 119.0(9) |
| C(50)-C(49)-P(2) | 121.4(8) |
| C(54)-C(49)-P(2) | 119.5(8) |
| C(51)-C(50)-C(49) | 119.9(10) |
| C(52)-C(51)-C(50) | 119.8(11) |
| C(51)-C(52)-C(53) | 122.2(11) |
| C(52)-C(53)-C(54) | 118.4(11) |
| C(53)-C(54)-C(49) | 120.7(11) |
| C(60)-C(55)-C(56) | 118.7(11) |
| C(60)-C(55)-P(2) | 121.8(9) |
| C(56)-C(55)-P(2) | 119.4(9) |
| C(57)-C(56)-C(55) | 122.4(14) |
| C(56)-C(57)-C(58) | 118.0(15) |
| C(57)-C(58)-C(59) | 121.5(15) |
| C(58)-C(59)-C(60) | 119.9(15) |
| C(55)-C(60)-C(59) | 119.4(14) |

Symmetry transformations used to generate equivalent atoms:

**Table 4.** Anisotropic displacement parameters (Å$^2$x 10$^3$) for str32m. The anisotropic displacement factor exponent takes the form: -2$\pi^2$[ h$^2$ a*$^2$U$^{11}$ + ... + 2 h k a* b* U$^{12}$ ]

| | U$^{11}$ | U$^{22}$ | U$^{33}$ | U$^{23}$ | U$^{13}$ | U$^{12}$ |
|---|---|---|---|---|---|---|
| Ru(1) | 36(1) | 41(1) | 35(1) | 1(1) | -2(1) | -5(1) |
| Fe(1) | 59(1) | 64(1) | 53(1) | 1(1) | 2(1) | 15(1) |
| P(1) | 40(2) | 46(2) | 37(1) | -3(1) | -1(1) | -4(1) |
| C(1) | 50(7) | 63(8) | 49(6) | 7(6) | -4(5) | 11(6) |
| N(1) | 43(5) | 51(5) | 37(4) | 3(4) | 1(4) | 2(4) |
| P(2) | 40(2) | 46(2) | 39(1) | -1(1) | -2(1) | -3(1) |
| C(2) | 52(7) | 57(7) | 61(7) | 0(6) | -5(6) | 6(6) |
| C(3) | 84(10) | 61(8) | 65(8) | 7(6) | 9(7) | 24(7) |
| C(4) | 65(8) | 78(9) | 56(7) | -5(6) | -5(6) | 27(7) |
| C(5) | 56(8) | 66(8) | 58(7) | 10(6) | 3(6) | 17(6) |
| C(6) | 190(20) | 113(16) | 75(12) | -23(11) | 52(15) | 3(18) |
| C(7) | 129(19) | 150(20) | 120(17) | -90(16) | -49(14) | 54(16) |
| C(8) | 120(18) | 79(12) | 160(20) | -49(13) | 21(14) | -7(11) |
| C(9) | 124(17) | 70(11) | 121(14) | -17(10) | -11(13) | 27(11) |
| C(10) | 58(11) | 130(17) | 200(20) | -105(17) | 32(14) | -6(12) |
| C(11) | 60(8) | 62(8) | 64(7) | 7(6) | 0(6) | -1(6) |
| C(12) | 45(7) | 90(9) | 64(7) | 11(7) | 2(6) | 12(6) |
| C(13) | 66(9) | 65(8) | 57(7) | 8(6) | -14(6) | 13(6) |
| C(14) | 52(8) | 108(11) | 72(8) | 40(8) | -2(6) | -3(7) |
| C(15) | 60(8) | 78(9) | 70(8) | 32(7) | 1(6) | -3(6) |
| C(16) | 55(7) | 50(7) | 40(6) | 8(5) | -5(5) | 2(5) |
| C(17) | 53(8) | 92(9) | 71(8) | 11(7) | 5(6) | 20(7) |
| C(18) | 67(9) | 115(11) | 58(7) | 43(7) | 5(6) | 26(8) |
| C(19) | 51(7) | 43(6) | 51(6) | -1(5) | 5(6) | 4(5) |
| C(20) | 55(8) | 53(8) | 88(9) | 0(7) | 1(6) | -20(6) |
| C(21) | 37(6) | 82(9) | 55(7) | 4(7) | -8(5) | -25(6) |
| C(22) | 44(7) | 56(7) | 63(7) | -8(6) | -2(5) | -8(5) |
| C(23) | 40(6) | 69(9) | 65(8) | -13(7) | 8(5) | -16(6) |
| C(24) | 50(7) | 93(10) | 52(7) | 11(7) | 4(5) | -29(7) |
| C(25) | 43(6) | 53(7) | 47(6) | -12(5) | 4(5) | 3(5) |
| C(26) | 77(9) | 56(8) | 65(8) | -5(7) | 0(6) | -2(6) |
| C(27) | 91(10) | 66(9) | 79(9) | -23(8) | 5(8) | -9(7) |
| C(28) | 74(10) | 83(11) | 143(15) | -72(11) | 16(10) | -18(8) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(29) | 117(12) | 95(11) | 56(8) | -37(8) | -6(7) | -24(9) |
| C(30) | 88(9) | 69(8) | 55(7) | -3(7) | -1(6) | -11(7) |
| C(31) | 46(7) | 57(7) | 33(5) | 1(5) | 6(5) | -1(5) |
| C(32) | 58(8) | 63(8) | 55(6) | 14(6) | 11(5) | 3(6) |
| C(33) | 61(9) | 93(10) | 76(8) | 23(8) | 10(7) | -1(7) |
| C(34) | 86(10) | 57(8) | 67(8) | 18(6) | -1(7) | -4(7) |
| C(35) | 57(8) | 80(9) | 75(8) | 21(7) | -2(6) | 7(7) |
| C(36) | 57(8) | 68(8) | 51(6) | 13(6) | 1(5) | -8(6) |
| C(37) | 41(6) | 48(6) | 47(6) | 0(5) | 4(5) | -2(5) |
| C(38) | 49(8) | 91(10) | 128(11) | -59(9) | 7(8) | 5(7) |
| C(39) | 51(9) | 98(12) | 173(16) | -37(11) | 10(10) | 14(8) |
| C(40) | 35(7) | 109(12) | 97(10) | 19(9) | 6(7) | 3(8) |
| C(41) | 43(8) | 127(12) | 57(7) | 12(8) | -2(6) | -22(8) |
| C(42) | 47(7) | 91(9) | 51(6) | -6(6) | 3(5) | -7(6) |
| C(43) | 51(7) | 40(6) | 71(7) | -7(6) | -1(6) | -3(5) |
| C(44) | 61(8) | 75(9) | 79(8) | 3(7) | 7(7) | 12(7) |
| C(45) | 58(10) | 97(12) | 190(20) | -23(13) | 33(11) | 15(9) |
| C(46) | 70(12) | 87(13) | 200(20) | 61(15) | -35(13) | -12(9) |
| C(47) | 82(12) | 85(11) | 128(14) | 35(11) | -21(10) | -6(9) |
| C(48) | 69(9) | 75(9) | 73(8) | 21(7) | -17(7) | 18(7) |
| C(49) | 44(6) | 56(7) | 40(6) | -7(5) | -5(5) | 7(5) |
| C(50) | 47(7) | 55(7) | 47(6) | -3(5) | -1(5) | -4(5) |
| C(51) | 63(8) | 81(9) | 43(7) | 6(6) | 3(5) | -10(6) |
| C(52) | 67(9) | 120(12) | 40(6) | -11(8) | 0(6) | 7(8) |
| C(53) | 93(10) | 85(10) | 49(7) | -26(7) | -2(7) | -11(8) |
| C(54) | 77(9) | 60(8) | 56(7) | 0(6) | -2(6) | -10(6) |
| C(55) | 47(7) | 56(7) | 55(6) | -12(6) | 6(5) | -16(5) |
| C(56) | 40(7) | 88(9) | 89(9) | -18(7) | -1(6) | -17(6) |
| C(57) | 91(12) | 126(14) | 91(11) | -20(10) | 13(9) | -46(10) |
| C(58) | 76(12) | 161(18) | 119(14) | -68(13) | 41(10) | -67(12) |
| C(59) | 144(16) | 98(12) | 83(10) | -14(9) | 46(11) | -50(12) |
| C(60) | 85(10) | 89(9) | 60(8) | 12(7) | 16(7) | -37(8) |

**Table 5**. Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters (Å$^2$x 10 $^3$) for str32m.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(2) | 18968 | -4650 | -20164 | 69 |
| H(3) | 17203 | -4469 | -21094 | 84 |
| H(4) | 15523 | -4946 | -20751 | 80 |
| H(5) | 16302 | -5453 | -19592 | 73 |
| H(6) | 18264 | -5234 | -22271 | 149 |
| H(7) | 16389 | -5619 | -22157 | 163 |
| H(8) | 16620 | -6156 | -20956 | 145 |
| H(9) | 18724 | -6138 | -20461 | 128 |
| H(10) | 19754 | -5601 | -21231 | 153 |
| H(11) | 19539 | -5244 | -19020 | 75 |
| H(12) | 17682 | -5614 | -18353 | 80 |
| H(14) | 18105 | -5899 | -16975 | 93 |
| H(15) | 19410 | -6189 | -15963 | 84 |
| H(17) | 22162 | -5891 | -17179 | 87 |
| H(18) | 20838 | -5637 | -18260 | 96 |
| H(20) | 24703 | -5856 | -14308 | 79 |
| H(21) | 25215 | -6475 | -13304 | 71 |
| H(22) | 25784 | -7167 | -14046 | 66 |
| H(23) | 25641 | -6969 | -15496 | 70 |
| H(24) | 25004 | -6169 | -15654 | 78 |
| H(26) | 22722 | -5748 | -13739 | 79 |
| H(27) | 23248 | -5158 | -12910 | 95 |
| H(28) | 23740 | -5279 | -11567 | 120 |
| H(29) | 23680 | -5990 | -11023 | 108 |
| H(30) | 23248 | -6617 | -11879 | 85 |
| H(32) | 20748 | -7276 | -12888 | 70 |
| H(33) | 20886 | -7923 | -12106 | 92 |
| H(34) | 22648 | -8224 | -11676 | 85 |
| H(35) | 24385 | -7914 | -12048 | 86 |
| H(36) | 24287 | -7272 | -12848 | 71 |
| H(38) | 20732 | -6099 | -13004 | 108 |
| H(39) | 18768 | -5958 | -13329 | 129 |

|  |  |  |  |  |
|---|---|---|---|---|
| H(40) | 17736 | -6300 | -14388 | 97 |
| H(41) | 18616 | -6897 | -14991 | 91 |
| H(42) | 20612 | -7031 | -14714 | 76 |
| H(44) | 25018 | -7877 | -16160 | 86 |
| H(45) | 26557 | -8417 | -15844 | 137 |
| H(46) | 26965 | -8660 | -14522 | 147 |
| H(47) | 25916 | -8368 | -13543 | 121 |
| H(48) | 24361 | -7913 | -13850 | 88 |
| H(50) | 23574 | -6781 | -16507 | 60 |
| H(51) | 23487 | -6811 | -17895 | 75 |
| H(52) | 22944 | -7467 | -18559 | 91 |
| H(53) | 22565 | -8118 | -17877 | 91 |
| H(54) | 22573 | -8090 | -16485 | 78 |
| H(56) | 20884 | -7519 | -15980 | 87 |
| H(57) | 19167 | -7878 | -15738 | 123 |
| H(58) | 19193 | -8359 | -14654 | 140 |
| H(59) | 20922 | -8502 | -13856 | 128 |
| H(60) | 22638 | -8114 | -14071 | 93 |

Table 6. Torsion angles [°] for str32m.

| | |
|---|---|
| N(1)-Ru(1)-P(1)-C(31) | 138.0(4) |
| C(22)-Ru(1)-P(1)-C(31) | -53.4(5) |
| C(21)-Ru(1)-P(1)-C(31) | -84.5(5) |
| C(23)-Ru(1)-P(1)-C(31) | -61.7(7) |
| C(24)-Ru(1)-P(1)-C(31) | -126.8(6) |
| C(20)-Ru(1)-P(1)-C(31) | -119.6(5) |
| P(2)-Ru(1)-P(1)-C(31) | 47.8(4) |
| N(1)-Ru(1)-P(1)-C(37) | 12.1(4) |
| C(22)-Ru(1)-P(1)-C(37) | -179.3(5) |
| C(21)-Ru(1)-P(1)-C(37) | 149.6(5) |
| C(23)-Ru(1)-P(1)-C(37) | 172.4(7) |
| C(24)-Ru(1)-P(1)-C(37) | 107.3(6) |
| C(20)-Ru(1)-P(1)-C(37) | 114.5(5) |
| P(2)-Ru(1)-P(1)-C(37) | -78.1(4) |
| N(1)-Ru(1)-P(1)-C(25) | -104.5(4) |
| C(22)-Ru(1)-P(1)-C(25) | 64.0(5) |
| C(21)-Ru(1)-P(1)-C(25) | 33.0(5) |
| C(23)-Ru(1)-P(1)-C(25) | 55.8(7) |
| C(24)-Ru(1)-P(1)-C(25) | -9.3(6) |
| C(20)-Ru(1)-P(1)-C(25) | -2.2(5) |
| P(2)-Ru(1)-P(1)-C(25) | 165.3(4) |
| C(10)-Fe(1)-C(1)-C(5) | -150.5(12) |
| C(9)-Fe(1)-C(1)-C(5) | -108.3(11) |
| C(6)-Fe(1)-C(1)-C(5) | 168.8(17) |
| C(8)-Fe(1)-C(1)-C(5) | -67.4(11) |
| C(7)-Fe(1)-C(1)-C(5) | -33(3) |
| C(3)-Fe(1)-C(1)-C(5) | 82.5(7) |
| C(4)-Fe(1)-C(1)-C(5) | 39.2(7) |
| C(2)-Fe(1)-C(1)-C(5) | 119.7(9) |
| C(10)-Fe(1)-C(1)-C(2) | 89.8(12) |
| C(9)-Fe(1)-C(1)-C(2) | 132.0(10) |
| C(6)-Fe(1)-C(1)-C(2) | 49.1(19) |
| C(8)-Fe(1)-C(1)-C(2) | 172.9(10) |
| C(7)-Fe(1)-C(1)-C(2) | -152(3) |
| C(5)-Fe(1)-C(1)-C(2) | -119.7(9) |
| C(3)-Fe(1)-C(1)-C(2) | -37.2(7) |
| C(4)-Fe(1)-C(1)-C(2) | -80.5(7) |
| C(10)-Fe(1)-C(1)-C(11) | -27.3(15) |
| C(9)-Fe(1)-C(1)-C(11) | 14.9(14) |
| C(6)-Fe(1)-C(1)-C(11) | -68(2) |
| C(8)-Fe(1)-C(1)-C(11) | 55.8(14) |
| C(7)-Fe(1)-C(1)-C(11) | 91(3) |
| C(5)-Fe(1)-C(1)-C(11) | 123.2(13) |
| C(3)-Fe(1)-C(1)-C(11) | -154.3(12) |
| C(4)-Fe(1)-C(1)-C(11) | 162.4(12) |
| C(2)-Fe(1)-C(1)-C(11) | -117.1(13) |
| C(22)-Ru(1)-N(1)-C(19) | 8(7) |
| C(21)-Ru(1)-N(1)-C(19) | 73(7) |
| C(23)-Ru(1)-N(1)-C(19) | -6(7) |
| C(24)-Ru(1)-N(1)-C(19) | 23(7) |
| C(20)-Ru(1)-N(1)-C(19) | 59(7) |
| P(1)-Ru(1)-N(1)-C(19) | 163(7) |
| P(2)-Ru(1)-N(1)-C(19) | -94(7) |
| N(1)-Ru(1)-P(2)-C(49) | 48.2(4) |
| C(22)-Ru(1)-P(2)-C(49) | -106.9(5) |
| C(21)-Ru(1)-P(2)-C(49) | -119.9(5) |
| C(23)-Ru(1)-P(2)-C(49) | -70.5(5) |
| C(24)-Ru(1)-P(2)-C(49) | -46.2(5) |
| C(20)-Ru(1)-P(2)-C(49) | -67.4(8) |
| P(1)-Ru(1)-P(2)-C(49) | 137.7(4) |
| N(1)-Ru(1)-P(2)-C(43) | 162.2(5) |
| C(22)-Ru(1)-P(2)-C(43) | 7.1(5) |
| C(21)-Ru(1)-P(2)-C(43) | -6.0(6) |
| C(23)-Ru(1)-P(2)-C(43) | 43.4(5) |
| C(24)-Ru(1)-P(2)-C(43) | 67.8(5) |
| C(20)-Ru(1)-P(2)-C(43) | 46.5(8) |
| P(1)-Ru(1)-P(2)-C(43) | -108.3(4) |
| N(1)-Ru(1)-P(2)-C(55) | -73.1(5) |
| C(22)-Ru(1)-P(2)-C(55) | 131.9(5) |
| C(21)-Ru(1)-P(2)-C(55) | 118.8(6) |
| C(23)-Ru(1)-P(2)-C(55) | 168.2(5) |
| C(24)-Ru(1)-P(2)-C(55) | -167.5(5) |
| C(20)-Ru(1)-P(2)-C(55) | 171.3(8) |
| P(1)-Ru(1)-P(2)-C(55) | 16.4(4) |
| C(5)-C(1)-C(2)-C(3) | 1.4(13) |

| | | | |
|---|---|---|---|
| C(11)-C(1)-C(2)-C(3) | -179.6(10) | C(1)-Fe(1)-C(3)-C(4) | -82.3(7) |
| Fe(1)-C(1)-C(2)-C(3) | 59.7(8) | C(2)-C(3)-C(4)-C(5) | -0.9(13) |
| C(5)-C(1)-C(2)-Fe(1) | -58.3(8) | Fe(1)-C(3)-C(4)-C(5) | 59.1(8) |
| C(11)-C(1)-C(2)-Fe(1) | 120.7(11) | C(2)-C(3)-C(4)-Fe(1) | -60.0(8) |
| C(10)-Fe(1)-C(2)-C(3) | 129.3(13) | C(10)-Fe(1)-C(4)-C(3) | -58(3) |
| C(9)-Fe(1)-C(2)-C(3) | 170.9(11) | C(9)-Fe(1)-C(4)-C(3) | 173.2(12) |
| C(6)-Fe(1)-C(2)-C(3) | 82.9(13) | C(6)-Fe(1)-C(4)-C(3) | -75.6(12) |
| C(8)-Fe(1)-C(2)-C(3) | -143(3) | C(8)-Fe(1)-C(4)-C(3) | -158.4(11) |
| C(7)-Fe(1)-C(2)-C(3) | 47.0(18) | C(7)-Fe(1)-C(4)-C(3) | -113.7(13) |
| C(5)-Fe(1)-C(2)-C(3) | -82.0(8) | C(5)-Fe(1)-C(4)-C(3) | 118.2(10) |
| C(4)-Fe(1)-C(2)-C(3) | -37.0(7) | C(2)-Fe(1)-C(4)-C(3) | 36.8(7) |
| C(1)-Fe(1)-C(2)-C(3) | -119.2(10) | C(1)-Fe(1)-C(4)-C(3) | 80.4(7) |
| C(10)-Fe(1)-C(2)-C(1) | -111.5(13) | C(10)-Fe(1)-C(4)-C(5) | -177(3) |
| C(9)-Fe(1)-C(2)-C(1) | -69.9(12) | C(9)-Fe(1)-C(4)-C(5) | 55.0(14) |
| C(6)-Fe(1)-C(2)-C(1) | -158.0(12) | C(6)-Fe(1)-C(4)-C(5) | 166.2(11) |
| C(8)-Fe(1)-C(2)-C(1) | -24(3) | C(8)-Fe(1)-C(4)-C(5) | 83.4(11) |
| C(7)-Fe(1)-C(2)-C(1) | 166.2(15) | C(7)-Fe(1)-C(4)-C(5) | 128.1(13) |
| C(5)-Fe(1)-C(2)-C(1) | 37.2(6) | C(3)-Fe(1)-C(4)-C(5) | -118.2(10) |
| C(3)-Fe(1)-C(2)-C(1) | 119.2(10) | C(2)-Fe(1)-C(4)-C(5) | -81.4(7) |
| C(4)-Fe(1)-C(2)-C(1) | 82.1(7) | C(1)-Fe(1)-C(4)-C(5) | -37.9(7) |
| C(1)-C(2)-C(3)-C(4) | -0.3(13) | C(2)-C(1)-C(5)-C(4) | -2.0(12) |
| Fe(1)-C(2)-C(3)-C(4) | 59.8(8) | C(11)-C(1)-C(5)-C(4) | 179.1(11) |
| C(1)-C(2)-C(3)-Fe(1) | -60.1(8) | Fe(1)-C(1)-C(5)-C(4) | -60.7(7) |
| C(10)-Fe(1)-C(3)-C(2) | -74.6(13) | C(2)-C(1)-C(5)-Fe(1) | 58.8(8) |
| C(9)-Fe(1)-C(3)-C(2) | -41(4) | C(11)-C(1)-C(5)-Fe(1) | -120.2(12) |
| C(6)-Fe(1)-C(3)-C(2) | -115.7(12) | C(3)-C(4)-C(5)-C(1) | 1.8(13) |
| C(8)-Fe(1)-C(3)-C(2) | 162.5(15) | Fe(1)-C(4)-C(5)-C(1) | 61.6(8) |
| C(7)-Fe(1)-C(3)-C(2) | -156.9(12) | C(3)-C(4)-C(5)-Fe(1) | -59.8(8) |
| C(5)-Fe(1)-C(3)-C(2) | 81.0(7) | C(10)-Fe(1)-C(5)-C(1) | 60.8(15) |
| C(4)-Fe(1)-C(3)-C(2) | 119.9(10) | C(9)-Fe(1)-C(5)-C(1) | 90.0(10) |
| C(1)-Fe(1)-C(3)-C(2) | 37.6(7) | C(6)-Fe(1)-C(5)-C(1) | -162(2) |
| C(10)-Fe(1)-C(3)-C(4) | 165.4(11) | C(8)-Fe(1)-C(5)-C(1) | 129.9(10) |
| C(9)-Fe(1)-C(3)-C(4) | -161(3) | C(7)-Fe(1)-C(5)-C(1) | 170.4(11) |
| C(6)-Fe(1)-C(3)-C(4) | 124.4(12) | C(3)-Fe(1)-C(5)-C(1) | -80.2(7) |
| C(8)-Fe(1)-C(3)-C(4) | 42.6(17) | C(4)-Fe(1)-C(5)-C(1) | -117.7(10) |
| C(7)-Fe(1)-C(3)-C(4) | 83.2(13) | C(2)-Fe(1)-C(5)-C(1) | -37.3(6) |
| C(5)-Fe(1)-C(3)-C(4) | -38.9(7) | C(10)-Fe(1)-C(5)-C(4) | 178.5(12) |
| C(2)-Fe(1)-C(3)-C(4) | -119.9(10) | C(9)-Fe(1)-C(5)-C(4) | -152.3(10) |

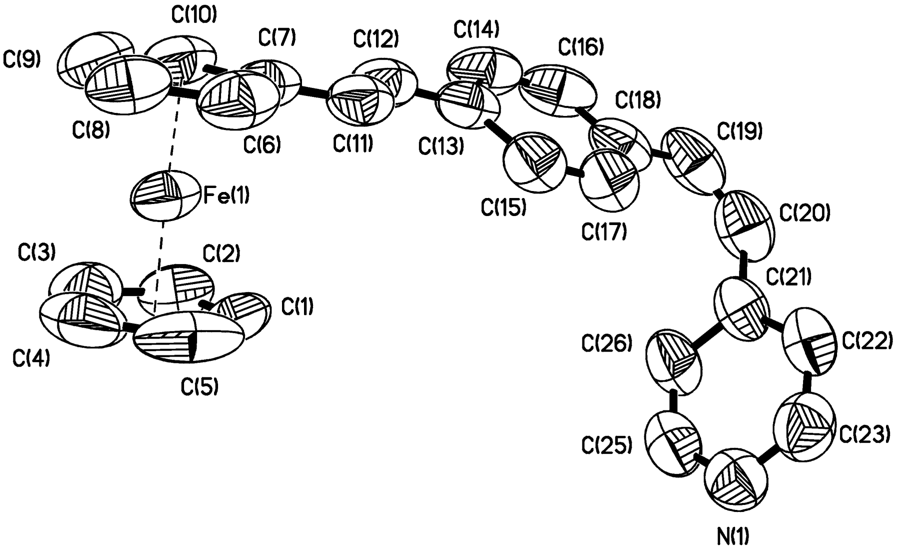
|  |  |  |  |
|---|---|---|---|
| C(6)-Fe(1)-C(5)-C(4) | -45(3) | C(4)-Fe(1)-C(7)-C(8) | -109.9(13) |
| C(8)-Fe(1)-C(5)-C(4) | -112.4(11) | C(2)-Fe(1)-C(7)-C(8) | 176.4(11) |
| C(7)-Fe(1)-C(5)-C(4) | -71.9(13) | C(1)-Fe(1)-C(7)-C(8) | -43(3) |
| C(3)-Fe(1)-C(5)-C(4) | 37.5(7) | C(6)-C(7)-C(8)-C(9) | -4(2) |
| C(2)-Fe(1)-C(5)-C(4) | 80.5(8) | Fe(1)-C(7)-C(8)-C(9) | -61.7(11) |
| C(1)-Fe(1)-C(5)-C(4) | 117.7(10) | C(6)-C(7)-C(8)-Fe(1) | 58.1(13) |
| C(10)-Fe(1)-C(6)-C(7) | 115.0(19) | C(10)-Fe(1)-C(8)-C(9) | 35.9(12) |
| C(9)-Fe(1)-C(6)-C(7) | 79.1(14) | C(6)-Fe(1)-C(8)-C(9) | 80.9(13) |
| C(8)-Fe(1)-C(6)-C(7) | 37.2(13) | C(7)-Fe(1)-C(8)-C(9) | 115.0(18) |
| C(5)-Fe(1)-C(6)-C(7) | -35(3) | C(5)-Fe(1)-C(8)-C(9) | -114.8(14) |
| C(3)-Fe(1)-C(6)-C(7) | -111.6(16) | C(3)-Fe(1)-C(8)-C(9) | 173.5(12) |
| C(4)-Fe(1)-C(6)-C(7) | -70.6(17) | C(4)-Fe(1)-C(8)-C(9) | -157.6(12) |
| C(2)-Fe(1)-C(6)-C(7) | -153.6(13) | C(2)-Fe(1)-C(8)-C(9) | -58(3) |
| C(1)-Fe(1)-C(6)-C(7) | 171.8(13) | C(1)-Fe(1)-C(8)-C(9) | -76.9(14) |
| C(9)-Fe(1)-C(6)-C(10) | -35.9(11) | C(10)-Fe(1)-C(8)-C(7) | -79.2(13) |
| C(8)-Fe(1)-C(6)-C(10) | -77.8(12) | C(9)-Fe(1)-C(8)-C(7) | -115.0(18) |
| C(7)-Fe(1)-C(6)-C(10) | -115.0(19) | C(6)-Fe(1)-C(8)-C(7) | -34.1(12) |
| C(5)-Fe(1)-C(6)-C(10) | -150(2) | C(5)-Fe(1)-C(8)-C(7) | 130.2(14) |
| C(3)-Fe(1)-C(6)-C(10) | 133.4(13) | C(3)-Fe(1)-C(8)-C(7) | 59(2) |
| C(4)-Fe(1)-C(6)-C(10) | 174.4(12) | C(4)-Fe(1)-C(8)-C(7) | 87.4(14) |
| C(2)-Fe(1)-C(6)-C(10) | 91.4(13) | C(2)-Fe(1)-C(8)-C(7) | -173(2) |
| C(1)-Fe(1)-C(6)-C(10) | 57(2) | C(1)-Fe(1)-C(8)-C(7) | 168.1(12) |
| C(10)-C(6)-C(7)-C(8) | 4(2) | C(7)-C(8)-C(9)-C(10) | 1.7(19) |
| Fe(1)-C(6)-C(7)-C(8) | -57.1(12) | Fe(1)-C(8)-C(9)-C(10) | -59.2(12) |
| C(10)-C(6)-C(7)-Fe(1) | 60.9(11) | C(7)-C(8)-C(9)-Fe(1) | 60.8(11) |
| C(10)-Fe(1)-C(7)-C(6) | -41.3(13) | C(10)-Fe(1)-C(9)-C(8) | -121.6(18) |
| C(9)-Fe(1)-C(7)-C(6) | -84.3(14) | C(6)-Fe(1)-C(9)-C(8) | -83.5(13) |
| C(8)-Fe(1)-C(7)-C(6) | -122.7(19) | C(7)-Fe(1)-C(9)-C(8) | -41.6(13) |
| C(5)-Fe(1)-C(7)-C(6) | 168.5(13) | C(5)-Fe(1)-C(9)-C(8) | 80.3(14) |
| C(3)-Fe(1)-C(7)-C(6) | 85.6(16) | C(3)-Fe(1)-C(9)-C(8) | -162(3) |
| C(4)-Fe(1)-C(7)-C(6) | 127.4(15) | C(4)-Fe(1)-C(9)-C(8) | 42.8(19) |
| C(2)-Fe(1)-C(7)-C(6) | 54(2) | C(2)-Fe(1)-C(9)-C(8) | 163.7(12) |
| C(1)-Fe(1)-C(7)-C(6) | -166(2) | C(1)-Fe(1)-C(9)-C(8) | 123.6(14) |
| C(10)-Fe(1)-C(7)-C(8) | 81.4(13) | C(6)-Fe(1)-C(9)-C(10) | 38.1(12) |
| C(9)-Fe(1)-C(7)-C(8) | 38.4(11) | C(8)-Fe(1)-C(9)-C(10) | 121.6(18) |
| C(6)-Fe(1)-C(7)-C(8) | 122.7(19) | C(7)-Fe(1)-C(9)-C(10) | 80.0(13) |
| C(5)-Fe(1)-C(7)-C(8) | -68.8(14) | C(5)-Fe(1)-C(9)-C(10) | -158.2(13) |
| C(3)-Fe(1)-C(7)-C(8) | -151.7(12) | C(3)-Fe(1)-C(9)-C(10) | -41(4) |

| | | | |
|---|---|---|---|
| C(4)-Fe(1)-C(9)-C(10) | 164.3(13) | C(14)-C(13)-C(18)-C(17) | -3(2) |
| C(2)-Fe(1)-C(9)-C(10) | -74.7(15) | C(12)-C(13)-C(18)-C(17) | 178.5(12) |
| C(1)-Fe(1)-C(9)-C(10) | -114.9(14) | C(16)-C(17)-C(18)-C(13) | 4(2) |
| C(8)-C(9)-C(10)-C(6) | 1(2) | Ru(1)-N(1)-C(19)-C(16) | 62(22) |
| Fe(1)-C(9)-C(10)-C(6) | -58.8(11) | C(17)-C(16)-C(19)-N(1) | -65(18) |
| C(8)-C(9)-C(10)-Fe(1) | 59.4(12) | C(15)-C(16)-C(19)-N(1) | 115(18) |
| C(7)-C(6)-C(10)-C(9) | -3(2) | N(1)-Ru(1)-C(20)-C(24) | -79.8(8) |
| Fe(1)-C(6)-C(10)-C(9) | 59.4(12) | C(22)-Ru(1)-C(20)-C(24) | 78.4(8) |
| C(7)-C(6)-C(10)-Fe(1) | -62.2(12) | C(21)-Ru(1)-C(20)-C(24) | 115.9(11) |
| C(6)-Fe(1)-C(10)-C(9) | -120.3(17) | C(23)-Ru(1)-C(20)-C(24) | 36.6(7) |
| C(8)-Fe(1)-C(10)-C(9) | -35.7(11) | P(1)-Ru(1)-C(20)-C(24) | -172.3(7) |
| C(7)-Fe(1)-C(10)-C(9) | -82.0(13) | P(2)-Ru(1)-C(20)-C(24) | 33.0(11) |
| C(5)-Fe(1)-C(10)-C(9) | 43.3(19) | N(1)-Ru(1)-C(20)-C(21) | 164.4(7) |
| C(3)-Fe(1)-C(10)-C(9) | 170.9(11) | C(22)-Ru(1)-C(20)-C(21) | -37.5(7) |
| C(4)-Fe(1)-C(10)-C(9) | -141(3) | C(23)-Ru(1)-C(20)-C(21) | -79.3(7) |
| C(2)-Fe(1)-C(10)-C(9) | 128.9(12) | C(24)-Ru(1)-C(20)-C(21) | -115.9(11) |
| C(1)-Fe(1)-C(10)-C(9) | 84.4(13) | P(1)-Ru(1)-C(20)-C(21) | 71.9(7) |
| C(9)-Fe(1)-C(10)-C(6) | 120.3(17) | P(2)-Ru(1)-C(20)-C(21) | -82.8(9) |
| C(8)-Fe(1)-C(10)-C(6) | 84.6(13) | C(24)-C(20)-C(21)-C(22) | -0.7(12) |
| C(7)-Fe(1)-C(10)-C(6) | 38.3(12) | Ru(1)-C(20)-C(21)-C(22) | 62.1(7) |
| C(5)-Fe(1)-C(10)-C(6) | 163.7(15) | C(24)-C(20)-C(21)-Ru(1) | -62.8(7) |
| C(3)-Fe(1)-C(10)-C(6) | -68.8(15) | N(1)-Ru(1)-C(21)-C(20) | -22.9(10) |
| C(4)-Fe(1)-C(10)-C(6) | -21(4) | C(22)-Ru(1)-C(21)-C(20) | 117.8(10) |
| C(2)-Fe(1)-C(10)-C(6) | -110.8(14) | C(23)-Ru(1)-C(21)-C(20) | 79.8(7) |
| C(1)-Fe(1)-C(10)-C(6) | -155.3(13) | C(24)-Ru(1)-C(21)-C(20) | 37.6(7) |
| C(5)-C(1)-C(11)-C(12) | -16(2) | P(1)-Ru(1)-C(21)-C(20) | -113.0(7) |
| C(2)-C(1)-C(11)-C(12) | 165.6(12) | P(2)-Ru(1)-C(21)-C(20) | 139.4(6) |
| Fe(1)-C(1)-C(11)-C(12) | -106.3(14) | N(1)-Ru(1)-C(21)-C(22) | -140.7(7) |
| C(1)-C(11)-C(12)-C(13) | -178.9(11) | C(23)-Ru(1)-C(21)-C(22) | -38.0(6) |
| C(11)-C(12)-C(13)-C(18) | -15(2) | C(24)-Ru(1)-C(21)-C(22) | -80.2(7) |
| C(11)-C(12)-C(13)-C(14) | 166.7(13) | C(20)-Ru(1)-C(21)-C(22) | -117.8(10) |
| C(18)-C(13)-C(14)-C(15) | 0(2) | P(1)-Ru(1)-C(21)-C(22) | 129.3(6) |
| C(12)-C(13)-C(14)-C(15) | 179.2(12) | P(2)-Ru(1)-C(21)-C(22) | 21.6(8) |
| C(13)-C(14)-C(15)-C(16) | 0(2) | C(20)-C(21)-C(22)-C(23) | 0.4(12) |
| C(14)-C(15)-C(16)-C(17) | 1.5(19) | Ru(1)-C(21)-C(22)-C(23) | 63.7(7) |
| C(14)-C(15)-C(16)-C(19) | -178.2(11) | C(20)-C(21)-C(22)-Ru(1) | -63.3(7) |
| C(15)-C(16)-C(17)-C(18) | -3.7(18) | N(1)-Ru(1)-C(22)-C(23) | -20.6(12) |
| C(19)-C(16)-C(17)-C(18) | 175.9(11) | C(21)-Ru(1)-C(22)-C(23) | -115.5(10) |

| | | | |
|---|---|---|---|
| C(24)-Ru(1)-C(22)-C(23) | -37.2(6) | C(22)-Ru(1)-C(24)-C(23) | 37.2(6) |
| C(20)-Ru(1)-C(22)-C(23) | -78.5(7) | C(21)-Ru(1)-C(24)-C(23) | 80.4(7) |
| P(1)-Ru(1)-C(22)-C(23) | -173.1(6) | C(20)-Ru(1)-C(24)-C(23) | 118.9(10) |
| P(2)-Ru(1)-C(22)-C(23) | 80.7(7) | P(1)-Ru(1)-C(24)-C(23) | 130.6(6) |
| N(1)-Ru(1)-C(22)-C(21) | 94.9(10) | P(2)-Ru(1)-C(24)-C(23) | -43.4(7) |
| C(23)-Ru(1)-C(22)-C(21) | 115.5(10) | C(31)-P(1)-C(25)-C(30) | 1.2(10) |
| C(24)-Ru(1)-C(22)-C(21) | 78.3(7) | C(37)-P(1)-C(25)-C(30) | 107.8(10) |
| C(20)-Ru(1)-C(22)-C(21) | 37.0(6) | Ru(1)-P(1)-C(25)-C(30) | -124.5(9) |
| P(1)-Ru(1)-C(22)-C(21) | -57.6(7) | C(31)-P(1)-C(25)-C(26) | -175.0(8) |
| P(2)-Ru(1)-C(22)-C(21) | -163.8(6) | C(37)-P(1)-C(25)-C(26) | -68.4(9) |
| C(21)-C(22)-C(23)-C(24) | 0.1(12) | Ru(1)-P(1)-C(25)-C(26) | 59.3(9) |
| Ru(1)-C(22)-C(23)-C(24) | 63.4(7) | C(30)-C(25)-C(26)-C(27) | 2.1(17) |
| C(21)-C(22)-C(23)-Ru(1) | -63.3(7) | P(1)-C(25)-C(26)-C(27) | 178.4(10) |
| N(1)-Ru(1)-C(23)-C(22) | 170.1(6) | C(25)-C(26)-C(27)-C(28) | -2(2) |
| C(21)-Ru(1)-C(23)-C(22) | 38.8(6) | C(26)-C(27)-C(28)-C(29) | -1(2) |
| C(24)-Ru(1)-C(23)-C(22) | 117.5(10) | C(27)-C(28)-C(29)-C(30) | 3(2) |
| C(20)-Ru(1)-C(23)-C(22) | 81.4(7) | C(26)-C(25)-C(30)-C(29) | -0.1(17) |
| P(1)-Ru(1)-C(23)-C(22) | 12.7(11) | P(1)-C(25)-C(30)-C(29) | -176.2(10) |
| P(2)-Ru(1)-C(23)-C(22) | -100.4(7) | C(28)-C(29)-C(30)-C(25) | -2(2) |
| N(1)-Ru(1)-C(23)-C(24) | 52.6(7) | C(37)-P(1)-C(31)-C(36) | 177.7(8) |
| C(22)-Ru(1)-C(23)-C(24) | -117.5(10) | C(25)-P(1)-C(31)-C(36) | -77.7(9) |
| C(21)-Ru(1)-C(23)-C(24) | -78.6(7) | Ru(1)-P(1)-C(31)-C(36) | 44.1(9) |
| C(20)-Ru(1)-C(23)-C(24) | -36.1(6) | C(37)-P(1)-C(31)-C(32) | -0.3(10) |
| P(1)-Ru(1)-C(23)-C(24) | -104.8(8) | C(25)-P(1)-C(31)-C(32) | 104.3(9) |
| P(2)-Ru(1)-C(23)-C(24) | 142.1(6) | Ru(1)-P(1)-C(31)-C(32) | -133.9(8) |
| C(21)-C(20)-C(24)-C(23) | 0.8(12) | C(36)-C(31)-C(32)-C(33) | -0.1(15) |
| Ru(1)-C(20)-C(24)-C(23) | -60.9(7) | P(1)-C(31)-C(32)-C(33) | 177.9(9) |
| C(21)-C(20)-C(24)-Ru(1) | 61.7(7) | C(31)-C(32)-C(33)-C(34) | 1.0(18) |
| C(22)-C(23)-C(24)-C(20) | -0.6(12) | C(32)-C(33)-C(34)-C(35) | -1(2) |
| Ru(1)-C(23)-C(24)-C(20) | 61.9(8) | C(33)-C(34)-C(35)-C(36) | 0.8(19) |
| C(22)-C(23)-C(24)-Ru(1) | -62.5(7) | C(32)-C(31)-C(36)-C(35) | -0.4(16) |
| N(1)-Ru(1)-C(24)-C(20) | 105.4(7) | P(1)-C(31)-C(36)-C(35) | -178.5(9) |
| C(22)-Ru(1)-C(24)-C(20) | -81.7(7) | C(34)-C(35)-C(36)-C(31) | 0.1(17) |
| C(21)-Ru(1)-C(24)-C(20) | -38.5(7) | C(31)-P(1)-C(37)-C(38) | 98.1(11) |
| C(23)-Ru(1)-C(24)-C(20) | -118.9(10) | C(25)-P(1)-C(37)-C(38) | -8.0(12) |
| P(1)-Ru(1)-C(24)-C(20) | 11.7(10) | Ru(1)-P(1)-C(37)-C(38) | -129.9(10) |
| P(2)-Ru(1)-C(24)-C(20) | -162.3(6) | C(31)-P(1)-C(37)-C(42) | -82.9(9) |
| N(1)-Ru(1)-C(24)-C(23) | -135.7(7) | C(25)-P(1)-C(37)-C(42) | 171.0(9) |

| | |
|---|---|
| Ru(1)-P(1)-C(37)-C(42) | 49.1(10) |
| C(42)-C(37)-C(38)-C(39) | -1(2) |
| P(1)-C(37)-C(38)-C(39) | 178.1(12) |
| C(37)-C(38)-C(39)-C(40) | -2(3) |
| C(38)-C(39)-C(40)-C(41) | 6(2) |
| C(39)-C(40)-C(41)-C(42) | -7(2) |
| C(40)-C(41)-C(42)-C(37) | 4.4(19) |
| C(38)-C(37)-C(42)-C(41) | -0.3(17) |
| P(1)-C(37)-C(42)-C(41) | -179.4(9) |
| C(49)-P(2)-C(43)-C(44) | 12.1(10) |
| C(55)-P(2)-C(43)-C(44) | 115.6(10) |
| Ru(1)-P(2)-C(43)-C(44) | -109.5(9) |
| C(49)-P(2)-C(43)-C(48) | -170.2(9) |
| C(55)-P(2)-C(43)-C(48) | -66.7(10) |
| Ru(1)-P(2)-C(43)-C(48) | 68.2(10) |
| C(48)-C(43)-C(44)-C(45) | 2.9(18) |
| P(2)-C(43)-C(44)-C(45) | -179.3(10) |
| C(43)-C(44)-C(45)-C(46) | -3(2) |
| C(44)-C(45)-C(46)-C(47) | -1(3) |
| C(45)-C(46)-C(47)-C(48) | 4(3) |
| C(46)-C(47)-C(48)-C(43) | -4(2) |
| C(44)-C(43)-C(48)-C(47) | 0.2(19) |
| P(2)-C(43)-C(48)-C(47) | -177.6(11) |
| C(43)-P(2)-C(49)-C(50) | -113.0(9) |
| C(55)-P(2)-C(49)-C(50) | 140.7(9) |
| Ru(1)-P(2)-C(49)-C(50) | 7.4(10) |
| C(43)-P(2)-C(49)-C(54) | 62.9(10) |
| C(55)-P(2)-C(49)-C(54) | -43.4(10) |
| Ru(1)-P(2)-C(49)-C(54) | -176.7(8) |
| C(54)-C(49)-C(50)-C(51) | -0.5(16) |
| P(2)-C(49)-C(50)-C(51) | 175.4(8) |
| C(49)-C(50)-C(51)-C(52) | 0.2(17) |
| C(50)-C(51)-C(52)-C(53) | -1.3(19) |
| C(51)-C(52)-C(53)-C(54) | 3(2) |
| C(52)-C(53)-C(54)-C(49) | -2.9(19) |
| C(50)-C(49)-C(54)-C(53) | 1.9(17) |
| P(2)-C(49)-C(54)-C(53) | -174.2(9) |
| C(49)-P(2)-C(55)-C(60) | 144.8(10) |
| C(43)-P(2)-C(55)-C(60) | 40.6(11) |
| Ru(1)-P(2)-C(55)-C(60) | -87.8(10) |
| C(49)-P(2)-C(55)-C(56) | -37.7(10) |
| C(43)-P(2)-C(55)-C(56) | -141.8(9) |
| Ru(1)-P(2)-C(55)-C(56) | 89.7(9) |
| C(60)-C(55)-C(56)-C(57) | 1.5(19) |
| P(2)-C(55)-C(56)-C(57) | -176.1(11) |
| C(55)-C(56)-C(57)-C(58) | -1(2) |
| C(56)-C(57)-C(58)-C(59) | -1(2) |
| C(57)-C(58)-C(59)-C(60) | 3(2) |
| C(56)-C(55)-C(60)-C(59) | 0.0(18) |
| P(2)-C(55)-C(60)-C(59) | 177.6(10) |
| C(58)-C(59)-C(60)-C(55) | -2(2) |

Symmetry transformations used to generate equivalent atoms:


C(10)
C(9)
C(7)
C(12)
C(14)
C(16)
C(18)
C(19)
C(8)
C(6)
C(11)
C(13)
Fe(1)
C(15)
C(17)
C(20)
C(3)
C(2)
C(1)
C(21)
C(4)
C(5)
C(26)
C(22)
C(25)
C(23)
N(1)

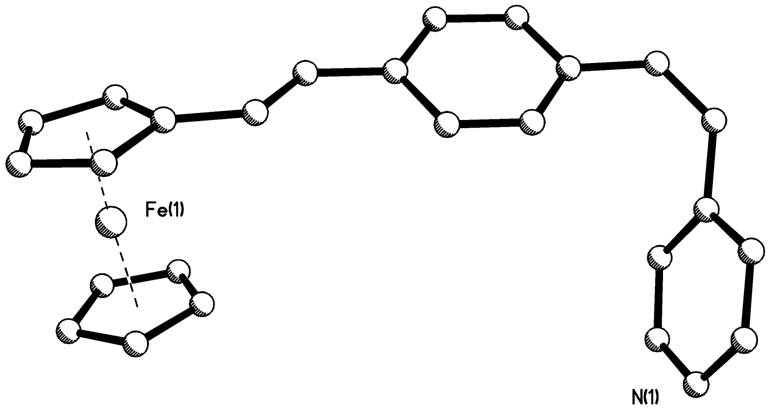

Fe(1)
N(1)

**Table 1**. Crystal data and structure refinement for str53m.

| | | |
|---|---|---|
| Identification code | str53m | |
| Empirical formula | C25 H21 Fe N | |
| Formula weight | 391.28 | |
| Temperature | 293(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | P2(1)/c | |
| Unit cell dimensions | a = 17.7672(18) Å | $\alpha$= 90°. |
| | b = 10.0114(9) Å | $\beta$= 106.027(2)°. |
| | c = 11.3680(11) Å | $\gamma$ = 90°. |
| Volume | 1943.5(3) Å$^3$ | |
| Z | 4 | |
| Density (calculated) | 1.337 Mg/m$^3$ | |
| Absorption coefficient | 0.784 mm$^{-1}$ | |
| F(000) | 816 | |
| Crystal size | 0.12 x 0.04 x 0.015 mm$^3$ | |
| Theta range for data collection | 1.19 to 20.81°. | |
| Index ranges | -17<=h<=17, -10<=k<=10, -7<=l<=11 | |
| Reflections collected | 7085 | |
| Independent reflections | 2025 [R(int) = 0.0329] | |
| Completeness to theta = 20.81° | 100.0 % | |
| Refinement method | Full-matrix least-squares on F$^2$ | |
| Data / restraints / parameters | 2025 / 0 / 244 | |
| Goodness-of-fit on F$^2$ | 1.023 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0318, wR2 = 0.0835 | |
| R indices (all data) | R1 = 0.0546, wR2 = 0.1071 | |
| Largest diff. peak and hole | 0.163 and -0.210 e.Å$^{-3}$ | |

**Table 2.** Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters (Å$^2$x $10^3$) for str53m. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| Fe(1) | 3882(1) | 371(1) | 6384(1) | 74(1) |
| C(1) | 3056(4) | 1718(6) | 6504(5) | 99(2) |
| N(1) | 827(2) | 4307(4) | 11420(5) | 94(1) |
| C(2) | 2742(3) | 860(5) | 5628(7) | 95(2) |
| C(3) | 3124(5) | 889(6) | 4768(6) | 108(2) |
| C(4) | 3728(4) | 1817(8) | 5108(9) | 124(2) |
| C(5) | 3690(4) | 2350(5) | 6268(8) | 118(2) |
| C(6) | 4121(3) | -777(4) | 7926(4) | 77(1) |
| C(7) | 4775(3) | 49(5) | 7910(5) | 90(2) |
| C(8) | 5015(3) | -261(5) | 6852(6) | 97(2) |
| C(9) | 4515(3) | -1279(5) | 6207(5) | 97(2) |
| C(10) | 3973(3) | -1595(4) | 6863(4) | 85(1) |
| C(11) | 3666(3) | -679(4) | 8796(4) | 78(1) |
| C(12) | 3082(3) | -1460(4) | 8884(4) | 83(1) |
| C(13) | 2583(3) | -1305(4) | 9701(4) | 78(1) |
| C(14) | 2077(3) | -2313(4) | 9860(5) | 94(2) |
| C(15) | 2576(3) | -130(4) | 10375(5) | 84(1) |
| C(16) | 1615(3) | -2157(5) | 10637(6) | 98(2) |
| C(17) | 2110(3) | 9(4) | 11132(5) | 85(1) |
| C(18) | 1601(3) | -990(5) | 11282(4) | 83(1) |
| C(19) | 1097(3) | -882(6) | 12102(5) | 104(2) |
| C(20) | 823(3) | 208(7) | 12496(5) | 105(2) |
| C(21) | 860(2) | 1618(5) | 12140(5) | 84(1) |
| C(22) | 1189(3) | 2612(6) | 12949(4) | 93(1) |
| C(23) | 1155(3) | 3907(6) | 12553(6) | 104(2) |
| C(25) | 508(3) | 3344(7) | 10653(5) | 98(2) |
| C(26) | 515(3) | 2025(6) | 10953(4) | 99(2) |

**Table 3**. Bond lengths [Å] and angles [°] for str53m.

| | | | |
|---|---|---|---|
| Fe(1)-C(5) | 2.009(5) | C(5)-Fe(1)-C(4) | 42.0(2) |
| Fe(1)-C(4) | 2.014(5) | C(5)-Fe(1)-C(3) | 68.2(2) |
| Fe(1)-C(3) | 2.023(5) | C(4)-Fe(1)-C(3) | 40.3(2) |
| Fe(1)-C(1) | 2.025(4) | C(5)-Fe(1)-C(1) | 40.0(2) |
| Fe(1)-C(7) | 2.027(4) | C(4)-Fe(1)-C(1) | 67.2(2) |
| Fe(1)-C(2) | 2.030(4) | C(3)-Fe(1)-C(1) | 65.0(2) |
| Fe(1)-C(10) | 2.036(4) | C(5)-Fe(1)-C(7) | 106.9(2) |
| Fe(1)-C(8) | 2.036(4) | C(4)-Fe(1)-C(7) | 130.5(3) |
| Fe(1)-C(9) | 2.039(4) | C(3)-Fe(1)-C(7) | 170.2(3) |
| Fe(1)-C(6) | 2.040(5) | C(1)-Fe(1)-C(7) | 117.3(2) |
| C(1)-C(2) | 1.316(6) | C(5)-Fe(1)-C(2) | 66.6(2) |
| C(1)-C(5) | 1.381(8) | C(4)-Fe(1)-C(2) | 66.4(2) |
| N(1)-C(25) | 1.319(6) | C(3)-Fe(1)-C(2) | 38.5(2) |
| N(1)-C(23) | 1.320(6) | C(1)-Fe(1)-C(2) | 37.89(18) |
| C(2)-C(3) | 1.336(7) | C(7)-Fe(1)-C(2) | 148.7(3) |
| C(3)-C(4) | 1.391(8) | C(5)-Fe(1)-C(10) | 166.0(4) |
| C(4)-C(5) | 1.442(8) | C(4)-Fe(1)-C(10) | 150.7(4) |
| C(6)-C(10) | 1.422(6) | C(3)-Fe(1)-C(10) | 118.3(2) |
| C(6)-C(7) | 1.430(6) | C(1)-Fe(1)-C(10) | 129.2(3) |
| C(6)-C(11) | 1.444(6) | C(7)-Fe(1)-C(10) | 68.42(18) |
| C(7)-C(8) | 1.418(7) | C(2)-Fe(1)-C(10) | 110.1(2) |
| C(8)-C(9) | 1.416(6) | C(5)-Fe(1)-C(8) | 117.5(3) |
| C(9)-C(10) | 1.408(6) | C(4)-Fe(1)-C(8) | 109.8(2) |
| C(11)-C(12) | 1.325(6) | C(3)-Fe(1)-C(8) | 132.8(3) |
| C(12)-C(13) | 1.458(6) | C(1)-Fe(1)-C(8) | 150.7(3) |
| C(13)-C(14) | 1.395(6) | C(7)-Fe(1)-C(8) | 40.85(19) |
| C(13)-C(15) | 1.405(6) | C(2)-Fe(1)-C(8) | 170.0(3) |
| C(14)-C(16) | 1.372(7) | C(10)-Fe(1)-C(8) | 68.3(2) |
| C(15)-C(17) | 1.357(6) | C(5)-Fe(1)-C(9) | 151.7(4) |
| C(16)-C(18) | 1.383(7) | C(4)-Fe(1)-C(9) | 118.7(3) |
| C(17)-C(18) | 1.391(6) | C(3)-Fe(1)-C(9) | 111.4(2) |
| C(18)-C(19) | 1.464(7) | C(1)-Fe(1)-C(9) | 167.4(3) |
| C(19)-C(20) | 1.322(7) | C(7)-Fe(1)-C(9) | 68.48(19) |
| C(20)-C(21) | 1.475(7) | C(2)-Fe(1)-C(9) | 131.8(3) |
| C(21)-C(22) | 1.372(6) | C(10)-Fe(1)-C(9) | 40.42(17) |
| C(21)-C(26) | 1.381(6) | C(8)-Fe(1)-C(9) | 40.66(18) |
| C(22)-C(23) | 1.368(6) | C(5)-Fe(1)-C(6) | 127.1(3) |
| C(25)-C(26) | 1.362(6) | C(4)-Fe(1)-C(6) | 168.1(4) |

|  |  |  |  |
|---|---|---|---|
| C(3)-Fe(1)-C(6) | 148.6(3) | C(6)-C(7)-Fe(1) | 69.9(3) |
| C(1)-Fe(1)-C(6) | 107.5(2) | C(9)-C(8)-C(7) | 107.7(5) |
| C(7)-Fe(1)-C(6) | 41.16(18) | C(9)-C(8)-Fe(1) | 69.8(3) |
| C(2)-Fe(1)-C(6) | 116.5(2) | C(7)-C(8)-Fe(1) | 69.2(3) |
| C(10)-Fe(1)-C(6) | 40.85(16) | C(10)-C(9)-C(8) | 108.1(5) |
| C(8)-Fe(1)-C(6) | 69.2(2) | C(10)-C(9)-Fe(1) | 69.7(3) |
| C(9)-Fe(1)-C(6) | 68.8(2) | C(8)-C(9)-Fe(1) | 69.6(3) |
| C(2)-C(1)-C(5) | 110.5(6) | C(9)-C(10)-C(6) | 109.1(5) |
| C(2)-C(1)-Fe(1) | 71.2(3) | C(9)-C(10)-Fe(1) | 69.9(3) |
| C(5)-C(1)-Fe(1) | 69.4(3) | C(6)-C(10)-Fe(1) | 69.7(2) |
| C(25)-N(1)-C(23) | 114.6(4) | C(12)-C(11)-C(6) | 127.6(4) |
| C(1)-C(2)-C(3) | 110.1(5) | C(11)-C(12)-C(13) | 127.7(4) |
| C(1)-C(2)-Fe(1) | 70.9(3) | C(14)-C(13)-C(15) | 115.6(5) |
| C(3)-C(2)-Fe(1) | 70.5(3) | C(14)-C(13)-C(12) | 122.1(5) |
| C(2)-C(3)-C(4) | 108.7(6) | C(15)-C(13)-C(12) | 122.3(4) |
| C(2)-C(3)-Fe(1) | 71.0(3) | C(16)-C(14)-C(13) | 121.5(5) |
| C(4)-C(3)-Fe(1) | 69.5(3) | C(17)-C(15)-C(13) | 122.0(5) |
| C(3)-C(4)-C(5) | 105.9(5) | C(14)-C(16)-C(18) | 122.6(5) |
| C(3)-C(4)-Fe(1) | 70.2(3) | C(15)-C(17)-C(18) | 122.4(5) |
| C(5)-C(4)-Fe(1) | 68.8(3) | C(16)-C(18)-C(17) | 115.8(5) |
| C(1)-C(5)-C(4) | 104.7(5) | C(16)-C(18)-C(19) | 120.2(5) |
| C(1)-C(5)-Fe(1) | 70.6(3) | C(17)-C(18)-C(19) | 123.9(5) |
| C(4)-C(5)-Fe(1) | 69.2(3) | C(20)-C(19)-C(18) | 128.6(5) |
| C(10)-C(6)-C(7) | 106.4(5) | C(19)-C(20)-C(21) | 130.4(5) |
| C(10)-C(6)-C(11) | 127.9(5) | C(22)-C(21)-C(26) | 115.7(5) |
| C(7)-C(6)-C(11) | 125.4(5) | C(22)-C(21)-C(20) | 123.6(5) |
| C(10)-C(6)-Fe(1) | 69.4(3) | C(26)-C(21)-C(20) | 120.6(5) |
| C(7)-C(6)-Fe(1) | 68.9(3) | C(23)-C(22)-C(21) | 119.7(5) |
| C(11)-C(6)-Fe(1) | 121.8(3) | N(1)-C(23)-C(22) | 125.2(5) |
| C(8)-C(7)-C(6) | 108.7(5) | N(1)-C(25)-C(26) | 124.8(5) |
| C(8)-C(7)-Fe(1) | 69.9(3) | C(25)-C(26)-C(21) | 120.1(5) |

---

Symmetry transformations used to generate equivalent atoms:

**Table 4**. Anisotropic displacement parameters ($Å^2 x 10^3$) for str53m. The anisotropic displacement factor exponent takes the form: $-2\pi^2[ h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12} ]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| Fe(1) | 70(1) | 59(1) | 84(1) | -2(1) | 4(1) | 17(1) |
| C(1) | 128(5) | 70(3) | 92(4) | -5(3) | 20(4) | 46(3) |
| N(1) | 86(3) | 103(3) | 93(3) | 8(3) | 26(3) | 9(2) |
| C(2) | 81(3) | 79(4) | 119(5) | 9(4) | 17(4) | 22(3) |
| C(3) | 126(5) | 96(4) | 84(4) | -1(3) | 1(4) | 39(4) |
| C(4) | 106(5) | 113(5) | 171(7) | 81(5) | 69(5) | 53(4) |
| C(5) | 92(4) | 49(3) | 170(7) | 5(4) | -35(4) | 3(3) |
| C(6) | 79(3) | 57(3) | 79(3) | -2(3) | -4(3) | 19(2) |
| C(7) | 75(3) | 77(3) | 101(4) | -4(3) | -6(3) | 17(3) |
| C(8) | 72(3) | 90(4) | 119(4) | 11(3) | 11(3) | 29(3) |
| C(9) | 101(4) | 77(3) | 104(4) | -9(3) | 13(4) | 34(3) |
| C(10) | 93(3) | 54(3) | 90(3) | -9(3) | -4(3) | 19(2) |
| C(11) | 92(3) | 52(3) | 73(3) | -4(2) | -7(3) | 8(3) |
| C(12) | 98(4) | 50(3) | 84(3) | -5(2) | -5(3) | 6(3) |
| C(13) | 83(3) | 55(3) | 76(3) | 6(3) | -8(3) | 4(3) |
| C(14) | 91(3) | 49(3) | 121(4) | 1(3) | -7(3) | -7(3) |
| C(15) | 101(4) | 61(3) | 82(3) | 1(2) | 15(3) | -21(2) |
| C(16) | 81(3) | 65(4) | 132(5) | 26(3) | 2(3) | -16(3) |
| C(17) | 103(4) | 69(3) | 79(3) | -1(2) | 18(3) | -26(3) |
| C(18) | 90(3) | 68(3) | 77(3) | 22(3) | -1(3) | -18(3) |
| C(19) | 112(4) | 108(5) | 83(4) | 30(3) | 13(3) | -39(4) |
| C(20) | 108(4) | 127(5) | 86(4) | 14(4) | 34(3) | -29(4) |
| C(21) | 77(3) | 107(4) | 73(3) | 13(3) | 29(3) | -15(3) |
| C(22) | 92(3) | 116(4) | 66(3) | -1(3) | 14(3) | -6(3) |
| C(23) | 100(4) | 111(5) | 95(4) | -15(4) | 17(3) | 0(3) |
| C(25) | 95(4) | 123(4) | 74(3) | 9(4) | 20(3) | 5(3) |
| C(26) | 110(4) | 111(5) | 68(4) | 4(3) | 11(3) | -16(3) |

**Table 5.** Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters (Å$^2$x $10^3$) for str53m.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1) | 2876 | 1877 | 7186 | 118 |
| H(2) | 2316 | 313 | 5611 | 114 |
| H(3) | 3005 | 375 | 4060 | 129 |
| H(4) | 4083 | 2046 | 4675 | 149 |
| H(5) | 4019 | 2981 | 6751 | 142 |
| H(7) | 5004 | 684 | 8497 | 108 |
| H(8) | 5427 | 133 | 6623 | 117 |
| H(9) | 4541 | -1670 | 5477 | 117 |
| H(10) | 3580 | -2235 | 6638 | 102 |
| H(11) | 3798 | 14 | 9361 | 94 |
| H(12) | 2978 | -2194 | 8363 | 100 |
| H(14) | 2053 | -3108 | 9428 | 113 |
| H(15) | 2902 | 573 | 10299 | 100 |
| H(16) | 1298 | -2864 | 10735 | 118 |
| H(17) | 2132 | 802 | 11566 | 102 |
| H(19) | 951 | -1687 | 12383 | 125 |
| H(20) | 566 | 61 | 13094 | 126 |
| H(22) | 1433 | 2408 | 13763 | 112 |
| H(23) | 1382 | 4557 | 13126 | 125 |
| H(25) | 260 | 3582 | 9848 | 117 |
| H(26) | 286 | 1399 | 10357 | 119 |

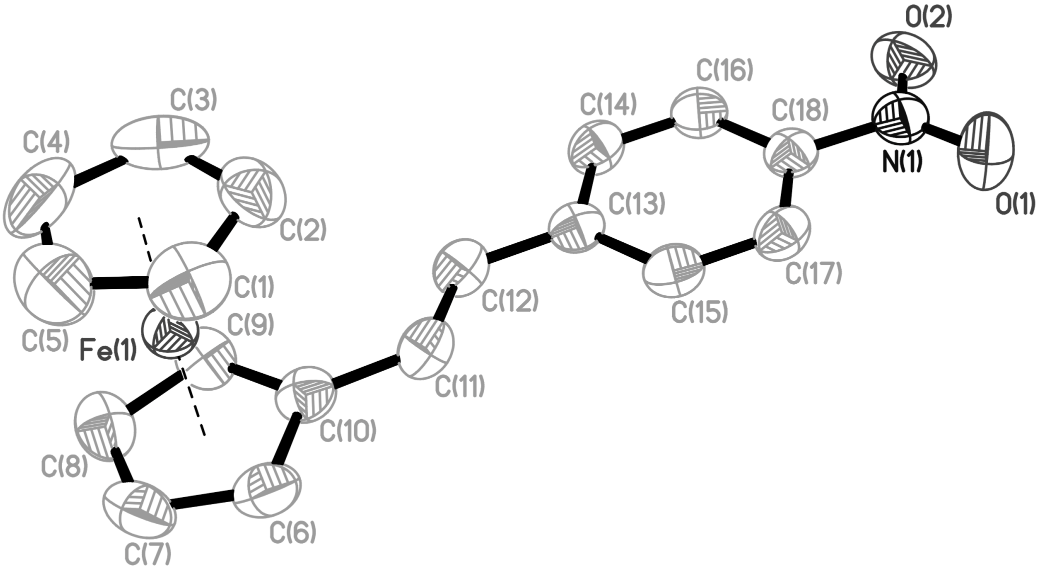

O(2)
C(16)
C(14)
C(18)
C(3)
C(4)
N(1)
C(13)
O(1)
C(2)
C(1)
C(12)
C(17)
C(15)
C(9)
C(5)
Fe(1)
C(11)
C(10)
C(8)
C(6)
C(7)

**Table 1.** Crystal data and structure refinement for str54m

| | | |
|---|---|---|
| Identification code | str54m | |
| Empirical formula | C18 H15 Fe N O2 | |
| Formula weight | 333.16 | |
| Temperature | 293(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | P2(1)/c | |
| Unit cell dimensions | a = 18.0285(13) Å | $\alpha$= 90°. |
| | b = 10.6208(7) Å | $\beta$= 98.223(2)°. |
| | c = 7.7084(5) Å | $\gamma$ = 90°. |
| Volume | 1460.81(17) Å$^3$ | |
| Z | 4 | |
| Density (calculated) | 1.515 Mg/m$^3$ | |
| Absorption coefficient | 1.038 mm$^{-1}$ | |
| F(000) | 688 | |
| Crystal size | 0.23 x 0.21 x 0.03 mm$^3$ | |
| Theta range for data collection | 1.14 to 26.37°. | |
| Index ranges | -22<=h<=13, -13<=k<=12, -9<=l<=9 | |
| Reflections collected | 9051 | |
| Independent reflections | 2990 [R(int) = 0.0364] | |
| Completeness to theta = 26.37° | 100.0 % | |
| Absorption correction | Bruker SADABS | |
| Refinement method | Full-matrix least-squares on F$^2$ | |
| Data / restraints / parameters | 2990 / 0 / 199 | |
| Goodness-of-fit on F$^2$ | 0.946 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0306, wR2 = 0.0679 | |
| R indices (all data) | R1 = 0.0591, wR2 = 0.0833 | |
| Largest diff. peak and hole | 0.236 and -0.294 e.Å$^{-3}$ | |

**Table 2**. Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters (Å$^2$x $10^3$) for tab54.ban. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| Fe(1) | 1402(1) | 72(1) | 2251(1) | 36(1) |
| N(1) | 5927(1) | -1529(2) | 9560(3) | 47(1) |
| O(1) | 6447(1) | -965(2) | 9059(3) | 71(1) |
| C(1) | 1833(2) | -230(3) | -23(3) | 59(1) |
| O(2) | 6014(1) | -2305(2) | 10754(3) | 61(1) |
| C(2) | 2131(2) | -1089(3) | 1239(4) | 57(1) |
| C(3) | 1537(2) | -1787(3) | 1772(4) | 69(1) |
| C(4) | 869(2) | -1334(3) | 791(5) | 75(1) |
| C(5) | 1059(2) | -379(3) | -303(4) | 71(1) |
| C(6) | 1788(2) | 1780(2) | 3195(3) | 50(1) |
| C(7) | 1003(2) | 1810(2) | 2768(3) | 55(1) |
| C(8) | 698(2) | 882(3) | 3767(3) | 52(1) |
| C(9) | 1299(2) | 269(2) | 4825(3) | 46(1) |
| C(10) | 1981(2) | 823(2) | 4493(3) | 43(1) |
| C(11) | 2743(2) | 486(2) | 5206(3) | 45(1) |
| C(12) | 2956(2) | -389(2) | 6419(3) | 42(1) |
| C(13) | 3720(1) | -689(2) | 7170(3) | 38(1) |
| C(14) | 3866(2) | -1648(2) | 8422(3) | 45(1) |
| C(15) | 4341(2) | -31(2) | 6734(3) | 42(1) |
| C(16) | 4577(2) | -1930(2) | 9198(3) | 43(1) |
| C(17) | 5056(2) | -305(2) | 7486(3) | 42(1) |
| C(18) | 5170(1) | -1261(2) | 8718(3) | 39(1) |

**Table 3**. Bond lengths [Å] and angles [°] for str54m.

| | |
|---|---|
| C(3)-Fe(1)-C(1) | 67.69(12) |
| C(8)-Fe(1)-C(1) | 154.78(12) |
| C(5)-Fe(1)-C(1) | 39.84(13) |
| C(2)-Fe(1)-C(1) | 39.69(11) |
| C(6)-Fe(1)-C(1) | 107.08(11) |
| C(7)-Fe(1)-C(1) | 119.86(12) |
| C(4)-Fe(1)-C(10) | 154.01(14) |
| C(9)-Fe(1)-C(10) | 40.73(10) |
| C(3)-Fe(1)-C(10) | 118.19(12) |
| C(8)-Fe(1)-C(10) | 68.59(11) |
| C(5)-Fe(1)-C(10) | 162.88(14) |
| C(2)-Fe(1)-C(10) | 106.28(11) |
| C(6)-Fe(1)-C(10) | 41.06(9) |
| C(7)-Fe(1)-C(10) | 68.56(11) |
| C(1)-Fe(1)-C(10) | 125.12(12) |
| O(1)-N(1)-O(2) | 123.0(2) |
| O(1)-N(1)-C(18) | 118.5(2) |
| O(2)-N(1)-C(18) | 118.5(2) |
| C(2)-C(1)-C(5) | 108.3(3) |
| C(2)-C(1)-Fe(1) | 69.95(15) |
| C(5)-C(1)-Fe(1) | 69.80(17) |
| C(1)-C(2)-C(3) | 108.5(3) |
| C(1)-C(2)-Fe(1) | 70.36(16) |
| C(3)-C(2)-Fe(1) | 69.47(16) |
| C(2)-C(3)-C(4) | 106.8(3) |
| C(2)-C(3)-Fe(1) | 69.95(15) |
| C(4)-C(3)-Fe(1) | 69.53(17) |
| C(5)-C(4)-C(3) | 107.9(3) |
| C(5)-C(4)-Fe(1) | 70.23(17) |
| C(3)-C(4)-Fe(1) | 69.75(16) |
| C(1)-C(5)-C(4) | 108.5(3) |
| C(1)-C(5)-Fe(1) | 70.36(16) |
| C(4)-C(5)-Fe(1) | 69.66(16) |
| C(7)-C(6)-C(10) | 108.3(2) |
| C(7)-C(6)-Fe(1) | 69.88(15) |
| C(10)-C(6)-Fe(1) | 69.81(14) |
| C(6)-C(7)-C(8) | 108.3(2) |
| C(6)-C(7)-Fe(1) | 69.76(14) |
| C(8)-C(7)-Fe(1) | 69.53(15) |
| C(7)-C(8)-C(9) | 108.1(3) |
| C(7)-C(8)-Fe(1) | 69.99(15) |
| C(9)-C(8)-Fe(1) | 69.40(14) |
| C(8)-C(9)-C(10) | 108.4(2) |
| C(8)-C(9)-Fe(1) | 69.78(14) |
| C(10)-C(9)-Fe(1) | 70.34(14) |
| C(9)-C(10)-C(6) | 106.9(2) |
| C(9)-C(10)-C(11) | 128.9(2) |
| C(6)-C(10)-C(11) | 124.2(3) |
| C(9)-C(10)-Fe(1) | 68.94(14) |
| C(6)-C(10)-Fe(1) | 69.13(13) |
| C(11)-C(10)-Fe(1) | 124.35(18) |
| C(12)-C(11)-C(10) | 126.9(3) |
| C(11)-C(12)-C(13) | 126.4(2) |
| C(15)-C(13)-C(14) | 116.8(2) |
| C(15)-C(13)-C(12) | 122.7(2) |
| C(14)-C(13)-C(12) | 120.5(2) |
| C(16)-C(14)-C(13) | 122.0(2) |
| C(17)-C(15)-C(13) | 121.9(2) |
| C(14)-C(16)-C(18) | 119.0(2) |
| C(15)-C(17)-C(18) | 119.0(2) |
| C(16)-C(18)-C(17) | 121.2(2) |
| C(16)-C(18)-N(1) | 119.6(2) |
| C(17)-C(18)-N(1) | 119.2(2) |

Symmetry transformations used to generate equivalent atoms:

**Table 4**. Anisotropic displacement parameters ($Å^2$x $10^3$) for tab54.ban. The anisotropic displacement factor exponent takes the form: $-2\pi^2$[ $h^2$ $a^{*2}U^{11}$ + ... + 2 h k a* b* $U^{12}$ ]

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| Fe(1) | 38(1) | 36(1) | 35(1) | -1(1) | 5(1) | 2(1) |
| N(1) | 48(2) | 46(1) | 47(1) | -13(1) | 5(1) | 2(1) |
| O(1) | 47(1) | 86(2) | 80(1) | 3(1) | 5(1) | -9(1) |
| C(1) | 72(2) | 64(2) | 46(2) | -7(1) | 20(2) | -1(2) |
| O(2) | 65(1) | 53(1) | 62(1) | 3(1) | -2(1) | 14(1) |
| C(2) | 49(2) | 62(2) | 59(2) | -13(1) | 6(2) | 15(2) |
| C(3) | 110(3) | 36(2) | 65(2) | -5(1) | 27(2) | 7(2) |
| C(4) | 53(2) | 76(2) | 99(3) | -49(2) | 22(2) | -22(2) |
| C(5) | 81(3) | 80(2) | 46(2) | -23(2) | -9(2) | 22(2) |
| C(6) | 64(2) | 35(1) | 48(2) | -2(1) | 2(1) | -6(1) |
| C(7) | 69(2) | 45(2) | 48(2) | -4(1) | 1(2) | 20(2) |
| C(8) | 47(2) | 66(2) | 44(1) | -9(1) | 8(1) | 9(2) |
| C(9) | 50(2) | 55(2) | 34(1) | 1(1) | 10(1) | 4(1) |
| C(10) | 53(2) | 41(1) | 35(1) | -4(1) | 3(1) | -3(1) |
| C(11) | 46(2) | 49(1) | 40(1) | -3(1) | 5(1) | -10(1) |
| C(12) | 45(2) | 46(1) | 37(1) | -1(1) | 10(1) | -7(1) |
| C(13) | 46(2) | 37(1) | 31(1) | -5(1) | 9(1) | -1(1) |
| C(14) | 48(2) | 44(1) | 44(1) | 2(1) | 13(1) | -8(1) |
| C(15) | 53(2) | 38(1) | 36(1) | 4(1) | 9(1) | -2(1) |
| C(16) | 50(2) | 39(1) | 41(1) | 4(1) | 7(1) | 0(1) |
| C(17) | 46(2) | 42(1) | 41(1) | -3(1) | 14(1) | -8(1) |
| C(18) | 44(2) | 38(1) | 35(1) | -8(1) | 6(1) | 0(1) |

**Table 5**. Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters (Å$^2$x 10 $^3$) for tab54.ban.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1) | 2104 | 347 | -587 | 71 |
| H(2) | 2637 | -1188 | 1664 | 68 |
| H(3) | 1578 | -2424 | 2609 | 83 |
| H(4) | 387 | -1622 | 863 | 89 |
| H(5) | 725 | 81 | -1089 | 85 |
| H(6) | 2125 | 2293 | 2716 | 60 |
| H(7) | 731 | 2349 | 1964 | 65 |
| H(8) | 192 | 704 | 3738 | 63 |
| H(9) | 1254 | -386 | 5604 | 55 |
| H(11) | 3123 | 925 | 4773 | 54 |
| H(12) | 2577 | -851 | 6823 | 51 |
| H(14) | 3466 | -2108 | 8735 | 54 |
| H(15) | 4264 | 612 | 5909 | 50 |
| H(16) | 4659 | -2563 | 10038 | 52 |
| H(17) | 5460 | 143 | 7175 | 51 |

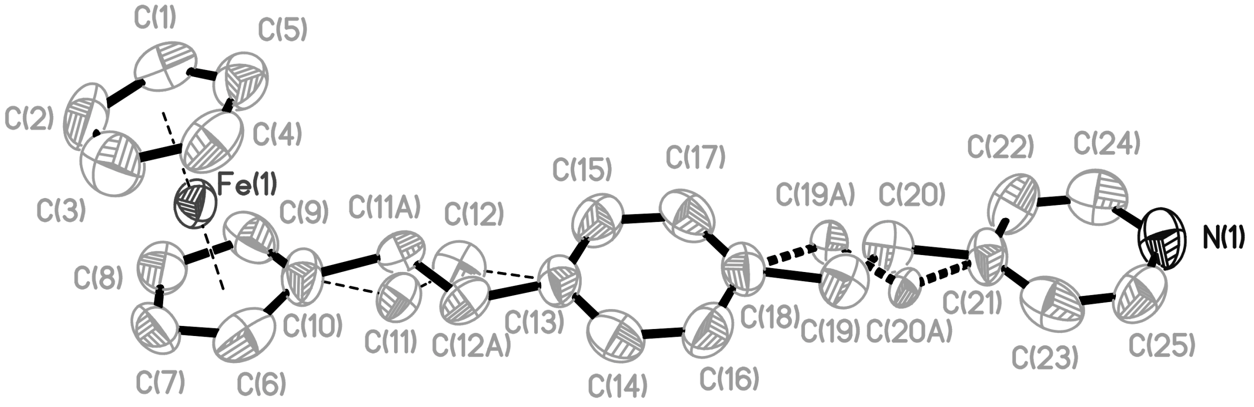
**Table 6**. Torsion angles [°] for str54m.

| | |
|---|---|
| C(4)-Fe(1)-C(1)-C(2) | -82.0(2) |
| C(9)-Fe(1)-C(1)-C(2) | 40.9(4) |
| C(3)-Fe(1)-C(1)-C(2) | -37.72(18) |
| C(8)-Fe(1)-C(1)-C(2) | -171.6(2) |
| C(5)-Fe(1)-C(1)-C(2) | -119.4(3) |
| C(6)-Fe(1)-C(1)-C(2) | 113.45(18) |
| C(7)-Fe(1)-C(1)-C(2) | 155.48(18) |
| C(10)-Fe(1)-C(1)-C(2) | 71.9(2) |
| C(4)-Fe(1)-C(1)-C(5) | 37.42(19) |
| C(9)-Fe(1)-C(1)-C(5) | 160.3(3) |
| C(3)-Fe(1)-C(1)-C(5) | 81.7(2) |
| C(8)-Fe(1)-C(1)-C(5) | -52.3(4) |
| C(2)-Fe(1)-C(1)-C(5) | 119.4(3) |
| C(6)-Fe(1)-C(1)-C(5) | -127.2(2) |
| C(7)-Fe(1)-C(1)-C(5) | -85.1(2) |
| C(10)-Fe(1)-C(1)-C(5) | -168.74(18) |
| C(5)-C(1)-C(2)-C(3) | -0.3(3) |
| Fe(1)-C(1)-C(2)-C(3) | 59.21(19) |
| C(5)-C(1)-C(2)-Fe(1) | -59.5(2) |
| C(4)-Fe(1)-C(2)-C(1) | 80.9(2) |
| C(9)-Fe(1)-C(2)-C(1) | -166.03(17) |
| C(3)-Fe(1)-C(2)-C(1) | 119.5(3) |
| C(8)-Fe(1)-C(2)-C(1) | 166.2(4) |
| C(5)-Fe(1)-C(2)-C(1) | 37.33(19) |
| C(6)-Fe(1)-C(2)-C(1) | -83.2(2) |
| C(7)-Fe(1)-C(2)-C(1) | -51.2(3) |
| C(10)-Fe(1)-C(2)-C(1) | -125.92(18) |
| C(4)-Fe(1)-C(2)-C(3) | -38.61(19) |
| C(9)-Fe(1)-C(2)-C(3) | 74.4(2) |
| C(8)-Fe(1)-C(2)-C(3) | 46.7(5) |
| C(5)-Fe(1)-C(2)-C(3) | -82.2(2) |
| C(6)-Fe(1)-C(2)-C(3) | 157.30(17) |
| C(7)-Fe(1)-C(2)-C(3) | -170.7(2) |
| C(1)-Fe(1)-C(2)-C(3) | -119.5(3) |
| C(10)-Fe(1)-C(2)-C(3) | 114.55(18) |
| C(1)-C(2)-C(3)-C(4) | 0.3(3) |
| Fe(1)-C(2)-C(3)-C(4) | 60.06(19) |
| C(1)-C(2)-C(3)-Fe(1) | -59.77(19) |
| C(4)-Fe(1)-C(3)-C(2) | 117.7(3) |
| C(9)-Fe(1)-C(3)-C(2) | -125.23(17) |
| C(8)-Fe(1)-C(3)-C(2) | -166.04(15) |
| C(5)-Fe(1)-C(3)-C(2) | 80.1(2) |
| C(6)-Fe(1)-C(3)-C(2) | -47.4(3) |
| C(7)-Fe(1)-C(3)-C(2) | 162.2(4) |
| C(1)-Fe(1)-C(3)-C(2) | 36.92(17) |
| C(10)-Fe(1)-C(3)-C(2) | -82.14(19) |
| C(9)-Fe(1)-C(3)-C(4) | 117.1(2) |
| C(8)-Fe(1)-C(3)-C(4) | 76.3(2) |
| C(5)-Fe(1)-C(3)-C(4) | -37.6(2) |
| C(2)-Fe(1)-C(3)-C(4) | -117.7(3) |
| C(6)-Fe(1)-C(3)-C(4) | -165.1(2) |
| C(7)-Fe(1)-C(3)-C(4) | 44.5(5) |
| C(1)-Fe(1)-C(3)-C(4) | -80.8(2) |
| C(10)-Fe(1)-C(3)-C(4) | 160.16(19) |
| C(2)-C(3)-C(4)-C(5) | -0.2(3) |
| Fe(1)-C(3)-C(4)-C(5) | 60.1(2) |
| C(2)-C(3)-C(4)-Fe(1) | -60.33(19) |
| C(9)-Fe(1)-C(4)-C(5) | 159.79(19) |
| C(3)-Fe(1)-C(4)-C(5) | -118.7(3) |
| C(8)-Fe(1)-C(4)-C(5) | 115.8(2) |
| C(2)-Fe(1)-C(4)-C(5) | -80.3(2) |
| C(6)-Fe(1)-C(4)-C(5) | 34.7(5) |
| C(7)-Fe(1)-C(4)-C(5) | 73.8(2) |
| C(1)-Fe(1)-C(4)-C(5) | -37.18(19) |
| C(10)-Fe(1)-C(4)-C(5) | -161.8(2) |
| C(9)-Fe(1)-C(4)-C(3) | -81.5(2) |
| C(8)-Fe(1)-C(4)-C(3) | -125.43(19) |
| C(5)-Fe(1)-C(4)-C(3) | 118.7(3) |
| C(2)-Fe(1)-C(4)-C(3) | 38.48(18) |
| C(6)-Fe(1)-C(4)-C(3) | 153.5(4) |
| C(7)-Fe(1)-C(4)-C(3) | -167.46(18) |
| C(1)-Fe(1)-C(4)-C(3) | 81.6(2) |
| C(10)-Fe(1)-C(4)-C(3) | -43.1(4) |
| C(2)-C(1)-C(5)-C(4) | 0.1(3) |

|  |  |  |  |
|---|---|---|---|
| Fe(1)-C(1)-C(5)-C(4) | -59.4(2) | Fe(1)-C(6)-C(7)-C(8) | 59.04(17) |
| C(2)-C(1)-C(5)-Fe(1) | 59.57(19) | C(10)-C(6)-C(7)-Fe(1) | -59.43(17) |
| C(3)-C(4)-C(5)-C(1) | 0.0(3) | C(4)-Fe(1)-C(7)-C(6) | -164.93(18) |
| Fe(1)-C(4)-C(5)-C(1) | 59.9(2) | C(9)-Fe(1)-C(7)-C(6) | 81.85(17) |
| C(3)-C(4)-C(5)-Fe(1) | -59.8(2) | C(3)-Fe(1)-C(7)-C(6) | 159.3(4) |
| C(4)-Fe(1)-C(5)-C(1) | -119.5(3) | C(8)-Fe(1)-C(7)-C(6) | 119.6(2) |
| C(9)-Fe(1)-C(5)-C(1) | -165.8(2) | C(5)-Fe(1)-C(7)-C(6) | -123.89(19) |
| C(3)-Fe(1)-C(5)-C(1) | -81.3(2) | C(2)-Fe(1)-C(7)-C(6) | -46.2(3) |
| C(8)-Fe(1)-C(5)-C(1) | 156.63(18) | C(1)-Fe(1)-C(7)-C(6) | -81.24(19) |
| C(2)-Fe(1)-C(5)-C(1) | -37.19(18) | C(10)-Fe(1)-C(7)-C(6) | 37.93(15) |
| C(6)-Fe(1)-C(5)-C(1) | 71.5(2) | C(4)-Fe(1)-C(7)-C(8) | 75.4(2) |
| C(7)-Fe(1)-C(5)-C(1) | 113.5(2) | C(9)-Fe(1)-C(7)-C(8) | -37.80(15) |
| C(10)-Fe(1)-C(5)-C(1) | 32.9(5) | C(3)-Fe(1)-C(7)-C(8) | 39.7(5) |
| C(9)-Fe(1)-C(5)-C(4) | -46.3(4) | C(5)-Fe(1)-C(7)-C(8) | 116.46(19) |
| C(3)-Fe(1)-C(5)-C(4) | 38.2(2) | C(2)-Fe(1)-C(7)-C(8) | -165.9(2) |
| C(8)-Fe(1)-C(5)-C(4) | -83.9(2) | C(6)-Fe(1)-C(7)-C(8) | -119.6(2) |
| C(2)-Fe(1)-C(5)-C(4) | 82.3(2) | C(1)-Fe(1)-C(7)-C(8) | 159.11(16) |
| C(6)-Fe(1)-C(5)-C(4) | -169.08(19) | C(10)-Fe(1)-C(7)-C(8) | -81.72(16) |
| C(7)-Fe(1)-C(5)-C(4) | -127.1(2) | C(6)-C(7)-C(8)-C(9) | 0.0(3) |
| C(1)-Fe(1)-C(5)-C(4) | 119.5(3) | Fe(1)-C(7)-C(8)-C(9) | 59.15(17) |
| C(10)-Fe(1)-C(5)-C(4) | 152.3(4) | C(6)-C(7)-C(8)-Fe(1) | -59.18(17) |
| C(4)-Fe(1)-C(6)-C(7) | 49.6(5) | C(4)-Fe(1)-C(8)-C(7) | -126.17(19) |
| C(9)-Fe(1)-C(6)-C(7) | -81.48(17) | C(9)-Fe(1)-C(8)-C(7) | 119.3(2) |
| C(3)-Fe(1)-C(6)-C(7) | -169.3(2) | C(3)-Fe(1)-C(8)-C(7) | -168.65(18) |
| C(8)-Fe(1)-C(6)-C(7) | -37.42(15) | C(5)-Fe(1)-C(8)-C(7) | -83.1(2) |
| C(5)-Fe(1)-C(6)-C(7) | 76.8(2) | C(2)-Fe(1)-C(8)-C(7) | 154.4(4) |
| C(2)-Fe(1)-C(6)-C(7) | 157.83(16) | C(6)-Fe(1)-C(8)-C(7) | 37.32(15) |
| C(1)-Fe(1)-C(6)-C(7) | 116.27(17) | C(1)-Fe(1)-C(8)-C(7) | -46.5(3) |
| C(10)-Fe(1)-C(6)-C(7) | -119.4(2) | C(10)-Fe(1)-C(8)-C(7) | 81.64(17) |
| C(4)-Fe(1)-C(6)-C(10) | 169.1(4) | C(4)-Fe(1)-C(8)-C(9) | 114.51(19) |
| C(9)-Fe(1)-C(6)-C(10) | 37.95(16) | C(3)-Fe(1)-C(8)-C(9) | 72.0(2) |
| C(3)-Fe(1)-C(6)-C(10) | -49.9(3) | C(5)-Fe(1)-C(8)-C(9) | 157.56(18) |
| C(8)-Fe(1)-C(6)-C(10) | 82.01(17) | C(2)-Fe(1)-C(8)-C(9) | 35.1(5) |
| C(5)-Fe(1)-C(6)-C(10) | -163.75(17) | C(6)-Fe(1)-C(8)-C(9) | -82.01(17) |
| C(2)-Fe(1)-C(6)-C(10) | -82.74(18) | C(7)-Fe(1)-C(8)-C(9) | -119.3(2) |
| C(7)-Fe(1)-C(6)-C(10) | 119.4(2) | C(1)-Fe(1)-C(8)-C(9) | -165.8(2) |
| C(1)-Fe(1)-C(6)-C(10) | -124.30(17) | C(10)-Fe(1)-C(8)-C(9) | -37.68(15) |
| C(10)-C(6)-C(7)-C(8) | -0.4(3) | C(7)-C(8)-C(9)-C(10) | 0.4(3) |

| | |
|---|---|
| Fe(1)-C(8)-C(9)-C(10) | 59.97(17) |
| C(7)-C(8)-C(9)-Fe(1) | -59.52(17) |
| C(4)-Fe(1)-C(9)-C(8) | -85.4(2) |
| C(3)-Fe(1)-C(9)-C(8) | -128.09(19) |
| C(5)-Fe(1)-C(9)-C(8) | -52.4(3) |
| C(2)-Fe(1)-C(9)-C(8) | -169.30(17) |
| C(6)-Fe(1)-C(9)-C(8) | 81.02(18) |
| C(7)-Fe(1)-C(9)-C(8) | 37.49(17) |
| C(1)-Fe(1)-C(9)-C(8) | 159.5(3) |
| C(10)-Fe(1)-C(9)-C(8) | 119.3(2) |
| C(4)-Fe(1)-C(9)-C(10) | 155.34(17) |
| C(3)-Fe(1)-C(9)-C(10) | 112.64(17) |
| C(8)-Fe(1)-C(9)-C(10) | -119.3(2) |
| C(5)-Fe(1)-C(9)-C(10) | -171.7(3) |
| C(2)-Fe(1)-C(9)-C(10) | 71.43(19) |
| C(6)-Fe(1)-C(9)-C(10) | -38.25(15) |
| C(7)-Fe(1)-C(9)-C(10) | -81.78(17) |
| C(1)-Fe(1)-C(9)-C(10) | 40.2(4) |
| C(8)-C(9)-C(10)-C(6) | -0.7(3) |
| Fe(1)-C(9)-C(10)-C(6) | 58.94(16) |
| C(8)-C(9)-C(10)-C(11) | -177.4(2) |
| Fe(1)-C(9)-C(10)-C(11) | -117.8(3) |
| C(8)-C(9)-C(10)-Fe(1) | -59.62(17) |
| C(7)-C(6)-C(10)-C(9) | 0.7(3) |
| Fe(1)-C(6)-C(10)-C(9) | -58.82(16) |
| C(7)-C(6)-C(10)-C(11) | 177.6(2) |
| Fe(1)-C(6)-C(10)-C(11) | 118.1(2) |
| C(7)-C(6)-C(10)-Fe(1) | 59.48(17) |
| C(4)-Fe(1)-C(10)-C(9) | -54.7(3) |
| C(3)-Fe(1)-C(10)-C(9) | -85.02(19) |
| C(8)-Fe(1)-C(10)-C(9) | 37.77(15) |
| C(5)-Fe(1)-C(10)-C(9) | 168.4(4) |
| C(2)-Fe(1)-C(10)-C(9) | -127.19(16) |
| C(6)-Fe(1)-C(10)-C(9) | 118.7(2) |
| C(7)-Fe(1)-C(10)-C(9) | 81.39(17) |
| C(1)-Fe(1)-C(10)-C(9) | -166.42(15) |
| C(4)-Fe(1)-C(10)-C(6) | -173.4(2) |
| C(9)-Fe(1)-C(10)-C(6) | -118.7(2) |
| C(3)-Fe(1)-C(10)-C(6) | 156.29(18) |
| C(8)-Fe(1)-C(10)-C(6) | -80.92(18) |
| C(5)-Fe(1)-C(10)-C(6) | 49.8(5) |
| C(2)-Fe(1)-C(10)-C(6) | 114.12(18) |
| C(7)-Fe(1)-C(10)-C(6) | -37.30(17) |
| C(1)-Fe(1)-C(10)-C(6) | 74.9(2) |
| C(4)-Fe(1)-C(10)-C(11) | 68.8(4) |
| C(9)-Fe(1)-C(10)-C(11) | 123.4(3) |
| C(3)-Fe(1)-C(10)-C(11) | 38.4(3) |
| C(8)-Fe(1)-C(10)-C(11) | 161.2(2) |
| C(5)-Fe(1)-C(10)-C(11) | -68.1(5) |
| C(2)-Fe(1)-C(10)-C(11) | -3.8(2) |
| C(6)-Fe(1)-C(10)-C(11) | -117.9(3) |
| C(7)-Fe(1)-C(10)-C(11) | -155.2(2) |
| C(1)-Fe(1)-C(10)-C(11) | -43.0(3) |
| C(9)-C(10)-C(11)-C(12) | -4.2(4) |
| C(6)-C(10)-C(11)-C(12) | 179.6(2) |
| Fe(1)-C(10)-C(11)-C(12) | -93.7(3) |
| C(10)-C(11)-C(12)-C(13) | -177.7(2) |
| C(11)-C(12)-C(13)-C(15) | 2.7(4) |
| C(11)-C(12)-C(13)-C(14) | -179.0(2) |
| C(15)-C(13)-C(14)-C(16) | 0.4(4) |
| C(12)-C(13)-C(14)-C(16) | -177.9(2) |
| C(14)-C(13)-C(15)-C(17) | 0.1(3) |
| C(12)-C(13)-C(15)-C(17) | 178.3(2) |
| C(13)-C(14)-C(16)-C(18) | -0.9(4) |
| C(13)-C(15)-C(17)-C(18) | -0.1(4) |
| C(14)-C(16)-C(18)-C(17) | 0.8(3) |
| C(14)-C(16)-C(18)-N(1) | 178.6(2) |
| C(15)-C(17)-C(18)-C(16) | -0.3(3) |
| C(15)-C(17)-C(18)-N(1) | -178.1(2) |
| O(1)-N(1)-C(18)-C(16) | 176.7(2) |
| O(2)-N(1)-C(18)-C(16) | -3.8(3) |
| O(1)-N(1)-C(18)-C(17) | -5.5(3) |
| O(2)-N(1)-C(18)-C(17) | 174.0(2) |

Symmetry transformations used to generate equivalent atoms:


C(1)
C(5)
C(2)
C(4)
C(3)
Fe(1)
C(9)
C(11A)
C(12)
C(15)
C(17)
C(19A)
C(20)
C(22)
C(24)
N(1)
C(8)
C(10)
C(11)
C(12A)
C(13)
C(18)
C(19)
C(20A)
C(21)
C(23)
C(25)
C(7)
C(6)
C(14)
C(16)

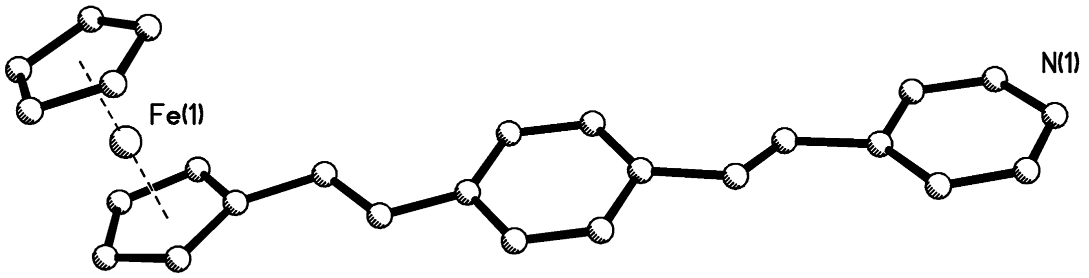

Fe(1)
N(1)

**Table 1.** Crystal data and structure refinement for str55m.

| | | |
|---|---|---|
| Identification code | str55m | |
| Empirical formula | C25 H21 Fe N | |
| Formula weight | 391.28 | |
| Temperature | 293(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | P2(1) | |
| Unit cell dimensions | a = 6.2814(4) Å | $\alpha$= 90°. |
| | b = 7.7253(6) Å | $\beta$= 95.394(2)°. |
| | c = 19.3917(14) Å | $\gamma$ = 90°. |
| Volume | 936.83(12) Å$^3$ | |
| Z | 2 | |
| Density (calculated) | 1.387 Mg/m$^3$ | |
| Absorption coefficient | 0.813 mm$^{-1}$ | |
| F(000) | 408 | |
| Crystal size | 0.41 x 0.18 x 0.02 mm$^3$ | |
| Theta range for data collection | 1.05 to 23.81°. | |
| Index ranges | -7<=h<=5, -8<=k<=8, -22<=l<=22 | |
| Reflections collected | 4833 | |
| Independent reflections | 2602 [R(int) = 0.0346] | |
| Completeness to theta = 23.81° | 100.0 % | |
| Refinement method | Full-matrix least-squares on F$^2$ | |
| Data / restraints / parameters | 2602 / 1 / 282 | |
| Goodness-of-fit on F$^2$ | 0.974 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0411, wR2 = 0.0896 | |
| R indices (all data) | R1 = 0.0593, wR2 = 0.1103 | |
| Absolute structure parameter | -0.03(4) | |
| Largest diff. peak and hole | 0.217 and -0.293 e.Å$^{-3}$ | |

**Table 2.** Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters (Å$^2$x $10^3$) for str55m. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| Fe(1) | 7504(1) | 8363(2) | 8887(1) | 48(1) |
| C(1) | 9901(11) | 7632(8) | 9605(3) | 66(2) |
| N(1) | 17849(10) | 9445(7) | 2351(3) | 72(2) |
| C(2) | 7906(13) | 7288(10) | 9837(3) | 75(2) |
| C(3) | 6881(13) | 6135(11) | 9366(5) | 86(3) |
| C(4) | 8232(16) | 5791(10) | 8843(4) | 71(2) |
| C(5) | 10065(11) | 6711(8) | 8997(3) | 67(2) |
| C(6) | 5423(12) | 9127(8) | 8073(3) | 71(2) |
| C(7) | 4774(10) | 9758(8) | 8704(3) | 65(2) |
| C(8) | 6371(12) | 10803(9) | 9008(4) | 64(2) |
| C(9) | 8027(12) | 10822(9) | 8564(4) | 67(2) |
| C(10) | 7447(11) | 9805(8) | 7988(3) | 64(2) |
| C(11) | 9085(19) | 9871(14) | 7460(8) | 47(4) |
| C(12) | 8570(20) | 9363(17) | 6812(10) | 53(4) |
| C(11A) | 7850(40) | 9120(30) | 7246(13) | 46(8) |
| C(12A) | 9400(50) | 9930(30) | 7013(12) | 38(6) |
| C(13) | 10056(10) | 9493(7) | 6282(3) | 54(2) |
| C(14) | 9224(9) | 8737(9) | 5676(3) | 64(2) |
| C(15) | 12097(11) | 10211(9) | 6295(3) | 67(2) |
| C(16) | 10317(11) | 8655(11) | 5101(3) | 69(2) |
| C(17) | 13200(10) | 10157(8) | 5710(4) | 68(2) |
| C(18) | 12330(11) | 9400(8) | 5106(3) | 62(2) |
| C(19A) | 14050(30) | 9770(30) | 4631(13) | 37(6) |
| C(20A) | 13650(40) | 9220(20) | 3944(12) | 35(6) |
| C(19) | 13070(30) | 9120(18) | 4385(10) | 57(5) |
| C(20) | 14670(30) | 9871(18) | 4206(11) | 60(5) |
| C(21) | 15454(11) | 9592(8) | 3493(3) | 61(2) |
| C(22) | 17377(12) | 10378(9) | 3488(3) | 74(2) |
| C(23) | 14727(10) | 8722(10) | 2902(4) | 76(2) |
| C(24) | 18495(11) | 10284(9) | 2927(4) | 77(2) |
| C(25) | 15950(12) | 8700(10) | 2344(3) | 73(2) |

**Table 3**. Bond lengths [Å] and angles [°] for str55m.

| | | | |
|---|---|---|---|
| Fe(1)-C(3) | 2.012(7) | C(3)-Fe(1)-C(6) | 117.8(3) |
| Fe(1)-C(2) | 2.014(6) | C(2)-Fe(1)-C(6) | 147.5(3) |
| Fe(1)-C(7) | 2.028(6) | C(7)-Fe(1)-C(6) | 40.6(2) |
| Fe(1)-C(1) | 2.032(6) | C(1)-Fe(1)-C(6) | 171.9(3) |
| Fe(1)-C(8) | 2.036(7) | C(8)-Fe(1)-C(6) | 67.4(3) |
| Fe(1)-C(9) | 2.036(7) | C(9)-Fe(1)-C(6) | 66.6(3) |
| Fe(1)-C(6) | 2.040(6) | C(3)-Fe(1)-C(4) | 40.6(3) |
| Fe(1)-C(4) | 2.043(8) | C(2)-Fe(1)-C(4) | 68.1(3) |
| Fe(1)-C(5) | 2.049(7) | C(7)-Fe(1)-C(4) | 134.3(4) |
| Fe(1)-C(10) | 2.066(5) | C(1)-Fe(1)-C(4) | 66.7(3) |
| C(1)-C(5) | 1.390(8) | C(8)-Fe(1)-C(4) | 170.9(4) |
| C(1)-C(2) | 1.396(9) | C(9)-Fe(1)-C(4) | 148.4(3) |
| N(1)-C(24) | 1.322(8) | C(6)-Fe(1)-C(4) | 112.3(3) |
| N(1)-C(25) | 1.323(8) | C(3)-Fe(1)-C(5) | 66.7(3) |
| C(2)-C(3) | 1.390(10) | C(2)-Fe(1)-C(5) | 67.6(3) |
| C(3)-C(4) | 1.407(11) | C(7)-Fe(1)-C(5) | 172.7(3) |
| C(4)-C(5) | 1.362(11) | C(1)-Fe(1)-C(5) | 39.8(2) |
| C(6)-C(10) | 1.399(9) | C(8)-Fe(1)-C(5) | 147.6(3) |
| C(6)-C(7) | 1.412(8) | C(9)-Fe(1)-C(5) | 117.7(3) |
| C(7)-C(8) | 1.376(9) | C(6)-Fe(1)-C(5) | 134.4(3) |
| C(8)-C(9) | 1.410(11) | C(4)-Fe(1)-C(5) | 38.9(3) |
| C(9)-C(10) | 1.386(10) | C(3)-Fe(1)-C(10) | 149.5(3) |
| C(10)-C(11) | 1.520(15) | C(2)-Fe(1)-C(10) | 169.8(3) |
| C(10)-C(11A) | 1.58(2) | C(7)-Fe(1)-C(10) | 67.6(2) |
| C(11)-C(12) | 1.33(3) | C(1)-Fe(1)-C(10) | 132.9(3) |
| C(12)-C(13) | 1.456(18) | C(8)-Fe(1)-C(10) | 67.6(3) |
| C(11A)-C(12A) | 1.28(6) | C(9)-Fe(1)-C(10) | 39.5(3) |
| C(12A)-C(13) | 1.55(2) | C(6)-Fe(1)-C(10) | 39.8(3) |
| C(13)-C(14) | 1.371(8) | C(4)-Fe(1)-C(10) | 118.4(3) |
| C(13)-C(15) | 1.395(9) | C(5)-Fe(1)-C(10) | 112.0(2) |
| C(14)-C(16) | 1.366(8) | C(5)-C(1)-C(2) | 108.4(6) |
| C(15)-C(17) | 1.385(9) | C(5)-C(1)-Fe(1) | 70.7(4) |
| C(16)-C(18) | 1.388(9) | C(2)-C(1)-Fe(1) | 69.1(4) |
| C(17)-C(18) | 1.375(9) | C(24)-N(1)-C(25) | 115.3(5) |
| C(18)-C(19A) | 1.51(2) | C(3)-C(2)-C(1) | 106.6(6) |
| C(18)-C(19) | 1.531(19) | C(3)-C(2)-Fe(1) | 69.7(4) |
| C(19A)-C(20A) | 1.40(5) | C(1)-C(2)-Fe(1) | 70.5(3) |
| C(20A)-C(21) | 1.52(2) | C(2)-C(3)-C(4) | 108.7(8) |
| C(19)-C(20) | 1.24(3) | C(2)-C(3)-Fe(1) | 69.9(4) |
| C(20)-C(21) | 1.53(2) | C(4)-C(3)-Fe(1) | 70.9(4) |
| C(21)-C(22) | 1.353(9) | C(5)-C(4)-C(3) | 107.4(7) |
| C(21)-C(23) | 1.370(9) | C(5)-C(4)-Fe(1) | 70.8(4) |
| C(22)-C(24) | 1.351(9) | C(3)-C(4)-Fe(1) | 68.5(4) |
| C(23)-C(25) | 1.385(9) | C(4)-C(5)-C(1) | 108.9(6) |
| C(3)-Fe(1)-C(2) | 40.4(3) | C(4)-C(5)-Fe(1) | 70.3(5) |
| C(3)-Fe(1)-C(7) | 109.7(3) | C(1)-C(5)-Fe(1) | 69.4(4) |
| C(2)-Fe(1)-C(7) | 114.2(3) | C(10)-C(6)-C(7) | 108.2(6) |
| C(3)-Fe(1)-C(1) | 67.0(3) | C(10)-C(6)-Fe(1) | 71.1(4) |
| C(2)-Fe(1)-C(1) | 40.4(3) | C(7)-C(6)-Fe(1) | 69.2(3) |
| C(7)-Fe(1)-C(1) | 145.8(3) | C(8)-C(7)-C(6) | 108.3(6) |
| C(3)-Fe(1)-C(8) | 130.9(3) | C(8)-C(7)-Fe(1) | 70.5(4) |
| C(2)-Fe(1)-C(8) | 107.0(3) | C(6)-C(7)-Fe(1) | 70.1(3) |
| C(7)-Fe(1)-C(8) | 39.6(3) | C(7)-C(8)-C(9) | 107.2(6) |
| C(1)-Fe(1)-C(8) | 115.0(3) | C(7)-C(8)-Fe(1) | 69.9(4) |
| C(3)-Fe(1)-C(9) | 169.8(4) | C(9)-C(8)-Fe(1) | 69.8(4) |
| C(2)-Fe(1)-C(9) | 131.0(3) | C(10)-C(9)-C(8) | 109.4(7) |
| C(7)-Fe(1)-C(9) | 67.0(3) | C(10)-C(9)-Fe(1) | 71.4(4) |
| C(1)-Fe(1)-C(9) | 109.8(3) | C(8)-C(9)-Fe(1) | 69.7(4) |
| C(8)-Fe(1)-C(9) | 40.5(3) | C(9)-C(10)-C(6) | 106.9(5) |

| | | | |
|---|---|---|---|
| C(9)-C(10)-C(11) | 112.4(8) | C(18)-C(17)-C(15) | 121.4(6) |
| C(6)-C(10)-C(11) | 140.6(9) | C(17)-C(18)-C(16) | 118.1(5) |
| C(9)-C(10)-C(11A) | 150.9(13) | C(17)-C(18)-C(19A) | 101.0(12) |
| C(6)-C(10)-C(11A) | 102.0(13) | C(16)-C(18)-C(19A) | 140.8(12) |
| C(11)-C(10)-C(11A) | 38.6(8) | C(17)-C(18)-C(19) | 135.0(10) |
| C(9)-C(10)-Fe(1) | 69.1(4) | C(16)-C(18)-C(19) | 106.9(10) |
| C(6)-C(10)-Fe(1) | 69.1(3) | C(19A)-C(18)-C(19) | 34.1(6) |
| C(11)-C(10)-Fe(1) | 128.9(5) | C(20A)-C(19A)-C(18) | 117(2) |
| C(11A)-C(10)-Fe(1) | 126.6(8) | C(19A)-C(20A)-C(21) | 114(2) |
| C(12)-C(11)-C(10) | 120.5(13) | C(20)-C(19)-C(18) | 121(2) |
| C(11)-C(12)-C(13) | 122.1(15) | C(19)-C(20)-C(21) | 122(2) |
| C(12A)-C(11A)-C(10) | 111(3) | C(22)-C(21)-C(23) | 116.2(5) |
| C(11A)-C(12A)-C(13) | 120(3) | C(22)-C(21)-C(20A) | 143.4(11) |
| C(14)-C(13)-C(15) | 117.4(5) | C(23)-C(21)-C(20A) | 100.4(11) |
| C(14)-C(13)-C(12) | 110.9(9) | C(22)-C(21)-C(20) | 108.0(10) |
| C(15)-C(13)-C(12) | 131.6(9) | C(23)-C(21)-C(20) | 135.8(10) |
| C(14)-C(13)-C(12A) | 139.7(13) | C(20A)-C(21)-C(20) | 35.4(6) |
| C(15)-C(13)-C(12A) | 102.8(13) | C(24)-C(22)-C(21) | 120.9(6) |
| C(12)-C(13)-C(12A) | 29.0(8) | C(21)-C(23)-C(25) | 119.6(6) |
| C(16)-C(14)-C(13) | 122.6(6) | N(1)-C(24)-C(22) | 124.4(6) |
| C(17)-C(15)-C(13) | 120.2(6) | N(1)-C(25)-C(23) | 123.5(6) |
| C(14)-C(16)-C(18) | 120.2(6) | | |

Symmetry transformations used to generate equivalent atoms:

**Table 4.** Anisotropic displacement parameters ($Å^2$x $10^3$) for str55m. The anisotropic displacement factor exponent takes the form: $-2\pi^2[ h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12} ]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| Fe(1) | 52(1) | 50(1) | 42(1) | 7(1) | 11(1) | 1(1) |
| C(1) | 71(4) | 61(4) | 61(4) | 8(3) | -14(3) | 2(3) |
| N(1) | 82(4) | 73(4) | 65(4) | 9(3) | 31(3) | -4(3) |
| C(2) | 104(6) | 76(5) | 48(4) | 14(3) | 28(4) | 13(4) |
| C(3) | 74(5) | 77(6) | 108(7) | 38(5) | 20(5) | -6(4) |
| C(4) | 103(6) | 50(4) | 57(5) | 4(3) | -3(4) | 1(4) |
| C(5) | 80(5) | 60(4) | 61(4) | 12(3) | 11(3) | 7(4) |
| C(6) | 91(5) | 61(4) | 56(4) | -3(3) | -14(4) | 6(3) |
| C(7) | 45(4) | 75(5) | 77(4) | 18(4) | 20(3) | 6(3) |
| C(8) | 72(5) | 58(4) | 62(4) | 7(3) | 14(4) | 17(4) |
| C(9) | 51(4) | 55(5) | 97(6) | 24(5) | 19(4) | 3(3) |
| C(10) | 83(5) | 59(4) | 54(4) | 18(3) | 28(4) | 27(4) |
| C(11) | 51(6) | 45(6) | 44(10) | 6(5) | -4(5) | 3(5) |
| C(12) | 63(8) | 53(7) | 40(10) | -10(6) | -8(7) | -7(5) |
| C(11A) | 59(15) | 39(10) | 39(13) | -8(8) | 3(10) | -2(9) |
| C(12A) | 66(15) | 47(13) | 1(11) | -6(8) | -4(9) | 4(10) |
| C(13) | 67(4) | 49(3) | 49(3) | 12(3) | 18(3) | 14(3) |
| C(14) | 53(3) | 57(6) | 81(4) | 2(3) | 8(3) | -2(3) |
| C(15) | 80(5) | 66(4) | 54(4) | -9(3) | 0(3) | 2(4) |
| C(16) | 85(4) | 72(6) | 48(3) | -8(4) | 0(3) | 11(4) |
| C(17) | 53(4) | 65(4) | 89(5) | 14(4) | 18(4) | -2(3) |
| C(18) | 73(5) | 63(4) | 54(4) | 14(3) | 22(3) | 23(3) |
| C(19A) | 36(10) | 38(9) | 38(13) | -6(8) | 9(8) | -15(7) |
| C(20A) | 40(10) | 43(9) | 23(12) | -8(7) | 2(8) | -1(7) |
| C(19) | 72(10) | 40(6) | 58(10) | -4(5) | 7(8) | 0(6) |
| C(20) | 66(10) | 50(7) | 65(11) | -3(7) | 6(9) | -3(7) |
| C(21) | 89(5) | 48(4) | 48(4) | 12(3) | 26(3) | 19(3) |
| C(22) | 99(6) | 66(5) | 57(4) | -10(3) | 2(4) | -17(4) |
| C(23) | 54(4) | 74(6) | 101(5) | 20(5) | 17(3) | -8(4) |
| C(24) | 62(4) | 72(5) | 96(6) | 2(4) | 7(4) | -23(3) |
| C(25) | 96(5) | 62(6) | 58(3) | -13(4) | -5(3) | -6(4) |

**Table 5.** Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters (Å$^2$x 10 $^3$) for str55m.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1) | 10944 | 8355 | 9821 | 79 |
| H(2) | 7368 | 7742 | 10229 | 90 |
| H(3) | 5526 | 5668 | 9392 | 103 |
| H(4) | 7929 | 5069 | 8463 | 85 |
| H(5) | 11236 | 6720 | 8737 | 80 |
| H(6) | 4640 | 8389 | 7767 | 85 |
| H(7) | 3486 | 9510 | 8884 | 78 |
| H(8) | 6361 | 11387 | 9427 | 76 |
| H(9) | 9309 | 11423 | 8646 | 80 |
| H(11) | 10460 | 10271 | 7591 | 57 |
| H(12) | 7212 | 8909 | 6693 | 63 |
| H(11A) | 7074 | 8236 | 7012 | 55 |
| H(12A) | 10125 | 10783 | 7279 | 46 |
| H(14) | 7860 | 8261 | 5656 | 77 |
| H(15) | 12718 | 10728 | 6698 | 81 |
| H(16) | 9712 | 8099 | 4705 | 82 |
| H(17) | 14558 | 10644 | 5725 | 82 |
| H(19A) | 15307 | 10332 | 4787 | 45 |
| H(20A) | 12391 | 8669 | 3776 | 42 |
| H(19) | 12312 | 8372 | 4077 | 68 |
| H(20) | 15410 | 10629 | 4514 | 72 |
| H(22) | 17938 | 10992 | 3876 | 89 |
| H(23) | 13419 | 8150 | 2875 | 91 |
| H(24) | 19808 | 10848 | 2947 | 92 |
| H(25) | 15408 | 8130 | 1943 | 88 |

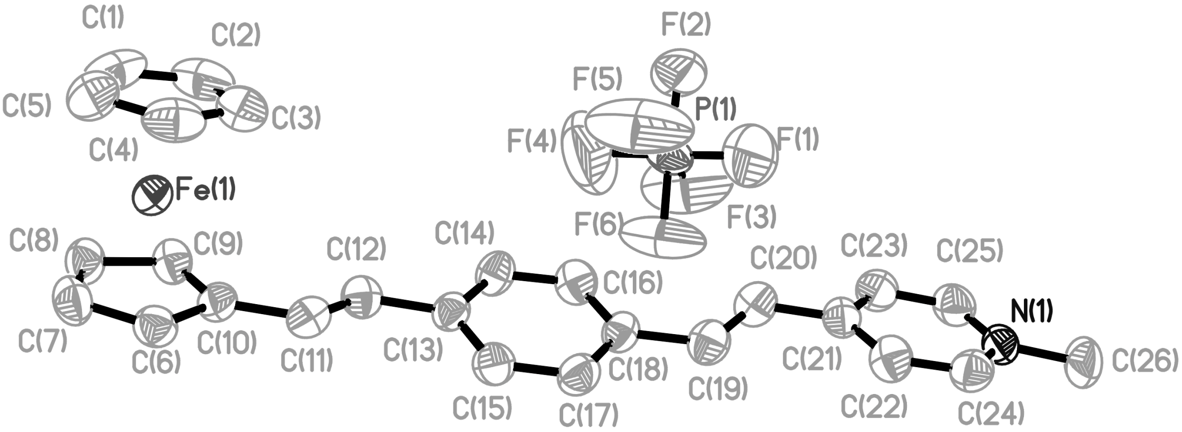

C(1)
C(2)
C(5)
C(3)
C(4)
Fe(1)
F(2)
F(5)
P(1)
F(4)
F(1)
F(6)
F(3)
C(8)
C(9)
C(12)
C(14)
C(16)
C(20)
C(23)
C(25)
N(1)
C(7)
C(6)
C(10)
C(11)
C(13)
C(15)
C(17)
C(18)
C(19)
C(21)
C(22)
C(24)
C(26)

**Table 1**. Crystal data and structure refinement for str57m.

| | | |
|---|---|---|
| Identification code | str57m | |
| Empirical formula | C26 H24 F6 Fe N P | |
| Formula weight | 551.28 | |
| Temperature | 293(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | P2(1)/c | |
| Unit cell dimensions | a = 12.0649(9) Å | $\alpha$= 90°. |
| | b = 15.7470(12) Å | $\beta$= 95.150(2)°. |
| | c = 12.5267(9) Å | $\gamma$ = 90°. |
| Volume | 2370.3(3) Å$^{3}$ | |
| Z | 4 | |
| Density (calculated) | 1.545 Mg/m$^{3}$ | |
| Absorption coefficient | 0.767 mm$^{-1}$ | |
| F(000) | 1128 | |
| Crystal size | 0.14 x 0.09 x 0.09 mm$^{3}$ | |
| Theta range for data collection | 1.69 to 23.26°. | |
| Index ranges | -13<=h<=12, -17<=k<=17, -13<=l<=13 | |
| Reflections collected | 11387 | |
| Independent reflections | 3400 [R(int) = 0.0571] | |
| Completeness to theta = 23.26° | 100.0 % | |
| Refinement method | Full-matrix least-squares on F$^{2}$ | |
| Data / restraints / parameters | 3400 / 0 / 316 | |
| Goodness-of-fit on F$^{2}$ | 1.060 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0548, wR2 = 0.1356 | |
| R indices (all data) | R1 = 0.0882, wR2 = 0.1502 | |
| Largest diff. peak and hole | 0.746 and -0.414 e.Å$^{-3}$ | |

**Table 2**. Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) for str57m. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| Fe(1) | 14906(1) | 2042(1) | 18423(1) | 39(1) |
| N(1) | 11400(4) | -387(3) | 7551(3) | 48(1) |
| C(1) | 15260(6) | 3288(4) | 18668(6) | 74(2) |
| P(1) | 9597(1) | 2743(1) | 11160(1) | 65(1) |
| F(2) | 9621(5) | 3692(3) | 10797(3) | 129(2) |
| C(2) | 14916(5) | 3145(4) | 17601(6) | 72(2) |
| C(3) | 15643(6) | 2582(4) | 17180(5) | 67(2) |
| F(3) | 8359(4) | 2646(4) | 10770(6) | 179(3) |
| C(4) | 16460(5) | 2370(4) | 18005(5) | 61(2) |
| F(4) | 9195(6) | 3019(5) | 12234(5) | 201(3) |
| C(5) | 16221(5) | 2812(4) | 18926(5) | 63(2) |
| F(5) | 10776(4) | 2866(4) | 11684(7) | 191(3) |
| C(6) | 14730(4) | 754(3) | 18618(4) | 46(1) |
| F(6) | 9646(4) | 1777(3) | 11486(5) | 134(2) |
| C(7) | 14599(4) | 1182(4) | 19586(4) | 53(1) |
| C(8) | 13715(4) | 1755(3) | 19420(4) | 49(1) |
| C(9) | 13278(4) | 1691(3) | 18340(4) | 45(1) |
| C(10) | 13894(4) | 1059(3) | 17834(4) | 42(1) |
| C(11) | 13749(4) | 770(3) | 16724(4) | 48(1) |
| C(12) | 12985(4) | 1033(3) | 15992(4) | 46(1) |
| C(13) | 12804(4) | 752(3) | 14871(4) | 41(1) |
| C(14) | 12100(4) | 1212(3) | 14154(4) | 48(1) |
| C(15) | 13306(4) | 40(3) | 14482(4) | 51(1) |
| C(16) | 11931(4) | 998(4) | 13097(4) | 51(1) |
| C(17) | 13128(4) | -192(3) | 13418(4) | 51(1) |
| C(18) | 12450(4) | 288(3) | 12701(4) | 42(1) |
| C(19) | 12324(4) | 37(4) | 11567(4) | 52(1) |
| C(20) | 11804(4) | 444(4) | 10767(4) | 53(1) |
| C(21) | 11702(4) | 156(3) | 9646(4) | 46(1) |
| C(22) | 12351(4) | -476(4) | 9263(4) | 52(1) |
| C(23) | 10905(5) | 519(4) | 8921(4) | 55(2) |
| C(24) | 12200(5) | -729(4) | 8215(4) | 54(2) |
| C(25) | 10765(5) | 232(4) | 7887(4) | 56(2) |
| C(26) | 11181(5) | -705(4) | 6441(4) | 72(2) |
| F(1) | 9925(9) | 2494(4) | 10078(5) | 230(4) |

**Table 3**. Bond lengths [Å] and angles [°] for  str57m.

| | |
|---|---|
| Fe(1)-C(2) | 2.020(6) |
| Fe(1)-C(1) | 2.026(6) |
| Fe(1)-C(9) | 2.033(5) |
| Fe(1)-C(8) | 2.037(5) |
| Fe(1)-C(3) | 2.046(6) |
| Fe(1)-C(7) | 2.046(5) |
| Fe(1)-C(5) | 2.051(5) |
| Fe(1)-C(6) | 2.055(5) |
| Fe(1)-C(4) | 2.058(5) |
| Fe(1)-C(10) | 2.066(5) |
| N(1)-C(25) | 1.330(7) |
| N(1)-C(24) | 1.331(7) |
| N(1)-C(26) | 1.479(6) |
| C(1)-C(2) | 1.381(9) |
| C(1)-C(5) | 1.394(9) |
| P(1)-F(1) | 1.498(6) |
| P(1)-F(5) | 1.525(5) |
| P(1)-F(4) | 1.533(6) |
| P(1)-F(3) | 1.536(5) |
| P(1)-F(2) | 1.564(4) |
| P(1)-F(6) | 1.575(4) |
| C(2)-C(3) | 1.385(9) |
| C(3)-C(4) | 1.402(8) |
| C(4)-C(5) | 1.399(8) |
| C(6)-C(7) | 1.408(7) |
| C(6)-C(10) | 1.426(7) |
| C(7)-C(8) | 1.398(7) |
| C(8)-C(9) | 1.411(7) |
| C(9)-C(10) | 1.425(7) |
| C(10)-C(11) | 1.458(7) |
| C(11)-C(12) | 1.308(6) |
| C(12)-C(13) | 1.470(7) |
| C(13)-C(15) | 1.383(7) |
| C(13)-C(14) | 1.384(7) |
| C(14)-C(16) | 1.364(7) |
| C(15)-C(17) | 1.380(7) |
| C(16)-C(18) | 1.394(7) |
| C(17)-C(18) | 1.385(7) |
| C(18)-C(19) | 1.469(7) |
| C(19)-C(20) | 1.302(7) |
| C(20)-C(21) | 1.470(7) |
| C(21)-C(22) | 1.380(7) |
| C(21)-C(23) | 1.386(7) |
| C(22)-C(24) | 1.368(7) |
| C(23)-C(25) | 1.368(7) |
| C(2)-Fe(1)-C(1) | 39.9(3) |
| C(2)-Fe(1)-C(9) | 104.9(2) |
| C(1)-Fe(1)-C(9) | 117.4(3) |
| C(2)-Fe(1)-C(8) | 122.7(3) |
| C(1)-Fe(1)-C(8) | 105.8(2) |
| C(9)-Fe(1)-C(8) | 40.56(19) |
| C(2)-Fe(1)-C(3) | 39.8(3) |
| C(1)-Fe(1)-C(3) | 67.2(3) |
| C(9)-Fe(1)-C(3) | 123.9(2) |
| C(8)-Fe(1)-C(3) | 159.6(3) |
| C(2)-Fe(1)-C(7) | 160.3(3) |
| C(1)-Fe(1)-C(7) | 125.6(3) |
| C(9)-Fe(1)-C(7) | 67.7(2) |
| C(8)-Fe(1)-C(7) | 40.0(2) |
| C(3)-Fe(1)-C(7) | 159.3(3) |
| C(2)-Fe(1)-C(5) | 66.9(3) |
| C(1)-Fe(1)-C(5) | 40.0(2) |
| C(9)-Fe(1)-C(5) | 153.3(2) |
| C(8)-Fe(1)-C(5) | 120.7(2) |
| C(3)-Fe(1)-C(5) | 67.1(3) |
| C(7)-Fe(1)-C(5) | 110.9(2) |
| C(2)-Fe(1)-C(6) | 156.1(3) |
| C(1)-Fe(1)-C(6) | 163.8(3) |
| C(9)-Fe(1)-C(6) | 68.2(2) |
| C(8)-Fe(1)-C(6) | 67.8(2) |
| C(3)-Fe(1)-C(6) | 123.8(2) |
| C(7)-Fe(1)-C(6) | 40.17(19) |
| C(5)-Fe(1)-C(6) | 129.2(2) |
| C(2)-Fe(1)-C(4) | 66.8(3) |
| C(1)-Fe(1)-C(4) | 67.1(2) |
| C(9)-Fe(1)-C(4) | 162.4(2) |

|  |  |  |  |
|---|---|---|---|
| C(8)-Fe(1)-C(4) | 157.0(2) | C(4)-C(3)-Fe(1) | 70.5(3) |
| C(3)-Fe(1)-C(4) | 40.0(2) | C(5)-C(4)-C(3) | 107.8(5) |
| C(7)-Fe(1)-C(4) | 125.0(2) | C(5)-C(4)-Fe(1) | 69.8(3) |
| C(5)-Fe(1)-C(4) | 39.8(2) | C(3)-C(4)-Fe(1) | 69.6(3) |
| C(6)-Fe(1)-C(4) | 112.6(2) | C(1)-C(5)-C(4) | 107.8(6) |
| C(2)-Fe(1)-C(10) | 119.5(3) | C(1)-C(5)-Fe(1) | 69.1(3) |
| C(1)-Fe(1)-C(10) | 152.8(3) | C(4)-C(5)-Fe(1) | 70.4(3) |
| C(9)-Fe(1)-C(10) | 40.7(2) | C(7)-C(6)-C(10) | 107.8(5) |
| C(8)-Fe(1)-C(10) | 68.1(2) | C(7)-C(6)-Fe(1) | 69.6(3) |
| C(3)-Fe(1)-C(10) | 108.8(2) | C(10)-C(6)-Fe(1) | 70.2(3) |
| C(7)-Fe(1)-C(10) | 67.7(2) | C(8)-C(7)-C(6) | 108.9(5) |
| C(5)-Fe(1)-C(10) | 165.6(2) | C(8)-C(7)-Fe(1) | 69.6(3) |
| C(6)-Fe(1)-C(10) | 40.50(19) | C(6)-C(7)-Fe(1) | 70.3(3) |
| C(4)-Fe(1)-C(10) | 128.3(2) | C(7)-C(8)-C(9) | 108.1(5) |
| C(25)-N(1)-C(24) | 120.3(5) | C(7)-C(8)-Fe(1) | 70.3(3) |
| C(25)-N(1)-C(26) | 119.1(5) | C(9)-C(8)-Fe(1) | 69.6(3) |
| C(24)-N(1)-C(26) | 120.5(5) | C(8)-C(9)-C(10) | 108.2(5) |
| C(2)-C(1)-C(5) | 107.9(6) | C(8)-C(9)-Fe(1) | 69.9(3) |
| C(2)-C(1)-Fe(1) | 69.8(3) | C(10)-C(9)-Fe(1) | 70.9(3) |
| C(5)-C(1)-Fe(1) | 70.9(3) | C(9)-C(10)-C(6) | 107.0(4) |
| F(1)-P(1)-F(5) | 96.4(5) | C(9)-C(10)-C(11) | 128.3(5) |
| F(1)-P(1)-F(4) | 176.5(5) | C(6)-C(10)-C(11) | 124.7(5) |
| F(5)-P(1)-F(4) | 86.7(4) | C(9)-C(10)-Fe(1) | 68.4(3) |
| F(1)-P(1)-F(3) | 90.8(5) | C(6)-C(10)-Fe(1) | 69.4(3) |
| F(5)-P(1)-F(3) | 172.8(5) | C(11)-C(10)-Fe(1) | 126.2(4) |
| F(4)-P(1)-F(3) | 86.1(4) | C(12)-C(11)-C(10) | 126.0(5) |
| F(1)-P(1)-F(2) | 88.5(3) | C(11)-C(12)-C(13) | 127.6(5) |
| F(5)-P(1)-F(2) | 87.8(3) | C(15)-C(13)-C(14) | 117.3(4) |
| F(4)-P(1)-F(2) | 89.9(4) | C(15)-C(13)-C(12) | 123.2(5) |
| F(3)-P(1)-F(2) | 92.6(3) | C(14)-C(13)-C(12) | 119.5(5) |
| F(1)-P(1)-F(6) | 88.6(4) | C(16)-C(14)-C(13) | 122.0(5) |
| F(5)-P(1)-F(6) | 89.9(3) | C(17)-C(15)-C(13) | 121.3(5) |
| F(4)-P(1)-F(6) | 93.1(4) | C(14)-C(16)-C(18) | 120.7(5) |
| F(3)-P(1)-F(6) | 90.0(3) | C(15)-C(17)-C(18) | 120.9(5) |
| F(2)-P(1)-F(6) | 176.1(3) | C(17)-C(18)-C(16) | 117.7(5) |
| C(1)-C(2)-C(3) | 109.1(6) | C(17)-C(18)-C(19) | 119.0(5) |
| C(1)-C(2)-Fe(1) | 70.3(4) | C(16)-C(18)-C(19) | 123.3(5) |
| C(3)-C(2)-Fe(1) | 71.1(4) | C(20)-C(19)-C(18) | 127.8(5) |
| C(2)-C(3)-C(4) | 107.4(6) | C(19)-C(20)-C(21) | 125.2(5) |
| C(2)-C(3)-Fe(1) | 69.1(4) | C(22)-C(21)-C(23) | 116.8(5) |

|  |  |  |  |
|---|---|---|---|
| C(22)-C(21)-C(20) | 123.6(5) | C(25)-C(23)-C(21) | 120.3(5) |
| C(23)-C(21)-C(20) | 119.6(5) | N(1)-C(24)-C(22) | 120.5(5) |
| C(24)-C(22)-C(21) | 120.9(5) | N(1)-C(25)-C(23) | 121.1(5) |

Symmetry transformations used to generate equivalent atoms:

**Table 4**. Anisotropic displacement parameters (Å$^2$x 10$^3$) for str57m. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| Fe(1) | 38(1) | 39(1) | 40(1) | -3(1) | 1(1) | -2(1) |
| N(1) | 52(3) | 54(3) | 38(3) | -2(2) | 5(2) | -15(2) |
| C(1) | 71(5) | 45(4) | 110(6) | -25(4) | 28(4) | -12(3) |
| P(1) | 62(1) | 65(1) | 65(1) | 20(1) | -9(1) | -10(1) |
| F(2) | 227(6) | 63(3) | 89(3) | 20(2) | -28(3) | -4(3) |
| C(2) | 61(4) | 54(4) | 99(5) | 28(4) | -1(4) | -6(3) |
| C(3) | 81(5) | 61(4) | 61(4) | 5(3) | 16(4) | -17(4) |
| F(3) | 97(4) | 142(5) | 277(8) | 30(5) | -87(5) | -4(3) |
| C(4) | 45(4) | 49(4) | 93(5) | 6(3) | 25(4) | -2(3) |
| F(4) | 223(8) | 281(9) | 110(4) | -1(5) | 71(5) | -40(6) |
| C(5) | 49(4) | 71(4) | 67(4) | -3(3) | -5(3) | -22(3) |
| F(5) | 80(4) | 141(5) | 335(9) | 92(5) | -78(5) | -45(3) |
| C(6) | 49(3) | 42(3) | 47(3) | 3(2) | 5(3) | 3(2) |
| F(6) | 89(3) | 86(3) | 218(5) | 69(3) | -36(3) | -28(2) |
| C(7) | 53(4) | 66(4) | 38(3) | 6(3) | -3(3) | -4(3) |
| C(8) | 51(3) | 58(4) | 40(3) | -4(3) | 11(3) | -3(3) |
| C(9) | 35(3) | 59(3) | 42(3) | 1(3) | 1(2) | -3(2) |
| C(10) | 43(3) | 42(3) | 41(3) | -3(2) | 3(2) | -8(2) |
| C(11) | 46(3) | 44(3) | 53(3) | -6(3) | 4(3) | -3(2) |
| C(12) | 42(3) | 50(3) | 46(3) | 0(3) | 7(3) | 1(2) |
| C(13) | 40(3) | 42(3) | 40(3) | -5(2) | 3(2) | -6(2) |
| C(14) | 44(3) | 51(3) | 47(3) | -9(3) | 2(3) | 7(3) |
| C(15) | 57(4) | 48(3) | 46(3) | 4(3) | -9(3) | -2(3) |
| C(16) | 44(3) | 60(4) | 49(3) | 2(3) | -5(3) | 2(3) |
| C(17) | 61(4) | 41(3) | 50(3) | -5(3) | -1(3) | 6(3) |
| C(18) | 38(3) | 46(3) | 41(3) | -7(2) | 3(2) | -3(2) |
| C(19) | 47(3) | 57(4) | 52(3) | -6(3) | 1(3) | -2(3) |
| C(20) | 48(3) | 54(4) | 55(4) | -5(3) | -1(3) | 4(3) |
| C(21) | 41(3) | 53(3) | 42(3) | -2(3) | 5(2) | -11(3) |
| C(22) | 43(3) | 63(4) | 47(3) | 0(3) | -6(3) | -1(3) |
| C(23) | 61(4) | 51(4) | 52(4) | 3(3) | 1(3) | 5(3) |
| C(24) | 52(4) | 53(4) | 57(4) | -5(3) | 9(3) | -10(3) |
| C(25) | 62(4) | 59(4) | 46(3) | 9(3) | -8(3) | -4(3) |
| C(26) | 92(5) | 86(5) | 39(3) | -14(3) | 2(3) | -26(4) |
| F(1) | 441(13) | 121(5) | 151(5) | -35(4) | 159(7) | -26(6) |

**Table 5**. Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters (Å$^2$x 10 $^3$) for str57m.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1) | 14912 | 3640 | 19132 | 89 |
| H(2) | 14296 | 3388 | 17226 | 86 |
| H(3) | 15598 | 2380 | 16480 | 81 |
| H(4) | 17055 | 2001 | 17950 | 73 |
| H(5) | 16629 | 2791 | 19592 | 76 |
| H(6) | 15265 | 346 | 18510 | 55 |
| H(7) | 15030 | 1098 | 20230 | 63 |
| H(8) | 13459 | 2115 | 19933 | 59 |
| H(9) | 12691 | 2007 | 18015 | 54 |
| H(11) | 14245 | 362 | 16518 | 57 |
| H(12) | 12500 | 1446 | 16205 | 55 |
| H(14) | 11730 | 1681 | 14401 | 57 |
| H(15) | 13773 | -288 | 14947 | 61 |
| H(16) | 11465 | 1330 | 12635 | 62 |
| H(17) | 13468 | -678 | 13180 | 61 |
| H(19) | 12656 | -473 | 11400 | 62 |
| H(20) | 11470 | 958 | 10917 | 63 |
| H(22) | 12898 | -734 | 9723 | 62 |
| H(23) | 10463 | 960 | 9138 | 66 |
| H(24) | 12661 | -1144 | 7965 | 64 |
| H(25) | 10217 | 473 | 7412 | 68 |
| H(26A) | 11705 | -1145 | 6317 | 108 |
| H(26B) | 11258 | -248 | 5946 | 108 |
| H(26C) | 10439 | -929 | 6340 | 108 |

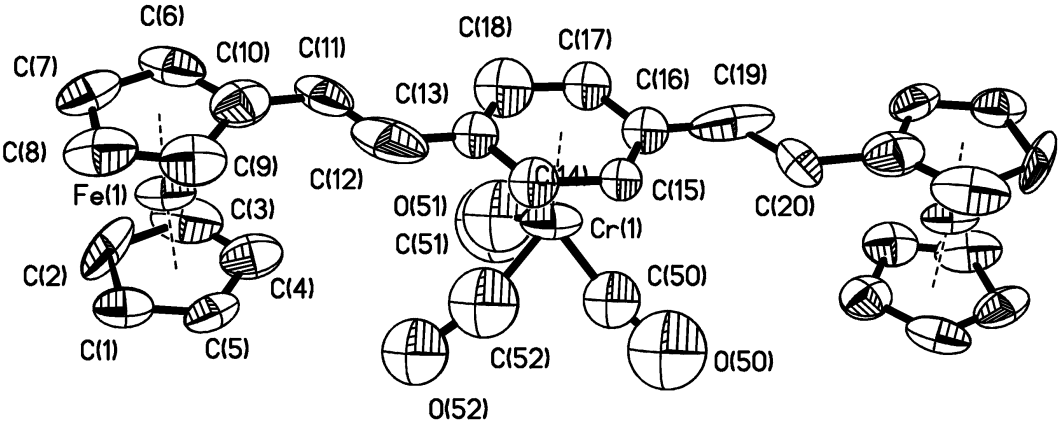

C(6)
C(7)
C(10)
C(11)
C(18)
C(17)
C(13)
C(16)
C(19)
C(8)
C(9)
C(12)
C(14)
C(15)
C(20)
Fe(1)
C(3)
O(51)
Cr(1)
C(51)
C(2)
C(4)
C(50)
C(1)
C(5)
C(52)
O(50)
O(52)

**Table 1**. Crystal data and structure refinement for str67m.

| | | |
|---|---|---|
| Identification code | str67m | |
| Empirical formula | C33 H26 Cr Fe2 O3 | |
| Formula weight | 634.24 | |
| Temperature | 293(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | P2(1)/c | |
| Unit cell dimensions | a = 17.131(3) Å | $\alpha$= 90°. |
| | b = 7.4568(13) Å | $\beta$= 99.780(4)°. |
| | c = 10.7432(19) Å | $\gamma$ = 90°. |
| Volume | 1352.4(4) Å$^3$ | |
| Z | 2 | |
| Density (calculated) | 1.557 Mg/m$^3$ | |
| Absorption coefficient | 1.487 mm$^{-1}$ | |
| F(000) | 648 | |
| Crystal size | 0.046 x 0.042 x 0.011 mm$^3$ | |
| Theta range for data collection | 1.21 to 24.70°. | |
| Index ranges | -11<=h<=11, -7<=k<=7, -7<=l<=12 | |
| Reflections collected | 4327 | |
| Independent reflections | 1353 [R(int) = 0.0790] | |
| Completeness to theta = 24.70° | 58.7 % | |
| Absorption correction | BRUKER | |
| Refinement method | Full-matrix least-squares on F$^2$ | |
| Data / restraints / parameters | 1353 / 0 / 182 | |
| Goodness-of-fit on F$^2$ | 1.082 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0699, wR2 = 0.1749 | |
| R indices (all data) | R1 = 0.1035, wR2 = 0.2007 | |
| Largest diff. peak and hole | 0.456 and -0.507 e.Å$^{-3}$ | |

**Table 2**. Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters (Å$^2$x $10^3$) for str67m. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| Fe(1) | 3533(1) | 5162(2) | 8181(1) | 55(1) |
| Cr(1) | 156(6) | 5347(7) | 5138(8) | 72(2) |
| C(1) | 3950(10) | 7635(13) | 8080(11) | 64(4) |
| C(2) | 4359(7) | 6442(19) | 7405(14) | 80(4) |
| C(3) | 3760(13) | 5748(16) | 6465(10) | 88(5) |
| C(4) | 3014(10) | 6462(16) | 6531(11) | 74(4) |
| C(5) | 3151(9) | 7652(13) | 7554(11) | 60(3) |
| C(6) | 3471(10) | 2516(14) | 8384(10) | 71(4) |
| C(7) | 4062(8) | 3182(13) | 9311(11) | 71(4) |
| C(8) | 3686(11) | 4391(14) | 10031(10) | 79(4) |
| C(9) | 2897(9) | 4466(15) | 9516(11) | 69(4) |
| C(10) | 2723(10) | 3243(15) | 8474(11) | 68(4) |
| C(11) | 2080(20) | 2970(30) | 7600(20) | 68(8) |
| C(12) | 1380(20) | 3840(30) | 7660(20) | 96(10) |
| C(13) | 710(10) | 3620(20) | 6723(14) | 53(5) |
| C(14) | 68(10) | 4555(18) | 7007(12) | 60(6) |
| C(15) | -660(9) | 4402(19) | 6238(14) | 43(6) |
| C(16) | -745(9) | 3320(20) | 5185(13) | 56(6) |
| C(17) | -103(10) | 2390(20) | 4901(14) | 62(6) |
| C(18) | 624(10) | 2540(20) | 5670(16) | 93(13) |
| C(19) | -1490(30) | 3040(30) | 4310(20) | 100(13) |
| C(20) | -2172(15) | 3840(30) | 4319(16) | 53(6) |
| C(50) | -419(19) | 7000(40) | 4560(30) | 87(9) |
| O(50) | -958(16) | 8040(40) | 4170(30) | 172(10) |
| O(51) | 1060(20) | 5460(40) | 3100(30) | 211(13) |
| C(51) | 870(30) | 5320(50) | 4070(50) | 151(18) |
| C(52) | 720(20) | 7180(50) | 5670(30) | 131(14) |
| O(52) | 1312(12) | 8300(30) | 6154(19) | 116(6) |

**Table 3**. Bond lengths [Å] and angles [°] for str67m.

| | |
|---|---|
| Fe(1)-C(1) | 1.987(10) |
| Fe(1)-C(6) | 1.990(10) |
| Fe(1)-C(3) | 1.996(11) |
| Fe(1)-C(2) | 2.002(11) |
| Fe(1)-C(9) | 2.010(11) |
| Fe(1)-C(7) | 2.026(10) |
| Fe(1)-C(8) | 2.042(10) |
| Fe(1)-C(5) | 2.044(10) |
| Fe(1)-C(10) | 2.054(12) |
| Fe(1)-C(4) | 2.082(11) |
| Cr(1)-Cr(1)#1 | 0.766(10) |
| Cr(1)-C(16)#1 | 1.50(2) |
| Cr(1)-C(50) | 1.63(4) |
| Cr(1)-C(17)#1 | 1.69(3) |
| Cr(1)-C(52) | 1.71(4) |
| Cr(1)-C(51) | 1.81(5) |
| Cr(1)-C(50)#1 | 1.82(3) |
| Cr(1)-C(15)#1 | 1.84(3) |
| Cr(1)-C(15) | 2.099(18) |
| Cr(1)-C(14) | 2.123(16) |
| Cr(1)-C(51)#1 | 2.14(5) |
| Cr(1)-C(18)#1 | 2.15(3) |
| C(1)-C(5) | 1.389(15) |
| C(1)-C(2) | 1.407(15) |
| C(2)-C(3) | 1.410(16) |
| C(3)-C(4) | 1.397(17) |
| C(4)-C(5) | 1.401(15) |
| C(4)-C(20)#1 | 1.59(2) |
| C(6)-C(7) | 1.386(15) |
| C(6)-C(10) | 1.410(15) |
| C(7)-C(8) | 1.412(14) |
| C(8)-C(9) | 1.372(16) |
| C(9)-C(10) | 1.435(16) |
| C(10)-C(11) | 1.34(2) |
| C(11)-C(12) | 1.37(3) |
| C(12)-C(13) | 1.40(3) |
| C(13)-C(14) | 1.378(9) |
| C(13)-C(18) | 1.378(9) |
| C(13)-C(50)#1 | 1.46(3) |
| C(13)-O(50)#1 | 1.67(3) |
| C(13)-Cr(1)#1 | 2.404(17) |
| C(14)-C(15) | 1.378(9) |
| C(14)-C(51)#1 | 1.82(5) |
| C(14)-O(51)#1 | 1.91(4) |
| C(14)-Cr(1)#1 | 2.273(16) |
| C(15)-C(51)#1 | 0.49(5) |
| C(15)-O(51)#1 | 1.07(4) |
| C(15)-C(16) | 1.378(9) |
| C(15)-Cr(1)#1 | 1.84(2) |
| C(16)-C(52)#1 | 0.99(4) |
| C(16)-C(51)#1 | 1.33(5) |
| C(16)-C(17) | 1.378(9) |
| C(16)-C(19) | 1.47(4) |
| C(16)-Cr(1)#1 | 1.500(19) |
| C(16)-C(50)#1 | 1.98(4) |
| C(17)-C(50)#1 | 1.08(3) |
| C(17)-C(52)#1 | 1.17(4) |
| C(17)-C(18) | 1.378(9) |
| C(17)-Cr(1)#1 | 1.693(17) |
| C(18)-C(50)#1 | 0.52(4) |
| C(18)-O(50)#1 | 0.72(3) |
| C(18)-Cr(1)#1 | 2.152(19) |
| C(19)-O(52)#1 | 1.18(3) |
| C(19)-C(20) | 1.30(3) |
| C(19)-C(52)#1 | 1.33(4) |
| C(20)-C(4)#1 | 1.59(2) |
| C(50)-C(18)#1 | 0.52(5) |
| C(50)-C(17)#1 | 1.08(4) |
| C(50)-O(50) | 1.23(4) |
| C(50)-C(13)#1 | 1.46(3) |
| C(50)-Cr(1)#1 | 1.82(3) |
| C(50)-C(16)#1 | 1.98(5) |
| O(50)-C(18)#1 | 0.72(4) |

| | |
|---|---|
| O(50)-C(13)#1 | 1.67(3) |
| O(51)-C(15)#1 | 1.07(4) |
| O(51)-C(51) | 1.15(6) |
| O(51)-C(14)#1 | 1.91(4) |
| C(51)-C(15)#1 | 0.49(6) |
| C(51)-C(16)#1 | 1.33(5) |
| C(51)-C(14)#1 | 1.82(6) |
| C(51)-Cr(1)#1 | 2.14(5) |
| C(52)-C(16)#1 | 0.99(5) |
| C(52)-C(17)#1 | 1.17(5) |
| C(52)-C(19)#1 | 1.33(4) |
| C(52)-O(52) | 1.35(4) |
| C(52)-Cr(1)#1 | 2.47(4) |
| O(52)-C(19)#1 | 1.18(3) |
| C(1)-Fe(1)-C(6) | 162.2(7) |
| C(1)-Fe(1)-C(3) | 67.6(5) |
| C(6)-Fe(1)-C(3) | 109.9(5) |
| C(1)-Fe(1)-C(2) | 41.3(4) |
| C(6)-Fe(1)-C(2) | 124.9(6) |
| C(3)-Fe(1)-C(2) | 41.3(5) |
| C(1)-Fe(1)-C(9) | 121.4(5) |
| C(6)-Fe(1)-C(9) | 67.7(5) |
| C(3)-Fe(1)-C(9) | 158.4(7) |
| C(2)-Fe(1)-C(9) | 157.9(6) |
| C(1)-Fe(1)-C(7) | 125.5(6) |
| C(6)-Fe(1)-C(7) | 40.4(4) |
| C(3)-Fe(1)-C(7) | 125.1(6) |
| C(2)-Fe(1)-C(7) | 108.7(5) |
| C(9)-Fe(1)-C(7) | 68.0(5) |
| C(1)-Fe(1)-C(8) | 109.0(5) |
| C(6)-Fe(1)-C(8) | 67.3(4) |
| C(3)-Fe(1)-C(8) | 161.3(7) |
| C(2)-Fe(1)-C(8) | 123.8(6) |
| C(9)-Fe(1)-C(8) | 39.6(5) |
| C(7)-Fe(1)-C(8) | 40.6(4) |
| C(1)-Fe(1)-C(5) | 40.3(4) |
| C(6)-Fe(1)-C(5) | 156.5(6) |
| C(3)-Fe(1)-C(5) | 66.3(5) |
| C(2)-Fe(1)-C(5) | 68.8(5) |
| C(9)-Fe(1)-C(5) | 106.7(5) |
| C(7)-Fe(1)-C(5) | 160.9(5) |
| C(8)-Fe(1)-C(5) | 123.9(5) |
| C(1)-Fe(1)-C(10) | 156.0(6) |
| C(6)-Fe(1)-C(10) | 40.8(4) |
| C(3)-Fe(1)-C(10) | 122.5(6) |
| C(2)-Fe(1)-C(10) | 159.9(6) |
| C(9)-Fe(1)-C(10) | 41.3(4) |
| C(7)-Fe(1)-C(10) | 69.2(5) |
| C(8)-Fe(1)-C(10) | 68.5(6) |
| C(5)-Fe(1)-C(10) | 119.8(6) |
| C(1)-Fe(1)-C(4) | 68.1(5) |
| C(6)-Fe(1)-C(4) | 122.1(5) |
| C(3)-Fe(1)-C(4) | 40.0(5) |
| C(2)-Fe(1)-C(4) | 69.7(5) |
| C(9)-Fe(1)-C(4) | 121.5(6) |
| C(7)-Fe(1)-C(4) | 158.8(5) |
| C(8)-Fe(1)-C(4) | 157.7(6) |
| C(5)-Fe(1)-C(4) | 39.7(4) |
| C(10)-Fe(1)-C(4) | 104.7(5) |
| Cr(1)#1-Cr(1)-C(16)#1 | 144.1(19) |
| Cr(1)#1-Cr(1)-C(50) | 91.5(18) |
| C(16)#1-Cr(1)-C(50) | 78.3(14) |
| Cr(1)#1-Cr(1)-C(17)#1 | 129(2) |
| C(16)#1-Cr(1)-C(17)#1 | 50.7(5) |
| C(50)-Cr(1)-C(17)#1 | 37.9(12) |
| Cr(1)#1-Cr(1)-C(52) | 169(2) |
| C(16)#1-Cr(1)-C(52) | 35.3(17) |
| C(50)-Cr(1)-C(52) | 78.1(16) |
| C(17)#1-Cr(1)-C(52) | 40.2(16) |
| Cr(1)#1-Cr(1)-C(51) | 104(2) |
| C(16)#1-Cr(1)-C(51) | 46.2(16) |
| C(50)-Cr(1)-C(51) | 101.3(18) |
| C(17)#1-Cr(1)-C(51) | 92.0(16) |
| C(52)-Cr(1)-C(51) | 79.3(19) |
| Cr(1)#1-Cr(1)-C(50)#1 | 63.6(15) |
| C(16)#1-Cr(1)-C(50)#1 | 121.5(16) |

| | | | |
|---|---|---|---|
| C(50)-Cr(1)-C(50)#1 | 155.1(7) | Cr(1)#1-Cr(1)-C(18)#1 | 89.6(17) |
| C(17)#1-Cr(1)-C(50)#1 | 166.9(14) | C(16)#1-Cr(1)-C(18)#1 | 79.4(7) |
| C(52)-Cr(1)-C(50)#1 | 126.8(17) | C(50)-Cr(1)-C(18)#1 | 2.0(12) |
| C(51)-Cr(1)-C(50)#1 | 85.9(17) | C(17)#1-Cr(1)-C(18)#1 | 39.8(5) |
| Cr(1)#1-Cr(1)-C(15)#1 | 98.5(17) | C(52)-Cr(1)-C(18)#1 | 80.0(15) |
| C(16)#1-Cr(1)-C(15)#1 | 47.3(6) | C(51)-Cr(1)-C(18)#1 | 101.1(17) |
| C(50)-Cr(1)-C(15)#1 | 87.3(14) | C(50)#1-Cr(1)-C(18)#1 | 153.2(12) |
| C(17)#1-Cr(1)-C(15)#1 | 84.8(7) | C(15)#1-Cr(1)-C(18)#1 | 86.8(7) |
| C(52)-Cr(1)-C(15)#1 | 82.5(16) | C(15)-Cr(1)-C(18)#1 | 92.6(13) |
| C(51)-Cr(1)-C(15)#1 | 15.5(19) | C(14)-Cr(1)-C(18)#1 | 116.5(12) |
| C(50)#1-Cr(1)-C(15)#1 | 96.0(13) | C(51)#1-Cr(1)-C(18)#1 | 80.4(15) |
| Cr(1)#1-Cr(1)-C(15) | 60.3(14) | C(5)-C(1)-C(2) | 109.8(13) |
| C(16)#1-Cr(1)-C(15) | 153.1(14) | C(5)-C(1)-Fe(1) | 72.1(7) |
| C(50)-Cr(1)-C(15) | 92.9(13) | C(2)-C(1)-Fe(1) | 69.9(6) |
| C(17)#1-Cr(1)-C(15) | 108.1(15) | C(1)-C(2)-C(3) | 103.6(11) |
| C(52)-Cr(1)-C(15) | 118.3(14) | C(1)-C(2)-Fe(1) | 68.8(6) |
| C(51)-Cr(1)-C(15) | 159.6(14) | C(3)-C(2)-Fe(1) | 69.1(7) |
| C(50)#1-Cr(1)-C(15) | 75.3(11) | C(4)-C(3)-C(2) | 112.6(12) |
| C(15)#1-Cr(1)-C(15) | 158.8(11) | C(4)-C(3)-Fe(1) | 73.4(8) |
| Cr(1)#1-Cr(1)-C(14) | 91.3(14) | C(2)-C(3)-Fe(1) | 69.6(6) |
| C(16)#1-Cr(1)-C(14) | 124.2(13) | C(3)-C(4)-C(5) | 104.4(12) |
| C(50)-Cr(1)-C(14) | 115.7(13) | C(3)-C(4)-C(20)#1 | 131.8(15) |
| C(17)#1-Cr(1)-C(14) | 106.8(13) | C(5)-C(4)-C(20)#1 | 123.8(16) |
| C(52)-Cr(1)-C(14) | 92.1(13) | C(3)-C(4)-Fe(1) | 66.7(6) |
| C(51)-Cr(1)-C(14) | 139.3(17) | C(5)-C(4)-Fe(1) | 68.7(6) |
| C(50)#1-Cr(1)-C(14) | 67.7(11) | C(20)#1-C(4)-Fe(1) | 129.6(9) |
| C(15)#1-Cr(1)-C(14) | 154.8(13) | C(1)-C(5)-C(4) | 109.6(12) |
| C(15)-Cr(1)-C(14) | 38.1(3) | C(1)-C(5)-Fe(1) | 67.7(6) |
| Cr(1)#1-Cr(1)-C(51)#1 | 55.3(19) | C(4)-C(5)-Fe(1) | 71.6(6) |
| C(16)#1-Cr(1)-C(51)#1 | 151.4(17) | C(7)-C(6)-C(10) | 112.0(12) |
| C(50)-Cr(1)-C(51)#1 | 80.9(16) | C(7)-C(6)-Fe(1) | 71.2(6) |
| C(17)#1-Cr(1)-C(51)#1 | 101.4(16) | C(10)-C(6)-Fe(1) | 72.0(7) |
| C(52)-Cr(1)-C(51)#1 | 120.7(18) | C(6)-C(7)-C(8) | 106.1(12) |
| C(51)-Cr(1)-C(51)#1 | 159.7(6) | C(6)-C(7)-Fe(1) | 68.4(6) |
| C(50)#1-Cr(1)-C(51)#1 | 84.3(15) | C(8)-C(7)-Fe(1) | 70.3(6) |
| C(15)#1-Cr(1)-C(51)#1 | 150.5(16) | C(9)-C(8)-C(7) | 108.4(13) |
| C(15)-Cr(1)-C(51)#1 | 13.4(13) | C(9)-C(8)-Fe(1) | 69.0(7) |
| C(14)-Cr(1)-C(51)#1 | 50.5(14) | C(7)-C(8)-Fe(1) | 69.1(6) |

| | |
|---|---|
| C(8)-C(9)-C(10) | 110.4(13) |
| C(8)-C(9)-Fe(1) | 71.5(7) |
| C(10)-C(9)-Fe(1) | 71.0(7) |
| C(11)-C(10)-C(6) | 122.9(18) |
| C(11)-C(10)-C(9) | 133.1(18) |
| C(6)-C(10)-C(9) | 103.1(13) |
| C(11)-C(10)-Fe(1) | 119.7(10) |
| C(6)-C(10)-Fe(1) | 67.2(7) |
| C(9)-C(10)-Fe(1) | 67.7(7) |
| C(10)-C(11)-C(12) | 121(2) |
| C(11)-C(12)-C(13) | 122(3) |
| C(14)-C(13)-C(18) | 120.0 |
| C(14)-C(13)-C(12) | 111.8(18) |
| C(18)-C(13)-C(12) | 128.0(18) |
| C(14)-C(13)-C(50)#1 | 102.3(16) |
| C(18)-C(13)-C(50)#1 | 21.0(16) |
| C(12)-C(13)-C(50)#1 | 145(3) |
| C(14)-C(13)-O(50)#1 | 142.5(13) |
| C(18)-C(13)-O(50)#1 | 24.9(12) |
| C(12)-C(13)-O(50)#1 | 103.9(19) |
| C(50)#1-C(13)-O(50)#1 | 45.5(17) |
| C(14)-C(13)-Cr(1) | 67.9(6) |
| C(18)-C(13)-Cr(1) | 74.8(5) |
| C(12)-C(13)-Cr(1) | 132.6(13) |
| C(50)#1-C(13)-Cr(1) | 54.9(15) |
| O(50)#1-C(13)-Cr(1) | 96.2(12) |
| C(14)-C(13)-Cr(1)#1 | 67.7(5) |
| C(18)-C(13)-Cr(1)#1 | 62.6(4) |
| C(12)-C(13)-Cr(1)#1 | 151.0(13) |
| C(50)#1-C(13)-Cr(1)#1 | 41.6(15) |
| O(50)#1-C(13)-Cr(1)#1 | 86.6(12) |
| Cr(1)-C(13)-Cr(1)#1 | 18.5(2) |
| C(13)-C(14)-C(15) | 120.0 |
| C(13)-C(14)-C(51)#1 | 122.5(17) |
| C(15)-C(14)-C(51)#1 | 8.1(17) |
| C(13)-C(14)-O(51)#1 | 145.0(12) |
| C(15)-C(14)-O(51)#1 | 33.3(12) |
| C(51)#1-C(14)-O(51)#1 | 35.9(18) |
| C(13)-C(14)-Cr(1) | 75.1(7) |
| C(15)-C(14)-Cr(1) | 70.0(6) |
| C(51)#1-C(14)-Cr(1) | 65.1(18) |
| O(51)#1-C(14)-Cr(1) | 100.4(13) |
| C(13)-C(14)-Cr(1)#1 | 78.2(6) |
| C(15)-C(14)-Cr(1)#1 | 54.2(6) |
| C(51)#1-C(14)-Cr(1)#1 | 51.2(17) |
| O(51)#1-C(14)-Cr(1)#1 | 86.9(12) |
| Cr(1)-C(14)-Cr(1)#1 | 19.7(3) |
| C(51)#1-C(15)-O(51)#1 | 86(7) |
| C(51)#1-C(15)-C(16) | 74(5) |
| O(51)#1-C(15)-C(16) | 128(2) |
| C(51)#1-C(15)-C(14) | 149(6) |
| O(51)#1-C(15)-C(14) | 102(2) |
| C(16)-C(15)-C(14) | 120.0 |
| C(51)#1-C(15)-Cr(1)#1 | 79(7) |
| O(51)#1-C(15)-Cr(1)#1 | 164(2) |
| C(16)-C(15)-Cr(1)#1 | 53.1(5) |
| C(14)-C(15)-Cr(1)#1 | 88.5(6) |
| C(51)#1-C(15)-Cr(1) | 88(7) |
| O(51)#1-C(15)-Cr(1) | 154(2) |
| C(16)-C(15)-Cr(1) | 73.9(5) |
| C(14)-C(15)-Cr(1) | 71.9(6) |
| Cr(1)#1-C(15)-Cr(1) | 21.2(3) |
| C(52)#1-C(16)-C(51)#1 | 151(3) |
| C(52)#1-C(16)-C(15) | 163(3) |
| C(51)#1-C(16)-C(15) | 21(2) |
| C(52)#1-C(16)-C(17) | 56(2) |
| C(51)#1-C(16)-C(17) | 137(2) |
| C(15)-C(16)-C(17) | 120.0 |
| C(52)#1-C(16)-C(19) | 62(2) |
| C(51)#1-C(16)-C(19) | 106(3) |
| C(15)-C(16)-C(19) | 124.4(15) |
| C(17)-C(16)-C(19) | 115.6(15) |
| C(52)#1-C(16)-Cr(1)#1 | 84(3) |
| C(51)#1-C(16)-Cr(1)#1 | 79(3) |
| C(15)-C(16)-Cr(1)#1 | 79.6(7) |
| C(17)-C(16)-Cr(1)#1 | 71.9(8) |

| | |
|---|---|
| C(19)-C(16)-Cr(1)#1 | 119.6(14) |
| C(52)#1-C(16)-C(50)#1 | 83(3) |
| C(51)#1-C(16)-C(50)#1 | 106(3) |
| C(15)-C(16)-C(50)#1 | 89.6(9) |
| C(17)-C(16)-C(50)#1 | 31.5(9) |
| C(19)-C(16)-C(50)#1 | 145.2(18) |
| Cr(1)#1-C(16)-C(50)#1 | 53.8(11) |
| C(52)#1-C(16)-Cr(1) | 96(3) |
| C(51)#1-C(16)-Cr(1) | 71(3) |
| C(15)-C(16)-Cr(1) | 68.5(6) |
| C(17)-C(16)-Cr(1) | 75.4(6) |
| C(19)-C(16)-Cr(1) | 129.1(13) |
| Cr(1)#1-C(16)-Cr(1) | 12.0(5) |
| C(50)#1-C(16)-Cr(1) | 51.9(10) |
| C(50)#1-C(17)-C(52)#1 | 139(3) |
| C(50)#1-C(17)-C(18) | 20(2) |
| C(52)#1-C(17)-C(18) | 159(2) |
| C(50)#1-C(17)-C(16) | 107(2) |
| C(52)#1-C(17)-C(16) | 45(2) |
| C(18)-C(17)-C(16) | 120.0 |
| C(50)#1-C(17)-Cr(1)#1 | 68(2) |
| C(52)#1-C(17)-Cr(1)#1 | 71(2) |
| C(18)-C(17)-Cr(1)#1 | 88.4(7) |
| C(16)-C(17)-Cr(1)#1 | 57.4(8) |
| C(50)#1-C(17)-Cr(1) | 53(2) |
| C(52)#1-C(17)-Cr(1) | 86(2) |
| C(18)-C(17)-Cr(1) | 73.2(6) |
| C(16)-C(17)-Cr(1) | 68.4(6) |
| Cr(1)#1-C(17)-Cr(1) | 15.2(6) |
| C(50)#1-C(18)-O(50)#1 | 163(6) |
| C(50)#1-C(18)-C(13) | 88(3) |
| O(50)#1-C(18)-C(13) | 101(3) |
| C(50)#1-C(18)-C(17) | 46(3) |
| O(50)#1-C(18)-C(17) | 134(3) |
| C(13)-C(18)-C(17) | 120.0 |
| C(50)#1-C(18)-Cr(1)#1 | 6(3) |
| O(50)#1-C(18)-Cr(1)#1 | 163(3) |
| C(13)-C(18)-Cr(1)#1 | 82.7(4) |
| C(17)-C(18)-Cr(1)#1 | 51.8(5) |
| C(50)#1-C(18)-Cr(1) | 26(3) |
| O(50)#1-C(18)-Cr(1) | 148(3) |
| C(13)-C(18)-Cr(1) | 69.6(5) |
| C(17)-C(18)-Cr(1) | 71.4(5) |
| Cr(1)#1-C(18)-Cr(1) | 19.7(3) |
| O(52)#1-C(19)-C(20) | 133(4) |
| O(52)#1-C(19)-C(52)#1 | 64(2) |
| C(20)-C(19)-C(52)#1 | 160(3) |
| O(52)#1-C(19)-C(16) | 97(3) |
| C(20)-C(19)-C(16) | 128(2) |
| C(52)#1-C(19)-C(16) | 41(2) |
| C(19)-C(20)-C(4)#1 | 131(2) |
| C(18)#1-C(50)-C(17)#1 | 114(5) |
| C(18)#1-C(50)-O(50) | 10(4) |
| C(17)#1-C(50)-O(50) | 115(3) |
| C(18)#1-C(50)-C(13)#1 | 71(4) |
| C(17)#1-C(50)-C(13)#1 | 139(3) |
| O(50)-C(50)-C(13)#1 | 76(2) |
| C(18)#1-C(50)-Cr(1) | 172(5) |
| C(17)#1-C(50)-Cr(1) | 74(2) |
| O(50)-C(50)-Cr(1) | 168(3) |
| C(13)#1-C(50)-Cr(1) | 102(2) |
| C(18)#1-C(50)-Cr(1)#1 | 147(5) |
| C(17)#1-C(50)-Cr(1)#1 | 99(3) |
| O(50)-C(50)-Cr(1)#1 | 145(2) |
| C(13)#1-C(50)-Cr(1)#1 | 84.0(16) |
| Cr(1)-C(50)-Cr(1)#1 | 24.9(7) |
| C(18)#1-C(50)-C(16)#1 | 136(5) |
| C(17)#1-C(50)-C(16)#1 | 41.8(17) |
| O(50)-C(50)-C(16)#1 | 144(3) |
| C(13)#1-C(50)-C(16)#1 | 105(2) |
| Cr(1)-C(50)-C(16)#1 | 47.9(11) |
| Cr(1)#1-C(50)-C(16)#1 | 69.4(15) |
| C(18)#1-O(50)-C(50) | 7(3) |
| C(18)#1-O(50)-C(13)#1 | 54(3) |
| C(50)-O(50)-C(13)#1 | 58.2(17) |
| C(15)#1-O(51)-C(51) | 25(3) |

| | |
|---|---|
| C(15)#1-O(51)-C(14)#1 | 45.0(18) |
| C(51)-O(51)-C(14)#1 | 68(3) |
| C(15)#1-C(51)-O(51) | 68(7) |
| C(15)#1-C(51)-C(16)#1 | 85(7) |
| O(51)-C(51)-C(16)#1 | 125(4) |
| C(15)#1-C(51)-Cr(1) | 86(7) |
| O(51)-C(51)-Cr(1) | 153(5) |
| C(16)#1-C(51)-Cr(1) | 54(2) |
| C(15)#1-C(51)-C(14)#1 | 23(4) |
| O(51)-C(51)-C(14)#1 | 76(3) |
| C(16)#1-C(51)-C(14)#1 | 97(3) |
| Cr(1)-C(51)-C(14)#1 | 77(2) |
| C(15)#1-C(51)-Cr(1)#1 | 79(7) |
| O(51)-C(51)-Cr(1)#1 | 139(4) |
| C(16)#1-C(51)-Cr(1)#1 | 73(3) |
| Cr(1)-C(51)-Cr(1)#1 | 20.3(6) |
| C(14)#1-C(51)-Cr(1)#1 | 64.3(18) |
| C(16)#1-C(52)-C(17)#1 | 79(3) |
| C(16)#1-C(52)-C(19)#1 | 77(4) |
| C(17)#1-C(52)-C(19)#1 | 148(4) |
| C(16)#1-C(52)-O(52) | 116(4) |
| C(17)#1-C(52)-O(52) | 126(4) |
| C(19)#1-C(52)-O(52) | 52.3(19) |
| C(16)#1-C(52)-Cr(1) | 61(2) |
| C(17)#1-C(52)-Cr(1) | 69(2) |
| C(19)#1-C(52)-Cr(1) | 114(3) |
| O(52)-C(52)-Cr(1) | 165(3) |
| C(16)#1-C(52)-Cr(1)#1 | 61(2) |
| C(17)#1-C(52)-Cr(1)#1 | 66(2) |
| C(19)#1-C(52)-Cr(1)#1 | 117(3) |
| O(52)-C(52)-Cr(1)#1 | 168(3) |
| Cr(1)-C(52)-Cr(1)#1 | 3.3(7) |
| C(19)#1-O(52)-C(52) | 63(2) |

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+1,-z+

**Table 4**. Anisotropic displacement parameters ($Å^2$x $10^3$) for str67m. The anisotropic displacement factor exponent takes the form: $-2\pi^2[ h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12} ]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| Fe(1) | 95(2) | 31(1) | 43(1) | 4(1) | 26(1) | 5(1) |
| Cr(1) | 102(8) | 37(4) | 83(4) | 13(3) | 26(4) | 1(4) |
| C(1) | 86(14) | 42(6) | 71(7) | 7(5) | 31(9) | 2(7) |
| C(2) | 32(10) | 110(11) | 110(11) | 66(9) | 44(9) | 34(9) |
| C(3) | 166(18) | 60(7) | 42(7) | 4(5) | 30(9) | -8(10) |
| C(4) | 102(15) | 56(7) | 71(8) | 22(6) | 32(9) | 7(8) |
| C(5) | 68(12) | 43(6) | 74(8) | 19(5) | 25(8) | 18(7) |
| C(6) | 125(15) | 39(6) | 51(7) | 1(5) | 21(8) | -20(8) |
| C(7) | 90(11) | 53(7) | 75(8) | 28(6) | 32(8) | 26(7) |
| C(8) | 142(16) | 56(7) | 43(6) | 6(5) | 25(8) | 13(9) |
| C(9) | 95(13) | 61(7) | 59(7) | 11(6) | 39(8) | -2(8) |
| C(10) | 79(13) | 57(7) | 72(9) | 23(6) | 29(9) | 1(8) |
| C(11) | 110(30) | 41(13) | 52(13) | 9(10) | -2(16) | -29(15) |
| C(12) | 160(30) | 50(15) | 73(16) | 16(12) | 15(19) | -36(18) |
| C(19) | 180(40) | 37(14) | 97(19) | 11(12) | 70(20) | 35(19) |
| C(20) | 60(20) | 59(14) | 38(11) | 2(9) | 4(12) | -25(14) |

**Table 5**. Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters (Å$^2$x 10 $^3$) for str67m.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1) | 4180 | 8310 | 8774 | 77 |
| H(2) | 4897 | 6174 | 7546 | 96 |
| H(3) | 3851 | 4907 | 5867 | 105 |
| H(5) | 2766 | 8347 | 7838 | 72 |
| H(6) | 3558 | 1687 | 7775 | 85 |
| H(7) | 4598 | 2891 | 9434 | 85 |
| H(8) | 3932 | 5028 | 10734 | 95 |
| H(9) | 2528 | 5206 | 9802 | 82 |
| H(11) | 2104 | 2178 | 6936 | 82 |
| H(12) | 1354 | 4594 | 8342 | 115 |
| H(20) | -2159 | 4739 | 4923 | 63 |

**Table 6**.  Torsion angles [°] for str67m.

| | |
|---|---|
| C(6)-Fe(1)-C(1)-C(5) | 164.7(13) |
| C(3)-Fe(1)-C(1)-C(5) | 79.4(9) |
| C(2)-Fe(1)-C(1)-C(5) | 119.8(11) |
| C(9)-Fe(1)-C(1)-C(5) | -78.5(9) |
| C(7)-Fe(1)-C(1)-C(5) | -162.6(7) |
| C(8)-Fe(1)-C(1)-C(5) | -120.3(8) |
| C(10)-Fe(1)-C(1)-C(5) | -40.6(15) |
| C(4)-Fe(1)-C(1)-C(5) | 36.0(7) |
| C(6)-Fe(1)-C(1)-C(2) | 44.9(18) |
| C(3)-Fe(1)-C(1)-C(2) | -40.4(8) |
| C(9)-Fe(1)-C(1)-C(2) | 161.7(8) |
| C(7)-Fe(1)-C(1)-C(2) | 77.6(9) |
| C(8)-Fe(1)-C(1)-C(2) | 119.9(9) |
| C(5)-Fe(1)-C(1)-C(2) | -119.8(11) |
| C(10)-Fe(1)-C(1)-C(2) | -160.4(11) |
| C(4)-Fe(1)-C(1)-C(2) | -83.8(8) |
| C(5)-C(1)-C(2)-C(3) | -0.5(11) |
| Fe(1)-C(1)-C(2)-C(3) | 60.8(7) |
| C(5)-C(1)-C(2)-Fe(1) | -61.3(7) |
| C(6)-Fe(1)-C(2)-C(1) | -164.8(8) |
| C(3)-Fe(1)-C(2)-C(1) | 114.7(11) |
| C(9)-Fe(1)-C(2)-C(1) | -45.4(16) |
| C(7)-Fe(1)-C(2)-C(1) | -122.9(9) |
| C(8)-Fe(1)-C(2)-C(1) | -80.4(9) |
| C(5)-Fe(1)-C(2)-C(1) | 37.0(7) |
| C(10)-Fe(1)-C(2)-C(1) | 156.6(14) |
| C(4)-Fe(1)-C(2)-C(1) | 79.5(8) |
| C(1)-Fe(1)-C(2)-C(3) | -114.7(11) |
| C(6)-Fe(1)-C(2)-C(3) | 80.5(10) |
| C(9)-Fe(1)-C(2)-C(3) | -160.2(13) |
| C(7)-Fe(1)-C(2)-C(3) | 122.4(9) |
| C(8)-Fe(1)-C(2)-C(3) | 164.8(8) |
| C(5)-Fe(1)-C(2)-C(3) | -77.8(8) |
| C(10)-Fe(1)-C(2)-C(3) | 41.8(18) |
| C(4)-Fe(1)-C(2)-C(3) | -35.2(8) |
| C(1)-C(2)-C(3)-C(4) | 0.3(12) |
| Fe(1)-C(2)-C(3)-C(4) | 60.9(8) |
| C(1)-C(2)-C(3)-Fe(1) | -60.6(7) |
| C(1)-Fe(1)-C(3)-C(4) | -82.2(8) |
| C(6)-Fe(1)-C(3)-C(4) | 116.7(8) |
| C(2)-Fe(1)-C(3)-C(4) | -122.7(11) |
| C(9)-Fe(1)-C(3)-C(4) | 37.1(16) |
| C(7)-Fe(1)-C(3)-C(4) | 159.3(7) |
| C(8)-Fe(1)-C(3)-C(4) | -165.4(13) |
| C(5)-Fe(1)-C(3)-C(4) | -38.3(7) |
| C(10)-Fe(1)-C(3)-C(4) | 73.1(9) |
| C(1)-Fe(1)-C(3)-C(2) | 40.4(7) |
| C(6)-Fe(1)-C(3)-C(2) | -120.7(9) |
| C(9)-Fe(1)-C(3)-C(2) | 159.7(11) |
| C(7)-Fe(1)-C(3)-C(2) | -78.1(9) |
| C(8)-Fe(1)-C(3)-C(2) | -42.7(18) |
| C(5)-Fe(1)-C(3)-C(2) | 84.4(8) |
| C(10)-Fe(1)-C(3)-C(2) | -164.3(8) |
| C(4)-Fe(1)-C(3)-C(2) | 122.7(11) |
| C(2)-C(3)-C(4)-C(5) | 0.0(12) |
| Fe(1)-C(3)-C(4)-C(5) | 58.7(7) |
| C(2)-C(3)-C(4)-C(20)#1 | 178.2(12) |
| Fe(1)-C(3)-C(4)-C(20)#1 | -123.1(13) |
| C(2)-C(3)-C(4)-Fe(1) | -58.7(8) |
| C(1)-Fe(1)-C(4)-C(3) | 80.7(8) |
| C(6)-Fe(1)-C(4)-C(3) | -82.9(9) |
| C(2)-Fe(1)-C(4)-C(3) | 36.3(8) |
| C(9)-Fe(1)-C(4)-C(3) | -164.9(7) |
| C(7)-Fe(1)-C(4)-C(3) | -53.3(17) |
| C(8)-Fe(1)-C(4)-C(3) | 167.7(12) |
| C(5)-Fe(1)-C(4)-C(3) | 117.3(11) |
| C(10)-Fe(1)-C(4)-C(3) | -123.5(8) |
| C(1)-Fe(1)-C(4)-C(5) | -36.6(7) |
| C(6)-Fe(1)-C(4)-C(5) | 159.8(9) |
| C(3)-Fe(1)-C(4)-C(5) | -117.3(11) |
| C(2)-Fe(1)-C(4)-C(5) | -80.9(8) |
| C(9)-Fe(1)-C(4)-C(5) | 77.8(9) |
| C(7)-Fe(1)-C(4)-C(5) | -170.5(12) |
| C(8)-Fe(1)-C(4)-C(5) | 50.4(17) |

|  |  |
|---|---|
| C(10)-Fe(1)-C(4)-C(5) | 119.3(9) |
| C(1)-Fe(1)-C(4)-C(20)#1 | -153.4(18) |
| C(6)-Fe(1)-C(4)-C(20)#1 | 42.9(18) |
| C(3)-Fe(1)-C(4)-C(20)#1 | 125.9(19) |
| C(2)-Fe(1)-C(4)-C(20)#1 | 162.2(18) |
| C(9)-Fe(1)-C(4)-C(20)#1 | -39.0(17) |
| C(7)-Fe(1)-C(4)-C(20)#1 | 73(2) |
| C(8)-Fe(1)-C(4)-C(20)#1 | -66(2) |
| C(5)-Fe(1)-C(4)-C(20)#1 | -117(2) |
| C(10)-Fe(1)-C(4)-C(20)#1 | 2.4(17) |
| C(2)-C(1)-C(5)-C(4) | 0.5(11) |
| Fe(1)-C(1)-C(5)-C(4) | -59.5(7) |
| C(2)-C(1)-C(5)-Fe(1) | 60.0(7) |
| C(3)-C(4)-C(5)-C(1) | -0.3(12) |
| C(20)#1-C(4)-C(5)-C(1) | -178.7(11) |
| Fe(1)-C(4)-C(5)-C(1) | 57.1(7) |
| C(3)-C(4)-C(5)-Fe(1) | -57.4(7) |
| C(20)#1-C(4)-C(5)-Fe(1) | 124.3(11) |
| C(6)-Fe(1)-C(5)-C(1) | -168.3(11) |
| C(3)-Fe(1)-C(5)-C(1) | -82.7(8) |
| C(2)-Fe(1)-C(5)-C(1) | -37.9(8) |
| C(9)-Fe(1)-C(5)-C(1) | 119.2(8) |
| C(7)-Fe(1)-C(5)-C(1) | 48.3(17) |
| C(8)-Fe(1)-C(5)-C(1) | 79.4(9) |
| C(10)-Fe(1)-C(5)-C(1) | 162.2(7) |
| C(4)-Fe(1)-C(5)-C(1) | -121.3(11) |
| C(1)-Fe(1)-C(5)-C(4) | 121.3(11) |
| C(6)-Fe(1)-C(5)-C(4) | -47.1(16) |
| C(3)-Fe(1)-C(5)-C(4) | 38.6(7) |
| C(2)-Fe(1)-C(5)-C(4) | 83.4(9) |
| C(9)-Fe(1)-C(5)-C(4) | -119.5(9) |
| C(7)-Fe(1)-C(5)-C(4) | 169.5(13) |
| C(8)-Fe(1)-C(5)-C(4) | -159.4(9) |
| C(10)-Fe(1)-C(5)-C(4) | -76.5(10) |
| C(1)-Fe(1)-C(6)-C(7) | 42.8(18) |
| C(3)-Fe(1)-C(6)-C(7) | 121.3(9) |
| C(2)-Fe(1)-C(6)-C(7) | 77.4(9) |
| C(9)-Fe(1)-C(6)-C(7) | -81.8(8) |
| C(8)-Fe(1)-C(6)-C(7) | -38.8(7) |
| C(5)-Fe(1)-C(6)-C(7) | -162.5(10) |
| C(10)-Fe(1)-C(6)-C(7) | -121.7(10) |
| C(4)-Fe(1)-C(6)-C(7) | 164.0(8) |
| C(1)-Fe(1)-C(6)-C(10) | 164.5(13) |
| C(3)-Fe(1)-C(6)-C(10) | -117.0(9) |
| C(2)-Fe(1)-C(6)-C(10) | -160.8(8) |
| C(9)-Fe(1)-C(6)-C(10) | 39.9(8) |
| C(7)-Fe(1)-C(6)-C(10) | 121.7(10) |
| C(8)-Fe(1)-C(6)-C(10) | 82.9(8) |
| C(5)-Fe(1)-C(6)-C(10) | -40.8(15) |
| C(4)-Fe(1)-C(6)-C(10) | -74.3(9) |
| C(10)-C(6)-C(7)-C(8) | -0.1(11) |
| Fe(1)-C(6)-C(7)-C(8) | 60.6(7) |
| C(10)-C(6)-C(7)-Fe(1) | -60.8(7) |
| C(1)-Fe(1)-C(7)-C(6) | -165.2(8) |
| C(3)-Fe(1)-C(7)-C(6) | -79.3(10) |
| C(2)-Fe(1)-C(7)-C(6) | -122.3(9) |
| C(9)-Fe(1)-C(7)-C(6) | 81.0(8) |
| C(8)-Fe(1)-C(7)-C(6) | 117.3(11) |
| C(5)-Fe(1)-C(7)-C(6) | 158.4(15) |
| C(10)-Fe(1)-C(7)-C(6) | 36.5(7) |
| C(4)-Fe(1)-C(7)-C(6) | -40.3(17) |
| C(1)-Fe(1)-C(7)-C(8) | 77.5(10) |
| C(6)-Fe(1)-C(7)-C(8) | -117.3(11) |
| C(3)-Fe(1)-C(7)-C(8) | 163.4(9) |
| C(2)-Fe(1)-C(7)-C(8) | 120.4(10) |
| C(9)-Fe(1)-C(7)-C(8) | -36.3(8) |
| C(5)-Fe(1)-C(7)-C(8) | 41.2(19) |
| C(10)-Fe(1)-C(7)-C(8) | -80.8(9) |
| C(4)-Fe(1)-C(7)-C(8) | -157.6(14) |
| C(6)-C(7)-C(8)-C(9) | -1.5(12) |
| Fe(1)-C(7)-C(8)-C(9) | 57.8(8) |
| C(6)-C(7)-C(8)-Fe(1) | -59.4(7) |
| C(1)-Fe(1)-C(8)-C(9) | 116.7(8) |
| C(6)-Fe(1)-C(8)-C(9) | -82.0(9) |
| C(3)-Fe(1)-C(8)-C(9) | -167.2(13) |
| C(2)-Fe(1)-C(8)-C(9) | 160.2(8) |

|  |  |  |  |
|---|---|---|---|
| C(7)-Fe(1)-C(8)-C(9) | -120.6(12) | C(8)-C(9)-C(10)-C(6) | -2.6(12) |
| C(5)-Fe(1)-C(8)-C(9) | 74.4(9) | Fe(1)-C(9)-C(10)-C(6) | 58.3(7) |
| C(10)-Fe(1)-C(8)-C(9) | -37.8(8) | C(8)-C(9)-C(10)-Fe(1) | -60.9(8) |
| C(4)-Fe(1)-C(8)-C(9) | 38.1(16) | C(1)-Fe(1)-C(10)-C(11) | 76(2) |
| C(1)-Fe(1)-C(8)-C(7) | -122.8(9) | C(6)-Fe(1)-C(10)-C(11) | -116(2) |
| C(6)-Fe(1)-C(8)-C(7) | 38.6(8) | C(3)-Fe(1)-C(10)-C(11) | -32.9(19) |
| C(3)-Fe(1)-C(8)-C(7) | -46.7(19) | C(2)-Fe(1)-C(10)-C(11) | -64(2) |
| C(2)-Fe(1)-C(8)-C(7) | -79.2(10) | C(9)-Fe(1)-C(10)-C(11) | 128(2) |
| C(9)-Fe(1)-C(8)-C(7) | 120.6(12) | C(7)-Fe(1)-C(10)-C(11) | -152.1(18) |
| C(5)-Fe(1)-C(8)-C(7) | -165.0(8) | C(8)-Fe(1)-C(10)-C(11) | 164.2(18) |
| C(10)-Fe(1)-C(8)-C(7) | 82.8(8) | C(5)-Fe(1)-C(10)-C(11) | 46.5(18) |
| C(4)-Fe(1)-C(8)-C(7) | 158.7(11) | C(4)-Fe(1)-C(10)-C(11) | 6.6(18) |
| C(7)-C(8)-C(9)-C(10) | 2.7(13) | C(1)-Fe(1)-C(10)-C(6) | -168.5(11) |
| Fe(1)-C(8)-C(9)-C(10) | 60.6(7) | C(3)-Fe(1)-C(10)-C(6) | 83.1(9) |
| C(7)-C(8)-C(9)-Fe(1) | -57.9(7) | C(2)-Fe(1)-C(10)-C(6) | 51.7(17) |
| C(1)-Fe(1)-C(9)-C(8) | -82.0(9) | C(9)-Fe(1)-C(10)-C(6) | -116.0(11) |
| C(6)-Fe(1)-C(9)-C(8) | 80.9(8) | C(7)-Fe(1)-C(10)-C(6) | -36.1(6) |
| C(3)-Fe(1)-C(9)-C(8) | 168.9(12) | C(8)-Fe(1)-C(10)-C(6) | -79.8(7) |
| C(2)-Fe(1)-C(9)-C(8) | -48.5(16) | C(5)-Fe(1)-C(10)-C(6) | 162.5(6) |
| C(7)-Fe(1)-C(9)-C(8) | 37.2(7) | C(4)-Fe(1)-C(10)-C(6) | 122.6(7) |
| C(5)-Fe(1)-C(9)-C(8) | -123.4(8) | C(1)-Fe(1)-C(10)-C(9) | -52.4(16) |
| C(10)-Fe(1)-C(9)-C(8) | 120.3(12) | C(6)-Fe(1)-C(10)-C(9) | 116.0(11) |
| C(4)-Fe(1)-C(9)-C(8) | -164.1(7) | C(3)-Fe(1)-C(10)-C(9) | -160.9(9) |
| C(1)-Fe(1)-C(9)-C(10) | 157.8(9) | C(2)-Fe(1)-C(10)-C(9) | 167.7(12) |
| C(6)-Fe(1)-C(9)-C(10) | -39.4(7) | C(7)-Fe(1)-C(10)-C(9) | 79.9(8) |
| C(3)-Fe(1)-C(9)-C(10) | 48.6(17) | C(8)-Fe(1)-C(10)-C(9) | 36.2(7) |
| C(2)-Fe(1)-C(9)-C(10) | -168.8(11) | C(5)-Fe(1)-C(10)-C(9) | -81.5(10) |
| C(7)-Fe(1)-C(9)-C(10) | -83.1(8) | C(4)-Fe(1)-C(10)-C(9) | -121.4(9) |
| C(8)-Fe(1)-C(9)-C(10) | -120.3(12) | C(6)-C(10)-C(11)-C(12) | -173.7(16) |
| C(5)-Fe(1)-C(9)-C(10) | 116.4(9) | C(9)-C(10)-C(11)-C(12) | -7(3) |
| C(4)-Fe(1)-C(9)-C(10) | 75.7(10) | Fe(1)-C(10)-C(11)-C(12) | -93(2) |
| C(7)-C(6)-C(10)-C(11) | 171.8(12) | C(10)-C(11)-C(12)-C(13) | 177.5(15) |
| Fe(1)-C(6)-C(10)-C(11) | 111.6(13) | C(11)-C(12)-C(13)-C(14) | 177.2(18) |
| C(7)-C(6)-C(10)-C(9) | 1.7(11) | C(11)-C(12)-C(13)-C(18) | 2(3) |
| Fe(1)-C(6)-C(10)-C(9) | -58.6(7) | C(11)-C(12)-C(13)-C(50)#1 | -16(5) |
| C(7)-C(6)-C(10)-Fe(1) | 60.3(7) | C(11)-C(12)-C(13)-O(50)#1 | 9(3) |
| C(8)-C(9)-C(10)-C(11) | -171.3(15) | C(11)-C(12)-C(13)-Cr(1) | -103(2) |
| Fe(1)-C(9)-C(10)-C(11) | -110.4(15) | C(11)-C(12)-C(13)-Cr(1)#1 | -100(4) |

| | |
|---|---|
| Cr(1)#1-Cr(1)-C(13)-C(14) | -85.5(17) |
| C(16)#1-Cr(1)-C(13)-C(14) | 120.5(17) |
| C(50)-Cr(1)-C(13)-C(14) | 17(3) |
| C(17)#1-Cr(1)-C(13)-C(14) | 65(2) |
| C(52)-Cr(1)-C(13)-C(14) | 88.5(15) |
| C(51)-Cr(1)-C(13)-C(14) | 168.3(15) |
| C(50)#1-Cr(1)-C(13)-C(14) | -124.4(18) |
| C(15)#1-Cr(1)-C(13)-C(14) | 172.0(14) |
| C(15)-Cr(1)-C(13)-C(14) | -30.7(3) |
| C(51)#1-Cr(1)-C(13)-C(14) | -32.0(13) |
| C(18)#1-Cr(1)-C(13)-C(14) | 13(3) |
| Cr(1)#1-Cr(1)-C(13)-C(18) | 46.5(17) |
| C(16)#1-Cr(1)-C(13)-C(18) | -107.5(18) |
| C(50)-Cr(1)-C(13)-C(18) | 149(3) |
| C(17)#1-Cr(1)-C(13)-C(18) | -163(2) |
| C(52)-Cr(1)-C(13)-C(18) | -139.5(16) |
| C(51)-Cr(1)-C(13)-C(18) | -59.6(15) |
| C(50)#1-Cr(1)-C(13)-C(18) | 7.7(18) |
| C(15)#1-Cr(1)-C(13)-C(18) | -56.0(15) |
| C(15)-Cr(1)-C(13)-C(18) | 101.4(4) |
| C(14)-Cr(1)-C(13)-C(18) | 132.1(3) |
| C(51)#1-Cr(1)-C(13)-C(18) | 100.0(12) |
| C(18)#1-Cr(1)-C(13)-C(18) | 145(2) |
| Cr(1)#1-Cr(1)-C(13)-C(12) | 175(3) |
| C(16)#1-Cr(1)-C(13)-C(12) | 21(3) |
| C(50)-Cr(1)-C(13)-C(12) | -83(4) |
| C(17)#1-Cr(1)-C(13)-C(12) | -35(3) |
| C(52)-Cr(1)-C(13)-C(12) | -11(3) |
| C(51)-Cr(1)-C(13)-C(12) | 68(3) |
| C(50)#1-Cr(1)-C(13)-C(12) | 136(3) |
| C(15)#1-Cr(1)-C(13)-C(12) | 72(2) |
| C(15)-Cr(1)-C(13)-C(12) | -131(2) |
| C(14)-Cr(1)-C(13)-C(12) | -100(3) |
| C(51)#1-Cr(1)-C(13)-C(12) | -132(3) |
| C(18)#1-Cr(1)-C(13)-C(12) | -87(3) |
| Cr(1)#1-Cr(1)-C(13)-C(50)#1 | 39(2) |
| C(16)#1-Cr(1)-C(13)-C(50)#1 | -115(2) |
| C(50)-Cr(1)-C(13)-C(50)#1 | 141.5(17) |
| C(17)#1-Cr(1)-C(13)-C(50)#1 | -171(2) |
| C(52)-Cr(1)-C(13)-C(50)#1 | -147(2) |
| C(51)-Cr(1)-C(13)-C(50)#1 | -67(2) |
| C(15)#1-Cr(1)-C(13)-C(50)#1 | -64(2) |
| C(15)-Cr(1)-C(13)-C(50)#1 | 93.7(18) |
| C(14)-Cr(1)-C(13)-C(50)#1 | 124.4(18) |
| C(51)#1-Cr(1)-C(13)-C(50)#1 | 92(2) |
| C(18)#1-Cr(1)-C(13)-C(50)#1 | 138(3) |
| Cr(1)#1-Cr(1)-C(13)-O(50)#1 | 59(2) |
| C(16)#1-Cr(1)-C(13)-O(50)#1 | -94.7(17) |
| C(50)-Cr(1)-C(13)-O(50)#1 | 162(2) |
| C(17)#1-Cr(1)-C(13)-O(50)#1 | -150.1(18) |
| C(52)-Cr(1)-C(13)-O(50)#1 | -126.7(19) |
| C(51)-Cr(1)-C(13)-O(50)#1 | -46.8(19) |
| C(50)#1-Cr(1)-C(13)-O(50)#1 | 20.5(17) |
| C(15)#1-Cr(1)-C(13)-O(50)#1 | -43.2(16) |
| C(15)-Cr(1)-C(13)-O(50)#1 | 114.2(13) |
| C(14)-Cr(1)-C(13)-O(50)#1 | 144.9(14) |
| C(51)#1-Cr(1)-C(13)-O(50)#1 | 112.8(17) |
| C(18)#1-Cr(1)-C(13)-O(50)#1 | 158(2) |
| C(16)#1-Cr(1)-C(13)-Cr(1)#1 | -154(2) |
| C(50)-Cr(1)-C(13)-Cr(1)#1 | 103(3) |
| C(17)#1-Cr(1)-C(13)-Cr(1)#1 | 151(3) |
| C(52)-Cr(1)-C(13)-Cr(1)#1 | 174(2) |
| C(51)-Cr(1)-C(13)-Cr(1)#1 | -106(2) |
| C(50)#1-Cr(1)-C(13)-Cr(1)#1 | -39(2) |
| C(15)#1-Cr(1)-C(13)-Cr(1)#1 | -102.5(18) |
| C(15)-Cr(1)-C(13)-Cr(1)#1 | 54.8(16) |
| C(14)-Cr(1)-C(13)-Cr(1)#1 | 85.5(17) |
| C(51)#1-Cr(1)-C(13)-Cr(1)#1 | 54(2) |
| C(18)#1-Cr(1)-C(13)-Cr(1)#1 | 99(3) |
| C(18)-C(13)-C(14)-C(15) | 0.0 |
| C(12)-C(13)-C(14)-C(15) | -175.5(14) |
| C(50)#1-C(13)-C(14)-C(15) | 12.1(16) |
| O(50)#1-C(13)-C(14)-C(15) | -14(2) |
| Cr(1)-C(13)-C(14)-C(15) | 55.8(5) |
| Cr(1)#1-C(13)-C(14)-C(15) | 35.8(4) |
| C(18)-C(13)-C(14)-C(51)#1 | -9(2) |

| | |
|---|---|
| C(12)-C(13)-C(14)-C(51)#1 | 175(2) |
| C(50)#1-C(13)-C(14)-C(51)#1 | 3(3) |
| O(50)#1-C(13)-C(14)-C(51)#1 | -23(3) |
| Cr(1)-C(13)-C(14)-C(51)#1 | 47(2) |
| Cr(1)#1-C(13)-C(14)-C(51)#1 | 27(2) |
| C(18)-C(13)-C(14)-O(51)#1 | 31(2) |
| C(12)-C(13)-C(14)-O(51)#1 | -145(2) |
| C(50)#1-C(13)-C(14)-O(51)#1 | 43(3) |
| O(50)#1-C(13)-C(14)-O(51)#1 | 17(4) |
| Cr(1)-C(13)-C(14)-O(51)#1 | 87(2) |
| Cr(1)#1-C(13)-C(14)-O(51)#1 | 67(2) |
| C(18)-C(13)-C(14)-Cr(1) | -55.8(5) |
| C(12)-C(13)-C(14)-Cr(1) | 128.6(14) |
| C(50)#1-C(13)-C(14)-Cr(1) | -43.7(15) |
| O(50)#1-C(13)-C(14)-Cr(1) | -70(2) |
| Cr(1)#1-C(13)-C(14)-Cr(1) | -20.0(3) |
| C(18)-C(13)-C(14)-Cr(1)#1 | -35.8(4) |
| C(12)-C(13)-C(14)-Cr(1)#1 | 148.7(14) |
| C(50)#1-C(13)-C(14)-Cr(1)#1 | -23.7(15) |
| O(50)#1-C(13)-C(14)-Cr(1)#1 | -50(2) |
| Cr(1)-C(13)-C(14)-Cr(1)#1 | 20.0(3) |
| Cr(1)#1-Cr(1)-C(14)-C(13) | 96.6(16) |
| C(16)#1-Cr(1)-C(14)-C(13) | -78(2) |
| C(50)-Cr(1)-C(14)-C(13) | -171.2(13) |
| C(17)#1-Cr(1)-C(14)-C(13) | -131.5(16) |
| C(52)-Cr(1)-C(14)-C(13) | -93.5(15) |
| C(51)-Cr(1)-C(14)-C(13) | -18(2) |
| C(50)#1-Cr(1)-C(14)-C(13) | 35.9(12) |
| C(15)#1-Cr(1)-C(14)-C(13) | -17(3) |
| C(15)-Cr(1)-C(14)-C(13) | 130.3(3) |
| C(51)#1-Cr(1)-C(14)-C(13) | 137.4(16) |
| C(18)#1-Cr(1)-C(14)-C(13) | -173.3(12) |
| Cr(1)#1-Cr(1)-C(14)-C(15) | -33.8(15) |
| C(16)#1-Cr(1)-C(14)-C(15) | 152(2) |
| C(50)-Cr(1)-C(14)-C(15) | 58.5(13) |
| C(17)#1-Cr(1)-C(14)-C(15) | 98.1(16) |
| C(52)-Cr(1)-C(14)-C(15) | 136.2(15) |
| C(51)-Cr(1)-C(14)-C(15) | -148(2) |
| C(50)#1-Cr(1)-C(14)-C(15) | -94.5(12) |
| C(15)#1-Cr(1)-C(14)-C(15) | -147(3) |
| C(51)#1-Cr(1)-C(14)-C(15) | 7.0(16) |
| C(18)#1-Cr(1)-C(14)-C(15) | 56.4(13) |
| Cr(1)#1-Cr(1)-C(14)-C(51)#1 | -41(2) |
| C(16)#1-Cr(1)-C(14)-C(51)#1 | 145(2) |
| C(50)-Cr(1)-C(14)-C(51)#1 | 51.5(19) |
| C(17)#1-Cr(1)-C(14)-C(51)#1 | 91.1(18) |
| C(52)-Cr(1)-C(14)-C(51)#1 | 129(2) |
| C(51)-Cr(1)-C(14)-C(51)#1 | -154.9(11) |
| C(50)#1-Cr(1)-C(14)-C(51)#1 | -101.5(18) |
| C(15)#1-Cr(1)-C(14)-C(51)#1 | -154(3) |
| C(15)-Cr(1)-C(14)-C(51)#1 | -7.0(16) |
| C(18)#1-Cr(1)-C(14)-C(51)#1 | 49.4(17) |
| Cr(1)#1-Cr(1)-C(14)-O(51)#1 | -47.8(19) |
| C(16)#1-Cr(1)-C(14)-O(51)#1 | 137.6(19) |
| C(50)-Cr(1)-C(14)-O(51)#1 | 44.5(16) |
| C(17)#1-Cr(1)-C(14)-O(51)#1 | 84.1(16) |
| C(52)-Cr(1)-C(14)-O(51)#1 | 122.2(17) |
| C(51)-Cr(1)-C(14)-O(51)#1 | -162(2) |
| C(50)#1-Cr(1)-C(14)-O(51)#1 | -108.5(15) |
| C(15)#1-Cr(1)-C(14)-O(51)#1 | -161(3) |
| C(15)-Cr(1)-C(14)-O(51)#1 | -14.0(12) |
| C(51)#1-Cr(1)-C(14)-O(51)#1 | -7.0(19) |
| C(18)#1-Cr(1)-C(14)-O(51)#1 | 42.4(15) |
| C(16)#1-Cr(1)-C(14)-Cr(1)#1 | -175(3) |
| C(50)-Cr(1)-C(14)-Cr(1)#1 | 92(2) |
| C(17)#1-Cr(1)-C(14)-Cr(1)#1 | 132(2) |
| C(52)-Cr(1)-C(14)-Cr(1)#1 | 170(2) |
| C(51)-Cr(1)-C(14)-Cr(1)#1 | -114(3) |
| C(50)#1-Cr(1)-C(14)-Cr(1)#1 | -60.7(18) |
| C(15)#1-Cr(1)-C(14)-Cr(1)#1 | -113(3) |
| C(15)-Cr(1)-C(14)-Cr(1)#1 | 33.8(15) |
| C(51)#1-Cr(1)-C(14)-Cr(1)#1 | 41(2) |
| C(18)#1-Cr(1)-C(14)-Cr(1)#1 | 90(2) |
| C(13)-C(14)-C(15)-C(51)#1 | -110(13) |
| O(51)#1-C(14)-C(15)-C(51)#1 | 102(12) |
| Cr(1)-C(14)-C(15)-C(51)#1 | -52(13) |

| | | | |
|---|---|---|---|
| Cr(1)#1-C(14)-C(15)-C(51)#1 | -65(13) | C(18)#1-Cr(1)-C(15)-O(51)#1 | -53(5) |
| C(13)-C(14)-C(15)-O(51)#1 | 147(2) | Cr(1)#1-Cr(1)-C(15)-C(16) | 10.3(14) |
| C(51)#1-C(14)-C(15)-O(51)#1 | -102(12) | C(16)#1-Cr(1)-C(15)-C(16) | 170(3) |
| Cr(1)-C(14)-C(15)-O(51)#1 | -154(2) | C(50)-Cr(1)-C(15)-C(16) | 100.3(11) |
| Cr(1)#1-C(14)-C(15)-O(51)#1 | -168(2) | C(17)#1-Cr(1)-C(15)-C(16) | 135.7(13) |
| C(13)-C(14)-C(15)-C(16) | 0.0 | C(52)-Cr(1)-C(15)-C(16) | 178.3(15) |
| C(51)#1-C(14)-C(15)-C(16) | 110(13) | C(51)-Cr(1)-C(15)-C(16) | -34(5) |
| O(51)#1-C(14)-C(15)-C(16) | -147(2) | C(50)#1-Cr(1)-C(15)-C(16) | -57.5(11) |
| Cr(1)-C(14)-C(15)-C(16) | 58.3(6) | C(15)#1-Cr(1)-C(15)-C(16) | 10(4) |
| Cr(1)#1-C(14)-C(15)-C(16) | 44.9(5) | C(14)-Cr(1)-C(15)-C(16) | -129.9(3) |
| C(13)-C(14)-C(15)-Cr(1)#1 | -44.9(5) | C(51)#1-Cr(1)-C(15)-C(16) | 74(5) |
| C(51)#1-C(14)-C(15)-Cr(1)#1 | 65(13) | C(18)#1-Cr(1)-C(15)-C(16) | 98.3(12) |
| O(51)#1-C(14)-C(15)-Cr(1)#1 | 168(2) | Cr(1)#1-Cr(1)-C(15)-C(14) | 140.2(16) |
| Cr(1)-C(14)-C(15)-Cr(1)#1 | 13.4(4) | C(16)#1-Cr(1)-C(15)-C(14) | -60(3) |
| C(13)-C(14)-C(15)-Cr(1) | -58.3(6) | C(50)-Cr(1)-C(15)-C(14) | -129.7(11) |
| C(51)#1-C(14)-C(15)-Cr(1) | 52(13) | C(17)#1-Cr(1)-C(15)-C(14) | -94.3(13) |
| O(51)#1-C(14)-C(15)-Cr(1) | 154(2) | C(52)-Cr(1)-C(15)-C(14) | -51.7(15) |
| Cr(1)#1-C(14)-C(15)-Cr(1) | -13.4(4) | C(51)-Cr(1)-C(15)-C(14) | 96(5) |
| Cr(1)#1-Cr(1)-C(15)-C(51)#1 | -64(5) | C(50)#1-Cr(1)-C(15)-C(14) | 72.5(11) |
| C(16)#1-Cr(1)-C(15)-C(51)#1 | 96(6) | C(15)#1-Cr(1)-C(15)-C(14) | 140(4) |
| C(50)-Cr(1)-C(15)-C(51)#1 | 26(5) | C(51)#1-Cr(1)-C(15)-C(14) | -156(5) |
| C(17)#1-Cr(1)-C(15)-C(51)#1 | 61(5) | C(18)#1-Cr(1)-C(15)-C(14) | -131.7(11) |
| C(52)-Cr(1)-C(15)-C(51)#1 | 104(5) | C(16)#1-Cr(1)-C(15)-Cr(1)#1 | 160(4) |
| C(51)-Cr(1)-C(15)-C(51)#1 | -109(6) | C(50)-Cr(1)-C(15)-Cr(1)#1 | 90.0(18) |
| C(50)#1-Cr(1)-C(15)-C(51)#1 | -132(5) | C(17)#1-Cr(1)-C(15)-Cr(1)#1 | 125(2) |
| C(15)#1-Cr(1)-C(15)-C(51)#1 | -64(7) | C(52)-Cr(1)-C(15)-Cr(1)#1 | 168(2) |
| C(14)-Cr(1)-C(15)-C(51)#1 | 156(5) | C(51)-Cr(1)-C(15)-Cr(1)#1 | -45(5) |
| C(18)#1-Cr(1)-C(15)-C(51)#1 | 24(5) | C(50)#1-Cr(1)-C(15)-Cr(1)#1 | -67.7(17) |
| Cr(1)#1-Cr(1)-C(15)-O(51)#1 | -141(5) | C(15)#1-Cr(1)-C(15)-Cr(1)#1 | 0(4) |
| C(16)#1-Cr(1)-C(15)-O(51)#1 | 19(7) | C(14)-Cr(1)-C(15)-Cr(1)#1 | -140.2(16) |
| C(50)-Cr(1)-C(15)-O(51)#1 | -51(5) | C(51)#1-Cr(1)-C(15)-Cr(1)#1 | 64(5) |
| C(17)#1-Cr(1)-C(15)-O(51)#1 | -15(5) | C(18)#1-Cr(1)-C(15)-Cr(1)#1 | 88.0(17) |
| C(52)-Cr(1)-C(15)-O(51)#1 | 27(6) | C(51)#1-C(15)-C(16)-C(52)#1 | 77(11) |
| C(51)-Cr(1)-C(15)-O(51)#1 | 175(7) | O(51)#1-C(15)-C(16)-C(52)#1 | 149(9) |
| C(50)#1-Cr(1)-C(15)-O(51)#1 | 152(5) | C(14)-C(15)-C(16)-C(52)#1 | -73(8) |
| C(15)#1-Cr(1)-C(15)-O(51)#1 | -141(5) | Cr(1)#1-C(15)-C(16)-C(52)#1 | -11(8) |
| C(14)-Cr(1)-C(15)-O(51)#1 | 79(5) | Cr(1)-C(15)-C(16)-C(52)#1 | -15(8) |
| C(51)#1-Cr(1)-C(15)-O(51)#1 | -77(7) | O(51)#1-C(15)-C(16)-C(51)#1 | 72(7) |

|  |  |  |  |
|---|---|---|---|
| C(14)-C(15)-C(16)-C(51)#1 | -149(8) | Cr(1)#1-Cr(1)-C(16)-C(51)#1 | -135(4) |
| Cr(1)#1-C(15)-C(16)-C(51)#1 | -88(7) | C(16)#1-Cr(1)-C(16)-C(51)#1 | -135(7) |
| Cr(1)-C(15)-C(16)-C(51)#1 | -92(7) | C(50)-Cr(1)-C(16)-C(51)#1 | -61(2) |
| C(51)#1-C(15)-C(16)-C(17) | 149(8) | C(17)#1-Cr(1)-C(16)-C(51)#1 | -40(3) |
| O(51)#1-C(15)-C(16)-C(17) | -138(3) | C(52)-Cr(1)-C(16)-C(51)#1 | 19(4) |
| C(14)-C(15)-C(16)-C(17) | 0.0 | C(51)-Cr(1)-C(16)-C(51)#1 | -171.6(8) |
| Cr(1)#1-C(15)-C(16)-C(17) | 61.9(8) | C(50)#1-Cr(1)-C(16)-C(51)#1 | 130(3) |
| Cr(1)-C(15)-C(16)-C(17) | 57.3(6) | C(15)#1-Cr(1)-C(16)-C(51)#1 | -153(3) |
| C(51)#1-C(15)-C(16)-C(19) | -31(7) | C(15)-Cr(1)-C(16)-C(51)#1 | 22(2) |
| O(51)#1-C(15)-C(16)-C(19) | 41(3) | C(14)-Cr(1)-C(16)-C(51)#1 | 53(2) |
| C(14)-C(15)-C(16)-C(19) | 179.3(17) | C(18)#1-Cr(1)-C(16)-C(51)#1 | -63(2) |
| Cr(1)#1-C(15)-C(16)-C(19) | -118.8(17) | Cr(1)#1-Cr(1)-C(16)-C(15) | -158(3) |
| Cr(1)-C(15)-C(16)-C(19) | -123.4(16) | C(16)#1-Cr(1)-C(16)-C(15) | -158(7) |
| C(51)#1-C(15)-C(16)-Cr(1)#1 | 88(7) | C(50)-Cr(1)-C(16)-C(15) | -83.6(12) |
| O(51)#1-C(15)-C(16)-Cr(1)#1 | 160(3) | C(17)#1-Cr(1)-C(16)-C(15) | -62.3(17) |
| C(14)-C(15)-C(16)-Cr(1)#1 | -61.9(8) | C(52)-Cr(1)-C(16)-C(15) | -4(3) |
| Cr(1)-C(15)-C(16)-Cr(1)#1 | -4.6(7) | C(51)-Cr(1)-C(16)-C(15) | 166(2) |
| C(51)#1-C(15)-C(16)-C(50)#1 | 141(7) | C(50)#1-Cr(1)-C(16)-C(15) | 107.5(12) |
| O(51)#1-C(15)-C(16)-C(50)#1 | -147(3) | C(15)#1-Cr(1)-C(16)-C(15) | -175.7(16) |
| C(14)-C(15)-C(16)-C(50)#1 | -8.7(12) | C(14)-Cr(1)-C(16)-C(15) | 30.8(3) |
| Cr(1)#1-C(15)-C(16)-C(50)#1 | 53.2(11) | C(51)#1-Cr(1)-C(16)-C(15) | -22(2) |
| Cr(1)-C(15)-C(16)-C(50)#1 | 48.6(11) | C(18)#1-Cr(1)-C(16)-C(15) | -85.0(13) |
| C(51)#1-C(15)-C(16)-Cr(1) | 92(7) | Cr(1)#1-Cr(1)-C(16)-C(17) | 71(3) |
| O(51)#1-C(15)-C(16)-Cr(1) | 165(3) | C(16)#1-Cr(1)-C(16)-C(17) | 71(7) |
| C(14)-C(15)-C(16)-Cr(1) | -57.3(6) | C(50)-Cr(1)-C(16)-C(17) | 145.3(13) |
| Cr(1)#1-C(15)-C(16)-Cr(1) | 4.6(7) | C(17)#1-Cr(1)-C(16)-C(17) | 166.6(17) |
| Cr(1)#1-Cr(1)-C(16)-C(52)#1 | 18(4) | C(52)-Cr(1)-C(16)-C(17) | -135(3) |
| C(16)#1-Cr(1)-C(16)-C(52)#1 | 18(8) | C(51)-Cr(1)-C(16)-C(17) | 35.0(19) |
| C(50)-Cr(1)-C(16)-C(52)#1 | 92(3) | C(50)#1-Cr(1)-C(16)-C(17) | -23.7(13) |
| C(17)#1-Cr(1)-C(16)-C(52)#1 | 113(3) | C(15)#1-Cr(1)-C(16)-C(17) | 53.2(18) |
| C(52)-Cr(1)-C(16)-C(52)#1 | 172.1(15) | C(15)-Cr(1)-C(16)-C(17) | -131.2(3) |
| C(51)-Cr(1)-C(16)-C(52)#1 | -18(3) | C(14)-Cr(1)-C(16)-C(17) | -100.4(5) |
| C(50)#1-Cr(1)-C(16)-C(52)#1 | -77(3) | C(51)#1-Cr(1)-C(16)-C(17) | -153(2) |
| C(15)#1-Cr(1)-C(16)-C(52)#1 | 0(3) | C(18)#1-Cr(1)-C(16)-C(17) | 143.8(14) |
| C(15)-Cr(1)-C(16)-C(52)#1 | 176(2) | Cr(1)#1-Cr(1)-C(16)-C(19) | -40(4) |
| C(14)-Cr(1)-C(16)-C(52)#1 | -154(2) | C(16)#1-Cr(1)-C(16)-C(19) | -40(8) |
| C(51)#1-Cr(1)-C(16)-C(52)#1 | 153(3) | C(50)-Cr(1)-C(16)-C(19) | 34(2) |
| C(18)#1-Cr(1)-C(16)-C(52)#1 | 91(3) | C(17)#1-Cr(1)-C(16)-C(19) | 55(2) |

| | |
|---|---|
| C(52)-Cr(1)-C(16)-C(19) | 114(3) |
| C(51)-Cr(1)-C(16)-C(19) | -76(3) |
| C(50)#1-Cr(1)-C(16)-C(19) | -135(2) |
| C(15)#1-Cr(1)-C(16)-C(19) | -58(2) |
| C(15)-Cr(1)-C(16)-C(19) | 118(2) |
| C(14)-Cr(1)-C(16)-C(19) | 148.3(19) |
| C(51)#1-Cr(1)-C(16)-C(19) | 95(3) |
| C(18)#1-Cr(1)-C(16)-C(19) | 32.5(19) |
| C(16)#1-Cr(1)-C(16)-Cr(1)#1 | 0(7) |
| C(50)-Cr(1)-C(16)-Cr(1)#1 | 74(3) |
| C(17)#1-Cr(1)-C(16)-Cr(1)#1 | 95(3) |
| C(52)-Cr(1)-C(16)-Cr(1)#1 | 154(5) |
| C(51)-Cr(1)-C(16)-Cr(1)#1 | -36(3) |
| C(50)#1-Cr(1)-C(16)-Cr(1)#1 | -95(3) |
| C(15)#1-Cr(1)-C(16)-Cr(1)#1 | -18(3) |
| C(15)-Cr(1)-C(16)-Cr(1)#1 | 158(3) |
| C(14)-Cr(1)-C(16)-Cr(1)#1 | -172(3) |
| C(51)#1-Cr(1)-C(16)-Cr(1)#1 | 135(4) |
| C(18)#1-Cr(1)-C(16)-Cr(1)#1 | 73(3) |
| Cr(1)#1-Cr(1)-C(16)-C(50)#1 | 95(3) |
| C(16)#1-Cr(1)-C(16)-C(50)#1 | 95(7) |
| C(50)-Cr(1)-C(16)-C(50)#1 | 168.9(6) |
| C(17)#1-Cr(1)-C(16)-C(50)#1 | -169.7(17) |
| C(52)-Cr(1)-C(16)-C(50)#1 | -111(4) |
| C(51)-Cr(1)-C(16)-C(50)#1 | 59(2) |
| C(15)#1-Cr(1)-C(16)-C(50)#1 | 76.9(18) |
| C(15)-Cr(1)-C(16)-C(50)#1 | -107.5(12) |
| C(14)-Cr(1)-C(16)-C(50)#1 | -76.7(12) |
| C(51)#1-Cr(1)-C(16)-C(50)#1 | -130(3) |
| C(18)#1-Cr(1)-C(16)-C(50)#1 | 167.5(15) |
| C(52)#1-C(16)-C(17)-C(50)#1 | 144(4) |
| C(51)#1-C(16)-C(17)-C(50)#1 | -1(5) |
| C(15)-C(16)-C(17)-C(50)#1 | -17(2) |
| C(19)-C(16)-C(17)-C(50)#1 | 164(3) |
| Cr(1)#1-C(16)-C(17)-C(50)#1 | 49(2) |
| Cr(1)-C(16)-C(17)-C(50)#1 | 37(2) |
| C(51)#1-C(16)-C(17)-C(52)#1 | -145(5) |
| C(15)-C(16)-C(17)-C(52)#1 | -161(3) |
| C(19)-C(16)-C(17)-C(52)#1 | 20(3) |
| Cr(1)#1-C(16)-C(17)-C(52)#1 | -95(3) |
| C(50)#1-C(16)-C(17)-C(52)#1 | -144(4) |
| Cr(1)-C(16)-C(17)-C(52)#1 | -107(3) |
| C(52)#1-C(16)-C(17)-C(18) | 161(3) |
| C(51)#1-C(16)-C(17)-C(18) | 15(4) |
| C(15)-C(16)-C(17)-C(18) | 0.0 |
| C(19)-C(16)-C(17)-C(18) | -179.3(16) |
| Cr(1)#1-C(16)-C(17)-C(18) | 65.9(6) |
| C(50)#1-C(16)-C(17)-C(18) | 17(2) |
| Cr(1)-C(16)-C(17)-C(18) | 54.0(5) |
| C(52)#1-C(16)-C(17)-Cr(1)#1 | 95(3) |
| C(51)#1-C(16)-C(17)-Cr(1)#1 | -50(4) |
| C(15)-C(16)-C(17)-Cr(1)#1 | -65.9(7) |
| C(19)-C(16)-C(17)-Cr(1)#1 | 114.8(16) |
| C(50)#1-C(16)-C(17)-Cr(1)#1 | -49(2) |
| Cr(1)-C(16)-C(17)-Cr(1)#1 | -11.9(6) |
| C(52)#1-C(16)-C(17)-Cr(1) | 107(3) |
| C(51)#1-C(16)-C(17)-Cr(1) | -38(4) |
| C(15)-C(16)-C(17)-Cr(1) | -54.0(5) |
| C(19)-C(16)-C(17)-Cr(1) | 126.7(15) |
| Cr(1)#1-C(16)-C(17)-Cr(1) | 11.9(6) |
| C(50)#1-C(16)-C(17)-Cr(1) | -37(2) |
| Cr(1)#1-Cr(1)-C(17)-C(50)#1 | -175(4) |
| C(16)#1-Cr(1)-C(17)-C(50)#1 | 64(3) |
| C(50)-Cr(1)-C(17)-C(50)#1 | -178.3(13) |
| C(17)#1-Cr(1)-C(17)-C(50)#1 | -175(5) |
| C(52)-Cr(1)-C(17)-C(50)#1 | 3(5) |
| C(51)-Cr(1)-C(17)-C(50)#1 | 75(3) |
| C(15)#1-Cr(1)-C(17)-C(50)#1 | 90(3) |
| C(15)-Cr(1)-C(17)-C(50)#1 | -103(2) |
| C(14)-Cr(1)-C(17)-C(50)#1 | -65(2) |
| C(51)#1-Cr(1)-C(17)-C(50)#1 | -117(3) |
| C(18)#1-Cr(1)-C(17)-C(50)#1 | -179(3) |
| Cr(1)#1-Cr(1)-C(17)-C(52)#1 | 1(3) |
| C(16)#1-Cr(1)-C(17)-C(52)#1 | -120(3) |
| C(50)-Cr(1)-C(17)-C(52)#1 | -2(3) |
| C(17)#1-Cr(1)-C(17)-C(52)#1 | 1(6) |

| | | | |
|---|---|---|---|
| C(52)-Cr(1)-C(17)-C(52)#1 | 179.2(18) | C(15)#1-Cr(1)-C(17)-Cr(1)#1 | -95(2) |
| C(51)-Cr(1)-C(17)-C(52)#1 | -109(3) | C(15)-Cr(1)-C(17)-Cr(1)#1 | 72(2) |
| C(50)#1-Cr(1)-C(17)-C(52)#1 | 176(4) | C(14)-Cr(1)-C(17)-Cr(1)#1 | 110(2) |
| C(15)#1-Cr(1)-C(17)-C(52)#1 | -94(2) | C(51)#1-Cr(1)-C(17)-Cr(1)#1 | 58(3) |
| C(15)-Cr(1)-C(17)-C(52)#1 | 73(2) | C(18)#1-Cr(1)-C(17)-Cr(1)#1 | -4(2) |
| C(14)-Cr(1)-C(17)-C(52)#1 | 111(2) | C(14)-C(13)-C(18)-C(50)#1 | 35(4) |
| C(51)#1-Cr(1)-C(17)-C(52)#1 | 59(2) | C(12)-C(13)-C(18)-C(50)#1 | -150(5) |
| C(18)#1-Cr(1)-C(17)-C(52)#1 | -3(3) | O(50)#1-C(13)-C(18)-C(50)#1 | -166(7) |
| Cr(1)#1-Cr(1)-C(17)-C(18) | -174(2) | Cr(1)-C(13)-C(18)-C(50)#1 | -18(4) |
| C(16)#1-Cr(1)-C(17)-C(18) | 64(2) | Cr(1)#1-C(13)-C(18)-C(50)#1 | -3(4) |
| C(50)-Cr(1)-C(17)-C(18) | -177.8(18) | C(14)-C(13)-C(18)-O(50)#1 | -159(3) |
| C(17)#1-Cr(1)-C(17)-C(18) | -174(5) | C(12)-C(13)-C(18)-O(50)#1 | 16(3) |
| C(52)-Cr(1)-C(17)-C(18) | 4(3) | C(50)#1-C(13)-C(18)-O(50)#1 | 166(7) |
| C(51)-Cr(1)-C(17)-C(18) | 75.3(16) | Cr(1)-C(13)-C(18)-O(50)#1 | 148(3) |
| C(50)#1-Cr(1)-C(17)-C(18) | 0(3) | Cr(1)#1-C(13)-C(18)-O(50)#1 | 163(3) |
| C(15)#1-Cr(1)-C(17)-C(18) | 90.5(15) | C(14)-C(13)-C(18)-C(17) | 0.0 |
| C(15)-Cr(1)-C(17)-C(18) | -102.8(4) | C(12)-C(13)-C(18)-C(17) | 174.7(17) |
| C(14)-Cr(1)-C(17)-C(18) | -64.6(5) | C(50)#1-C(13)-C(18)-C(17) | -35(4) |
| C(51)#1-Cr(1)-C(17)-C(18) | -116.7(14) | O(50)#1-C(13)-C(18)-C(17) | 159(3) |
| C(18)#1-Cr(1)-C(17)-C(18) | -178.6(17) | Cr(1)-C(13)-C(18)-C(17) | -52.6(6) |
| Cr(1)#1-Cr(1)-C(17)-C(16) | -41(2) | Cr(1)#1-C(13)-C(18)-C(17) | -37.6(5) |
| C(16)#1-Cr(1)-C(17)-C(16) | -162.7(19) | C(14)-C(13)-C(18)-Cr(1)#1 | 37.6(5) |
| C(50)-Cr(1)-C(17)-C(16) | -44.8(17) | C(12)-C(13)-C(18)-Cr(1)#1 | -147.7(16) |
| C(17)#1-Cr(1)-C(17)-C(16) | -41(5) | C(50)#1-C(13)-C(18)-Cr(1)#1 | 3(4) |
| C(52)-Cr(1)-C(17)-C(16) | 137(4) | O(50)#1-C(13)-C(18)-Cr(1)#1 | -163(3) |
| C(51)-Cr(1)-C(17)-C(16) | -151.7(16) | Cr(1)-C(13)-C(18)-Cr(1)#1 | -15.0(5) |
| C(50)#1-Cr(1)-C(17)-C(16) | 133(2) | C(14)-C(13)-C(18)-Cr(1) | 52.6(6) |
| C(15)#1-Cr(1)-C(17)-C(16) | -136.5(15) | C(12)-C(13)-C(18)-Cr(1) | -132.6(16) |
| C(15)-Cr(1)-C(17)-C(16) | 30.1(3) | C(50)#1-C(13)-C(18)-Cr(1) | 18(4) |
| C(14)-Cr(1)-C(17)-C(16) | 68.4(5) | O(50)#1-C(13)-C(18)-Cr(1) | -148(3) |
| C(51)#1-Cr(1)-C(17)-C(16) | 16.3(14) | Cr(1)#1-C(13)-C(18)-Cr(1) | 15.0(5) |
| C(18)#1-Cr(1)-C(17)-C(16) | -45.6(17) | C(52)#1-C(17)-C(18)-C(50)#1 | -13(8) |
| C(16)#1-Cr(1)-C(17)-Cr(1)#1 | -121(3) | C(16)-C(17)-C(18)-C(50)#1 | -53(6) |
| C(50)-Cr(1)-C(17)-Cr(1)#1 | -3(2) | Cr(1)#1-C(17)-C(18)-C(50)#1 | -3(6) |
| C(17)#1-Cr(1)-C(17)-Cr(1)#1 | 0(5) | Cr(1)-C(17)-C(18)-C(50)#1 | -1(6) |
| C(52)-Cr(1)-C(17)-Cr(1)#1 | 178(5) | C(50)#1-C(17)-C(18)-O(50)#1 | -157(9) |
| C(51)-Cr(1)-C(17)-Cr(1)#1 | -110(3) | C(52)#1-C(17)-C(18)-O(50)#1 | -170(8) |
| C(50)#1-Cr(1)-C(17)-Cr(1)#1 | 175(4) | C(16)-C(17)-C(18)-O(50)#1 | 151(5) |

| | |
|---|---|
| Cr(1)#1-C(17)-C(18)-O(50)#1 | -159(5) |
| Cr(1)-C(17)-C(18)-O(50)#1 | -158(5) |
| C(50)#1-C(17)-C(18)-C(13) | 53(6) |
| C(52)#1-C(17)-C(18)-C(13) | 40(6) |
| C(16)-C(17)-C(18)-C(13) | 0.0 |
| Cr(1)#1-C(17)-C(18)-C(13) | 50.3(7) |
| Cr(1)-C(17)-C(18)-C(13) | 51.7(6) |
| C(50)#1-C(17)-C(18)-Cr(1)#1 | 3(6) |
| C(52)#1-C(17)-C(18)-Cr(1)#1 | -11(6) |
| C(16)-C(17)-C(18)-Cr(1)#1 | -50.3(7) |
| Cr(1)-C(17)-C(18)-Cr(1)#1 | 1.5(7) |
| C(50)#1-C(17)-C(18)-Cr(1) | 1(6) |
| C(52)#1-C(17)-C(18)-Cr(1) | -12(6) |
| C(16)-C(17)-C(18)-Cr(1) | -51.8(6) |
| Cr(1)#1-C(17)-C(18)-Cr(1) | -1.5(7) |
| Cr(1)#1-Cr(1)-C(18)-C(50)#1 | 5(10) |
| C(16)#1-Cr(1)-C(18)-C(50)#1 | -136(10) |
| C(50)-Cr(1)-C(18)-C(50)#1 | 8(14) |
| C(17)#1-Cr(1)-C(18)-C(50)#1 | 178(9) |
| C(52)-Cr(1)-C(18)-C(50)#1 | -176(10) |
| C(51)-Cr(1)-C(18)-C(50)#1 | -102(10) |
| C(15)#1-Cr(1)-C(18)-C(50)#1 | -92(10) |
| C(15)-Cr(1)-C(18)-C(50)#1 | 68(10) |
| C(14)-Cr(1)-C(18)-C(50)#1 | 106(10) |
| C(51)#1-Cr(1)-C(18)-C(50)#1 | 59(10) |
| C(18)#1-Cr(1)-C(18)-C(50)#1 | 5(12) |
| Cr(1)#1-Cr(1)-C(18)-O(50)#1 | 152(6) |
| C(16)#1-Cr(1)-C(18)-O(50)#1 | 11(6) |
| C(50)-Cr(1)-C(18)-O(50)#1 | 155(6) |
| C(17)#1-Cr(1)-C(18)-O(50)#1 | -35(8) |
| C(52)-Cr(1)-C(18)-O(50)#1 | -29(6) |
| C(51)-Cr(1)-C(18)-O(50)#1 | 45(6) |
| C(50)#1-Cr(1)-C(18)-O(50)#1 | 147(13) |
| C(15)#1-Cr(1)-C(18)-O(50)#1 | 55(5) |
| C(15)-Cr(1)-C(18)-O(50)#1 | -145(6) |
| C(14)-Cr(1)-C(18)-O(50)#1 | -107(6) |
| C(51)#1-Cr(1)-C(18)-O(50)#1 | -154(6) |
| C(18)#1-Cr(1)-C(18)-O(50)#1 | 152(5) |
| Cr(1)#1-Cr(1)-C(18)-C(13) | -130.0(17) |
| C(16)#1-Cr(1)-C(18)-C(13) | 88.3(16) |
| C(50)-Cr(1)-C(18)-C(13) | -128(5) |
| C(17)#1-Cr(1)-C(18)-C(13) | 42(4) |
| C(52)-Cr(1)-C(18)-C(13) | 48.3(17) |
| C(51)-Cr(1)-C(18)-C(13) | 122.5(15) |
| C(50)#1-Cr(1)-C(18)-C(13) | -135(10) |
| C(15)#1-Cr(1)-C(18)-C(13) | 133.0(13) |
| C(15)-Cr(1)-C(18)-C(13) | -67.5(4) |
| C(14)-Cr(1)-C(18)-C(13) | -29.4(2) |
| C(51)#1-Cr(1)-C(18)-C(13) | -76.3(13) |
| C(18)#1-Cr(1)-C(18)-C(13) | -130(4) |
| Cr(1)#1-Cr(1)-C(18)-C(17) | 3.4(15) |
| C(16)#1-Cr(1)-C(18)-C(17) | -138.3(15) |
| C(50)-Cr(1)-C(18)-C(17) | 6(5) |
| C(17)#1-Cr(1)-C(18)-C(17) | 176(4) |
| C(52)-Cr(1)-C(18)-C(17) | -178.3(17) |
| C(51)-Cr(1)-C(18)-C(17) | -104.0(15) |
| C(50)#1-Cr(1)-C(18)-C(17) | -2(10) |
| C(15)#1-Cr(1)-C(18)-C(17) | -93.6(14) |
| C(15)-Cr(1)-C(18)-C(17) | 66.0(4) |
| C(14)-Cr(1)-C(18)-C(17) | 104.1(4) |
| C(51)#1-Cr(1)-C(18)-C(17) | 57.1(13) |
| C(18)#1-Cr(1)-C(18)-C(17) | 3(4) |
| C(16)#1-Cr(1)-C(18)-Cr(1)#1 | -142(2) |
| C(50)-Cr(1)-C(18)-Cr(1)#1 | 2(4) |
| C(17)#1-Cr(1)-C(18)-Cr(1)#1 | 172(5) |
| C(52)-Cr(1)-C(18)-Cr(1)#1 | 178(2) |
| C(51)-Cr(1)-C(18)-Cr(1)#1 | -107(2) |
| C(50)#1-Cr(1)-C(18)-Cr(1)#1 | -5(10) |
| C(15)#1-Cr(1)-C(18)-Cr(1)#1 | -97.0(17) |
| C(15)-Cr(1)-C(18)-Cr(1)#1 | 62.5(15) |
| C(14)-Cr(1)-C(18)-Cr(1)#1 | 100.6(16) |
| C(51)#1-Cr(1)-C(18)-Cr(1)#1 | 53.7(19) |
| C(18)#1-Cr(1)-C(18)-Cr(1)#1 | 0(4) |
| C(52)#1-C(16)-C(19)-O(52)#1 | 37(3) |
| C(51)#1-C(16)-C(19)-O(52)#1 | -172(3) |
| C(15)-C(16)-C(19)-O(52)#1 | -161.1(15) |

| | |
|---|---|
| C(17)-C(16)-C(19)-O(52)#1 | 18(2) |
| Cr(1)#1-C(16)-C(19)-O(52)#1 | 101.1(19) |
| C(50)#1-C(16)-C(19)-O(52)#1 | 33(4) |
| Cr(1)-C(16)-C(19)-O(52)#1 | 109.9(19) |
| C(52)#1-C(16)-C(19)-C(20) | -157(4) |
| C(51)#1-C(16)-C(19)-C(20) | -6(4) |
| C(15)-C(16)-C(19)-C(20) | 5(3) |
| C(17)-C(16)-C(19)-C(20) | -175(2) |
| Cr(1)#1-C(16)-C(19)-C(20) | -93(3) |
| C(50)#1-C(16)-C(19)-C(20) | -161(3) |
| Cr(1)-C(16)-C(19)-C(20) | -84(3) |
| C(51)#1-C(16)-C(19)-C(52)#1 | 151(4) |
| C(15)-C(16)-C(19)-C(52)#1 | 162(3) |
| C(17)-C(16)-C(19)-C(52)#1 | -19(3) |
| Cr(1)#1-C(16)-C(19)-C(52)#1 | 64(3) |
| C(50)#1-C(16)-C(19)-C(52)#1 | -4(4) |
| Cr(1)-C(16)-C(19)-C(52)#1 | 73(3) |
| O(52)#1-C(19)-C(20)-C(4)#1 | -14(4) |
| C(52)#1-C(19)-C(20)-C(4)#1 | 135(8) |
| C(16)-C(19)-C(20)-C(4)#1 | -175.7(16) |
| Cr(1)#1-Cr(1)-C(50)-C(18)#1 | -21(39) |
| C(16)#1-Cr(1)-C(50)-C(18)#1 | 124(40) |
| C(17)#1-Cr(1)-C(50)-C(18)#1 | 163(41) |
| C(52)-Cr(1)-C(50)-C(18)#1 | 161(39) |
| C(51)-Cr(1)-C(50)-C(18)#1 | 84(39) |
| C(50)#1-Cr(1)-C(50)-C(18)#1 | -21(39) |
| C(15)#1-Cr(1)-C(50)-C(18)#1 | 78(39) |
| C(15)-Cr(1)-C(50)-C(18)#1 | -81(39) |
| C(14)-Cr(1)-C(50)-C(18)#1 | -113(39) |
| C(51)#1-Cr(1)-C(50)-C(18)#1 | -75(39) |
| Cr(1)#1-Cr(1)-C(50)-C(17)#1 | 177(3) |
| C(16)#1-Cr(1)-C(50)-C(17)#1 | -38.1(16) |
| C(52)-Cr(1)-C(50)-C(17)#1 | -2(2) |
| C(51)-Cr(1)-C(50)-C(17)#1 | -78(2) |
| C(50)#1-Cr(1)-C(50)-C(17)#1 | 177(3) |
| C(15)#1-Cr(1)-C(50)-C(17)#1 | -85(2) |
| C(15)-Cr(1)-C(50)-C(17)#1 | 116(2) |
| C(14)-Cr(1)-C(50)-C(17)#1 | 84(2) |
| C(51)#1-Cr(1)-C(50)-C(17)#1 | 122(2) |
| C(18)#1-Cr(1)-C(50)-C(17)#1 | -163(41) |
| Cr(1)#1-Cr(1)-C(50)-O(50) | 34(13) |
| C(16)#1-Cr(1)-C(50)-O(50) | 179(13) |
| C(17)#1-Cr(1)-C(50)-O(50) | -142(14) |
| C(52)-Cr(1)-C(50)-O(50) | -144(13) |
| C(51)-Cr(1)-C(50)-O(50) | 139(13) |
| C(50)#1-Cr(1)-C(50)-O(50) | 34(13) |
| C(15)#1-Cr(1)-C(50)-O(50) | 133(13) |
| C(15)-Cr(1)-C(50)-O(50) | -26(13) |
| C(14)-Cr(1)-C(50)-O(50) | -58(13) |
| C(51)#1-Cr(1)-C(50)-O(50) | -20(13) |
| C(18)#1-Cr(1)-C(50)-O(50) | 55(35) |
| Cr(1)#1-Cr(1)-C(50)-C(13)#1 | -45(2) |
| C(16)#1-Cr(1)-C(50)-C(13)#1 | 100(2) |
| C(17)#1-Cr(1)-C(50)-C(13)#1 | 138(3) |
| C(52)-Cr(1)-C(50)-C(13)#1 | 136(2) |
| C(51)-Cr(1)-C(50)-C(13)#1 | 60(2) |
| C(50)#1-Cr(1)-C(50)-C(13)#1 | -45(2) |
| C(15)#1-Cr(1)-C(50)-C(13)#1 | 53(2) |
| C(15)-Cr(1)-C(50)-C(13)#1 | -105.5(18) |
| C(14)-Cr(1)-C(50)-C(13)#1 | -137.3(14) |
| C(51)#1-Cr(1)-C(50)-C(13)#1 | -100(2) |
| C(18)#1-Cr(1)-C(50)-C(13)#1 | -24(38) |
| C(16)#1-Cr(1)-C(50)-Cr(1)#1 | 145(2) |
| C(17)#1-Cr(1)-C(50)-Cr(1)#1 | -177(3) |
| C(52)-Cr(1)-C(50)-Cr(1)#1 | -179(2) |
| C(51)-Cr(1)-C(50)-Cr(1)#1 | 105(2) |
| C(50)#1-Cr(1)-C(50)-Cr(1)#1 | 0.000(4) |
| C(15)#1-Cr(1)-C(50)-Cr(1)#1 | 98.4(17) |
| C(15)-Cr(1)-C(50)-Cr(1)#1 | -60.4(15) |
| C(14)-Cr(1)-C(50)-Cr(1)#1 | -92.1(18) |
| C(51)#1-Cr(1)-C(50)-Cr(1)#1 | -54.5(19) |
| C(18)#1-Cr(1)-C(50)-Cr(1)#1 | 21(39) |
| Cr(1)#1-Cr(1)-C(50)-C(16)#1 | -145(2) |
| C(17)#1-Cr(1)-C(50)-C(16)#1 | 38.1(16) |
| C(52)-Cr(1)-C(50)-C(16)#1 | 36.0(17) |
| C(51)-Cr(1)-C(50)-C(16)#1 | -40.3(17) |

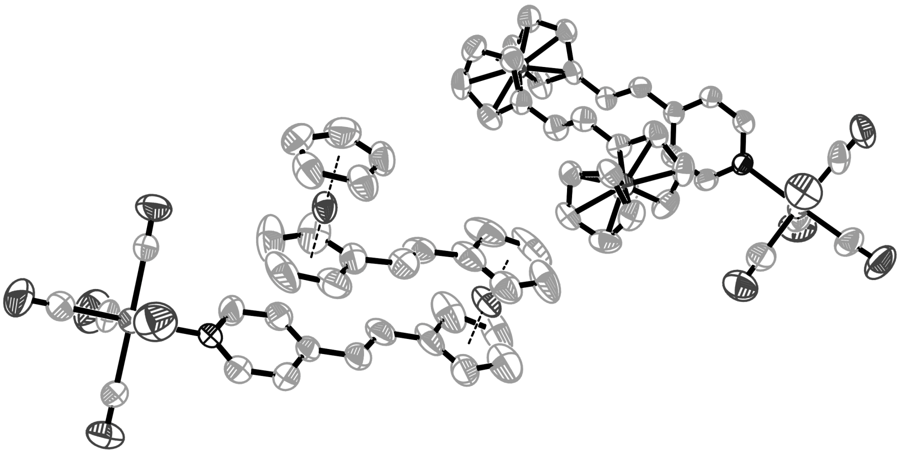
| | |
|---|---|
| C(50)#1-Cr(1)-C(50)-C(16)#1 | -145(2) |
| C(15)#1-Cr(1)-C(50)-C(16)#1 | -46.9(7) |
| C(15)-Cr(1)-C(50)-C(16)#1 | 154.3(13) |
| C(14)-Cr(1)-C(50)-C(16)#1 | 122.5(15) |
| C(51)#1-Cr(1)-C(50)-C(16)#1 | 160.2(16) |
| C(18)#1-Cr(1)-C(50)-C(16)#1 | -124(40) |
| C(17)#1-C(50)-O(50)-C(18)#1 | 86(22) |
| C(13)#1-C(50)-O(50)-C(18)#1 | -53(21) |
| Cr(1)-C(50)-O(50)-C(18)#1 | -134(25) |
| Cr(1)#1-C(50)-O(50)-C(18)#1 | -110(22) |
| C(16)#1-C(50)-O(50)-C(18)#1 | 45(21) |
| C(18)#1-C(50)-O(50)-C(13)#1 | 53(21) |
| C(17)#1-C(50)-O(50)-C(13)#1 | 138(4) |
| Cr(1)-C(50)-O(50)-C(13)#1 | -82(13) |
| Cr(1)#1-C(50)-O(50)-C(13)#1 | -58(4) |
| C(16)#1-C(50)-O(50)-C(13)#1 | 97(4) |
| C(14)#1-O(51)-C(51)-C(15)#1 | -23(4) |
| C(15)#1-O(51)-C(51)-C(16)#1 | -67(6) |
| C(14)#1-O(51)-C(51)-C(16)#1 | -89(6) |
| C(15)#1-O(51)-C(51)-Cr(1) | 13(7) |
| C(14)#1-O(51)-C(51)-Cr(1) | -10(8) |
| C(15)#1-O(51)-C(51)-C(14)#1 | 23(4) |
| C(15)#1-O(51)-C(51)-Cr(1)#1 | 39(5) |
| C(14)#1-O(51)-C(51)-Cr(1)#1 | 16(4) |
| Cr(1)#1-Cr(1)-C(51)-C(15)#1 | 69(6) |
| C(16)#1-Cr(1)-C(51)-C(15)#1 | -87(6) |
| C(50)-Cr(1)-C(51)-C(15)#1 | -25(6) |
| C(17)#1-Cr(1)-C(51)-C(15)#1 | -62(5) |
| C(52)-Cr(1)-C(51)-C(15)#1 | -101(6) |
| C(50)#1-Cr(1)-C(51)-C(15)#1 | 131(6) |
| C(15)-Cr(1)-C(51)-C(15)#1 | 108(6) |
| C(14)-Cr(1)-C(51)-C(15)#1 | 179(5) |
| C(51)#1-Cr(1)-C(51)-C(15)#1 | 69(6) |
| C(18)#1-Cr(1)-C(51)-C(15)#1 | -23(5) |
| Cr(1)#1-Cr(1)-C(51)-O(51) | 57(9) |
| C(16)#1-Cr(1)-C(51)-O(51) | -98(9) |
| C(50)-Cr(1)-C(51)-O(51) | -37(9) |
| C(17)#1-Cr(1)-C(51)-O(51) | -74(8) |
| C(52)-Cr(1)-C(51)-O(51) | -112(9) |
| C(50)#1-Cr(1)-C(51)-O(51) | 119(9) |
| C(15)#1-Cr(1)-C(51)-O(51) | -12(6) |
| C(15)-Cr(1)-C(51)-O(51) | 97(9) |
| C(14)-Cr(1)-C(51)-O(51) | 167(7) |
| C(51)#1-Cr(1)-C(51)-O(51) | 57(9) |
| C(18)#1-Cr(1)-C(51)-O(51) | -35(9) |
| Cr(1)#1-Cr(1)-C(51)-C(16)#1 | 156(2) |
| C(50)-Cr(1)-C(51)-C(16)#1 | 61(2) |
| C(17)#1-Cr(1)-C(51)-C(16)#1 | 24.4(18) |
| C(52)-Cr(1)-C(51)-C(16)#1 | -14(2) |
| C(50)#1-Cr(1)-C(51)-C(16)#1 | -143(2) |
| C(15)#1-Cr(1)-C(51)-C(16)#1 | 87(6) |
| C(15)-Cr(1)-C(51)-C(16)#1 | -165(4) |
| C(14)-Cr(1)-C(51)-C(16)#1 | -95(3) |
| C(51)#1-Cr(1)-C(51)-C(16)#1 | 156(2) |
| C(18)#1-Cr(1)-C(51)-C(16)#1 | 63(2) |
| Cr(1)#1-Cr(1)-C(51)-C(14)#1 | 47(2) |
| C(16)#1-Cr(1)-C(51)-C(14)#1 | -109(3) |
| C(50)-Cr(1)-C(51)-C(14)#1 | -47.3(18) |
| C(17)#1-Cr(1)-C(51)-C(14)#1 | -84.3(14) |
| C(52)-Cr(1)-C(51)-C(14)#1 | -123(2) |
| C(50)#1-Cr(1)-C(51)-C(14)#1 | 108.7(17) |
| C(15)#1-Cr(1)-C(51)-C(14)#1 | -22(4) |
| C(15)-Cr(1)-C(51)-C(14)#1 | 86(5) |
| C(14)-Cr(1)-C(51)-C(14)#1 | 156.8(16) |
| C(51)#1-Cr(1)-C(51)-C(14)#1 | 47(2) |
| C(18)#1-Cr(1)-C(51)-C(14)#1 | -45.2(13) |
| C(16)#1-Cr(1)-C(51)-Cr(1)#1 | -156(2) |
| C(50)-Cr(1)-C(51)-Cr(1)#1 | -94.5(19) |
| C(17)#1-Cr(1)-C(51)-Cr(1)#1 | -132(2) |
| C(52)-Cr(1)-C(51)-Cr(1)#1 | -170(2) |
| C(50)#1-Cr(1)-C(51)-Cr(1)#1 | 61.4(16) |
| C(15)#1-Cr(1)-C(51)-Cr(1)#1 | -69(6) |
| C(15)-Cr(1)-C(51)-Cr(1)#1 | 39(4) |
| C(14)-Cr(1)-C(51)-Cr(1)#1 | 110(2) |
| C(51)#1-Cr(1)-C(51)-Cr(1)#1 | 0.000(4) |
| C(18)#1-Cr(1)-C(51)-Cr(1)#1 | -92.5(18) |

| | |
|---|---|
| Cr(1)#1-Cr(1)-C(52)-C(16)#1 | -94(12) |
| C(50)-Cr(1)-C(52)-C(16)#1 | -87(3) |
| C(17)#1-Cr(1)-C(52)-C(16)#1 | -88(3) |
| C(51)-Cr(1)-C(52)-C(16)#1 | 18(3) |
| C(50)#1-Cr(1)-C(52)-C(16)#1 | 94(3) |
| C(15)#1-Cr(1)-C(52)-C(16)#1 | 2(2) |
| C(15)-Cr(1)-C(52)-C(16)#1 | -173(3) |
| C(14)-Cr(1)-C(52)-C(16)#1 | 158(3) |
| C(51)#1-Cr(1)-C(52)-C(16)#1 | -158(3) |
| C(18)#1-Cr(1)-C(52)-C(16)#1 | -86(2) |
| Cr(1)#1-Cr(1)-C(52)-C(17)#1 | -6(13) |
| C(16)#1-Cr(1)-C(52)-C(17)#1 | 88(3) |
| C(50)-Cr(1)-C(52)-C(17)#1 | 2(2) |
| C(51)-Cr(1)-C(52)-C(17)#1 | 106(3) |
| C(50)#1-Cr(1)-C(52)-C(17)#1 | -177(2) |
| C(15)#1-Cr(1)-C(52)-C(17)#1 | 91(2) |
| C(15)-Cr(1)-C(52)-C(17)#1 | -85(3) |
| C(14)-Cr(1)-C(52)-C(17)#1 | -114(2) |
| C(51)#1-Cr(1)-C(52)-C(17)#1 | -70(3) |
| C(18)#1-Cr(1)-C(52)-C(17)#1 | 2.6(15) |
| Cr(1)#1-Cr(1)-C(52)-C(19)#1 | -151(11) |
| C(16)#1-Cr(1)-C(52)-C(19)#1 | -57(3) |
| C(50)-Cr(1)-C(52)-C(19)#1 | -144(3) |
| C(17)#1-Cr(1)-C(52)-C(19)#1 | -146(4) |
| C(51)-Cr(1)-C(52)-C(19)#1 | -40(3) |
| C(50)#1-Cr(1)-C(52)-C(19)#1 | 37(4) |
| C(15)#1-Cr(1)-C(52)-C(19)#1 | -55(3) |
| C(15)-Cr(1)-C(52)-C(19)#1 | 129(2) |
| C(14)-Cr(1)-C(52)-C(19)#1 | 100(3) |
| C(51)#1-Cr(1)-C(52)-C(19)#1 | 144(3) |
| C(18)#1-Cr(1)-C(52)-C(19)#1 | -143(3) |
| Cr(1)#1-Cr(1)-C(52)-O(52) | -175(10) |
| C(16)#1-Cr(1)-C(52)-O(52) | -81(12) |
| C(50)-Cr(1)-C(52)-O(52) | -168(12) |
| C(17)#1-Cr(1)-C(52)-O(52) | -170(13) |
| C(51)-Cr(1)-C(52)-O(52) | -64(12) |
| C(50)#1-Cr(1)-C(52)-O(52) | 13(13) |
| C(15)#1-Cr(1)-C(52)-O(52) | -79(12) |
| C(15)-Cr(1)-C(52)-O(52) | 105(12) |
| C(14)-Cr(1)-C(52)-O(52) | 76(12) |
| C(51)#1-Cr(1)-C(52)-O(52) | 120(12) |
| C(18)#1-Cr(1)-C(52)-O(52) | -167(12) |
| C(16)#1-Cr(1)-C(52)-Cr(1)#1 | 94(12) |
| C(50)-Cr(1)-C(52)-Cr(1)#1 | 7(12) |
| C(17)#1-Cr(1)-C(52)-Cr(1)#1 | 6(13) |
| C(51)-Cr(1)-C(52)-Cr(1)#1 | 112(12) |
| C(50)#1-Cr(1)-C(52)-Cr(1)#1 | -172(13) |
| C(15)#1-Cr(1)-C(52)-Cr(1)#1 | 96(12) |
| C(15)-Cr(1)-C(52)-Cr(1)#1 | -79(12) |
| C(14)-Cr(1)-C(52)-Cr(1)#1 | -108(12) |
| C(51)#1-Cr(1)-C(52)-Cr(1)#1 | -64(12) |
| C(18)#1-Cr(1)-C(52)-Cr(1)#1 | 8(12) |
| C(16)#1-C(52)-O(52)-C(19)#1 | -46(4) |
| C(17)#1-C(52)-O(52)-C(19)#1 | -140(5) |
| Cr(1)-C(52)-O(52)-C(19)#1 | 28(11) |
| Cr(1)#1-C(52)-O(52)-C(19)#1 | 27(13) |

---

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+1,-z+1



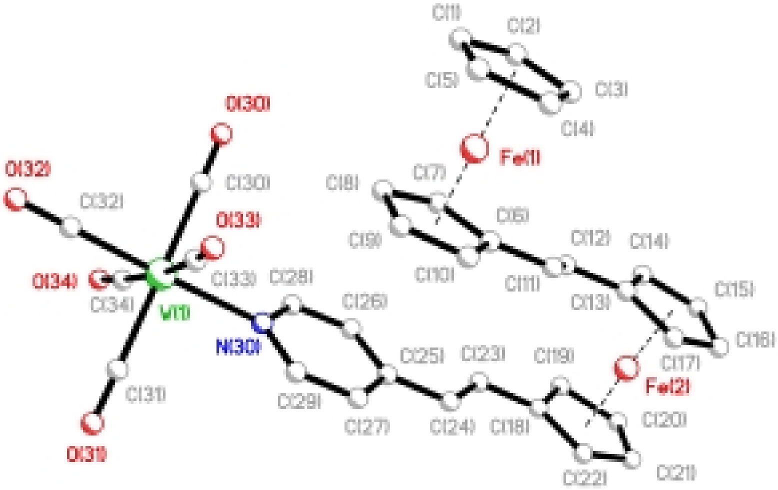

C(1)
C(2)
C(5)
C(3)
C(4)
O(30)
Fe(1)
O(32)
C(32)
C(30)
C(8)
C(7)
O(33)
C(6)
C(12)
C(14)
C(9)
C(10)
O(34)
C(33)
C(28)
C(11)
C(13)
C(15)
C(34)
V(1)
C(26)
N(30)
C(16)
C(25)
C(23)
C(19)
C(17)
Fe(2)
C(31)
C(29)
C(20)
C(27)
C(24)
C(18)
O(31)
C(22)
C(21)

**Table 1**. Crystal data and structure refinement for str75m.

| | | |
|---|---|---|
| Identification code | str75m | |
| Empirical formula | C34 H25 Fe2 N O5 W | |
| Formula weight | 823.10 | |
| Temperature | 293(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Triclinic | |
| Space group | -1 | |
| Unit cell dimensions | a = 10.4332(6) Å | $\alpha$= 83.0560(10)°. |
| | b = 15.1577(8) Å | $\beta$= 76.9510(10)°. |
| | c = 20.3793(11) Å | $\gamma$ = 84.6140(10)°. |
| Volume | 3109.2(3) Å$^3$ | |
| Z | 4 | |
| Density (calculated) | 1.758 Mg/m$^3$ | |
| Absorption coefficient | 4.653 mm$^{-1}$ | |
| F(000) | 1608 | |
| Crystal size | 0.23 x 0.13 x 0.05 mm$^3$ | |
| Theta range for data collection | 1.03 to 26.37°. | |
| Index ranges | -12<=h<=13, -17<=k<=18, -25<=l<=15 | |
| Reflections collected | 19707 | |
| Independent reflections | 12656 [R(int) = 0.0441] | |
| Completeness to theta = 26.37° | 99.8 % | |
| Absorption correction | BRUKER | |
| Refinement method | Full-matrix least-squares on F$^2$ | |
| Data / restraints / parameters | 12656 / 0 / 775 | |
| Goodness-of-fit on F$^2$ | 0.902 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0409, wR2 = 0.0928 | |
| R indices (all data) | R1 = 0.0761, wR2 = 0.1002 | |
| Largest diff. peak and hole | 1.406 and -1.421 e.Å$^{-3}$ | |

**Table 2**. Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters (Å$^2$x $10^3$) for str75m. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| W(1) | -5586(1) | 18065(1) | 739(1) | 61(1) |
| C(1) | -7679(9) | 14650(6) | 3532(4) | 85(2) |
| Fe(1) | -6478(1) | 14317(1) | 2648(1) | 55(1) |
| W(2) | 8707(1) | 6819(1) | 3050(1) | 58(1) |
| Fe(2) | -84(1) | 12231(1) | 1360(1) | 74(1) |
| C(2) | -6657(9) | 14048(6) | 3660(4) | 93(3) |
| Fe(3) | 4142(1) | 10120(1) | 3156(1) | 43(1) |
| C(3) | -6721(7) | 13272(5) | 3389(4) | 71(2) |
| Fe(4) | 7402(1) | 12927(1) | 4780(1) | 49(1) |
| C(4) | -7789(7) | 13391(5) | 3075(4) | 70(2) |
| C(5) | -8380(7) | 14265(5) | 3166(4) | 79(2) |
| C(6) | -4771(7) | 14052(5) | 1948(3) | 63(2) |
| C(7) | -4725(8) | 14843(6) | 2215(4) | 88(3) |
| C(8) | -5762(10) | 15440(6) | 2097(6) | 119(4) |
| C(9) | -6480(9) | 15006(7) | 1730(5) | 106(4) |
| C(10) | -5875(8) | 14164(6) | 1648(4) | 81(2) |
| C(11) | -3875(7) | 13257(5) | 1927(3) | 66(2) |
| C(12) | -2757(7) | 13172(5) | 2082(3) | 70(2) |
| C(13) | -1836(7) | 12359(6) | 2050(4) | 77(2) |
| C(14) | -737(8) | 12226(7) | 2371(4) | 100(3) |
| C(15) | -96(9) | 11397(8) | 2212(5) | 127(5) |
| C(16) | -731(9) | 11019(7) | 1792(5) | 112(4) |
| C(17) | -1777(8) | 11618(6) | 1690(4) | 81(2) |
| C(18) | 174(8) | 13356(6) | 695(4) | 85(3) |
| C(19) | 1243(8) | 13181(7) | 1055(5) | 111(3) |
| C(20) | 1793(10) | 12288(8) | 847(7) | 139(6) |
| C(21) | 1112(12) | 11973(9) | 453(6) | 132(5) |
| C(22) | 118(9) | 12610(6) | 340(4) | 97(3) |
| C(23) | -713(7) | 14189(5) | 759(3) | 75(2) |
| C(24) | -1642(7) | 14435(5) | 436(3) | 66(2) |
| C(25) | -2485(7) | 15264(4) | 498(3) | 55(2) |
| C(26) | -2330(7) | 15933(5) | 873(3) | 74(2) |
| C(27) | -3471(7) | 15446(4) | 152(3) | 65(2) |

| | | | | |
|---|---|---|---|---|
| C(28) | -3164(8) | 16692(5) | 912(4) | 77(2) |
| C(29) | -4273(7) | 16207(5) | 209(3) | 63(2) |
| N(30) | -4160(5) | 16841(3) | 596(2) | 54(1) |
| O(30) | -5566(6) | 17806(4) | 2297(3) | 94(2) |
| C(30) | -5603(7) | 17884(4) | 1751(3) | 58(2) |
| O(31) | -5414(6) | 18421(4) | -840(3) | 110(2) |
| C(31) | -5465(8) | 18291(5) | -276(4) | 78(2) |
| C(32) | -6875(9) | 19103(6) | 885(4) | 93(3) |
| O(32) | -7628(8) | 19703(5) | 966(3) | 144(3) |
| O(33) | -8074(7) | 16931(5) | 956(3) | 111(2) |
| C(33) | -7135(9) | 17312(6) | 869(4) | 79(2) |
| C(34) | -4163(10) | 18921(5) | 651(4) | 84(3) |
| O(34) | -3412(8) | 19449(5) | 627(4) | 138(3) |
| C(51) | 2635(7) | 9775(5) | 2763(4) | 65(2) |
| C(52) | 3406(7) | 10368(6) | 2303(3) | 72(2) |
| C(53) | 3371(7) | 11150(5) | 2605(3) | 63(2) |
| C(54) | 2571(6) | 11043(4) | 3264(3) | 57(2) |
| C(55) | 2124(6) | 10194(4) | 3351(3) | 58(2) |
| C(56) | 5465(6) | 10404(4) | 3715(3) | 50(2) |
| C(57) | 4880(6) | 9588(4) | 3976(3) | 59(2) |
| C(58) | 5147(7) | 9006(4) | 3480(4) | 66(2) |
| C(59) | 5904(7) | 9418(5) | 2897(4) | 68(2) |
| C(60) | 6095(6) | 10287(5) | 3033(3) | 62(2) |
| C(61) | 5401(6) | 11179(4) | 4075(3) | 55(2) |
| C(62) | 6118(6) | 11854(4) | 3877(3) | 57(2) |
| C(63) | 6086(6) | 12644(4) | 4225(3) | 51(2) |
| C(64) | 5425(6) | 12810(4) | 4889(3) | 60(2) |
| C(65) | 5686(7) | 13689(5) | 4996(4) | 71(2) |
| C(66) | 6505(7) | 14059(4) | 4398(4) | 69(2) |
| C(67) | 6777(7) | 13420(5) | 3919(4) | 65(2) |
| C(68) | 8820(6) | 11890(4) | 4785(3) | 50(2) |
| C(69) | 8080(7) | 11995(4) | 5453(3) | 61(2) |
| C(70) | 8246(9) | 12868(5) | 5597(4) | 77(2) |
| C(71) | 9066(9) | 13292(5) | 5031(5) | 83(3) |
| C(72) | 9394(7) | 12704(5) | 4530(4) | 70(2) |
| C(73) | 8879(5) | 11118(4) | 4417(3) | 46(1) |
| C(74) | 8455(6) | 10331(4) | 4664(3) | 49(2) |
| C(75) | 8477(6) | 9564(4) | 4306(3) | 47(1) |

|  |  |  |  |  |
|---|---|---|---|---|
| C(76) | 8866(6) | 9586(4) | 3601(3) | 54(2) |
| C(77) | 8120(6) | 8749(4) | 4635(3) | 56(2) |
| C(78) | 8882(6) | 8835(4) | 3284(3) | 55(2) |
| N(79) | 8541(5) | 8040(3) | 3617(2) | 48(1) |
| C(79) | 8153(6) | 8020(4) | 4288(3) | 57(2) |
| O(80) | 9023(7) | 5101(4) | 2319(3) | 128(3) |
| C(80) | 8899(8) | 5756(6) | 2582(4) | 86(3) |
| O(81) | 8437(8) | 7985(5) | 1688(3) | 131(3) |
| C(81) | 8526(9) | 7573(6) | 2181(5) | 88(3) |
| O(82) | 9005(6) | 5536(3) | 4356(3) | 96(2) |
| C(82) | 8908(8) | 6015(5) | 3895(4) | 75(2) |
| C(83) | 6728(8) | 6694(5) | 3267(4) | 70(2) |
| O(83) | 5634(6) | 6572(4) | 3360(3) | 105(2) |
| C(84) | 10683(8) | 6926(5) | 2789(4) | 69(2) |
| O(84) | 11784(6) | 7001(5) | 2626(3) | 113(2) |

**Table 3**. Bond lengths [Å] and angles [°] for str75m.

| | |
|---|---|
| W(1)-C(32) | 1.977(8) |
| W(1)-C(33) | 2.016(10) |
| W(1)-C(34) | 2.026(10) |
| W(1)-C(31) | 2.032(7) |
| W(1)-C(30) | 2.044(7) |
| W(1)-N(30) | 2.271(5) |
| C(1)-C(5) | 1.365(11) |
| C(1)-C(2) | 1.386(10) |
| C(1)-Fe(1) | 2.037(7) |
| Fe(1)-C(2) | 2.023(8) |
| Fe(1)-C(10) | 2.027(7) |
| Fe(1)-C(8) | 2.028(9) |
| Fe(1)-C(4) | 2.031(7) |
| Fe(1)-C(5) | 2.030(7) |
| Fe(1)-C(9) | 2.029(8) |
| Fe(1)-C(7) | 2.034(7) |
| Fe(1)-C(3) | 2.044(7) |
| Fe(1)-C(6) | 2.056(7) |
| W(2)-C(80) | 1.943(8) |
| W(2)-C(81) | 2.024(9) |
| W(2)-C(82) | 2.026(8) |
| W(2)-C(84) | 2.027(9) |
| W(2)-C(83) | 2.033(9) |
| W(2)-N(79) | 2.271(5) |
| Fe(2)-C(20) | 2.005(9) |
| Fe(2)-C(17) | 2.014(8) |
| Fe(2)-C(14) | 2.019(8) |
| Fe(2)-C(15) | 2.019(8) |
| Fe(2)-C(19) | 2.036(9) |
| Fe(2)-C(21) | 2.042(11) |
| Fe(2)-C(16) | 2.044(10) |
| Fe(2)-C(18) | 2.045(7) |
| Fe(2)-C(13) | 2.048(7) |
| Fe(2)-C(22) | 2.057(8) |
| C(2)-C(3) | 1.372(11) |
| Fe(3)-C(53) | 2.023(6) |
| Fe(3)-C(58) | 2.025(6) |
| Fe(3)-C(59) | 2.030(7) |
| Fe(3)-C(60) | 2.032(6) |
| Fe(3)-C(52) | 2.036(6) |
| Fe(3)-C(54) | 2.043(6) |
| Fe(3)-C(57) | 2.043(6) |
| Fe(3)-C(55) | 2.047(6) |
| Fe(3)-C(51) | 2.052(6) |
| Fe(3)-C(56) | 2.079(6) |
| C(3)-C(4) | 1.393(9) |
| Fe(4)-C(65) | 2.029(7) |
| Fe(4)-C(72) | 2.030(7) |
| Fe(4)-C(66) | 2.032(6) |
| Fe(4)-C(69) | 2.039(6) |
| Fe(4)-C(67) | 2.042(6) |
| Fe(4)-C(70) | 2.042(6) |
| Fe(4)-C(64) | 2.046(7) |
| Fe(4)-C(68) | 2.055(6) |
| Fe(4)-C(71) | 2.057(7) |
| Fe(4)-C(63) | 2.068(6) |
| C(4)-C(5) | 1.423(10) |
| C(6)-C(7) | 1.385(10) |
| C(6)-C(10) | 1.410(10) |
| C(6)-C(11) | 1.452(9) |
| C(7)-C(8) | 1.389(12) |
| C(8)-C(9) | 1.420(14) |
| C(9)-C(10) | 1.381(11) |
| C(11)-C(12) | 1.267(9) |
| C(12)-C(13) | 1.488(10) |
| C(13)-C(17) | 1.403(11) |
| C(13)-C(14) | 1.432(10) |
| C(14)-C(15) | 1.406(13) |
| C(15)-C(16) | 1.393(15) |
| C(16)-C(17) | 1.388(10) |
| C(18)-C(22) | 1.427(12) |
| C(18)-C(19) | 1.456(12) |
| C(18)-C(23) | 1.494(10) |

| | |
|---|---|
| C(19)-C(20) | 1.490(15) |
| C(20)-C(21) | 1.339(17) |
| C(21)-C(22) | 1.388(13) |
| C(23)-C(24) | 1.294(9) |
| C(24)-C(25) | 1.466(9) |
| C(25)-C(27) | 1.363(9) |
| C(25)-C(26) | 1.382(9) |
| C(26)-C(28) | 1.375(9) |
| C(27)-C(29) | 1.361(9) |
| C(28)-N(30) | 1.329(8) |
| C(29)-N(30) | 1.344(8) |
| O(30)-C(30) | 1.113(7) |
| O(31)-C(31) | 1.133(7) |
| C(32)-O(32) | 1.146(9) |
| O(33)-C(33) | 1.153(10) |
| C(34)-O(34) | 1.160(10) |
| C(51)-C(52) | 1.388(10) |
| C(51)-C(55) | 1.399(9) |
| C(52)-C(53) | 1.395(9) |
| C(53)-C(54) | 1.411(9) |
| C(54)-C(55) | 1.388(9) |
| C(56)-C(57) | 1.421(9) |
| C(56)-C(60) | 1.420(8) |
| C(56)-C(61) | 1.447(8) |
| C(57)-C(58) | 1.386(9) |
| C(58)-C(59) | 1.384(10) |
| C(59)-C(60) | 1.419(9) |
| C(61)-C(62) | 1.295(8) |
| C(62)-C(63) | 1.459(8) |
| C(63)-C(64) | 1.414(8) |
| C(63)-C(67) | 1.439(9) |
| C(64)-C(65) | 1.436(9) |
| C(65)-C(66) | 1.409(10) |
| C(66)-C(67) | 1.422(9) |
| C(68)-C(72) | 1.411(9) |
| C(68)-C(69) | 1.425(9) |
| C(68)-C(73) | 1.454(8) |
| C(69)-C(70) | 1.424(9) |
| C(70)-C(71) | 1.398(11) |
| C(71)-C(72) | 1.399(10) |
| C(73)-C(74) | 1.313(8) |
| C(74)-C(75) | 1.441(8) |
| C(75)-C(77) | 1.375(8) |
| C(75)-C(76) | 1.400(8) |
| C(76)-C(78) | 1.373(8) |
| C(77)-C(79) | 1.376(8) |
| C(78)-N(79) | 1.347(7) |
| N(79)-C(79) | 1.333(7) |
| O(80)-C(80) | 1.167(8) |
| O(81)-C(81) | 1.136(9) |
| O(82)-C(82) | 1.133(8) |
| C(83)-O(83) | 1.143(8) |
| C(84)-O(84) | 1.134(9) |
| C(32)-W(1)-C(33) | 87.4(4) |
| C(32)-W(1)-C(34) | 87.0(4) |
| C(33)-W(1)-C(34) | 174.1(3) |
| C(32)-W(1)-C(31) | 90.2(3) |
| C(33)-W(1)-C(31) | 92.1(3) |
| C(34)-W(1)-C(31) | 89.5(3) |
| C(32)-W(1)-C(30) | 90.1(3) |
| C(33)-W(1)-C(30) | 91.6(3) |
| C(34)-W(1)-C(30) | 86.8(3) |
| C(31)-W(1)-C(30) | 176.3(3) |
| C(32)-W(1)-N(30) | 177.9(3) |
| C(33)-W(1)-N(30) | 90.8(3) |
| C(34)-W(1)-N(30) | 94.8(3) |
| C(31)-W(1)-N(30) | 90.9(2) |
| C(30)-W(1)-N(30) | 88.9(2) |
| C(5)-C(1)-C(2) | 108.4(8) |
| C(5)-C(1)-Fe(1) | 70.1(4) |
| C(2)-C(1)-Fe(1) | 69.5(5) |
| C(2)-Fe(1)-C(10) | 158.8(3) |
| C(2)-Fe(1)-C(8) | 124.7(5) |
| C(10)-Fe(1)-C(8) | 67.8(4) |
| C(2)-Fe(1)-C(4) | 66.6(4) |
| C(10)-Fe(1)-C(4) | 108.2(3) |

| | |
|---|---|
| C(8)-Fe(1)-C(4) | 158.8(4) |
| C(2)-Fe(1)-C(5) | 66.8(3) |
| C(10)-Fe(1)-C(5) | 123.8(4) |
| C(8)-Fe(1)-C(5) | 122.6(3) |
| C(4)-Fe(1)-C(5) | 41.0(3) |
| C(2)-Fe(1)-C(9) | 160.6(4) |
| C(10)-Fe(1)-C(9) | 39.8(3) |
| C(8)-Fe(1)-C(9) | 41.0(4) |
| C(4)-Fe(1)-C(9) | 122.6(4) |
| C(5)-Fe(1)-C(9) | 107.8(3) |
| C(2)-Fe(1)-C(7) | 110.5(4) |
| C(10)-Fe(1)-C(7) | 66.7(4) |
| C(8)-Fe(1)-C(7) | 40.0(3) |
| C(4)-Fe(1)-C(7) | 159.4(3) |
| C(5)-Fe(1)-C(7) | 158.6(3) |
| C(9)-Fe(1)-C(7) | 67.3(4) |
| C(2)-Fe(1)-C(1) | 39.9(3) |
| C(10)-Fe(1)-C(1) | 159.2(3) |
| C(8)-Fe(1)-C(1) | 109.0(4) |
| C(4)-Fe(1)-C(1) | 67.0(3) |
| C(5)-Fe(1)-C(1) | 39.2(3) |
| C(9)-Fe(1)-C(1) | 124.2(4) |
| C(7)-Fe(1)-C(1) | 124.9(4) |
| C(2)-Fe(1)-C(3) | 39.4(3) |
| C(10)-Fe(1)-C(3) | 123.3(3) |
| C(8)-Fe(1)-C(3) | 159.7(5) |
| C(4)-Fe(1)-C(3) | 40.0(3) |
| C(5)-Fe(1)-C(3) | 67.8(3) |
| C(9)-Fe(1)-C(3) | 158.1(4) |
| C(7)-Fe(1)-C(3) | 124.6(3) |
| C(1)-Fe(1)-C(3) | 67.0(3) |
| C(2)-Fe(1)-C(6) | 123.8(3) |
| C(10)-Fe(1)-C(6) | 40.4(3) |
| C(8)-Fe(1)-C(6) | 67.8(3) |
| C(4)-Fe(1)-C(6) | 123.5(3) |
| C(5)-Fe(1)-C(6) | 160.0(4) |
| C(9)-Fe(1)-C(6) | 67.8(3) |
| C(7)-Fe(1)-C(6) | 39.6(3) |
| C(1)-Fe(1)-C(6) | 159.3(3) |
| C(3)-Fe(1)-C(6) | 108.5(3) |
| C(80)-W(2)-C(81) | 89.5(3) |
| C(80)-W(2)-C(82) | 87.8(3) |
| C(81)-W(2)-C(82) | 177.3(3) |
| C(80)-W(2)-C(84) | 90.4(3) |
| C(81)-W(2)-C(84) | 89.3(3) |
| C(82)-W(2)-C(84) | 90.3(3) |
| C(80)-W(2)-C(83) | 87.4(3) |
| C(81)-W(2)-C(83) | 88.9(3) |
| C(82)-W(2)-C(83) | 91.3(3) |
| C(84)-W(2)-C(83) | 177.3(3) |
| C(80)-W(2)-N(79) | 177.9(2) |
| C(81)-W(2)-N(79) | 92.1(3) |
| C(82)-W(2)-N(79) | 90.6(2) |
| C(84)-W(2)-N(79) | 88.2(2) |
| C(83)-W(2)-N(79) | 94.0(2) |
| C(20)-Fe(2)-C(17) | 152.7(5) |
| C(20)-Fe(2)-C(14) | 126.4(5) |
| C(17)-Fe(2)-C(14) | 68.4(4) |
| C(20)-Fe(2)-C(15) | 107.7(4) |
| C(17)-Fe(2)-C(15) | 67.1(4) |
| C(14)-Fe(2)-C(15) | 40.7(4) |
| C(20)-Fe(2)-C(19) | 43.3(4) |
| C(17)-Fe(2)-C(19) | 162.7(3) |
| C(14)-Fe(2)-C(19) | 107.4(4) |
| C(15)-Fe(2)-C(19) | 121.4(5) |
| C(20)-Fe(2)-C(21) | 38.6(5) |
| C(17)-Fe(2)-C(21) | 119.5(5) |
| C(14)-Fe(2)-C(21) | 159.6(4) |
| C(15)-Fe(2)-C(21) | 122.0(4) |
| C(19)-Fe(2)-C(21) | 70.5(5) |
| C(20)-Fe(2)-C(16) | 118.5(4) |
| C(17)-Fe(2)-C(16) | 40.0(3) |
| C(14)-Fe(2)-C(16) | 68.7(4) |
| C(15)-Fe(2)-C(16) | 40.1(4) |
| C(19)-Fe(2)-C(16) | 155.8(4) |
| C(21)-Fe(2)-C(16) | 104.5(5) |

| | |
|---|---|
| C(20)-Fe(2)-C(18) | 68.3(4) |
| C(17)-Fe(2)-C(18) | 125.8(3) |
| C(14)-Fe(2)-C(18) | 124.5(4) |
| C(15)-Fe(2)-C(18) | 159.7(5) |
| C(19)-Fe(2)-C(18) | 41.8(3) |
| C(21)-Fe(2)-C(18) | 68.2(4) |
| C(16)-Fe(2)-C(18) | 159.7(5) |
| C(20)-Fe(2)-C(13) | 165.1(6) |
| C(17)-Fe(2)-C(13) | 40.4(3) |
| C(14)-Fe(2)-C(13) | 41.2(3) |
| C(15)-Fe(2)-C(13) | 68.1(3) |
| C(19)-Fe(2)-C(13) | 125.5(4) |
| C(21)-Fe(2)-C(13) | 155.9(5) |
| C(16)-Fe(2)-C(13) | 68.3(4) |
| C(18)-Fe(2)-C(13) | 110.3(3) |
| C(20)-Fe(2)-C(22) | 66.0(5) |
| C(17)-Fe(2)-C(22) | 108.0(4) |
| C(14)-Fe(2)-C(22) | 160.2(3) |
| C(15)-Fe(2)-C(22) | 157.5(5) |
| C(19)-Fe(2)-C(22) | 70.0(4) |
| C(21)-Fe(2)-C(22) | 39.6(4) |
| C(16)-Fe(2)-C(22) | 121.9(5) |
| C(18)-Fe(2)-C(22) | 40.7(3) |
| C(13)-Fe(2)-C(22) | 123.4(3) |
| C(3)-C(2)-C(1) | 109.5(8) |
| C(3)-C(2)-Fe(1) | 71.1(4) |
| C(1)-C(2)-Fe(1) | 70.6(4) |
| C(53)-Fe(3)-C(58) | 165.9(3) |
| C(53)-Fe(3)-C(59) | 127.9(3) |
| C(58)-Fe(3)-C(59) | 39.9(3) |
| C(53)-Fe(3)-C(60) | 107.5(3) |
| C(58)-Fe(3)-C(60) | 67.7(3) |
| C(59)-Fe(3)-C(60) | 40.9(3) |
| C(53)-Fe(3)-C(52) | 40.2(3) |
| C(58)-Fe(3)-C(52) | 128.6(3) |
| C(59)-Fe(3)-C(52) | 106.6(3) |
| C(60)-Fe(3)-C(52) | 115.8(3) |
| C(53)-Fe(3)-C(54) | 40.6(3) |
| C(58)-Fe(3)-C(54) | 152.3(3) |
| C(59)-Fe(3)-C(54) | 167.2(3) |
| C(60)-Fe(3)-C(54) | 129.8(3) |
| C(52)-Fe(3)-C(54) | 67.9(3) |
| C(53)-Fe(3)-C(57) | 152.1(3) |
| C(58)-Fe(3)-C(57) | 39.8(3) |
| C(59)-Fe(3)-C(57) | 67.1(3) |
| C(60)-Fe(3)-C(57) | 67.2(3) |
| C(52)-Fe(3)-C(57) | 167.5(3) |
| C(54)-Fe(3)-C(57) | 120.5(3) |
| C(53)-Fe(3)-C(55) | 66.9(3) |
| C(58)-Fe(3)-C(55) | 120.1(3) |
| C(59)-Fe(3)-C(55) | 150.3(3) |
| C(60)-Fe(3)-C(55) | 168.7(3) |
| C(52)-Fe(3)-C(55) | 66.9(3) |
| C(54)-Fe(3)-C(55) | 39.7(2) |
| C(57)-Fe(3)-C(55) | 112.8(3) |
| C(53)-Fe(3)-C(51) | 67.0(3) |
| C(58)-Fe(3)-C(51) | 109.7(3) |
| C(59)-Fe(3)-C(51) | 116.4(3) |
| C(60)-Fe(3)-C(51) | 148.6(3) |
| C(52)-Fe(3)-C(51) | 39.7(3) |
| C(54)-Fe(3)-C(51) | 67.4(3) |
| C(57)-Fe(3)-C(51) | 132.0(3) |
| C(55)-Fe(3)-C(51) | 39.9(3) |
| C(53)-Fe(3)-C(56) | 117.6(3) |
| C(58)-Fe(3)-C(56) | 68.0(3) |
| C(59)-Fe(3)-C(56) | 68.5(3) |
| C(60)-Fe(3)-C(56) | 40.4(2) |
| C(52)-Fe(3)-C(56) | 149.2(3) |
| C(54)-Fe(3)-C(56) | 109.9(2) |
| C(57)-Fe(3)-C(56) | 40.3(2) |
| C(55)-Fe(3)-C(56) | 132.1(3) |
| C(51)-Fe(3)-C(56) | 170.2(3) |
| C(2)-C(3)-C(4) | 107.2(7) |
| C(2)-C(3)-Fe(1) | 69.4(4) |
| C(4)-C(3)-Fe(1) | 69.5(4) |
| C(65)-Fe(4)-C(72) | 154.9(3) |

| | |
|---|---|
| C(65)-Fe(4)-C(66) | 40.6(3) |
| C(72)-Fe(4)-C(66) | 120.5(3) |
| C(65)-Fe(4)-C(69) | 124.6(3) |
| C(72)-Fe(4)-C(69) | 68.1(3) |
| C(66)-Fe(4)-C(69) | 160.7(3) |
| C(65)-Fe(4)-C(67) | 68.7(3) |
| C(72)-Fe(4)-C(67) | 107.9(3) |
| C(66)-Fe(4)-C(67) | 40.9(3) |
| C(69)-Fe(4)-C(67) | 157.5(3) |
| C(65)-Fe(4)-C(70) | 106.7(3) |
| C(72)-Fe(4)-C(70) | 67.5(3) |
| C(66)-Fe(4)-C(70) | 123.3(3) |
| C(69)-Fe(4)-C(70) | 40.8(3) |
| C(67)-Fe(4)-C(70) | 160.1(3) |
| C(65)-Fe(4)-C(64) | 41.3(3) |
| C(72)-Fe(4)-C(64) | 162.6(3) |
| C(66)-Fe(4)-C(64) | 68.6(3) |
| C(69)-Fe(4)-C(64) | 108.3(3) |
| C(67)-Fe(4)-C(64) | 68.5(3) |
| C(70)-Fe(4)-C(64) | 121.7(3) |
| C(65)-Fe(4)-C(68) | 162.4(3) |
| C(72)-Fe(4)-C(68) | 40.4(2) |
| C(66)-Fe(4)-C(68) | 156.3(3) |
| C(69)-Fe(4)-C(68) | 40.7(2) |
| C(67)-Fe(4)-C(68) | 121.8(3) |
| C(70)-Fe(4)-C(68) | 68.2(3) |
| C(64)-Fe(4)-C(68) | 125.9(3) |
| C(65)-Fe(4)-C(71) | 119.9(3) |
| C(72)-Fe(4)-C(71) | 40.0(3) |
| C(66)-Fe(4)-C(71) | 106.7(3) |
| C(69)-Fe(4)-C(71) | 67.9(3) |
| C(67)-Fe(4)-C(71) | 124.2(3) |
| C(70)-Fe(4)-C(71) | 39.9(3) |
| C(64)-Fe(4)-C(71) | 156.1(3) |
| C(68)-Fe(4)-C(71) | 67.7(3) |
| C(65)-Fe(4)-C(63) | 68.6(3) |
| C(72)-Fe(4)-C(63) | 126.1(3) |
| C(66)-Fe(4)-C(63) | 68.6(3) |
| C(69)-Fe(4)-C(63) | 122.2(2) |
| C(67)-Fe(4)-C(63) | 41.0(2) |
| C(70)-Fe(4)-C(63) | 157.2(3) |
| C(64)-Fe(4)-C(63) | 40.2(2) |
| C(68)-Fe(4)-C(63) | 109.1(2) |
| C(71)-Fe(4)-C(63) | 162.0(3) |
| C(3)-C(4)-C(5) | 107.7(7) |
| C(3)-C(4)-Fe(1) | 70.5(4) |
| C(5)-C(4)-Fe(1) | 69.5(4) |
| C(1)-C(5)-C(4) | 107.3(7) |
| C(1)-C(5)-Fe(1) | 70.7(5) |
| C(4)-C(5)-Fe(1) | 69.5(4) |
| C(7)-C(6)-C(10) | 106.0(7) |
| C(7)-C(6)-C(11) | 130.1(7) |
| C(10)-C(6)-C(11) | 123.8(7) |
| C(7)-C(6)-Fe(1) | 69.4(4) |
| C(10)-C(6)-Fe(1) | 68.7(4) |
| C(11)-C(6)-Fe(1) | 128.7(5) |
| C(6)-C(7)-C(8) | 110.5(9) |
| C(6)-C(7)-Fe(1) | 71.1(4) |
| C(8)-C(7)-Fe(1) | 69.8(5) |
| C(7)-C(8)-C(9) | 106.5(9) |
| C(7)-C(8)-Fe(1) | 70.2(5) |
| C(9)-C(8)-Fe(1) | 69.5(5) |
| C(10)-C(9)-C(8) | 107.6(9) |
| C(10)-C(9)-Fe(1) | 70.0(4) |
| C(8)-C(9)-Fe(1) | 69.5(6) |
| C(9)-C(10)-C(6) | 109.4(9) |
| C(9)-C(10)-Fe(1) | 70.2(5) |
| C(6)-C(10)-Fe(1) | 70.9(4) |
| C(12)-C(11)-C(6) | 126.7(8) |
| C(11)-C(12)-C(13) | 126.4(8) |
| C(17)-C(13)-C(14) | 106.1(7) |
| C(17)-C(13)-C(12) | 130.0(7) |
| C(14)-C(13)-C(12) | 123.8(9) |
| C(17)-C(13)-Fe(2) | 68.5(4) |
| C(14)-C(13)-Fe(2) | 68.3(4) |
| C(12)-C(13)-Fe(2) | 124.7(5) |

| | | | |
|---|---|---|---|
| C(15)-C(14)-C(13) | 106.8(10) | N(30)-C(29)-C(27) | 123.8(6) |
| C(15)-C(14)-Fe(2) | 69.6(5) | C(28)-N(30)-C(29) | 115.1(6) |
| C(13)-C(14)-Fe(2) | 70.5(4) | C(28)-N(30)-W(1) | 121.6(4) |
| C(16)-C(15)-C(14) | 110.0(9) | C(29)-N(30)-W(1) | 123.3(4) |
| C(16)-C(15)-Fe(2) | 70.9(6) | O(30)-C(30)-W(1) | 177.0(6) |
| C(14)-C(15)-Fe(2) | 69.7(5) | O(31)-C(31)-W(1) | 179.1(7) |
| C(17)-C(16)-C(15) | 106.4(10) | O(32)-C(32)-W(1) | 179.5(8) |
| C(17)-C(16)-Fe(2) | 68.8(5) | O(33)-C(33)-W(1) | 175.4(8) |
| C(15)-C(16)-Fe(2) | 69.0(6) | O(34)-C(34)-W(1) | 175.3(8) |
| C(16)-C(17)-C(13) | 110.7(9) | C(52)-C(51)-C(55) | 107.7(6) |
| C(16)-C(17)-Fe(2) | 71.2(5) | C(52)-C(51)-Fe(3) | 69.5(4) |
| C(13)-C(17)-Fe(2) | 71.1(5) | C(55)-C(51)-Fe(3) | 69.8(4) |
| C(22)-C(18)-C(19) | 109.1(8) | C(51)-C(52)-C(53) | 107.9(6) |
| C(22)-C(18)-C(23) | 129.5(8) | C(51)-C(52)-Fe(3) | 70.8(4) |
| C(19)-C(18)-C(23) | 121.2(9) | C(53)-C(52)-Fe(3) | 69.4(4) |
| C(22)-C(18)-Fe(2) | 70.1(4) | C(52)-C(53)-C(54) | 108.6(6) |
| C(19)-C(18)-Fe(2) | 68.7(4) | C(52)-C(53)-Fe(3) | 70.4(4) |
| C(23)-C(18)-Fe(2) | 124.3(5) | C(54)-C(53)-Fe(3) | 70.4(3) |
| C(18)-C(19)-C(20) | 101.0(10) | C(55)-C(54)-C(53) | 106.5(6) |
| C(18)-C(19)-Fe(2) | 69.4(5) | C(55)-C(54)-Fe(3) | 70.3(4) |
| C(20)-C(19)-Fe(2) | 67.3(6) | C(53)-C(54)-Fe(3) | 68.9(4) |
| C(21)-C(20)-C(19) | 112.5(11) | C(54)-C(55)-C(51) | 109.2(6) |
| C(21)-C(20)-Fe(2) | 72.2(7) | C(54)-C(55)-Fe(3) | 70.0(4) |
| C(19)-C(20)-Fe(2) | 69.5(5) | C(51)-C(55)-Fe(3) | 70.3(4) |
| C(20)-C(21)-C(22) | 108.4(13) | C(57)-C(56)-C(60) | 105.0(6) |
| C(20)-C(21)-Fe(2) | 69.2(7) | C(57)-C(56)-C(61) | 126.5(6) |
| C(22)-C(21)-Fe(2) | 70.8(6) | C(60)-C(56)-C(61) | 128.5(6) |
| C(21)-C(22)-C(18) | 108.9(10) | C(57)-C(56)-Fe(3) | 68.5(3) |
| C(21)-C(22)-Fe(2) | 69.6(6) | C(60)-C(56)-Fe(3) | 68.0(3) |
| C(18)-C(22)-Fe(2) | 69.2(4) | C(61)-C(56)-Fe(3) | 127.0(4) |
| C(24)-C(23)-C(18) | 126.4(8) | C(58)-C(57)-C(56) | 109.8(6) |
| C(23)-C(24)-C(25) | 125.5(7) | C(58)-C(57)-Fe(3) | 69.4(4) |
| C(27)-C(25)-C(26) | 114.6(6) | C(56)-C(57)-Fe(3) | 71.2(3) |
| C(27)-C(25)-C(24) | 120.9(6) | C(57)-C(58)-C(59) | 108.8(6) |
| C(26)-C(25)-C(24) | 124.5(6) | C(57)-C(58)-Fe(3) | 70.8(4) |
| C(28)-C(26)-C(25) | 121.3(6) | C(59)-C(58)-Fe(3) | 70.3(4) |
| C(29)-C(27)-C(25) | 121.7(7) | C(58)-C(59)-C(60) | 107.4(6) |
| N(30)-C(28)-C(26) | 123.3(6) | C(58)-C(59)-Fe(3) | 69.8(4) |

| | |
|---|---|
| C(60)-C(59)-Fe(3) | 69.6(4) |
| C(59)-C(60)-C(56) | 109.0(6) |
| C(59)-C(60)-Fe(3) | 69.5(4) |
| C(56)-C(60)-Fe(3) | 71.6(4) |
| C(62)-C(61)-C(56) | 125.8(6) |
| C(61)-C(62)-C(63) | 127.4(7) |
| C(64)-C(63)-C(67) | 107.6(6) |
| C(64)-C(63)-C(62) | 129.2(6) |
| C(67)-C(63)-C(62) | 123.2(6) |
| C(64)-C(63)-Fe(4) | 69.1(3) |
| C(67)-C(63)-Fe(4) | 68.5(3) |
| C(62)-C(63)-Fe(4) | 127.4(4) |
| C(63)-C(64)-C(65) | 108.3(6) |
| C(63)-C(64)-Fe(4) | 70.7(4) |
| C(65)-C(64)-Fe(4) | 68.7(4) |
| C(66)-C(65)-C(64) | 107.9(6) |
| C(66)-C(65)-Fe(4) | 69.8(4) |
| C(64)-C(65)-Fe(4) | 70.0(4) |
| C(65)-C(66)-C(67) | 108.5(6) |
| C(65)-C(66)-Fe(4) | 69.6(4) |
| C(67)-C(66)-Fe(4) | 69.9(4) |
| C(66)-C(67)-C(63) | 107.8(6) |
| C(66)-C(67)-Fe(4) | 69.2(4) |
| C(63)-C(67)-Fe(4) | 70.5(3) |
| C(72)-C(68)-C(69) | 106.9(6) |
| C(72)-C(68)-C(73) | 126.6(6) |
| C(69)-C(68)-C(73) | 126.3(6) |
| C(72)-C(68)-Fe(4) | 68.9(4) |
| C(69)-C(68)-Fe(4) | 69.0(4) |
| C(73)-C(68)-Fe(4) | 123.4(4) |
| C(70)-C(69)-C(68) | 107.5(7) |
| C(70)-C(69)-Fe(4) | 69.7(4) |
| C(68)-C(69)-Fe(4) | 70.2(3) |
| C(71)-C(70)-C(69) | 108.3(7) |
| C(71)-C(70)-Fe(4) | 70.6(4) |
| C(69)-C(70)-Fe(4) | 69.5(3) |
| C(70)-C(71)-C(72) | 108.1(6) |
| C(70)-C(71)-Fe(4) | 69.5(4) |
| C(72)-C(71)-Fe(4) | 69.0(4) |
| C(71)-C(72)-C(68) | 109.2(7) |
| C(71)-C(72)-Fe(4) | 71.0(5) |
| C(68)-C(72)-Fe(4) | 70.7(4) |
| C(74)-C(73)-C(68) | 127.1(6) |
| C(73)-C(74)-C(75) | 128.0(6) |
| C(77)-C(75)-C(76) | 114.7(5) |
| C(77)-C(75)-C(74) | 122.3(6) |
| C(76)-C(75)-C(74) | 123.0(6) |
| C(78)-C(76)-C(75) | 120.8(6) |
| C(75)-C(77)-C(79) | 121.7(6) |
| N(79)-C(78)-C(76) | 123.4(6) |
| C(79)-N(79)-C(78) | 115.9(5) |
| C(79)-N(79)-W(2) | 123.4(4) |
| C(78)-N(79)-W(2) | 120.7(4) |
| N(79)-C(79)-C(77) | 123.4(6) |
| O(80)-C(80)-W(2) | 177.8(7) |
| O(81)-C(81)-W(2) | 178.8(8) |
| O(82)-C(82)-W(2) | 177.1(6) |
| O(83)-C(83)-W(2) | 174.9(7) |
| O(84)-C(84)-W(2) | 178.0(7) |

---

Symmetry transformations used to generate equivalent atoms:

**Table 4**. Anisotropic displacement parameters (Å$^2$x 10$^3$) for str75m. The anisotropic displacement factor exponent takes the form: $-2\pi^2[ h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12} ]$

| | U$^{11}$ | U$^{22}$ | U$^{33}$ | U$^{23}$ | U$^{13}$ | U$^{12}$ |
|---|---|---|---|---|---|---|
| W(1) | 79(1) | 55(1) | 46(1) | -5(1) | -16(1) | 16(1) |
| C(1) | 89(6) | 86(6) | 68(5) | -19(4) | 1(4) | 23(5) |
| Fe(1) | 42(1) | 47(1) | 68(1) | 0(1) | -1(1) | 7(1) |
| W(2) | 62(1) | 53(1) | 66(1) | -18(1) | -29(1) | 8(1) |
| Fe(2) | 47(1) | 87(1) | 62(1) | 29(1) | 13(1) | 25(1) |
| C(2) | 97(7) | 116(8) | 67(5) | -17(5) | -26(5) | 22(6) |
| Fe(3) | 38(1) | 44(1) | 48(1) | -4(1) | -13(1) | -4(1) |
| C(3) | 65(5) | 55(5) | 77(5) | 8(4) | 2(4) | 17(4) |
| Fe(4) | 59(1) | 39(1) | 55(1) | -5(1) | -23(1) | -6(1) |
| C(4) | 56(5) | 64(5) | 81(5) | 15(4) | -8(4) | -7(4) |
| C(5) | 47(4) | 84(6) | 82(6) | 20(4) | 8(4) | 19(4) |
| C(6) | 53(4) | 59(5) | 64(4) | 5(3) | 5(3) | 3(4) |
| C(7) | 49(5) | 75(6) | 129(7) | -5(5) | 7(4) | -17(4) |
| C(8) | 90(8) | 59(6) | 168(11) | 21(6) | 33(7) | 4(6) |
| C(9) | 66(6) | 118(8) | 95(7) | 54(6) | 20(5) | 26(6) |
| C(10) | 71(5) | 103(6) | 58(5) | 8(4) | -7(4) | 16(5) |
| C(11) | 49(4) | 77(5) | 66(4) | -2(4) | -4(3) | 2(4) |
| C(12) | 55(5) | 97(6) | 47(4) | 0(4) | 4(3) | 4(4) |
| C(13) | 45(4) | 106(7) | 57(5) | 26(4) | 11(3) | 10(4) |
| C(14) | 56(5) | 165(9) | 57(5) | 27(5) | 6(4) | 11(6) |
| C(15) | 64(6) | 163(11) | 100(8) | 88(7) | 22(5) | 42(7) |
| C(16) | 68(7) | 97(7) | 126(9) | 48(6) | 22(5) | 36(6) |
| C(17) | 66(5) | 89(6) | 72(5) | 15(5) | 1(4) | 5(5) |
| C(18) | 67(5) | 91(6) | 66(5) | 36(4) | 15(4) | 25(5) |
| C(19) | 59(6) | 117(8) | 123(8) | 48(6) | 17(5) | -2(5) |
| C(20) | 53(7) | 131(11) | 160(12) | 80(9) | 57(6) | 47(6) |
| C(21) | 109(10) | 133(10) | 99(9) | 32(7) | 45(6) | 51(9) |
| C(22) | 113(8) | 80(6) | 67(5) | 9(5) | 19(5) | 33(5) |
| C(23) | 76(5) | 85(5) | 49(4) | 17(4) | -2(4) | 5(4) |
| C(24) | 74(5) | 61(4) | 52(4) | 5(3) | 2(4) | 5(4) |
| C(25) | 64(4) | 47(4) | 44(4) | 6(3) | 0(3) | -2(3) |
| C(26) | 78(5) | 81(5) | 67(5) | -13(4) | -36(4) | 27(4) |
| C(27) | 78(5) | 55(4) | 59(4) | -9(3) | -11(4) | 1(4) |

|  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|
| C(28) | 105(6) | 60(4) | 79(5) | -19(4) | -50(5) | 19(4) |
| C(29) | 68(5) | 63(4) | 57(4) | -5(3) | -18(3) | 2(4) |
| N(30) | 70(4) | 48(3) | 42(3) | 0(2) | -15(3) | 6(3) |
| O(30) | 148(6) | 86(4) | 55(3) | -8(3) | -34(3) | -15(4) |
| C(30) | 74(5) | 45(4) | 56(4) | -7(3) | -16(4) | 1(3) |
| O(31) | 145(6) | 126(5) | 51(3) | -3(3) | -21(3) | 21(4) |
| C(31) | 100(6) | 75(5) | 50(4) | -13(4) | -10(4) | 32(4) |
| C(32) | 122(8) | 91(6) | 70(5) | -22(4) | -47(5) | 43(6) |
| O(32) | 178(7) | 137(6) | 119(5) | -54(4) | -64(5) | 103(6) |
| O(33) | 101(5) | 131(6) | 109(5) | -22(4) | -37(4) | -10(5) |
| C(33) | 86(6) | 93(6) | 61(5) | -15(4) | -30(4) | 23(5) |
| C(34) | 114(8) | 48(5) | 82(6) | -13(4) | -10(5) | 20(5) |
| O(34) | 167(8) | 84(5) | 153(7) | -17(5) | -3(5) | -31(5) |
| C(51) | 55(4) | 63(4) | 86(5) | -22(4) | -30(4) | -1(4) |
| C(52) | 67(5) | 102(6) | 49(4) | -4(4) | -25(4) | 9(5) |
| C(53) | 70(5) | 55(4) | 61(4) | 16(4) | -17(4) | -7(4) |
| C(54) | 64(4) | 50(4) | 59(4) | -4(3) | -26(3) | 11(3) |
| C(55) | 43(4) | 62(4) | 69(4) | 10(4) | -20(3) | 0(3) |
| C(56) | 36(3) | 60(4) | 57(4) | -7(3) | -16(3) | -4(3) |
| C(57) | 58(4) | 60(4) | 65(4) | 1(4) | -32(3) | 1(4) |
| C(58) | 56(5) | 46(4) | 106(6) | -10(4) | -39(4) | 4(3) |
| C(59) | 47(4) | 74(5) | 87(5) | -33(4) | -15(4) | 10(4) |
| C(60) | 45(4) | 64(5) | 75(5) | -4(4) | -9(3) | -11(3) |
| C(61) | 45(4) | 65(4) | 59(4) | -5(3) | -20(3) | -2(3) |
| C(62) | 52(4) | 62(4) | 64(4) | -3(3) | -26(3) | -5(4) |
| C(63) | 48(4) | 47(4) | 63(4) | -5(3) | -24(3) | 0(3) |
| C(64) | 51(4) | 57(4) | 65(4) | -3(3) | -8(3) | 4(3) |
| C(65) | 73(5) | 65(5) | 77(5) | -26(4) | -19(4) | 12(4) |
| C(66) | 75(5) | 41(4) | 98(6) | -5(4) | -38(5) | 8(4) |
| C(67) | 67(5) | 65(5) | 66(4) | 11(4) | -31(4) | -4(4) |
| C(68) | 51(4) | 41(4) | 58(4) | 2(3) | -20(3) | 0(3) |
| C(69) | 81(5) | 47(4) | 60(4) | 0(3) | -32(4) | -5(4) |
| C(70) | 114(7) | 56(5) | 79(5) | -16(4) | -60(5) | 3(5) |
| C(71) | 109(7) | 47(4) | 116(7) | 0(5) | -71(6) | -24(5) |
| C(72) | 56(5) | 62(5) | 95(6) | 10(4) | -28(4) | -17(4) |
| C(73) | 35(3) | 46(4) | 55(4) | -2(3) | -6(3) | -4(3) |
| C(74) | 49(4) | 55(4) | 43(3) | -8(3) | -11(3) | 2(3) |
| C(75) | 41(3) | 46(4) | 54(4) | -4(3) | -16(3) | 3(3) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(76) | 57(4) | 51(4) | 51(4) | 0(3) | -6(3) | -9(3) |
| C(77) | 68(5) | 49(4) | 45(4) | -5(3) | 0(3) | -7(3) |
| C(78) | 59(4) | 58(4) | 47(4) | -10(3) | -8(3) | -5(3) |
| N(79) | 53(3) | 43(3) | 50(3) | -10(2) | -16(2) | 3(2) |
| C(79) | 67(5) | 46(4) | 55(4) | 2(3) | -7(3) | -12(3) |
| O(80) | 184(7) | 98(5) | 135(5) | -63(4) | -99(5) | 43(5) |
| C(80) | 99(7) | 85(6) | 89(6) | -34(5) | -50(5) | 14(5) |
| O(81) | 184(8) | 124(5) | 101(5) | 2(4) | -78(5) | -3(5) |
| C(81) | 104(7) | 91(6) | 86(6) | -17(5) | -56(5) | 17(5) |
| O(82) | 130(5) | 63(3) | 108(4) | 16(3) | -58(4) | -25(3) |
| C(82) | 80(6) | 49(4) | 114(7) | -11(4) | -55(5) | -5(4) |
| C(83) | 76(6) | 55(4) | 88(5) | -14(4) | -36(4) | 6(4) |
| O(83) | 74(4) | 128(5) | 119(5) | -5(4) | -32(4) | -19(4) |
| C(84) | 69(5) | 70(5) | 71(5) | -25(4) | -22(4) | 24(4) |
| O(84) | 68(4) | 164(6) | 95(4) | -18(4) | 1(3) | 11(4) |

**Table 5**. Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters ($Å^2$x $10^{3}$) for str75m.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1) | -7856 | 15219 | 3672 | 102 |
| H(2) | -6026 | 14154 | 3893 | 112 |
| H(3) | -6157 | 12761 | 3411 | 86 |
| H(4) | -8065 | 12974 | 2846 | 84 |
| H(5) | -9109 | 14525 | 3006 | 95 |
| H(7) | -4089 | 14959 | 2442 | 105 |
| H(8) | -5950 | 16011 | 2231 | 142 |
| H(9) | -7223 | 15245 | 1573 | 128 |
| H(10) | -6154 | 13737 | 1429 | 98 |
| H(11) | -4151 | 12760 | 1785 | 79 |
| H(12) | -2485 | 13666 | 2229 | 84 |
| H(14) | -493 | 12614 | 2635 | 120 |
| H(15) | 642 | 11138 | 2363 | 152 |
| H(16) | -501 | 10474 | 1616 | 134 |
| H(17) | -2359 | 11538 | 1421 | 97 |
| H(19) | 1509 | 13530 | 1338 | 133 |
| H(20) | 2527 | 11984 | 977 | 167 |
| H(21) | 1277 | 11421 | 283 | 158 |
| H(22) | -487 | 12558 | 76 | 116 |
| H(23) | -585 | 14568 | 1062 | 90 |
| H(24) | -1786 | 14054 | 139 | 80 |
| H(26) | -1647 | 15868 | 1103 | 88 |
| H(27) | -3599 | 15040 | -130 | 78 |
| H(28) | -3025 | 17122 | 1172 | 93 |
| H(29) | -4938 | 16294 | -34 | 75 |
| H(51) | 2485 | 9202 | 2693 | 78 |
| H(52) | 3866 | 10262 | 1869 | 86 |
| H(53) | 3802 | 11657 | 2406 | 76 |
| H(54) | 2380 | 11460 | 3578 | 68 |
| H(55) | 1573 | 9943 | 3740 | 70 |
| H(57) | 4391 | 9464 | 4415 | 71 |
| H(58) | 4863 | 8433 | 3531 | 79 |

| | | | | |
|---|---|---|---|---|
| H(59) | 6228 | 9170 | 2491 | 82 |
| H(60) | 6558 | 10711 | 2725 | 74 |
| H(61) | 4791 | 11193 | 4484 | 66 |
| H(62) | 6723 | 11832 | 3466 | 69 |
| H(64) | 4911 | 12417 | 5203 | 71 |
| H(65) | 5369 | 13966 | 5390 | 85 |
| H(66) | 6816 | 14625 | 4328 | 83 |
| H(67) | 7307 | 13491 | 3486 | 78 |
| H(69) | 7580 | 11571 | 5742 | 73 |
| H(70) | 7874 | 13114 | 6000 | 92 |
| H(71) | 9345 | 13864 | 4993 | 99 |
| H(72) | 9908 | 12829 | 4098 | 83 |
| H(73) | 9260 | 11188 | 3957 | 55 |
| H(74) | 8095 | 10261 | 5127 | 59 |
| H(76) | 9117 | 10117 | 3344 | 65 |
| H(77) | 7849 | 8688 | 5105 | 67 |
| H(78) | 9141 | 8878 | 2814 | 66 |
| H(79) | 7890 | 7485 | 4534 | 69 |

**Table 6**. Torsion angles [°] for str75m.

| | |
|---|---|
| C(5)-C(1)-Fe(1)-C(2) | -119.6(8) |
| C(5)-C(1)-Fe(1)-C(10) | 41.5(12) |
| C(2)-C(1)-Fe(1)-C(10) | 161.1(9) |
| C(5)-C(1)-Fe(1)-C(8) | 118.6(6) |
| C(2)-C(1)-Fe(1)-C(8) | -121.8(7) |
| C(5)-C(1)-Fe(1)-C(4) | -39.1(5) |
| C(2)-C(1)-Fe(1)-C(4) | 80.5(6) |
| C(2)-C(1)-Fe(1)-C(5) | 119.6(8) |
| C(5)-C(1)-Fe(1)-C(9) | 75.7(7) |
| C(2)-C(1)-Fe(1)-C(9) | -164.7(6) |
| C(5)-C(1)-Fe(1)-C(7) | 160.2(5) |
| C(2)-C(1)-Fe(1)-C(7) | -80.2(7) |
| C(5)-C(1)-Fe(1)-C(3) | -82.7(5) |
| C(2)-C(1)-Fe(1)-C(3) | 36.9(5) |
| C(5)-C(1)-Fe(1)-C(6) | -164.1(7) |
| C(2)-C(1)-Fe(1)-C(6) | -44.6(11) |
| C(5)-C(1)-C(2)-C(3) | -1.3(10) |
| Fe(1)-C(1)-C(2)-C(3) | -60.8(6) |
| C(5)-C(1)-C(2)-Fe(1) | 59.5(6) |
| C(10)-Fe(1)-C(2)-C(3) | -41.9(12) |
| C(8)-Fe(1)-C(2)-C(3) | -162.6(5) |
| C(4)-Fe(1)-C(2)-C(3) | 38.0(5) |
| C(5)-Fe(1)-C(2)-C(3) | 82.8(5) |
| C(9)-Fe(1)-C(2)-C(3) | 160.4(11) |
| C(7)-Fe(1)-C(2)-C(3) | -120.0(5) |
| C(1)-Fe(1)-C(2)-C(3) | 119.6(8) |
| C(6)-Fe(1)-C(2)-C(3) | -77.8(6) |
| C(10)-Fe(1)-C(2)-C(1) | -161.5(9) |
| C(8)-Fe(1)-C(2)-C(1) | 77.8(7) |
| C(4)-Fe(1)-C(2)-C(1) | -81.6(6) |
| C(5)-Fe(1)-C(2)-C(1) | -36.7(5) |
| C(9)-Fe(1)-C(2)-C(1) | 40.9(14) |
| C(7)-Fe(1)-C(2)-C(1) | 120.4(6) |
| C(3)-Fe(1)-C(2)-C(1) | -119.6(8) |
| C(6)-Fe(1)-C(2)-C(1) | 162.6(5) |
| C(1)-C(2)-C(3)-C(4) | 1.0(10) |
| Fe(1)-C(2)-C(3)-C(4) | -59.5(5) |
| C(1)-C(2)-C(3)-Fe(1) | 60.5(6) |
| C(10)-Fe(1)-C(3)-C(2) | 163.2(5) |
| C(8)-Fe(1)-C(3)-C(2) | 45.1(12) |
| C(4)-Fe(1)-C(3)-C(2) | -118.5(7) |
| C(5)-Fe(1)-C(3)-C(2) | -80.0(5) |
| C(9)-Fe(1)-C(3)-C(2) | -162.7(8) |
| C(7)-Fe(1)-C(3)-C(2) | 80.2(6) |
| C(1)-Fe(1)-C(3)-C(2) | -37.3(5) |
| C(6)-Fe(1)-C(3)-C(2) | 121.0(5) |
| C(2)-Fe(1)-C(3)-C(4) | 118.5(7) |
| C(10)-Fe(1)-C(3)-C(4) | -78.3(5) |
| C(8)-Fe(1)-C(3)-C(4) | 163.6(9) |
| C(5)-Fe(1)-C(3)-C(4) | 38.5(5) |
| C(9)-Fe(1)-C(3)-C(4) | -44.2(10) |
| C(7)-Fe(1)-C(3)-C(4) | -161.3(5) |
| C(1)-Fe(1)-C(3)-C(4) | 81.2(5) |
| C(6)-Fe(1)-C(3)-C(4) | -120.5(5) |
| C(2)-C(3)-C(4)-C(5) | -0.3(9) |
| Fe(1)-C(3)-C(4)-C(5) | -59.8(5) |
| C(2)-C(3)-C(4)-Fe(1) | 59.5(6) |
| C(2)-Fe(1)-C(4)-C(3) | -37.4(4) |
| C(10)-Fe(1)-C(4)-C(3) | 120.6(5) |
| C(8)-Fe(1)-C(4)-C(3) | -164.2(11) |
| C(5)-Fe(1)-C(4)-C(3) | -118.5(7) |
| C(9)-Fe(1)-C(4)-C(3) | 162.0(5) |
| C(7)-Fe(1)-C(4)-C(3) | 48.6(11) |
| C(1)-Fe(1)-C(4)-C(3) | -81.1(5) |
| C(6)-Fe(1)-C(4)-C(3) | 78.6(5) |
| C(2)-Fe(1)-C(4)-C(5) | 81.0(5) |
| C(10)-Fe(1)-C(4)-C(5) | -121.0(5) |
| C(8)-Fe(1)-C(4)-C(5) | -45.8(13) |
| C(9)-Fe(1)-C(4)-C(5) | -79.5(6) |
| C(7)-Fe(1)-C(4)-C(5) | 167.1(9) |
| C(1)-Fe(1)-C(4)-C(5) | 37.4(5) |
| C(3)-Fe(1)-C(4)-C(5) | 118.5(7) |
| C(6)-Fe(1)-C(4)-C(5) | -162.9(5) |
| C(2)-C(1)-C(5)-C(4) | 1.1(9) |

| | |
|---|---|
| Fe(1)-C(1)-C(5)-C(4) | 60.2(5) |
| C(2)-C(1)-C(5)-Fe(1) | -59.1(6) |
| C(3)-C(4)-C(5)-C(1) | -0.5(9) |
| Fe(1)-C(4)-C(5)-C(1) | -60.9(6) |
| C(3)-C(4)-C(5)-Fe(1) | 60.5(5) |
| C(2)-Fe(1)-C(5)-C(1) | 37.4(5) |
| C(10)-Fe(1)-C(5)-C(1) | -163.6(5) |
| C(8)-Fe(1)-C(5)-C(1) | -80.0(7) |
| C(4)-Fe(1)-C(5)-C(1) | 117.8(7) |
| C(9)-Fe(1)-C(5)-C(1) | -122.7(6) |
| C(7)-Fe(1)-C(5)-C(1) | -49.7(11) |
| C(3)-Fe(1)-C(5)-C(1) | 80.2(5) |
| C(6)-Fe(1)-C(5)-C(1) | 163.6(7) |
| C(2)-Fe(1)-C(5)-C(4) | -80.4(5) |
| C(10)-Fe(1)-C(5)-C(4) | 78.6(5) |
| C(8)-Fe(1)-C(5)-C(4) | 162.1(6) |
| C(9)-Fe(1)-C(5)-C(4) | 119.5(6) |
| C(7)-Fe(1)-C(5)-C(4) | -167.5(8) |
| C(1)-Fe(1)-C(5)-C(4) | -117.8(7) |
| C(3)-Fe(1)-C(5)-C(4) | -37.6(4) |
| C(6)-Fe(1)-C(5)-C(4) | 45.8(10) |
| C(2)-Fe(1)-C(6)-C(7) | -81.5(6) |
| C(10)-Fe(1)-C(6)-C(7) | 117.6(7) |
| C(8)-Fe(1)-C(6)-C(7) | 36.3(6) |
| C(4)-Fe(1)-C(6)-C(7) | -164.0(5) |
| C(5)-Fe(1)-C(6)-C(7) | 161.7(8) |
| C(9)-Fe(1)-C(6)-C(7) | 80.8(6) |
| C(1)-Fe(1)-C(6)-C(7) | -48.7(10) |
| C(3)-Fe(1)-C(6)-C(7) | -122.3(5) |
| C(2)-Fe(1)-C(6)-C(10) | 160.9(5) |
| C(8)-Fe(1)-C(6)-C(10) | -81.3(6) |
| C(4)-Fe(1)-C(6)-C(10) | 78.4(5) |
| C(5)-Fe(1)-C(6)-C(10) | 44.1(10) |
| C(9)-Fe(1)-C(6)-C(10) | -36.9(6) |
| C(7)-Fe(1)-C(6)-C(10) | -117.6(7) |
| C(1)-Fe(1)-C(6)-C(10) | -166.3(8) |
| C(3)-Fe(1)-C(6)-C(10) | 120.0(5) |
| C(2)-Fe(1)-C(6)-C(11) | 44.0(9) |
| C(10)-Fe(1)-C(6)-C(11) | -116.9(9) |
| C(8)-Fe(1)-C(6)-C(11) | 161.8(9) |
| C(4)-Fe(1)-C(6)-C(11) | -38.5(8) |
| C(5)-Fe(1)-C(6)-C(11) | -72.9(11) |
| C(9)-Fe(1)-C(6)-C(11) | -153.8(9) |
| C(7)-Fe(1)-C(6)-C(11) | 125.4(9) |
| C(1)-Fe(1)-C(6)-C(11) | 76.8(12) |
| C(3)-Fe(1)-C(6)-C(11) | 3.1(8) |
| C(10)-C(6)-C(7)-C(8) | 0.4(9) |
| C(11)-C(6)-C(7)-C(8) | 177.4(7) |
| Fe(1)-C(6)-C(7)-C(8) | -58.8(6) |
| C(10)-C(6)-C(7)-Fe(1) | 59.2(5) |
| C(11)-C(6)-C(7)-Fe(1) | -123.7(7) |
| C(2)-Fe(1)-C(7)-C(6) | 118.7(5) |
| C(10)-Fe(1)-C(7)-C(6) | -38.7(4) |
| C(8)-Fe(1)-C(7)-C(6) | -121.4(9) |
| C(4)-Fe(1)-C(7)-C(6) | 40.9(12) |
| C(5)-Fe(1)-C(7)-C(6) | -162.9(8) |
| C(9)-Fe(1)-C(7)-C(6) | -82.1(6) |
| C(1)-Fe(1)-C(7)-C(6) | 161.1(4) |
| C(3)-Fe(1)-C(7)-C(6) | 76.8(6) |
| C(2)-Fe(1)-C(7)-C(8) | -120.0(7) |
| C(10)-Fe(1)-C(7)-C(8) | 82.7(7) |
| C(4)-Fe(1)-C(7)-C(8) | 162.3(9) |
| C(5)-Fe(1)-C(7)-C(8) | -41.5(13) |
| C(9)-Fe(1)-C(7)-C(8) | 39.2(6) |
| C(1)-Fe(1)-C(7)-C(8) | -77.5(8) |
| C(3)-Fe(1)-C(7)-C(8) | -161.9(7) |
| C(6)-Fe(1)-C(7)-C(8) | 121.4(9) |
| C(6)-C(7)-C(8)-C(9) | -0.8(10) |
| Fe(1)-C(7)-C(8)-C(9) | -60.4(6) |
| C(6)-C(7)-C(8)-Fe(1) | 59.6(6) |
| C(2)-Fe(1)-C(8)-C(7) | 80.6(7) |
| C(10)-Fe(1)-C(8)-C(7) | -79.8(6) |
| C(4)-Fe(1)-C(8)-C(7) | -162.7(9) |
| C(5)-Fe(1)-C(8)-C(7) | 163.4(6) |
| C(9)-Fe(1)-C(8)-C(7) | -117.1(9) |
| C(1)-Fe(1)-C(8)-C(7) | 122.2(6) |

| | |
|---|---|
| C(3)-Fe(1)-C(8)-C(7) | 47.5(13) |
| C(6)-Fe(1)-C(8)-C(7) | -36.0(6) |
| C(2)-Fe(1)-C(8)-C(9) | -162.3(5) |
| C(10)-Fe(1)-C(8)-C(9) | 37.4(5) |
| C(4)-Fe(1)-C(8)-C(9) | -45.6(14) |
| C(5)-Fe(1)-C(8)-C(9) | -79.5(7) |
| C(7)-Fe(1)-C(8)-C(9) | 117.1(9) |
| C(1)-Fe(1)-C(8)-C(9) | -120.7(6) |
| C(3)-Fe(1)-C(8)-C(9) | 164.6(8) |
| C(6)-Fe(1)-C(8)-C(9) | 81.1(6) |
| C(7)-C(8)-C(9)-C(10) | 1.0(11) |
| Fe(1)-C(8)-C(9)-C(10) | -59.9(6) |
| C(7)-C(8)-C(9)-Fe(1) | 60.8(6) |
| C(2)-Fe(1)-C(9)-C(10) | 167.6(10) |
| C(8)-Fe(1)-C(9)-C(10) | 118.7(8) |
| C(4)-Fe(1)-C(9)-C(10) | -79.2(6) |
| C(5)-Fe(1)-C(9)-C(10) | -121.8(6) |
| C(7)-Fe(1)-C(9)-C(10) | 80.4(6) |
| C(1)-Fe(1)-C(9)-C(10) | -161.9(5) |
| C(3)-Fe(1)-C(9)-C(10) | -47.0(11) |
| C(6)-Fe(1)-C(9)-C(10) | 37.4(5) |
| C(2)-Fe(1)-C(9)-C(8) | 48.9(14) |
| C(10)-Fe(1)-C(9)-C(8) | -118.7(8) |
| C(4)-Fe(1)-C(9)-C(8) | 162.2(5) |
| C(5)-Fe(1)-C(9)-C(8) | 119.5(6) |
| C(7)-Fe(1)-C(9)-C(8) | -38.3(6) |
| C(1)-Fe(1)-C(9)-C(8) | 79.4(7) |
| C(3)-Fe(1)-C(9)-C(8) | -165.7(7) |
| C(6)-Fe(1)-C(9)-C(8) | -81.3(6) |
| C(8)-C(9)-C(10)-C(6) | -0.8(10) |
| Fe(1)-C(9)-C(10)-C(6) | -60.3(5) |
| C(8)-C(9)-C(10)-Fe(1) | 59.6(7) |
| C(7)-C(6)-C(10)-C(9) | 0.3(9) |
| C(11)-C(6)-C(10)-C(9) | -177.1(6) |
| Fe(1)-C(6)-C(10)-C(9) | 59.9(5) |
| C(7)-C(6)-C(10)-Fe(1) | -59.6(5) |
| C(11)-C(6)-C(10)-Fe(1) | 123.1(7) |
| C(2)-Fe(1)-C(10)-C(9) | -168.6(10) |
| C(8)-Fe(1)-C(10)-C(9) | -38.4(6) |
| C(4)-Fe(1)-C(10)-C(9) | 119.4(6) |
| C(5)-Fe(1)-C(10)-C(9) | 76.8(7) |
| C(7)-Fe(1)-C(10)-C(9) | -81.9(6) |
| C(1)-Fe(1)-C(10)-C(9) | 46.5(13) |
| C(3)-Fe(1)-C(10)-C(9) | 160.9(6) |
| C(6)-Fe(1)-C(10)-C(9) | -119.9(8) |
| C(2)-Fe(1)-C(10)-C(6) | -48.7(12) |
| C(8)-Fe(1)-C(10)-C(6) | 81.4(5) |
| C(4)-Fe(1)-C(10)-C(6) | -120.7(5) |
| C(5)-Fe(1)-C(10)-C(6) | -163.4(4) |
| C(9)-Fe(1)-C(10)-C(6) | 119.9(8) |
| C(7)-Fe(1)-C(10)-C(6) | 37.9(4) |
| C(1)-Fe(1)-C(10)-C(6) | 166.3(9) |
| C(3)-Fe(1)-C(10)-C(6) | -79.3(6) |
| C(7)-C(6)-C(11)-C(12) | -9.5(13) |
| C(10)-C(6)-C(11)-C(12) | 167.1(7) |
| Fe(1)-C(6)-C(11)-C(12) | -104.3(9) |
| C(6)-C(11)-C(12)-C(13) | -179.1(6) |
| C(11)-C(12)-C(13)-C(17) | 19.4(12) |
| C(11)-C(12)-C(13)-C(14) | -165.1(7) |
| C(11)-C(12)-C(13)-Fe(2) | 109.3(9) |
| C(20)-Fe(2)-C(13)-C(17) | -156.5(13) |
| C(14)-Fe(2)-C(13)-C(17) | -118.5(7) |
| C(15)-Fe(2)-C(13)-C(17) | -79.8(6) |
| C(19)-Fe(2)-C(13)-C(17) | 166.4(5) |
| C(21)-Fe(2)-C(13)-C(17) | 40.2(12) |
| C(16)-Fe(2)-C(13)-C(17) | -36.5(5) |
| C(18)-Fe(2)-C(13)-C(17) | 121.8(5) |
| C(22)-Fe(2)-C(13)-C(17) | 78.3(6) |
| C(20)-Fe(2)-C(13)-C(14) | -38.0(16) |
| C(17)-Fe(2)-C(13)-C(14) | 118.5(7) |
| C(15)-Fe(2)-C(13)-C(14) | 38.7(6) |
| C(19)-Fe(2)-C(13)-C(14) | -75.1(7) |
| C(21)-Fe(2)-C(13)-C(14) | 158.7(10) |
| C(16)-Fe(2)-C(13)-C(14) | 82.0(6) |
| C(18)-Fe(2)-C(13)-C(14) | -119.7(6) |
| C(22)-Fe(2)-C(13)-C(14) | -163.2(6) |

| | | | |
|---|---|---|---|
| C(20)-Fe(2)-C(13)-C(12) | 79.0(15) | C(18)-Fe(2)-C(15)-C(16) | 171.3(8) |
| C(17)-Fe(2)-C(13)-C(12) | -124.5(9) | C(13)-Fe(2)-C(15)-C(16) | 81.8(6) |
| C(14)-Fe(2)-C(13)-C(12) | 117.0(10) | C(22)-Fe(2)-C(15)-C(16) | -43.6(13) |
| C(15)-Fe(2)-C(13)-C(12) | 155.6(10) | C(20)-Fe(2)-C(15)-C(14) | 125.6(7) |
| C(19)-Fe(2)-C(13)-C(12) | 41.9(9) | C(17)-Fe(2)-C(15)-C(14) | -83.0(6) |
| C(21)-Fe(2)-C(13)-C(12) | -84.4(13) | C(19)-Fe(2)-C(15)-C(14) | 80.1(7) |
| C(16)-Fe(2)-C(13)-C(12) | -161.0(9) | C(21)-Fe(2)-C(15)-C(14) | 165.5(7) |
| C(18)-Fe(2)-C(13)-C(12) | -2.7(9) | C(16)-Fe(2)-C(15)-C(14) | -120.9(9) |
| C(22)-Fe(2)-C(13)-C(12) | -46.3(9) | C(18)-Fe(2)-C(15)-C(14) | 50.3(12) |
| C(17)-C(13)-C(14)-C(15) | -2.1(8) | C(13)-Fe(2)-C(15)-C(14) | -39.1(6) |
| C(12)-C(13)-C(14)-C(15) | -178.6(6) | C(22)-Fe(2)-C(15)-C(14) | -164.6(9) |
| Fe(2)-C(13)-C(14)-C(15) | -60.4(5) | C(14)-C(15)-C(16)-C(17) | -0.1(11) |
| C(17)-C(13)-C(14)-Fe(2) | 58.3(5) | Fe(2)-C(15)-C(16)-C(17) | -58.9(6) |
| C(12)-C(13)-C(14)-Fe(2) | -118.2(6) | C(14)-C(15)-C(16)-Fe(2) | 58.8(6) |
| C(20)-Fe(2)-C(14)-C(15) | -74.0(9) | C(20)-Fe(2)-C(16)-C(17) | -157.9(7) |
| C(17)-Fe(2)-C(14)-C(15) | 79.5(7) | C(14)-Fe(2)-C(16)-C(17) | 81.3(6) |
| C(19)-Fe(2)-C(14)-C(15) | -118.2(7) | C(15)-Fe(2)-C(16)-C(17) | 118.2(9) |
| C(21)-Fe(2)-C(14)-C(15) | -37.5(18) | C(19)-Fe(2)-C(16)-C(17) | 166.4(9) |
| C(16)-Fe(2)-C(14)-C(15) | 36.4(6) | C(21)-Fe(2)-C(16)-C(17) | -118.9(7) |
| C(18)-Fe(2)-C(14)-C(15) | -161.1(7) | C(18)-Fe(2)-C(16)-C(17) | -53.0(13) |
| C(13)-Fe(2)-C(14)-C(15) | 117.3(9) | C(13)-Fe(2)-C(16)-C(17) | 36.8(5) |
| C(22)-Fe(2)-C(14)-C(15) | 162.5(12) | C(22)-Fe(2)-C(16)-C(17) | -79.9(7) |
| C(20)-Fe(2)-C(14)-C(13) | 168.6(6) | C(20)-Fe(2)-C(16)-C(15) | 83.9(8) |
| C(17)-Fe(2)-C(14)-C(13) | -37.8(5) | C(17)-Fe(2)-C(16)-C(15) | -118.2(9) |
| C(15)-Fe(2)-C(14)-C(13) | -117.3(9) | C(14)-Fe(2)-C(16)-C(15) | -36.9(6) |
| C(19)-Fe(2)-C(14)-C(13) | 124.5(6) | C(19)-Fe(2)-C(16)-C(15) | 48.2(13) |
| C(21)-Fe(2)-C(14)-C(13) | -154.8(14) | C(21)-Fe(2)-C(16)-C(15) | 122.8(7) |
| C(16)-Fe(2)-C(14)-C(13) | -80.9(6) | C(18)-Fe(2)-C(16)-C(15) | -171.3(8) |
| C(18)-Fe(2)-C(14)-C(13) | 81.6(6) | C(13)-Fe(2)-C(16)-C(15) | -81.4(6) |
| C(22)-Fe(2)-C(14)-C(13) | 45.2(15) | C(22)-Fe(2)-C(16)-C(15) | 161.9(6) |
| C(13)-C(14)-C(15)-C(16) | 1.4(10) | C(15)-C(16)-C(17)-C(13) | -1.4(10) |
| Fe(2)-C(14)-C(15)-C(16) | -59.6(7) | Fe(2)-C(16)-C(17)-C(13) | -60.3(6) |
| C(13)-C(14)-C(15)-Fe(2) | 61.0(5) | C(15)-C(16)-C(17)-Fe(2) | 59.0(7) |
| C(20)-Fe(2)-C(15)-C(16) | -113.4(7) | C(14)-C(13)-C(17)-C(16) | 2.2(9) |
| C(17)-Fe(2)-C(15)-C(16) | 38.0(6) | C(12)-C(13)-C(17)-C(16) | 178.4(7) |
| C(14)-Fe(2)-C(15)-C(16) | 120.9(9) | Fe(2)-C(13)-C(17)-C(16) | 60.4(6) |
| C(19)-Fe(2)-C(15)-C(16) | -159.0(6) | C(14)-C(13)-C(17)-Fe(2) | -58.2(5) |
| C(21)-Fe(2)-C(15)-C(16) | -73.6(8) | C(12)-C(13)-C(17)-Fe(2) | 118.0(7) |

| | |
|---|---|
| C(20)-Fe(2)-C(17)-C(16) | 46.2(12) |
| C(14)-Fe(2)-C(17)-C(16) | -82.2(7) |
| C(15)-Fe(2)-C(17)-C(16) | -38.1(7) |
| C(19)-Fe(2)-C(17)-C(16) | -161.0(12) |
| C(21)-Fe(2)-C(17)-C(16) | 76.8(8) |
| C(18)-Fe(2)-C(17)-C(16) | 160.0(7) |
| C(13)-Fe(2)-C(17)-C(16) | -120.8(8) |
| C(22)-Fe(2)-C(17)-C(16) | 118.5(7) |
| C(20)-Fe(2)-C(17)-C(13) | 167.0(9) |
| C(14)-Fe(2)-C(17)-C(13) | 38.5(5) |
| C(15)-Fe(2)-C(17)-C(13) | 82.7(6) |
| C(19)-Fe(2)-C(17)-C(13) | -40.2(14) |
| C(21)-Fe(2)-C(17)-C(13) | -162.4(5) |
| C(16)-Fe(2)-C(17)-C(13) | 120.8(8) |
| C(18)-Fe(2)-C(17)-C(13) | -79.2(6) |
| C(22)-Fe(2)-C(17)-C(13) | -120.7(5) |
| C(20)-Fe(2)-C(18)-C(22) | 77.9(7) |
| C(17)-Fe(2)-C(18)-C(22) | -75.3(6) |
| C(14)-Fe(2)-C(18)-C(22) | -162.0(5) |
| C(15)-Fe(2)-C(18)-C(22) | 160.4(9) |
| C(19)-Fe(2)-C(18)-C(22) | 121.0(7) |
| C(21)-Fe(2)-C(18)-C(22) | 36.2(6) |
| C(16)-Fe(2)-C(18)-C(22) | -36.0(12) |
| C(13)-Fe(2)-C(18)-C(22) | -118.0(5) |
| C(20)-Fe(2)-C(18)-C(19) | -43.1(7) |
| C(17)-Fe(2)-C(18)-C(19) | 163.8(6) |
| C(14)-Fe(2)-C(18)-C(19) | 77.0(6) |
| C(15)-Fe(2)-C(18)-C(19) | 39.4(12) |
| C(21)-Fe(2)-C(18)-C(19) | -84.8(7) |
| C(16)-Fe(2)-C(18)-C(19) | -157.0(9) |
| C(13)-Fe(2)-C(18)-C(19) | 121.0(6) |
| C(22)-Fe(2)-C(18)-C(19) | -121.0(7) |
| C(20)-Fe(2)-C(18)-C(23) | -157.2(10) |
| C(17)-Fe(2)-C(18)-C(23) | 49.7(10) |
| C(14)-Fe(2)-C(18)-C(23) | -37.1(10) |
| C(15)-Fe(2)-C(18)-C(23) | -74.7(13) |
| C(19)-Fe(2)-C(18)-C(23) | -114.1(11) |
| C(21)-Fe(2)-C(18)-C(23) | 161.1(10) |
| C(16)-Fe(2)-C(18)-C(23) | 88.9(13) |
| C(13)-Fe(2)-C(18)-C(23) | 6.9(9) |
| C(22)-Fe(2)-C(18)-C(23) | 124.9(10) |
| C(22)-C(18)-C(19)-C(20) | 1.9(8) |
| C(23)-C(18)-C(19)-C(20) | 178.5(7) |
| Fe(2)-C(18)-C(19)-C(20) | 60.4(5) |
| C(22)-C(18)-C(19)-Fe(2) | -58.6(5) |
| C(23)-C(18)-C(19)-Fe(2) | 118.1(6) |
| C(20)-Fe(2)-C(19)-C(18) | 112.2(9) |
| C(17)-Fe(2)-C(19)-C(18) | -49.9(15) |
| C(14)-Fe(2)-C(19)-C(18) | -122.7(6) |
| C(15)-Fe(2)-C(19)-C(18) | -165.1(6) |
| C(21)-Fe(2)-C(19)-C(18) | 78.7(6) |
| C(16)-Fe(2)-C(19)-C(18) | 160.7(10) |
| C(13)-Fe(2)-C(19)-C(18) | -80.9(6) |
| C(22)-Fe(2)-C(19)-C(18) | 36.5(5) |
| C(17)-Fe(2)-C(19)-C(20) | -162.2(12) |
| C(14)-Fe(2)-C(19)-C(20) | 125.0(7) |
| C(15)-Fe(2)-C(19)-C(20) | 82.7(8) |
| C(21)-Fe(2)-C(19)-C(20) | -33.6(6) |
| C(16)-Fe(2)-C(19)-C(20) | 48.5(14) |
| C(18)-Fe(2)-C(19)-C(20) | -112.2(9) |
| C(13)-Fe(2)-C(19)-C(20) | 166.9(7) |
| C(22)-Fe(2)-C(19)-C(20) | -75.7(7) |
| C(18)-C(19)-C(20)-C(21) | -2.6(12) |
| Fe(2)-C(19)-C(20)-C(21) | 59.4(9) |
| C(18)-C(19)-C(20)-Fe(2) | -62.0(5) |
| C(17)-Fe(2)-C(20)-C(21) | 45.2(13) |
| C(14)-Fe(2)-C(20)-C(21) | 160.6(7) |
| C(15)-Fe(2)-C(20)-C(21) | 119.4(9) |
| C(19)-Fe(2)-C(20)-C(21) | -123.4(11) |
| C(16)-Fe(2)-C(20)-C(21) | 77.1(9) |
| C(18)-Fe(2)-C(20)-C(21) | -81.8(8) |
| C(13)-Fe(2)-C(20)-C(21) | -169.2(11) |
| C(22)-Fe(2)-C(20)-C(21) | -37.5(8) |
| C(17)-Fe(2)-C(20)-C(19) | 168.6(7) |
| C(14)-Fe(2)-C(20)-C(19) | -76.0(7) |
| C(15)-Fe(2)-C(20)-C(19) | -117.3(7) |

| | |
|---|---|
| C(21)-Fe(2)-C(20)-C(19) | 123.4(11) |
| C(16)-Fe(2)-C(20)-C(19) | -159.5(6) |
| C(18)-Fe(2)-C(20)-C(19) | 41.6(6) |
| C(13)-Fe(2)-C(20)-C(19) | -45.8(17) |
| C(22)-Fe(2)-C(20)-C(19) | 85.9(6) |
| C(19)-C(20)-C(21)-C(22) | 2.3(14) |
| Fe(2)-C(20)-C(21)-C(22) | 60.2(8) |
| C(19)-C(20)-C(21)-Fe(2) | -57.8(8) |
| C(17)-Fe(2)-C(21)-C(20) | -158.1(7) |
| C(14)-Fe(2)-C(21)-C(20) | -50(2) |
| C(15)-Fe(2)-C(21)-C(20) | -78.1(10) |
| C(19)-Fe(2)-C(21)-C(20) | 37.4(8) |
| C(16)-Fe(2)-C(21)-C(20) | -117.8(8) |
| C(18)-Fe(2)-C(21)-C(20) | 82.1(9) |
| C(13)-Fe(2)-C(21)-C(20) | 173.2(7) |
| C(22)-Fe(2)-C(21)-C(20) | 119.3(13) |
| C(20)-Fe(2)-C(21)-C(22) | -119.3(13) |
| C(17)-Fe(2)-C(21)-C(22) | 82.6(8) |
| C(14)-Fe(2)-C(21)-C(22) | -169.5(12) |
| C(15)-Fe(2)-C(21)-C(22) | 162.6(7) |
| C(19)-Fe(2)-C(21)-C(22) | -81.9(7) |
| C(16)-Fe(2)-C(21)-C(22) | 122.9(8) |
| C(18)-Fe(2)-C(21)-C(22) | -37.2(7) |
| C(13)-Fe(2)-C(21)-C(22) | 53.9(15) |
| C(20)-C(21)-C(22)-C(18) | -1.0(13) |
| Fe(2)-C(21)-C(22)-C(18) | 58.2(6) |
| C(20)-C(21)-C(22)-Fe(2) | -59.2(9) |
| C(19)-C(18)-C(22)-C(21) | -0.7(10) |
| C(23)-C(18)-C(22)-C(21) | -176.9(8) |
| Fe(2)-C(18)-C(22)-C(21) | -58.4(7) |
| C(19)-C(18)-C(22)-Fe(2) | 57.7(5) |
| C(23)-C(18)-C(22)-Fe(2) | -118.5(8) |
| C(20)-Fe(2)-C(22)-C(21) | 36.6(9) |
| C(17)-Fe(2)-C(22)-C(21) | -114.9(8) |
| C(14)-Fe(2)-C(22)-C(21) | 169.2(12) |
| C(15)-Fe(2)-C(22)-C(21) | -41.6(15) |
| C(19)-Fe(2)-C(22)-C(21) | 83.3(8) |
| C(16)-Fe(2)-C(22)-C(21) | -73.2(9) |
| C(18)-Fe(2)-C(22)-C(21) | 120.7(10) |
| C(13)-Fe(2)-C(22)-C(21) | -156.7(8) |
| C(20)-Fe(2)-C(22)-C(18) | -84.1(7) |
| C(17)-Fe(2)-C(22)-C(18) | 124.4(5) |
| C(14)-Fe(2)-C(22)-C(18) | 48.5(14) |
| C(15)-Fe(2)-C(22)-C(18) | -162.3(10) |
| C(19)-Fe(2)-C(22)-C(18) | -37.4(5) |
| C(21)-Fe(2)-C(22)-C(18) | -120.7(10) |
| C(16)-Fe(2)-C(22)-C(18) | 166.1(5) |
| C(13)-Fe(2)-C(22)-C(18) | 82.6(6) |
| C(22)-C(18)-C(23)-C(24) | -8.2(12) |
| C(19)-C(18)-C(23)-C(24) | 176.0(7) |
| Fe(2)-C(18)-C(23)-C(24) | -99.8(9) |
| C(18)-C(23)-C(24)-C(25) | -178.8(6) |
| C(23)-C(24)-C(25)-C(27) | -177.5(7) |
| C(23)-C(24)-C(25)-C(26) | 5.5(11) |
| C(27)-C(25)-C(26)-C(28) | 3.3(11) |
| C(24)-C(25)-C(26)-C(28) | -179.6(7) |
| C(26)-C(25)-C(27)-C(29) | -3.5(10) |
| C(24)-C(25)-C(27)-C(29) | 179.2(6) |
| C(25)-C(26)-C(28)-N(30) | -0.4(13) |
| C(25)-C(27)-C(29)-N(30) | 0.8(11) |
| C(26)-C(28)-N(30)-C(29) | -2.4(11) |
| C(26)-C(28)-N(30)-W(1) | 175.8(6) |
| C(27)-C(29)-N(30)-C(28) | 2.2(10) |
| C(27)-C(29)-N(30)-W(1) | -176.0(5) |
| C(32)-W(1)-N(30)-C(28) | -103(7) |
| C(33)-W(1)-N(30)-C(28) | -133.6(6) |
| C(34)-W(1)-N(30)-C(28) | 44.7(6) |
| C(31)-W(1)-N(30)-C(28) | 134.3(6) |
| C(30)-W(1)-N(30)-C(28) | -42.0(6) |
| C(32)-W(1)-N(30)-C(29) | 75(7) |
| C(33)-W(1)-N(30)-C(29) | 44.4(5) |
| C(34)-W(1)-N(30)-C(29) | -137.3(5) |
| C(31)-W(1)-N(30)-C(29) | -47.7(6) |
| C(30)-W(1)-N(30)-C(29) | 136.0(5) |
| C(32)-W(1)-C(30)-O(30) | -94(12) |
| C(33)-W(1)-C(30)-O(30) | 179(100) |

| | |
|---|---|
| C(34)-W(1)-C(30)-O(30) | -7(12) |
| C(31)-W(1)-C(30)-O(30) | 1(15) |
| N(30)-W(1)-C(30)-O(30) | 88(12) |
| C(32)-W(1)-C(31)-O(31) | -35(52) |
| C(33)-W(1)-C(31)-O(31) | 53(52) |
| C(34)-W(1)-C(31)-O(31) | -122(52) |
| C(30)-W(1)-C(31)-O(31) | -130(51) |
| N(30)-W(1)-C(31)-O(31) | 143(52) |
| C(33)-W(1)-C(32)-O(32) | -47(100) |
| C(34)-W(1)-C(32)-O(32) | 135(100) |
| C(31)-W(1)-C(32)-O(32) | 45(100) |
| C(30)-W(1)-C(32)-O(32) | -138(100) |
| N(30)-W(1)-C(32)-O(32) | -77(100) |
| C(32)-W(1)-C(33)-O(33) | -9(9) |
| C(34)-W(1)-C(33)-O(33) | 7(11) |
| C(31)-W(1)-C(33)-O(33) | -99(9) |
| C(30)-W(1)-C(33)-O(33) | 81(9) |
| N(30)-W(1)-C(33)-O(33) | 170(9) |
| C(32)-W(1)-C(34)-O(34) | 24(10) |
| C(33)-W(1)-C(34)-O(34) | 9(12) |
| C(31)-W(1)-C(34)-O(34) | 115(10) |
| C(30)-W(1)-C(34)-O(34) | -66(10) |
| N(30)-W(1)-C(34)-O(34) | -155(10) |
| C(53)-Fe(3)-C(51)-C(52) | 38.0(4) |
| C(58)-Fe(3)-C(51)-C(52) | -127.3(5) |
| C(59)-Fe(3)-C(51)-C(52) | -84.4(5) |
| C(60)-Fe(3)-C(51)-C(52) | -48.2(7) |
| C(54)-Fe(3)-C(51)-C(52) | 82.2(5) |
| C(57)-Fe(3)-C(51)-C(52) | -166.5(4) |
| C(55)-Fe(3)-C(51)-C(52) | 118.9(6) |
| C(56)-Fe(3)-C(51)-C(52) | 158.0(14) |
| C(53)-Fe(3)-C(51)-C(55) | -80.9(4) |
| C(58)-Fe(3)-C(51)-C(55) | 113.8(4) |
| C(59)-Fe(3)-C(51)-C(55) | 156.7(4) |
| C(60)-Fe(3)-C(51)-C(55) | -167.1(5) |
| C(52)-Fe(3)-C(51)-C(55) | -118.9(6) |
| C(54)-Fe(3)-C(51)-C(55) | -36.7(4) |
| C(57)-Fe(3)-C(51)-C(55) | 74.6(5) |
| C(56)-Fe(3)-C(51)-C(55) | 39.1(17) |
| C(55)-C(51)-C(52)-C(53) | -0.1(7) |
| Fe(3)-C(51)-C(52)-C(53) | -59.7(5) |
| C(55)-C(51)-C(52)-Fe(3) | 59.6(4) |
| C(53)-Fe(3)-C(52)-C(51) | -118.6(6) |
| C(58)-Fe(3)-C(52)-C(51) | 73.3(5) |
| C(59)-Fe(3)-C(52)-C(51) | 111.5(5) |
| C(60)-Fe(3)-C(52)-C(51) | 154.5(4) |
| C(54)-Fe(3)-C(52)-C(51) | -80.7(4) |
| C(57)-Fe(3)-C(52)-C(51) | 53.5(15) |
| C(55)-Fe(3)-C(52)-C(51) | -37.6(4) |
| C(56)-Fe(3)-C(52)-C(51) | -172.8(5) |
| C(58)-Fe(3)-C(52)-C(53) | -168.0(4) |
| C(59)-Fe(3)-C(52)-C(53) | -129.9(5) |
| C(60)-Fe(3)-C(52)-C(53) | -86.9(5) |
| C(54)-Fe(3)-C(52)-C(53) | 37.9(4) |
| C(57)-Fe(3)-C(52)-C(53) | 172.2(12) |
| C(55)-Fe(3)-C(52)-C(53) | 81.0(5) |
| C(51)-Fe(3)-C(52)-C(53) | 118.6(6) |
| C(56)-Fe(3)-C(52)-C(53) | -54.2(7) |
| C(51)-C(52)-C(53)-C(54) | 0.2(8) |
| Fe(3)-C(52)-C(53)-C(54) | -60.4(5) |
| C(51)-C(52)-C(53)-Fe(3) | 60.6(5) |
| C(58)-Fe(3)-C(53)-C(52) | 41.7(13) |
| C(59)-Fe(3)-C(53)-C(52) | 68.9(5) |
| C(60)-Fe(3)-C(53)-C(52) | 109.5(5) |
| C(54)-Fe(3)-C(53)-C(52) | -119.0(6) |
| C(57)-Fe(3)-C(53)-C(52) | -176.4(6) |
| C(55)-Fe(3)-C(53)-C(52) | -81.0(5) |
| C(51)-Fe(3)-C(53)-C(52) | -37.5(4) |
| C(56)-Fe(3)-C(53)-C(52) | 152.1(4) |
| C(58)-Fe(3)-C(53)-C(54) | 160.7(10) |
| C(59)-Fe(3)-C(53)-C(54) | -172.1(4) |
| C(60)-Fe(3)-C(53)-C(54) | -131.5(4) |
| C(52)-Fe(3)-C(53)-C(54) | 119.0(6) |
| C(57)-Fe(3)-C(53)-C(54) | -57.4(8) |
| C(55)-Fe(3)-C(53)-C(54) | 38.0(4) |
| C(51)-Fe(3)-C(53)-C(54) | 81.5(4) |

| | |
|---|---|
| C(56)-Fe(3)-C(53)-C(54) | -88.9(4) |
| C(52)-C(53)-C(54)-C(55) | -0.3(7) |
| Fe(3)-C(53)-C(54)-C(55) | -60.6(4) |
| C(52)-C(53)-C(54)-Fe(3) | 60.4(5) |
| C(53)-Fe(3)-C(54)-C(55) | 117.5(6) |
| C(58)-Fe(3)-C(54)-C(55) | -52.6(7) |
| C(59)-Fe(3)-C(54)-C(55) | 146.9(11) |
| C(60)-Fe(3)-C(54)-C(55) | -174.2(4) |
| C(52)-Fe(3)-C(54)-C(55) | 80.0(4) |
| C(57)-Fe(3)-C(54)-C(55) | -89.7(4) |
| C(51)-Fe(3)-C(54)-C(55) | 36.9(4) |
| C(56)-Fe(3)-C(54)-C(55) | -133.0(4) |
| C(58)-Fe(3)-C(54)-C(53) | -170.0(5) |
| C(59)-Fe(3)-C(54)-C(53) | 29.4(14) |
| C(60)-Fe(3)-C(54)-C(53) | 68.4(5) |
| C(52)-Fe(3)-C(54)-C(53) | -37.5(4) |
| C(57)-Fe(3)-C(54)-C(53) | 152.8(4) |
| C(55)-Fe(3)-C(54)-C(53) | -117.5(6) |
| C(51)-Fe(3)-C(54)-C(53) | -80.6(4) |
| C(56)-Fe(3)-C(54)-C(53) | 109.5(4) |
| C(53)-C(54)-C(55)-C(51) | 0.2(7) |
| Fe(3)-C(54)-C(55)-C(51) | -59.5(4) |
| C(53)-C(54)-C(55)-Fe(3) | 59.7(4) |
| C(52)-C(51)-C(55)-C(54) | -0.1(7) |
| Fe(3)-C(51)-C(55)-C(54) | 59.3(4) |
| C(52)-C(51)-C(55)-Fe(3) | -59.4(5) |
| C(53)-Fe(3)-C(55)-C(54) | -38.9(4) |
| C(58)-Fe(3)-C(55)-C(54) | 154.8(4) |
| C(59)-Fe(3)-C(55)-C(54) | -165.9(5) |
| C(60)-Fe(3)-C(55)-C(54) | 23.5(15) |
| C(52)-Fe(3)-C(55)-C(54) | -82.8(4) |
| C(57)-Fe(3)-C(55)-C(54) | 110.8(4) |
| C(51)-Fe(3)-C(55)-C(54) | -120.2(6) |
| C(56)-Fe(3)-C(55)-C(54) | 68.1(5) |
| C(53)-Fe(3)-C(55)-C(51) | 81.3(4) |
| C(58)-Fe(3)-C(55)-C(51) | -85.0(5) |
| C(59)-Fe(3)-C(55)-C(51) | -45.7(7) |
| C(60)-Fe(3)-C(55)-C(51) | 143.7(13) |
| C(52)-Fe(3)-C(55)-C(51) | 37.4(4) |
| C(54)-Fe(3)-C(55)-C(51) | 120.2(6) |
| C(57)-Fe(3)-C(55)-C(51) | -129.0(4) |
| C(56)-Fe(3)-C(55)-C(51) | -171.7(4) |
| C(53)-Fe(3)-C(56)-C(57) | 157.8(4) |
| C(58)-Fe(3)-C(56)-C(57) | -36.4(4) |
| C(59)-Fe(3)-C(56)-C(57) | -79.5(4) |
| C(60)-Fe(3)-C(56)-C(57) | -117.3(6) |
| C(52)-Fe(3)-C(56)-C(57) | -166.0(5) |
| C(54)-Fe(3)-C(56)-C(57) | 114.0(4) |
| C(55)-Fe(3)-C(56)-C(57) | 75.0(5) |
| C(51)-Fe(3)-C(56)-C(57) | 41.9(16) |
| C(53)-Fe(3)-C(56)-C(60) | -84.8(5) |
| C(58)-Fe(3)-C(56)-C(60) | 80.9(4) |
| C(59)-Fe(3)-C(56)-C(60) | 37.8(4) |
| C(52)-Fe(3)-C(56)-C(60) | -48.7(7) |
| C(54)-Fe(3)-C(56)-C(60) | -128.7(4) |
| C(57)-Fe(3)-C(56)-C(60) | 117.3(6) |
| C(55)-Fe(3)-C(56)-C(60) | -167.7(4) |
| C(51)-Fe(3)-C(56)-C(60) | 159.3(14) |
| C(53)-Fe(3)-C(56)-C(61) | 37.6(7) |
| C(58)-Fe(3)-C(56)-C(61) | -156.6(7) |
| C(59)-Fe(3)-C(56)-C(61) | 160.3(7) |
| C(60)-Fe(3)-C(56)-C(61) | 122.5(8) |
| C(52)-Fe(3)-C(56)-C(61) | 73.8(8) |
| C(54)-Fe(3)-C(56)-C(61) | -6.2(6) |
| C(57)-Fe(3)-C(56)-C(61) | -120.2(7) |
| C(55)-Fe(3)-C(56)-C(61) | -45.2(7) |
| C(51)-Fe(3)-C(56)-C(61) | -78.3(17) |
| C(60)-C(56)-C(57)-C(58) | 0.3(7) |
| C(61)-C(56)-C(57)-C(58) | 179.6(5) |
| Fe(3)-C(56)-C(57)-C(58) | 58.8(4) |
| C(60)-C(56)-C(57)-Fe(3) | -58.5(4) |
| C(61)-C(56)-C(57)-Fe(3) | 120.8(6) |
| C(53)-Fe(3)-C(57)-C(58) | -166.4(6) |
| C(59)-Fe(3)-C(57)-C(58) | -37.5(4) |
| C(60)-Fe(3)-C(57)-C(58) | -82.0(5) |
| C(52)-Fe(3)-C(57)-C(58) | 24.4(16) |

| | | | |
|---|---|---|---|
| C(54)-Fe(3)-C(57)-C(58) | 154.1(4) | C(57)-Fe(3)-C(59)-C(58) | 37.4(4) |
| C(55)-Fe(3)-C(57)-C(58) | 110.2(5) | C(55)-Fe(3)-C(59)-C(58) | -58.7(7) |
| C(51)-Fe(3)-C(57)-C(58) | 68.1(6) | C(51)-Fe(3)-C(59)-C(58) | -89.5(5) |
| C(56)-Fe(3)-C(57)-C(58) | -120.7(6) | C(56)-Fe(3)-C(59)-C(58) | 81.1(4) |
| C(53)-Fe(3)-C(57)-C(56) | -45.7(8) | C(53)-Fe(3)-C(59)-C(60) | 71.5(5) |
| C(58)-Fe(3)-C(57)-C(56) | 120.7(6) | C(58)-Fe(3)-C(59)-C(60) | -118.5(6) |
| C(59)-Fe(3)-C(57)-C(56) | 83.2(4) | C(52)-Fe(3)-C(59)-C(60) | 110.4(5) |
| C(60)-Fe(3)-C(57)-C(56) | 38.7(4) | C(54)-Fe(3)-C(59)-C(60) | 47.6(14) |
| C(52)-Fe(3)-C(57)-C(56) | 145.1(13) | C(57)-Fe(3)-C(59)-C(60) | -81.1(4) |
| C(54)-Fe(3)-C(57)-C(56) | -85.2(4) | C(55)-Fe(3)-C(59)-C(60) | -177.2(5) |
| C(55)-Fe(3)-C(57)-C(56) | -129.0(4) | C(51)-Fe(3)-C(59)-C(60) | 152.0(4) |
| C(51)-Fe(3)-C(57)-C(56) | -171.2(4) | C(56)-Fe(3)-C(59)-C(60) | -37.4(4) |
| C(56)-C(57)-C(58)-C(59) | 0.4(7) | C(58)-C(59)-C(60)-C(56) | 1.1(7) |
| Fe(3)-C(57)-C(58)-C(59) | 60.3(5) | Fe(3)-C(59)-C(60)-C(56) | 60.9(4) |
| C(56)-C(57)-C(58)-Fe(3) | -59.9(4) | C(58)-C(59)-C(60)-Fe(3) | -59.8(5) |
| C(53)-Fe(3)-C(58)-C(57) | 153.2(11) | C(57)-C(56)-C(60)-C(59) | -0.8(7) |
| C(59)-Fe(3)-C(58)-C(57) | 119.1(6) | C(61)-C(56)-C(60)-C(59) | 179.9(6) |
| C(60)-Fe(3)-C(58)-C(57) | 80.6(4) | Fe(3)-C(56)-C(60)-C(59) | -59.7(4) |
| C(52)-Fe(3)-C(58)-C(57) | -173.4(4) | C(57)-C(56)-C(60)-Fe(3) | 58.8(4) |
| C(54)-Fe(3)-C(58)-C(57) | -54.3(7) | C(61)-C(56)-C(60)-Fe(3) | -120.5(6) |
| C(55)-Fe(3)-C(58)-C(57) | -90.2(5) | C(53)-Fe(3)-C(60)-C(59) | -128.3(5) |
| C(51)-Fe(3)-C(58)-C(57) | -132.9(4) | C(58)-Fe(3)-C(60)-C(59) | 37.6(4) |
| C(56)-Fe(3)-C(58)-C(57) | 36.9(4) | C(52)-Fe(3)-C(60)-C(59) | -85.8(5) |
| C(53)-Fe(3)-C(58)-C(59) | 34.1(13) | C(54)-Fe(3)-C(60)-C(59) | -167.7(4) |
| C(60)-Fe(3)-C(58)-C(59) | -38.5(4) | C(57)-Fe(3)-C(60)-C(59) | 80.8(4) |
| C(52)-Fe(3)-C(58)-C(59) | 67.5(5) | C(55)-Fe(3)-C(60)-C(59) | 172.9(12) |
| C(54)-Fe(3)-C(58)-C(59) | -173.4(5) | C(51)-Fe(3)-C(60)-C(59) | -53.9(7) |
| C(57)-Fe(3)-C(58)-C(59) | -119.1(6) | C(56)-Fe(3)-C(60)-C(59) | 119.4(6) |
| C(55)-Fe(3)-C(58)-C(59) | 150.7(4) | C(53)-Fe(3)-C(60)-C(56) | 112.2(4) |
| C(51)-Fe(3)-C(58)-C(59) | 108.0(5) | C(58)-Fe(3)-C(60)-C(56) | -81.9(4) |
| C(56)-Fe(3)-C(58)-C(59) | -82.2(4) | C(59)-Fe(3)-C(60)-C(56) | -119.4(6) |
| C(57)-C(58)-C(59)-C(60) | -0.9(7) | C(52)-Fe(3)-C(60)-C(56) | 154.7(4) |
| Fe(3)-C(58)-C(59)-C(60) | 59.7(5) | C(54)-Fe(3)-C(60)-C(56) | 72.8(5) |
| C(57)-C(58)-C(59)-Fe(3) | -60.6(4) | C(57)-Fe(3)-C(60)-C(56) | -38.6(4) |
| C(53)-Fe(3)-C(59)-C(58) | -170.0(4) | C(55)-Fe(3)-C(60)-C(56) | 53.5(15) |
| C(60)-Fe(3)-C(59)-C(58) | 118.5(6) | C(51)-Fe(3)-C(60)-C(56) | -173.3(5) |
| C(52)-Fe(3)-C(59)-C(58) | -131.1(5) | C(57)-C(56)-C(61)-C(62) | 167.1(6) |
| C(54)-Fe(3)-C(59)-C(58) | 166.1(11) | C(60)-C(56)-C(61)-C(62) | -13.8(10) |

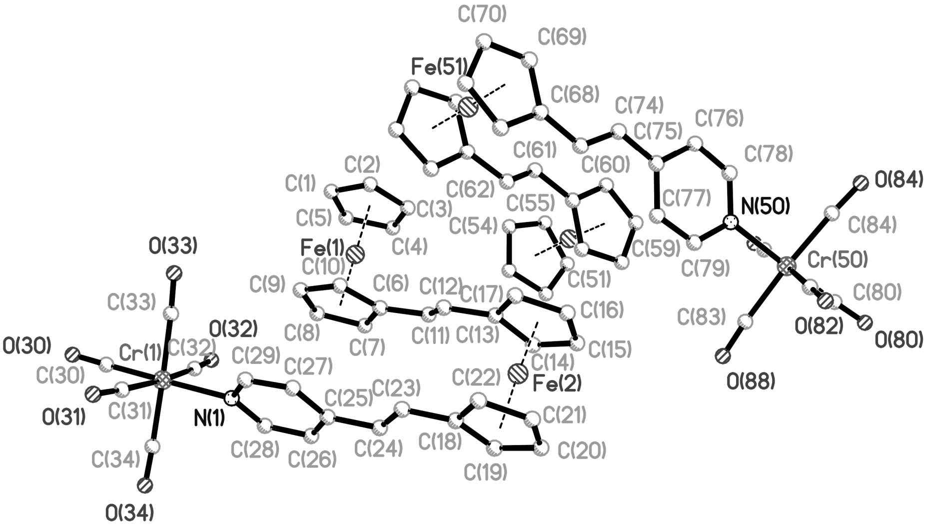
| | |
|---|---|
| Fe(3)-C(56)-C(61)-C(62) | -103.8(7) |
| C(56)-C(61)-C(62)-C(63) | -179.9(5) |
| C(61)-C(62)-C(63)-C(64) | 10.1(10) |
| C(61)-C(62)-C(63)-C(67) | -170.3(6) |
| C(61)-C(62)-C(63)-Fe(4) | 102.6(7) |
| C(65)-Fe(4)-C(63)-C(64) | -38.1(4) |
| C(72)-Fe(4)-C(63)-C(64) | 165.3(4) |
| C(66)-Fe(4)-C(63)-C(64) | -81.8(4) |
| C(69)-Fe(4)-C(63)-C(64) | 80.2(5) |
| C(67)-Fe(4)-C(63)-C(64) | -119.9(6) |
| C(70)-Fe(4)-C(63)-C(64) | 44.2(9) |
| C(68)-Fe(4)-C(63)-C(64) | 123.4(4) |
| C(71)-Fe(4)-C(63)-C(64) | -159.9(8) |
| C(65)-Fe(4)-C(63)-C(67) | 81.8(4) |
| C(72)-Fe(4)-C(63)-C(67) | -74.9(5) |
| C(66)-Fe(4)-C(63)-C(67) | 38.0(4) |
| C(69)-Fe(4)-C(63)-C(67) | -160.0(4) |
| C(70)-Fe(4)-C(63)-C(67) | 164.1(7) |
| C(64)-Fe(4)-C(63)-C(67) | 119.9(6) |
| C(68)-Fe(4)-C(63)-C(67) | -116.8(4) |
| C(71)-Fe(4)-C(63)-C(67) | -40.1(10) |
| C(65)-Fe(4)-C(63)-C(62) | -162.1(7) |
| C(72)-Fe(4)-C(63)-C(62) | 41.2(7) |
| C(66)-Fe(4)-C(63)-C(62) | 154.2(7) |
| C(69)-Fe(4)-C(63)-C(62) | -43.8(7) |
| C(67)-Fe(4)-C(63)-C(62) | 116.1(8) |
| C(70)-Fe(4)-C(63)-C(62) | -79.8(10) |
| C(64)-Fe(4)-C(63)-C(62) | -124.0(8) |
| C(68)-Fe(4)-C(63)-C(62) | -0.7(7) |
| C(71)-Fe(4)-C(63)-C(62) | 76.0(11) |
| C(67)-C(63)-C(64)-C(65) | 0.8(7) |
| C(62)-C(63)-C(64)-C(65) | -179.5(6) |
| Fe(4)-C(63)-C(64)-C(65) | 58.7(4) |
| C(67)-C(63)-C(64)-Fe(4) | -57.8(4) |
| C(62)-C(63)-C(64)-Fe(4) | 121.9(6) |
| C(65)-Fe(4)-C(64)-C(63) | 119.5(6) |
| C(72)-Fe(4)-C(64)-C(63) | -43.5(11) |
| C(66)-Fe(4)-C(64)-C(63) | 81.7(4) |
| C(69)-Fe(4)-C(64)-C(63) | -118.6(4) |
| C(67)-Fe(4)-C(64)-C(63) | 37.7(4) |
| C(70)-Fe(4)-C(64)-C(63) | -161.5(4) |
| C(68)-Fe(4)-C(64)-C(63) | -76.8(4) |
| C(71)-Fe(4)-C(64)-C(63) | 164.8(6) |
| C(72)-Fe(4)-C(64)-C(65) | -163.0(8) |
| C(66)-Fe(4)-C(64)-C(65) | -37.8(4) |
| C(69)-Fe(4)-C(64)-C(65) | 121.9(4) |
| C(67)-Fe(4)-C(64)-C(65) | -81.8(4) |
| C(70)-Fe(4)-C(64)-C(65) | 79.0(5) |
| C(68)-Fe(4)-C(64)-C(65) | 163.7(4) |
| C(71)-Fe(4)-C(64)-C(65) | 45.3(9) |
| C(63)-Fe(4)-C(64)-C(65) | -119.5(6) |
| C(63)-C(64)-C(65)-C(66) | -0.1(8) |
| Fe(4)-C(64)-C(65)-C(66) | 59.8(5) |
| C(63)-C(64)-C(65)-Fe(4) | -59.9(4) |
| C(72)-Fe(4)-C(65)-C(66) | 49.3(9) |
| C(69)-Fe(4)-C(65)-C(66) | 163.2(4) |
| C(67)-Fe(4)-C(65)-C(66) | -37.5(4) |
| C(70)-Fe(4)-C(65)-C(66) | 122.0(5) |
| C(64)-Fe(4)-C(65)-C(66) | -118.8(6) |
| C(68)-Fe(4)-C(65)-C(66) | -167.6(8) |
| C(71)-Fe(4)-C(65)-C(66) | 80.7(5) |
| C(63)-Fe(4)-C(65)-C(66) | -81.6(4) |
| C(72)-Fe(4)-C(65)-C(64) | 168.1(6) |
| C(66)-Fe(4)-C(65)-C(64) | 118.8(6) |
| C(69)-Fe(4)-C(65)-C(64) | -78.1(5) |
| C(67)-Fe(4)-C(65)-C(64) | 81.2(4) |
| C(70)-Fe(4)-C(65)-C(64) | -119.3(4) |
| C(68)-Fe(4)-C(65)-C(64) | -48.8(10) |
| C(71)-Fe(4)-C(65)-C(64) | -160.6(4) |
| C(63)-Fe(4)-C(65)-C(64) | 37.1(4) |
| C(64)-C(65)-C(66)-C(67) | -0.7(8) |
| Fe(4)-C(65)-C(66)-C(67) | 59.3(5) |
| C(64)-C(65)-C(66)-Fe(4) | -59.9(5) |
| C(72)-Fe(4)-C(66)-C(65) | -158.1(4) |
| C(69)-Fe(4)-C(66)-C(65) | -46.1(11) |
| C(67)-Fe(4)-C(66)-C(65) | 119.8(6) |

| | | | |
|---|---|---|---|
| C(70)-Fe(4)-C(66)-C(65) | -76.3(6) | C(66)-Fe(4)-C(68)-C(72) | 43.5(8) |
| C(64)-Fe(4)-C(66)-C(65) | 38.4(4) | C(69)-Fe(4)-C(68)-C(72) | -118.8(6) |
| C(68)-Fe(4)-C(66)-C(65) | 170.7(6) | C(67)-Fe(4)-C(68)-C(72) | 80.1(5) |
| C(71)-Fe(4)-C(66)-C(65) | -116.8(5) | C(70)-Fe(4)-C(68)-C(72) | -80.5(5) |
| C(63)-Fe(4)-C(66)-C(65) | 81.7(4) | C(64)-Fe(4)-C(68)-C(72) | 165.4(4) |
| C(65)-Fe(4)-C(66)-C(67) | -119.8(6) | C(71)-Fe(4)-C(68)-C(72) | -37.3(4) |
| C(72)-Fe(4)-C(66)-C(67) | 82.1(5) | C(63)-Fe(4)-C(68)-C(72) | 123.7(4) |
| C(69)-Fe(4)-C(66)-C(67) | -165.9(8) | C(65)-Fe(4)-C(68)-C(69) | -38.1(10) |
| C(70)-Fe(4)-C(66)-C(67) | 163.8(5) | C(72)-Fe(4)-C(68)-C(69) | 118.8(6) |
| C(64)-Fe(4)-C(66)-C(67) | -81.5(4) | C(66)-Fe(4)-C(68)-C(69) | 162.3(6) |
| C(68)-Fe(4)-C(66)-C(67) | 50.9(8) | C(67)-Fe(4)-C(68)-C(69) | -161.0(4) |
| C(71)-Fe(4)-C(66)-C(67) | 123.4(5) | C(70)-Fe(4)-C(68)-C(69) | 38.3(4) |
| C(63)-Fe(4)-C(66)-C(67) | -38.1(4) | C(64)-Fe(4)-C(68)-C(69) | -75.8(5) |
| C(65)-C(66)-C(67)-C(63) | 1.2(7) | C(71)-Fe(4)-C(68)-C(69) | 81.5(4) |
| Fe(4)-C(66)-C(67)-C(63) | 60.2(4) | C(63)-Fe(4)-C(68)-C(69) | -117.5(4) |
| C(65)-C(66)-C(67)-Fe(4) | -59.0(5) | C(65)-Fe(4)-C(68)-C(73) | 82.4(10) |
| C(64)-C(63)-C(67)-C(66) | -1.2(7) | C(72)-Fe(4)-C(68)-C(73) | -120.7(7) |
| C(62)-C(63)-C(67)-C(66) | 179.0(5) | C(66)-Fe(4)-C(68)-C(73) | -77.2(9) |
| Fe(4)-C(63)-C(67)-C(66) | -59.4(4) | C(69)-Fe(4)-C(68)-C(73) | 120.5(7) |
| C(64)-C(63)-C(67)-Fe(4) | 58.2(4) | C(67)-Fe(4)-C(68)-C(73) | -40.6(6) |
| C(62)-C(63)-C(67)-Fe(4) | -121.6(6) | C(70)-Fe(4)-C(68)-C(73) | 158.8(6) |
| C(65)-Fe(4)-C(67)-C(66) | 37.3(4) | C(64)-Fe(4)-C(68)-C(73) | 44.6(6) |
| C(72)-Fe(4)-C(67)-C(66) | -116.3(5) | C(71)-Fe(4)-C(68)-C(73) | -158.0(6) |
| C(69)-Fe(4)-C(67)-C(66) | 167.9(7) | C(63)-Fe(4)-C(68)-C(73) | 3.0(6) |
| C(70)-Fe(4)-C(67)-C(66) | -43.1(11) | C(72)-C(68)-C(69)-C(70) | -1.4(7) |
| C(64)-Fe(4)-C(67)-C(66) | 81.7(5) | C(73)-C(68)-C(69)-C(70) | -176.8(5) |
| C(68)-Fe(4)-C(67)-C(66) | -158.5(4) | Fe(4)-C(68)-C(69)-C(70) | -60.0(4) |
| C(71)-Fe(4)-C(67)-C(66) | -75.2(6) | C(72)-C(68)-C(69)-Fe(4) | 58.7(4) |
| C(63)-Fe(4)-C(67)-C(66) | 118.7(6) | C(73)-C(68)-C(69)-Fe(4) | -116.7(6) |
| C(65)-Fe(4)-C(67)-C(63) | -81.4(4) | C(65)-Fe(4)-C(69)-C(70) | -74.8(6) |
| C(72)-Fe(4)-C(67)-C(63) | 125.0(4) | C(72)-Fe(4)-C(69)-C(70) | 80.5(5) |
| C(66)-Fe(4)-C(67)-C(63) | -118.7(6) | C(66)-Fe(4)-C(69)-C(70) | -40.1(11) |
| C(69)-Fe(4)-C(67)-C(63) | 49.2(9) | C(67)-Fe(4)-C(69)-C(70) | 164.4(7) |
| C(70)-Fe(4)-C(67)-C(63) | -161.9(9) | C(64)-Fe(4)-C(69)-C(70) | -117.6(5) |
| C(64)-Fe(4)-C(67)-C(63) | -37.0(4) | C(68)-Fe(4)-C(69)-C(70) | 118.3(6) |
| C(68)-Fe(4)-C(67)-C(63) | 82.8(4) | C(71)-Fe(4)-C(69)-C(70) | 37.2(5) |
| C(71)-Fe(4)-C(67)-C(63) | 166.0(4) | C(63)-Fe(4)-C(69)-C(70) | -159.7(5) |
| C(65)-Fe(4)-C(68)-C(72) | -156.9(8) | C(65)-Fe(4)-C(69)-C(68) | 166.9(4) |

| | | | |
|---|---|---|---|
| C(72)-Fe(4)-C(69)-C(68) | -37.7(4) | C(66)-Fe(4)-C(71)-C(72) | -117.8(5) |
| C(66)-Fe(4)-C(69)-C(68) | -158.3(8) | C(69)-Fe(4)-C(71)-C(72) | 81.8(4) |
| C(67)-Fe(4)-C(69)-C(68) | 46.2(9) | C(67)-Fe(4)-C(71)-C(72) | -76.5(5) |
| C(70)-Fe(4)-C(69)-C(68) | -118.3(6) | C(70)-Fe(4)-C(71)-C(72) | 119.9(6) |
| C(64)-Fe(4)-C(69)-C(68) | 124.1(4) | C(64)-Fe(4)-C(71)-C(72) | 167.3(6) |
| C(71)-Fe(4)-C(69)-C(68) | -81.1(5) | C(68)-Fe(4)-C(71)-C(72) | 37.7(4) |
| C(63)-Fe(4)-C(69)-C(68) | 82.1(4) | C(63)-Fe(4)-C(71)-C(72) | -45.8(10) |
| C(68)-C(69)-C(70)-C(71) | 0.2(8) | C(70)-C(71)-C(72)-C(68) | -2.0(8) |
| Fe(4)-C(69)-C(70)-C(71) | -60.2(5) | Fe(4)-C(71)-C(72)-C(68) | -60.7(5) |
| C(68)-C(69)-C(70)-Fe(4) | 60.3(4) | C(70)-C(71)-C(72)-Fe(4) | 58.7(5) |
| C(65)-Fe(4)-C(70)-C(71) | -116.9(5) | C(69)-C(68)-C(72)-C(71) | 2.1(7) |
| C(72)-Fe(4)-C(70)-C(71) | 37.1(4) | C(73)-C(68)-C(72)-C(71) | 177.4(6) |
| C(66)-Fe(4)-C(70)-C(71) | -75.6(6) | Fe(4)-C(68)-C(72)-C(71) | 60.8(5) |
| C(69)-Fe(4)-C(70)-C(71) | 119.2(7) | C(69)-C(68)-C(72)-Fe(4) | -58.8(4) |
| C(67)-Fe(4)-C(70)-C(71) | -43.3(12) | C(73)-C(68)-C(72)-Fe(4) | 116.6(6) |
| C(64)-Fe(4)-C(70)-C(71) | -159.5(4) | C(65)-Fe(4)-C(72)-C(71) | 44.5(9) |
| C(68)-Fe(4)-C(70)-C(71) | 80.9(5) | C(66)-Fe(4)-C(72)-C(71) | 79.5(5) |
| C(63)-Fe(4)-C(70)-C(71) | 168.6(6) | C(69)-Fe(4)-C(72)-C(71) | -81.2(5) |
| C(65)-Fe(4)-C(70)-C(69) | 123.9(5) | C(67)-Fe(4)-C(72)-C(71) | 122.4(5) |
| C(72)-Fe(4)-C(70)-C(69) | -82.0(5) | C(70)-Fe(4)-C(72)-C(71) | -37.0(4) |
| C(66)-Fe(4)-C(70)-C(69) | 165.3(5) | C(64)-Fe(4)-C(72)-C(71) | -162.6(8) |
| C(67)-Fe(4)-C(70)-C(69) | -162.4(8) | C(68)-Fe(4)-C(72)-C(71) | -119.3(6) |
| C(64)-Fe(4)-C(70)-C(69) | 81.4(5) | C(63)-Fe(4)-C(72)-C(71) | 164.1(4) |
| C(68)-Fe(4)-C(70)-C(69) | -38.3(4) | C(65)-Fe(4)-C(72)-C(68) | 163.8(6) |
| C(71)-Fe(4)-C(70)-C(69) | -119.2(7) | C(66)-Fe(4)-C(72)-C(68) | -161.3(4) |
| C(63)-Fe(4)-C(70)-C(69) | 49.4(10) | C(69)-Fe(4)-C(72)-C(68) | 38.0(4) |
| C(69)-C(70)-C(71)-C(72) | 1.1(8) | C(67)-Fe(4)-C(72)-C(68) | -118.4(4) |
| Fe(4)-C(70)-C(71)-C(72) | -58.4(5) | C(70)-Fe(4)-C(72)-C(68) | 82.3(4) |
| C(69)-C(70)-C(71)-Fe(4) | 59.5(5) | C(64)-Fe(4)-C(72)-C(68) | -43.3(11) |
| C(65)-Fe(4)-C(71)-C(70) | 80.2(5) | C(71)-Fe(4)-C(72)-C(68) | 119.3(6) |
| C(72)-Fe(4)-C(71)-C(70) | -119.9(6) | C(63)-Fe(4)-C(72)-C(68) | -76.7(5) |
| C(66)-Fe(4)-C(71)-C(70) | 122.3(5) | C(72)-C(68)-C(73)-C(74) | 173.3(6) |
| C(69)-Fe(4)-C(71)-C(70) | -38.0(4) | C(69)-C(68)-C(73)-C(74) | -12.2(10) |
| C(67)-Fe(4)-C(71)-C(70) | 163.6(4) | Fe(4)-C(68)-C(73)-C(74) | -99.5(7) |
| C(64)-Fe(4)-C(71)-C(70) | 47.4(9) | C(68)-C(73)-C(74)-C(75) | 178.5(5) |
| C(68)-Fe(4)-C(71)-C(70) | -82.2(4) | C(73)-C(74)-C(75)-C(77) | 173.4(6) |
| C(63)-Fe(4)-C(71)-C(70) | -165.7(7) | C(73)-C(74)-C(75)-C(76) | -6.4(10) |
| C(65)-Fe(4)-C(71)-C(72) | -160.0(4) | C(77)-C(75)-C(76)-C(78) | -0.3(9) |

| | |
|---|---|
| C(74)-C(75)-C(76)-C(78) | 179.5(6) |
| C(76)-C(75)-C(77)-C(79) | 0.2(9) |
| C(74)-C(75)-C(77)-C(79) | -179.6(6) |
| C(75)-C(76)-C(78)-N(79) | -0.4(10) |
| C(76)-C(78)-N(79)-C(79) | 1.3(9) |
| C(76)-C(78)-N(79)-W(2) | -176.6(5) |
| C(80)-W(2)-N(79)-C(79) | -65(8) |
| C(81)-W(2)-N(79)-C(79) | 156.8(5) |
| C(82)-W(2)-N(79)-C(79) | -23.6(5) |
| C(84)-W(2)-N(79)-C(79) | -113.9(5) |
| C(83)-W(2)-N(79)-C(79) | 67.7(5) |
| C(80)-W(2)-N(79)-C(78) | 113(8) |
| C(81)-W(2)-N(79)-C(78) | -25.4(5) |
| C(82)-W(2)-N(79)-C(78) | 154.2(5) |
| C(84)-W(2)-N(79)-C(78) | 63.9(5) |
| C(83)-W(2)-N(79)-C(78) | -114.5(5) |
| C(78)-N(79)-C(79)-C(77) | -1.5(9) |
| W(2)-N(79)-C(79)-C(77) | 176.4(5) |
| C(75)-C(77)-C(79)-N(79) | 0.8(10) |
| C(81)-W(2)-C(80)-O(80) | 174(23) |
| C(82)-W(2)-C(80)-O(80) | -5(23) |
| C(84)-W(2)-C(80)-O(80) | 85(23) |
| C(83)-W(2)-C(80)-O(80) | -97(23) |
| N(79)-W(2)-C(80)-O(80) | 36(29) |
| C(80)-W(2)-C(81)-O(81) | -25(41) |
| C(82)-W(2)-C(81)-O(81) | -18(46) |
| C(84)-W(2)-C(81)-O(81) | 65(41) |
| C(83)-W(2)-C(81)-O(81) | -113(41) |
| N(79)-W(2)-C(81)-O(81) | 153(41) |
| C(80)-W(2)-C(82)-O(82) | -22(16) |
| C(81)-W(2)-C(82)-O(82) | -29(20) |
| C(84)-W(2)-C(82)-O(82) | -112(16) |
| C(83)-W(2)-C(82)-O(82) | 65(16) |
| N(79)-W(2)-C(82)-O(82) | 159(16) |
| C(80)-W(2)-C(83)-O(83) | -6(8) |
| C(81)-W(2)-C(83)-O(83) | 84(8) |
| C(82)-W(2)-C(83)-O(83) | -94(8) |
| C(84)-W(2)-C(83)-O(83) | 33(12) |
| N(79)-W(2)-C(83)-O(83) | 176(8) |
| C(80)-W(2)-C(84)-O(84) | 91(21) |
| C(81)-W(2)-C(84)-O(84) | 1(21) |
| C(82)-W(2)-C(84)-O(84) | 179(100) |
| C(83)-W(2)-C(84)-O(84) | 52(24) |
| N(79)-W(2)-C(84)-O(84) | -91(21) |

Symmetry transformations used to generate equivalent atoms:


C(70)
C(69)
Fe(51)
C(68)
C(74)
C(75)
C(76)
C(78)
C(61)
C(60)
C(2)
C(1)
C(62)
O(84)
C(3)
C(55)
C(77)
N(50)
C(5)
C(54)
C(84)
C(4)
C(59)
O(33)
Fe(1)
C(79)
Cr(50)
C(10)
C(51)
C(9)
C(6)
C(12)
C(17)
C(16)
C(80)
C(33)
C(83)
O(82)
O(80)
O(32)
C(8)
C(11)
C(13)
O(30)
Cr(1)
C(32)
C(7)
C(15)
C(29)
C(14)
C(30)
C(27)
C(22)
Fe(2)
O(88)
C(23)
C(25)
C(21)
O(31)
C(31)
N(1)
C(18)
C(28)
C(26)
C(24)
C(20)
C(34)
C(19)
O(34)

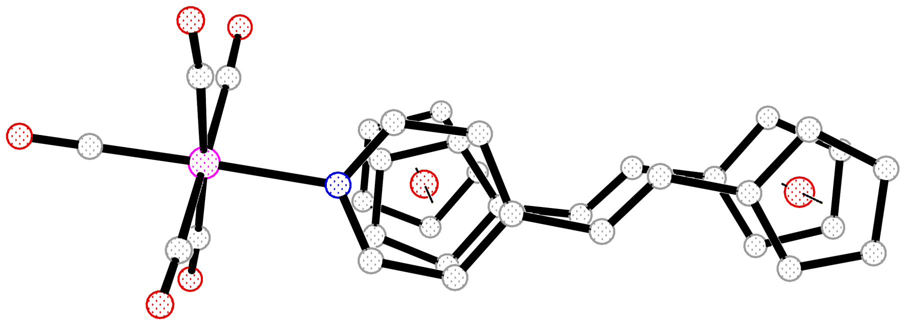


**Table 1**. Crystal data and structure refinement for str76m.

| | | |
|---|---|---|
| Identification code | str76m | |
| Empirical formula | C34 H25 Cr Fe2 N O5 | |
| Formula weight | 691.25 | |
| Temperature | 293(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Triclinic | |
| Space group | P-1 | |
| Unit cell dimensions | a = 10.4406(8) Å | $\alpha$= 83.488(2)°. |
| | b = 15.0730(12) Å | $\beta$= 77.095(2)°. |
| | c = 20.1531(16) Å | $\gamma$ = 84.630(2)°. |
| Volume | 3063.8(4) Å$^3$ | |
| Z | 4 | |
| Density (calculated) | 1.499 Mg/m$^3$ | |
| Absorption coefficient | 1.325 mm$^{-1}$ | |
| F(000) | 1408 | |
| Crystal size | 0.19 x 0.19 x 0.12 mm$^3$ | |
| Theta range for data collection | 1.04 to 23.25°. | |
| Index ranges | -11<=h<=11, -16<=k<=16, -22<=l<=14 | |
| Reflections collected | 15180 | |
| Independent reflections | 8820 [R(int) = 0.0466] | |
| Completeness to theta = 23.25° | 99.9 % | |
| Refinement method | Full-matrix least-squares on F$^2$ | |
| Data / restraints / parameters | 8820 / 0 / 775 | |
| Goodness-of-fit on F$^2$ | 0.906 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0416, wR2 = 0.0835 | |
| R indices (all data) | R1 = 0.0929, wR2 = 0.1062 | |
| Largest diff. peak and hole | 0.339 and -0.295 e.Å$^{-3}$ | |

**Table 2**. Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) for str76m. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| Fe(1) | 6499(1) | 662(1) | 2326(1) | 55(1) |
| Cr(1) | 5602(1) | -3050(1) | 4270(1) | 61(1) |
| N(1) | 4224(4) | -1891(3) | 4405(2) | 51(1) |
| C(1) | 7691(7) | 321(4) | 1443(3) | 86(2) |
| Fe(2) | 112(1) | 2742(1) | 3659(1) | 68(1) |
| C(2) | 6653(6) | 935(5) | 1299(3) | 85(2) |
| C(3) | 6728(6) | 1707(4) | 1594(3) | 69(2) |
| C(4) | 7804(5) | 1585(4) | 1908(3) | 70(2) |
| C(5) | 8403(5) | 721(4) | 1816(3) | 77(2) |
| C(6) | 4806(5) | 931(4) | 3037(3) | 62(2) |
| C(7) | 5907(6) | 804(5) | 3344(3) | 82(2) |
| C(8) | 6517(7) | -52(6) | 3226(4) | 107(3) |
| C(9) | 5791(8) | -469(5) | 2879(5) | 114(3) |
| C(10) | 4749(6) | 143(5) | 2752(4) | 93(2) |
| C(11) | 3905(5) | 1725(4) | 3061(3) | 70(2) |
| C(12) | 2772(6) | 1810(4) | 2915(3) | 73(2) |
| C(13) | 1852(5) | 2618(5) | 2954(3) | 71(2) |
| C(14) | 1811(6) | 3359(5) | 3330(3) | 83(2) |
| C(15) | 728(7) | 3952(5) | 3227(4) | 103(3) |
| C(16) | 93(7) | 3586(6) | 2808(4) | 108(3) |
| C(17) | 758(6) | 2746(5) | 2637(3) | 91(2) |
| C(18) | -126(6) | 1598(4) | 4316(3) | 73(2) |
| C(19) | -79(6) | 2340(5) | 4674(3) | 82(2) |
| C(20) | -1098(8) | 2976(5) | 4573(4) | 109(3) |
| C(21) | -1781(6) | 2640(6) | 4152(4) | 109(3) |
| C(22) | -1180(6) | 1789(5) | 3973(3) | 92(2) |
| C(23) | 744(5) | 771(4) | 4248(3) | 69(2) |
| C(24) | 1677(5) | 522(4) | 4574(3) | 64(2) |
| C(25) | 2537(5) | -317(3) | 4509(2) | 52(1) |
| C(26) | 3534(5) | -486(4) | 4854(3) | 63(2) |
| C(27) | 2381(6) | -980(4) | 4118(3) | 71(2) |
| C(28) | 4329(5) | -1261(4) | 4788(3) | 59(1) |

| | | | | |
|---|---|---|---|---|
| C(29) | 3231(6) | -1741(4) | 4083(3) | 69(2) |
| O(30) | 7598(5) | -4606(4) | 4068(3) | 131(2) |
| C(30) | 6831(7) | -4017(4) | 4150(3) | 85(2) |
| C(31) | 4266(8) | -3854(4) | 4351(3) | 85(2) |
| O(31) | 3546(6) | -4386(3) | 4388(3) | 131(2) |
| O(32) | 7965(5) | -1953(3) | 4066(2) | 102(2) |
| C(32) | 7036(7) | -2349(4) | 4157(3) | 73(2) |
| O(33) | 5657(5) | -2836(3) | 2752(2) | 88(1) |
| C(33) | 5642(5) | -2894(3) | 3321(3) | 62(2) |
| O(34) | 5420(5) | -3389(3) | 5797(2) | 112(2) |
| C(34) | 5475(6) | -3246(4) | 5229(3) | 74(2) |
| N(50) | 1426(4) | 6978(3) | 1432(2) | 46(1) |
| Fe(50) | 5868(1) | 4863(1) | 1859(1) | 43(1) |
| Cr(50) | 1247(1) | 8141(1) | 1985(1) | 61(1) |
| Fe(51) | 2602(1) | 2074(1) | 191(1) | 49(1) |
| C(51) | 7368(5) | 5204(4) | 2254(3) | 62(2) |
| C(52) | 6595(6) | 4608(5) | 2721(3) | 69(2) |
| C(53) | 6635(5) | 3814(4) | 2405(3) | 67(2) |
| C(54) | 7422(5) | 3933(3) | 1752(3) | 56(1) |
| C(55) | 7879(5) | 4784(4) | 1653(3) | 55(1) |
| C(56) | 4556(5) | 4591(3) | 1296(3) | 49(1) |
| C(57) | 3929(5) | 4690(4) | 1982(3) | 62(2) |
| C(58) | 4116(5) | 5565(4) | 2129(3) | 70(2) |
| C(59) | 4875(5) | 5995(4) | 1544(3) | 64(2) |
| C(60) | 5146(5) | 5397(4) | 1032(3) | 57(1) |
| C(61) | 4613(5) | 3809(4) | 916(3) | 54(1) |
| C(62) | 3902(5) | 3126(4) | 1116(3) | 56(1) |
| C(63) | 3923(5) | 2337(3) | 753(3) | 52(1) |
| C(64) | 3265(5) | 1555(4) | 1039(3) | 60(2) |
| C(65) | 3535(6) | 932(4) | 551(3) | 70(2) |
| C(66) | 4334(6) | 1325(4) | -47(3) | 71(2) |
| C(67) | 4566(5) | 2197(4) | 76(3) | 61(2) |
| C(68) | 1199(5) | 3125(3) | 206(3) | 48(1) |
| C(69) | 1897(6) | 3018(3) | -469(3) | 60(2) |
| C(70) | 1735(6) | 2149(4) | -624(3) | 71(2) |
| C(71) | 956(6) | 1710(4) | -51(4) | 78(2) |
| C(72) | 603(5) | 2299(4) | 468(3) | 66(2) |
| C(73) | 1120(4) | 3883(3) | 591(3) | 49(1) |

| | | | | |
|---|---|---|---|---|
| C(74) | 1546(5) | 4684(3) | 343(2) | 49(1) |
| C(75) | 1507(4) | 5444(3) | 723(2) | 43(1) |
| C(76) | 1878(5) | 6271(3) | 397(3) | 56(1) |
| C(77) | 1107(5) | 5424(3) | 1427(3) | 54(1) |
| C(78) | 1832(5) | 6993(3) | 755(3) | 57(1) |
| C(79) | 1065(5) | 6179(4) | 1753(3) | 56(1) |
| O(80) | 929(6) | 9794(3) | 2707(3) | 130(2) |
| C(80) | 1037(7) | 9143(5) | 2441(3) | 90(2) |
| O(81) | 4183(5) | 8356(3) | 1707(2) | 106(2) |
| C(81) | 3109(7) | 8244(4) | 1786(3) | 75(2) |
| O(82) | -1691(4) | 7989(4) | 2379(2) | 112(2) |
| C(82) | -603(6) | 8035(4) | 2226(3) | 70(2) |
| C(83) | 1395(6) | 7440(4) | 2814(3) | 79(2) |
| O(84) | 997(4) | 9422(3) | 743(2) | 90(1) |
| C(84) | 1082(5) | 8914(4) | 1195(3) | 62(2) |
| O(88) | 1469(6) | 7062(3) | 3327(3) | 121(2) |

**Table 3**. Bond lengths [Å] and angles [°] for str76m.

| | |
|---|---|
| Fe(1)-C(8) | 2.005(6) |
| Fe(1)-C(1) | 2.019(6) |
| Fe(1)-C(4) | 2.020(5) |
| Fe(1)-C(3) | 2.024(5) |
| Fe(1)-C(10) | 2.025(6) |
| Fe(1)-C(5) | 2.029(5) |
| Fe(1)-C(9) | 2.033(7) |
| Fe(1)-C(7) | 2.036(6) |
| Fe(1)-C(2) | 2.036(6) |
| Fe(1)-C(6) | 2.052(5) |
| Cr(1)-C(30) | 1.849(7) |
| Cr(1)-C(32) | 1.870(8) |
| Cr(1)-C(33) | 1.893(6) |
| Cr(1)-C(34) | 1.898(6) |
| Cr(1)-C(31) | 1.901(8) |
| Cr(1)-N(1) | 2.159(4) |
| N(1)-C(28) | 1.316(6) |
| N(1)-C(29) | 1.330(6) |
| C(1)-C(5) | 1.384(8) |
| C(1)-C(2) | 1.417(8) |
| Fe(2)-C(22) | 2.016(6) |
| Fe(2)-C(21) | 2.016(6) |
| Fe(2)-C(17) | 2.019(6) |
| Fe(2)-C(16) | 2.019(6) |
| Fe(2)-C(14) | 2.023(6) |
| Fe(2)-C(15) | 2.025(7) |
| Fe(2)-C(20) | 2.034(7) |
| Fe(2)-C(19) | 2.037(6) |
| Fe(2)-C(13) | 2.049(5) |
| Fe(2)-C(18) | 2.051(5) |
| C(2)-C(3) | 1.381(8) |
| C(3)-C(4) | 1.395(7) |
| C(4)-C(5) | 1.405(7) |
| C(6)-C(10) | 1.388(8) |
| C(6)-C(7) | 1.410(7) |
| C(6)-C(11) | 1.450(7) |
| C(7)-C(8) | 1.406(9) |
| C(8)-C(9) | 1.373(10) |
| C(9)-C(10) | 1.408(9) |
| C(11)-C(12) | 1.273(7) |
| C(12)-C(13) | 1.477(8) |
| C(13)-C(14) | 1.412(8) |
| C(13)-C(17) | 1.416(8) |
| C(14)-C(15) | 1.412(8) |
| C(15)-C(16) | 1.371(10) |
| C(16)-C(17) | 1.425(9) |
| C(18)-C(19) | 1.408(8) |
| C(18)-C(22) | 1.416(8) |
| C(18)-C(23) | 1.473(8) |
| C(19)-C(20) | 1.398(8) |
| C(20)-C(21) | 1.385(10) |
| C(21)-C(22) | 1.423(9) |
| C(23)-C(24) | 1.298(7) |
| C(24)-C(25) | 1.481(7) |
| C(25)-C(26) | 1.366(7) |
| C(25)-C(27) | 1.384(7) |
| C(26)-C(28) | 1.369(7) |
| C(27)-C(29) | 1.382(7) |
| O(30)-C(30) | 1.140(6) |
| C(31)-O(31) | 1.134(7) |
| O(32)-C(32) | 1.156(7) |
| O(33)-C(33) | 1.137(5) |
| O(34)-C(34) | 1.129(6) |
| N(50)-C(78) | 1.333(6) |
| N(50)-C(79) | 1.345(6) |
| N(50)-Cr(50) | 2.155(4) |
| Fe(50)-C(57) | 2.022(5) |
| Fe(50)-C(58) | 2.022(5) |
| Fe(50)-C(59) | 2.027(5) |
| Fe(50)-C(53) | 2.028(5) |
| Fe(50)-C(52) | 2.031(5) |
| Fe(50)-C(54) | 2.032(5) |
| Fe(50)-C(60) | 2.034(5) |

| | |
|---|---|
| Fe(50)-C(51) | 2.038(5) |
| Fe(50)-C(55) | 2.042(5) |
| Fe(50)-C(56) | 2.058(5) |
| Cr(50)-C(80) | 1.825(7) |
| Cr(50)-C(84) | 1.893(6) |
| Cr(50)-C(82) | 1.901(7) |
| Cr(50)-C(83) | 1.902(7) |
| Cr(50)-C(81) | 1.913(7) |
| Fe(51)-C(71) | 2.026(6) |
| Fe(51)-C(66) | 2.031(5) |
| Fe(51)-C(64) | 2.033(5) |
| Fe(51)-C(70) | 2.034(5) |
| Fe(51)-C(67) | 2.036(5) |
| Fe(51)-C(69) | 2.037(5) |
| Fe(51)-C(65) | 2.039(5) |
| Fe(51)-C(72) | 2.043(5) |
| Fe(51)-C(68) | 2.053(5) |
| Fe(51)-C(63) | 2.061(5) |
| C(51)-C(52) | 1.397(7) |
| C(51)-C(55) | 1.405(7) |
| C(52)-C(53) | 1.411(7) |
| C(53)-C(54) | 1.389(7) |
| C(54)-C(55) | 1.388(7) |
| C(56)-C(57) | 1.410(7) |
| C(56)-C(60) | 1.410(7) |
| C(56)-C(61) | 1.466(7) |
| C(57)-C(58) | 1.424(7) |
| C(58)-C(59) | 1.394(7) |
| C(59)-C(60) | 1.411(7) |
| C(61)-C(62) | 1.299(7) |
| C(62)-C(63) | 1.462(7) |
| C(63)-C(67) | 1.410(7) |
| C(63)-C(64) | 1.419(7) |
| C(64)-C(65) | 1.401(7) |
| C(65)-C(66) | 1.407(7) |
| C(66)-C(67) | 1.416(7) |
| C(68)-C(69) | 1.411(7) |
| C(68)-C(72) | 1.438(7) |
| C(68)-C(73) | 1.439(6) |
| C(69)-C(70) | 1.415(7) |
| C(70)-C(71) | 1.392(8) |
| C(71)-C(72) | 1.413(8) |
| C(73)-C(74) | 1.330(6) |
| C(74)-C(75) | 1.442(6) |
| C(75)-C(77) | 1.384(6) |
| C(75)-C(76) | 1.388(6) |
| C(76)-C(78) | 1.364(7) |
| C(77)-C(79) | 1.369(7) |
| O(80)-C(80) | 1.156(6) |
| O(81)-C(81) | 1.122(6) |
| O(82)-C(82) | 1.115(6) |
| C(83)-O(88) | 1.136(6) |
| O(84)-C(84) | 1.136(6) |
| C(8)-Fe(1)-C(1) | 122.4(3) |
| C(8)-Fe(1)-C(4) | 122.9(3) |
| C(1)-Fe(1)-C(4) | 67.4(3) |
| C(8)-Fe(1)-C(3) | 159.1(4) |
| C(1)-Fe(1)-C(3) | 67.8(2) |
| C(4)-Fe(1)-C(3) | 40.4(2) |
| C(8)-Fe(1)-C(10) | 67.6(3) |
| C(1)-Fe(1)-C(10) | 124.8(3) |
| C(4)-Fe(1)-C(10) | 159.2(3) |
| C(3)-Fe(1)-C(10) | 124.0(3) |
| C(8)-Fe(1)-C(5) | 106.8(3) |
| C(1)-Fe(1)-C(5) | 40.0(2) |
| C(4)-Fe(1)-C(5) | 40.6(2) |
| C(3)-Fe(1)-C(5) | 68.3(2) |
| C(10)-Fe(1)-C(5) | 159.3(3) |
| C(8)-Fe(1)-C(9) | 39.8(3) |
| C(1)-Fe(1)-C(9) | 108.6(3) |
| C(4)-Fe(1)-C(9) | 158.3(3) |
| C(3)-Fe(1)-C(9) | 160.0(4) |
| C(10)-Fe(1)-C(9) | 40.6(3) |
| C(5)-Fe(1)-C(9) | 122.5(3) |
| C(8)-Fe(1)-C(7) | 40.7(3) |
| C(1)-Fe(1)-C(7) | 158.3(3) |

| | | | |
|---|---|---|---|
| C(4)-Fe(1)-C(7) | 108.1(3) | C(28)-N(1)-Cr(1) | 122.8(4) |
| C(3)-Fe(1)-C(7) | 123.5(3) | C(29)-N(1)-Cr(1) | 122.3(4) |
| C(10)-Fe(1)-C(7) | 66.9(3) | C(5)-C(1)-C(2) | 108.8(6) |
| C(5)-Fe(1)-C(7) | 122.7(3) | C(5)-C(1)-Fe(1) | 70.4(4) |
| C(9)-Fe(1)-C(7) | 67.3(3) | C(2)-C(1)-Fe(1) | 70.2(3) |
| C(8)-Fe(1)-C(2) | 159.2(3) | C(22)-Fe(2)-C(21) | 41.3(3) |
| C(1)-Fe(1)-C(2) | 40.9(2) | C(22)-Fe(2)-C(17) | 108.1(3) |
| C(4)-Fe(1)-C(2) | 67.3(3) | C(21)-Fe(2)-C(17) | 124.4(3) |
| C(3)-Fe(1)-C(2) | 39.8(2) | C(22)-Fe(2)-C(16) | 122.1(3) |
| C(10)-Fe(1)-C(2) | 109.5(3) | C(21)-Fe(2)-C(16) | 106.7(3) |
| C(5)-Fe(1)-C(2) | 68.2(3) | C(17)-Fe(2)-C(16) | 41.3(3) |
| C(9)-Fe(1)-C(2) | 124.6(4) | C(22)-Fe(2)-C(14) | 162.0(3) |
| C(7)-Fe(1)-C(2) | 159.0(3) | C(21)-Fe(2)-C(14) | 155.2(4) |
| C(8)-Fe(1)-C(6) | 68.5(2) | C(17)-Fe(2)-C(14) | 68.6(3) |
| C(1)-Fe(1)-C(6) | 160.0(3) | C(16)-Fe(2)-C(14) | 67.9(3) |
| C(4)-Fe(1)-C(6) | 123.3(2) | C(22)-Fe(2)-C(15) | 156.0(3) |
| C(3)-Fe(1)-C(6) | 108.3(2) | C(21)-Fe(2)-C(15) | 119.6(3) |
| C(10)-Fe(1)-C(6) | 39.8(2) | C(17)-Fe(2)-C(15) | 68.5(3) |
| C(5)-Fe(1)-C(6) | 158.8(3) | C(16)-Fe(2)-C(15) | 39.6(3) |
| C(9)-Fe(1)-C(6) | 68.0(3) | C(14)-Fe(2)-C(15) | 40.8(2) |
| C(7)-Fe(1)-C(6) | 40.4(2) | C(22)-Fe(2)-C(20) | 68.8(3) |
| C(2)-Fe(1)-C(6) | 123.5(2) | C(21)-Fe(2)-C(20) | 40.0(3) |
| C(30)-Cr(1)-C(32) | 86.3(3) | C(17)-Fe(2)-C(20) | 159.4(3) |
| C(30)-Cr(1)-C(33) | 90.7(2) | C(16)-Fe(2)-C(20) | 121.8(3) |
| C(32)-Cr(1)-C(33) | 91.4(2) | C(14)-Fe(2)-C(20) | 120.7(4) |
| C(30)-Cr(1)-C(34) | 89.6(2) | C(15)-Fe(2)-C(20) | 105.7(3) |
| C(32)-Cr(1)-C(34) | 91.9(3) | C(22)-Fe(2)-C(19) | 68.3(3) |
| C(33)-Cr(1)-C(34) | 176.7(3) | C(21)-Fe(2)-C(19) | 67.3(3) |
| C(30)-Cr(1)-C(31) | 88.2(3) | C(17)-Fe(2)-C(19) | 159.2(3) |
| C(32)-Cr(1)-C(31) | 174.4(3) | C(16)-Fe(2)-C(19) | 158.2(4) |
| C(33)-Cr(1)-C(31) | 87.2(3) | C(14)-Fe(2)-C(19) | 108.2(3) |
| C(34)-Cr(1)-C(31) | 89.5(3) | C(15)-Fe(2)-C(19) | 123.4(4) |
| C(30)-Cr(1)-N(1) | 178.0(3) | C(20)-Fe(2)-C(19) | 40.2(2) |
| C(32)-Cr(1)-N(1) | 91.7(2) | C(22)-Fe(2)-C(13) | 125.5(3) |
| C(33)-Cr(1)-N(1) | 89.24(19) | C(21)-Fe(2)-C(13) | 162.2(4) |
| C(34)-Cr(1)-N(1) | 90.53(19) | C(17)-Fe(2)-C(13) | 40.7(2) |
| C(31)-Cr(1)-N(1) | 93.8(2) | C(16)-Fe(2)-C(13) | 68.4(2) |
| C(28)-N(1)-C(29) | 114.8(5) | C(14)-Fe(2)-C(13) | 40.6(2) |

| | |
|---|---|
| C(15)-Fe(2)-C(13) | 68.4(3) |
| C(20)-Fe(2)-C(13) | 157.3(4) |
| C(19)-Fe(2)-C(13) | 123.6(2) |
| C(22)-Fe(2)-C(18) | 40.7(2) |
| C(21)-Fe(2)-C(18) | 68.1(2) |
| C(17)-Fe(2)-C(18) | 123.6(3) |
| C(16)-Fe(2)-C(18) | 159.2(4) |
| C(14)-Fe(2)-C(18) | 125.3(2) |
| C(15)-Fe(2)-C(18) | 160.7(3) |
| C(20)-Fe(2)-C(18) | 68.1(3) |
| C(19)-Fe(2)-C(18) | 40.3(2) |
| C(13)-Fe(2)-C(18) | 109.9(2) |
| C(3)-C(2)-C(1) | 107.3(6) |
| C(3)-C(2)-Fe(1) | 69.6(3) |
| C(1)-C(2)-Fe(1) | 68.9(3) |
| C(2)-C(3)-C(4) | 108.2(5) |
| C(2)-C(3)-Fe(1) | 70.6(3) |
| C(4)-C(3)-Fe(1) | 69.7(3) |
| C(3)-C(4)-C(5) | 108.7(6) |
| C(3)-C(4)-Fe(1) | 70.0(3) |
| C(5)-C(4)-Fe(1) | 70.0(3) |
| C(1)-C(5)-C(4) | 106.9(5) |
| C(1)-C(5)-Fe(1) | 69.6(4) |
| C(4)-C(5)-Fe(1) | 69.4(3) |
| C(10)-C(6)-C(7) | 106.3(6) |
| C(10)-C(6)-C(11) | 128.7(6) |
| C(7)-C(6)-C(11) | 124.9(6) |
| C(10)-C(6)-Fe(1) | 69.1(3) |
| C(7)-C(6)-Fe(1) | 69.2(3) |
| C(11)-C(6)-Fe(1) | 128.6(4) |
| C(8)-C(7)-C(6) | 108.3(7) |
| C(8)-C(7)-Fe(1) | 68.5(4) |
| C(6)-C(7)-Fe(1) | 70.4(3) |
| C(9)-C(8)-C(7) | 108.4(7) |
| C(9)-C(8)-Fe(1) | 71.2(4) |
| C(7)-C(8)-Fe(1) | 70.8(3) |
| C(8)-C(9)-C(10) | 107.4(7) |
| C(8)-C(9)-Fe(1) | 69.0(4) |
| C(10)-C(9)-Fe(1) | 69.4(4) |
| C(6)-C(10)-C(9) | 109.5(7) |
| C(6)-C(10)-Fe(1) | 71.1(3) |
| C(9)-C(10)-Fe(1) | 70.0(4) |
| C(12)-C(11)-C(6) | 127.3(7) |
| C(11)-C(12)-C(13) | 126.7(7) |
| C(14)-C(13)-C(17) | 107.2(6) |
| C(14)-C(13)-C(12) | 128.8(6) |
| C(17)-C(13)-C(12) | 123.8(7) |
| C(14)-C(13)-Fe(2) | 68.7(3) |
| C(17)-C(13)-Fe(2) | 68.5(3) |
| C(12)-C(13)-Fe(2) | 124.7(4) |
| C(13)-C(14)-C(15) | 108.3(7) |
| C(13)-C(14)-Fe(2) | 70.7(4) |
| C(15)-C(14)-Fe(2) | 69.7(4) |
| C(16)-C(15)-C(14) | 108.3(8) |
| C(16)-C(15)-Fe(2) | 69.9(5) |
| C(14)-C(15)-Fe(2) | 69.5(4) |
| C(15)-C(16)-C(17) | 109.0(6) |
| C(15)-C(16)-Fe(2) | 70.4(4) |
| C(17)-C(16)-Fe(2) | 69.3(3) |
| C(13)-C(17)-C(16) | 107.2(7) |
| C(13)-C(17)-Fe(2) | 70.8(3) |
| C(16)-C(17)-Fe(2) | 69.3(4) |
| C(19)-C(18)-C(22) | 107.3(6) |
| C(19)-C(18)-C(23) | 130.0(6) |
| C(22)-C(18)-C(23) | 122.6(7) |
| C(19)-C(18)-Fe(2) | 69.3(3) |
| C(22)-C(18)-Fe(2) | 68.3(3) |
| C(23)-C(18)-Fe(2) | 125.2(4) |
| C(20)-C(19)-C(18) | 109.1(7) |
| C(20)-C(19)-Fe(2) | 69.8(4) |
| C(18)-C(19)-Fe(2) | 70.4(3) |
| C(21)-C(20)-C(19) | 107.6(8) |
| C(21)-C(20)-Fe(2) | 69.3(4) |
| C(19)-C(20)-Fe(2) | 70.0(4) |
| C(20)-C(21)-C(22) | 109.1(6) |
| C(20)-C(21)-Fe(2) | 70.7(4) |

| | |
|---|---|
| C(22)-C(21)-Fe(2) | 69.3(3) |
| C(18)-C(22)-C(21) | 106.8(7) |
| C(18)-C(22)-Fe(2) | 71.0(4) |
| C(21)-C(22)-Fe(2) | 69.4(4) |
| C(24)-C(23)-C(18) | 126.4(6) |
| C(23)-C(24)-C(25) | 126.0(6) |
| C(26)-C(25)-C(27) | 115.7(5) |
| C(26)-C(25)-C(24) | 120.8(5) |
| C(27)-C(25)-C(24) | 123.5(5) |
| C(25)-C(26)-C(28) | 120.4(5) |
| C(29)-C(27)-C(25) | 119.8(5) |
| N(1)-C(28)-C(26) | 125.1(5) |
| N(1)-C(29)-C(27) | 124.2(5) |
| O(30)-C(30)-Cr(1) | 179.1(7) |
| O(31)-C(31)-Cr(1) | 174.5(7) |
| O(32)-C(32)-Cr(1) | 176.2(6) |
| O(33)-C(33)-Cr(1) | 177.2(5) |
| O(34)-C(34)-Cr(1) | 177.8(5) |
| C(78)-N(50)-C(79) | 114.9(4) |
| C(78)-N(50)-Cr(50) | 123.8(3) |
| C(79)-N(50)-Cr(50) | 121.3(3) |
| C(57)-Fe(50)-C(58) | 41.2(2) |
| C(57)-Fe(50)-C(59) | 68.6(2) |
| C(58)-Fe(50)-C(59) | 40.3(2) |
| C(57)-Fe(50)-C(53) | 106.8(2) |
| C(58)-Fe(50)-C(53) | 127.7(3) |
| C(59)-Fe(50)-C(53) | 165.9(3) |
| C(57)-Fe(50)-C(52) | 115.3(2) |
| C(58)-Fe(50)-C(52) | 106.1(2) |
| C(59)-Fe(50)-C(52) | 128.0(3) |
| C(53)-Fe(50)-C(52) | 40.7(2) |
| C(57)-Fe(50)-C(54) | 129.1(2) |
| C(58)-Fe(50)-C(54) | 166.5(2) |
| C(59)-Fe(50)-C(54) | 152.8(2) |
| C(53)-Fe(50)-C(54) | 40.01(19) |
| C(52)-Fe(50)-C(54) | 67.7(2) |
| C(57)-Fe(50)-C(60) | 67.8(2) |
| C(58)-Fe(50)-C(60) | 67.8(2) |
| C(59)-Fe(50)-C(60) | 40.6(2) |
| C(53)-Fe(50)-C(60) | 151.4(3) |
| C(52)-Fe(50)-C(60) | 167.7(3) |
| C(54)-Fe(50)-C(60) | 120.5(2) |
| C(57)-Fe(50)-C(51) | 148.8(2) |
| C(58)-Fe(50)-C(51) | 116.3(2) |
| C(59)-Fe(50)-C(51) | 108.9(2) |
| C(53)-Fe(50)-C(51) | 67.6(2) |
| C(52)-Fe(50)-C(51) | 40.2(2) |
| C(54)-Fe(50)-C(51) | 67.3(2) |
| C(60)-Fe(50)-C(51) | 131.6(2) |
| C(57)-Fe(50)-C(55) | 168.0(2) |
| C(58)-Fe(50)-C(55) | 150.6(3) |
| C(59)-Fe(50)-C(55) | 119.6(2) |
| C(53)-Fe(50)-C(55) | 67.4(2) |
| C(52)-Fe(50)-C(55) | 67.7(2) |
| C(54)-Fe(50)-C(55) | 39.84(19) |
| C(60)-Fe(50)-C(55) | 111.9(2) |
| C(51)-Fe(50)-C(55) | 40.30(19) |
| C(57)-Fe(50)-C(56) | 40.41(19) |
| C(58)-Fe(50)-C(56) | 68.5(2) |
| C(59)-Fe(50)-C(56) | 68.5(2) |
| C(53)-Fe(50)-C(56) | 117.3(2) |
| C(52)-Fe(50)-C(56) | 149.1(2) |
| C(54)-Fe(50)-C(56) | 110.2(2) |
| C(60)-Fe(50)-C(56) | 40.31(19) |
| C(51)-Fe(50)-C(56) | 169.9(2) |
| C(55)-Fe(50)-C(56) | 131.6(2) |
| C(80)-Cr(50)-C(84) | 87.0(2) |
| C(80)-Cr(50)-C(82) | 89.9(3) |
| C(84)-Cr(50)-C(82) | 91.2(2) |
| C(80)-Cr(50)-C(83) | 88.8(3) |
| C(84)-Cr(50)-C(83) | 175.8(2) |
| C(82)-Cr(50)-C(83) | 88.8(3) |
| C(80)-Cr(50)-C(81) | 88.8(3) |
| C(84)-Cr(50)-C(81) | 91.0(2) |
| C(82)-Cr(50)-C(81) | 177.4(2) |
| C(83)-Cr(50)-C(81) | 89.0(3) |

| | |
|---|---|
| C(80)-Cr(50)-N(50) | 177.7(2) |
| C(84)-Cr(50)-N(50) | 91.5(2) |
| C(82)-Cr(50)-N(50) | 88.3(2) |
| C(83)-Cr(50)-N(50) | 92.7(2) |
| C(81)-Cr(50)-N(50) | 93.0(2) |
| C(71)-Fe(51)-C(66) | 120.5(3) |
| C(71)-Fe(51)-C(64) | 124.0(2) |
| C(66)-Fe(51)-C(64) | 68.0(2) |
| C(71)-Fe(51)-C(70) | 40.1(2) |
| C(66)-Fe(51)-C(70) | 107.2(2) |
| C(64)-Fe(51)-C(70) | 159.8(2) |
| C(71)-Fe(51)-C(67) | 156.3(3) |
| C(66)-Fe(51)-C(67) | 40.8(2) |
| C(64)-Fe(51)-C(67) | 68.1(2) |
| C(70)-Fe(51)-C(67) | 121.9(3) |
| C(71)-Fe(51)-C(69) | 68.1(2) |
| C(66)-Fe(51)-C(69) | 124.5(2) |
| C(64)-Fe(51)-C(69) | 158.1(2) |
| C(70)-Fe(51)-C(69) | 40.67(19) |
| C(67)-Fe(51)-C(69) | 108.4(2) |
| C(71)-Fe(51)-C(65) | 106.8(2) |
| C(66)-Fe(51)-C(65) | 40.5(2) |
| C(64)-Fe(51)-C(65) | 40.3(2) |
| C(70)-Fe(51)-C(65) | 123.5(2) |
| C(67)-Fe(51)-C(65) | 68.2(2) |
| C(69)-Fe(51)-C(65) | 160.5(2) |
| C(71)-Fe(51)-C(72) | 40.6(2) |
| C(66)-Fe(51)-C(72) | 155.9(2) |
| C(64)-Fe(51)-C(72) | 107.9(2) |
| C(70)-Fe(51)-C(72) | 68.0(2) |
| C(67)-Fe(51)-C(72) | 161.9(2) |
| C(69)-Fe(51)-C(72) | 68.3(2) |
| C(65)-Fe(51)-C(72) | 121.0(2) |
| C(71)-Fe(51)-C(68) | 68.6(2) |
| C(66)-Fe(51)-C(68) | 161.2(2) |
| C(64)-Fe(51)-C(68) | 122.5(2) |
| C(70)-Fe(51)-C(68) | 68.3(2) |
| C(67)-Fe(51)-C(68) | 124.9(2) |
| C(69)-Fe(51)-C(68) | 40.37(18) |
| C(65)-Fe(51)-C(68) | 157.3(2) |
| C(72)-Fe(51)-C(68) | 41.10(19) |
| C(71)-Fe(51)-C(63) | 161.3(3) |
| C(66)-Fe(51)-C(63) | 68.0(2) |
| C(64)-Fe(51)-C(63) | 40.56(19) |
| C(70)-Fe(51)-C(63) | 157.8(2) |
| C(67)-Fe(51)-C(63) | 40.27(19) |
| C(69)-Fe(51)-C(63) | 122.8(2) |
| C(65)-Fe(51)-C(63) | 67.9(2) |
| C(72)-Fe(51)-C(63) | 125.3(2) |
| C(68)-Fe(51)-C(63) | 108.9(2) |
| C(52)-C(51)-C(55) | 108.2(5) |
| C(52)-C(51)-Fe(50) | 69.7(3) |
| C(55)-C(51)-Fe(50) | 70.0(3) |
| C(51)-C(52)-C(53) | 107.4(5) |
| C(51)-C(52)-Fe(50) | 70.2(3) |
| C(53)-C(52)-Fe(50) | 69.5(3) |
| C(54)-C(53)-C(52) | 107.9(5) |
| C(54)-C(53)-Fe(50) | 70.2(3) |
| C(52)-C(53)-Fe(50) | 69.8(3) |
| C(55)-C(54)-C(53) | 108.7(5) |
| C(55)-C(54)-Fe(50) | 70.5(3) |
| C(53)-C(54)-Fe(50) | 69.8(3) |
| C(54)-C(55)-C(51) | 107.7(5) |
| C(54)-C(55)-Fe(50) | 69.7(3) |
| C(51)-C(55)-Fe(50) | 69.7(3) |
| C(57)-C(56)-C(60) | 106.7(5) |
| C(57)-C(56)-C(61) | 127.9(5) |
| C(60)-C(56)-C(61) | 125.4(5) |
| C(57)-C(56)-Fe(50) | 68.4(3) |
| C(60)-C(56)-Fe(50) | 68.9(3) |
| C(61)-C(56)-Fe(50) | 127.2(3) |
| C(56)-C(57)-C(58) | 108.3(5) |
| C(56)-C(57)-Fe(50) | 71.2(3) |
| C(58)-C(57)-Fe(50) | 69.4(3) |
| C(59)-C(58)-C(57) | 108.1(5) |
| C(59)-C(58)-Fe(50) | 70.1(3) |

| | |
|---|---|
| C(57)-C(58)-Fe(50) | 69.4(3) |
| C(58)-C(59)-C(60) | 107.6(5) |
| C(58)-C(59)-Fe(50) | 69.7(3) |
| C(60)-C(59)-Fe(50) | 69.9(3) |
| C(56)-C(60)-C(59) | 109.3(5) |
| C(56)-C(60)-Fe(50) | 70.8(3) |
| C(59)-C(60)-Fe(50) | 69.4(3) |
| C(62)-C(61)-C(56) | 125.4(5) |
| C(61)-C(62)-C(63) | 127.1(5) |
| C(67)-C(63)-C(64) | 107.3(5) |
| C(67)-C(63)-C(62) | 128.2(5) |
| C(64)-C(63)-C(62) | 124.5(5) |
| C(67)-C(63)-Fe(51) | 68.9(3) |
| C(64)-C(63)-Fe(51) | 68.7(3) |
| C(62)-C(63)-Fe(51) | 127.4(3) |
| C(65)-C(64)-C(63) | 108.6(5) |
| C(65)-C(64)-Fe(51) | 70.1(3) |
| C(63)-C(64)-Fe(51) | 70.8(3) |
| C(64)-C(65)-C(66) | 108.0(5) |
| C(64)-C(65)-Fe(51) | 69.6(3) |
| C(66)-C(65)-Fe(51) | 69.5(3) |
| C(65)-C(66)-C(67) | 108.0(5) |
| C(65)-C(66)-Fe(51) | 70.1(3) |
| C(67)-C(66)-Fe(51) | 69.8(3) |
| C(63)-C(67)-C(66) | 108.1(5) |
| C(63)-C(67)-Fe(51) | 70.8(3) |
| C(66)-C(67)-Fe(51) | 69.5(3) |
| C(69)-C(68)-C(72) | 106.9(5) |
| C(69)-C(68)-C(73) | 128.4(5) |
| C(72)-C(68)-C(73) | 124.6(5) |
| C(69)-C(68)-Fe(51) | 69.2(3) |
| C(72)-C(68)-Fe(51) | 69.1(3) |
| C(73)-C(68)-Fe(51) | 124.5(3) |
| C(68)-C(69)-C(70) | 108.5(5) |
| C(68)-C(69)-Fe(51) | 70.4(3) |
| C(70)-C(69)-Fe(51) | 69.6(3) |
| C(71)-C(70)-C(69) | 108.3(5) |
| C(71)-C(70)-Fe(51) | 69.6(3) |
| C(69)-C(70)-Fe(51) | 69.8(3) |
| C(70)-C(71)-C(72) | 108.7(6) |
| C(70)-C(71)-Fe(51) | 70.3(3) |
| C(72)-C(71)-Fe(51) | 70.3(3) |
| C(71)-C(72)-C(68) | 107.5(5) |
| C(71)-C(72)-Fe(51) | 69.0(3) |
| C(68)-C(72)-Fe(51) | 69.8(3) |
| C(74)-C(73)-C(68) | 125.8(5) |
| C(73)-C(74)-C(75) | 126.7(5) |
| C(77)-C(75)-C(76) | 114.4(5) |
| C(77)-C(75)-C(74) | 124.2(4) |
| C(76)-C(75)-C(74) | 121.4(5) |
| C(78)-C(76)-C(75) | 121.5(5) |
| C(79)-C(77)-C(75) | 121.0(5) |
| N(50)-C(78)-C(76) | 124.1(5) |
| N(50)-C(79)-C(77) | 124.1(5) |
| O(80)-C(80)-Cr(50) | 177.5(7) |
| O(81)-C(81)-Cr(50) | 174.3(6) |
| O(82)-C(82)-Cr(50) | 178.1(6) |
| O(88)-C(83)-Cr(50) | 176.3(6) |
| O(84)-C(84)-Cr(50) | 175.6(5) |

**Table 4**. Anisotropic displacement parameters ($Å^2$x $10^3$) for str76m. The anisotropic displacement factor exponent takes the form: $-2\pi^2[ h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12} ]$

|  | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| Fe(1) | 41(1) | 45(1) | 73(1) | -1(1) | -4(1) | 8(1) |
| Cr(1) | 72(1) | 56(1) | 55(1) | -5(1) | -18(1) | 11(1) |
| N(1) | 60(3) | 53(3) | 41(3) | -4(2) | -17(2) | 1(2) |
| C(1) | 82(5) | 80(5) | 84(5) | -22(4) | 3(4) | 23(4) |
| Fe(2) | 41(1) | 80(1) | 63(1) | 22(1) | 4(1) | 20(1) |
| C(2) | 74(5) | 107(6) | 76(5) | -9(4) | -23(3) | 8(4) |
| C(3) | 62(4) | 55(4) | 84(4) | 4(3) | -13(3) | 8(3) |
| C(4) | 54(4) | 55(4) | 96(5) | 12(3) | -17(3) | -2(3) |
| C(5) | 44(4) | 82(5) | 90(5) | 17(4) | -1(3) | 15(4) |
| C(6) | 48(4) | 62(4) | 65(4) | 3(3) | 4(3) | 8(3) |
| C(7) | 62(4) | 107(6) | 66(4) | 3(4) | -8(3) | 16(4) |
| C(8) | 67(5) | 113(7) | 103(6) | 53(5) | 16(4) | 27(5) |
| C(9) | 78(6) | 61(5) | 170(9) | 25(5) | 25(5) | -7(5) |
| C(10) | 51(4) | 73(5) | 139(6) | 0(4) | 11(4) | -13(4) |
| C(11) | 45(4) | 86(5) | 68(4) | 4(3) | 1(3) | 2(3) |
| C(12) | 58(4) | 98(5) | 55(4) | 10(3) | 0(3) | -7(4) |
| C(13) | 43(3) | 97(5) | 55(4) | 23(3) | 6(3) | 11(4) |
| C(14) | 56(4) | 86(5) | 90(5) | 23(4) | -1(3) | 4(4) |
| C(15) | 67(5) | 88(6) | 125(7) | 38(5) | 8(4) | 20(4) |
| C(16) | 50(4) | 150(8) | 87(6) | 68(5) | 12(4) | 26(5) |
| C(17) | 64(4) | 143(7) | 52(4) | 23(4) | -6(3) | 6(5) |
| C(18) | 54(4) | 79(5) | 61(4) | 28(3) | 12(3) | 15(4) |
| C(19) | 81(5) | 84(5) | 63(4) | 8(4) | 8(3) | 24(4) |
| C(20) | 88(6) | 105(6) | 94(6) | 16(5) | 34(4) | 42(5) |
| C(21) | 39(4) | 123(7) | 124(7) | 59(5) | 23(4) | 25(4) |
| C(22) | 49(4) | 101(6) | 108(5) | 31(4) | 0(4) | 2(4) |
| C(23) | 57(4) | 85(5) | 53(4) | 14(3) | 2(3) | -3(3) |
| C(24) | 67(4) | 75(4) | 45(3) | 3(3) | -7(3) | -4(3) |
| C(25) | 58(4) | 51(4) | 41(3) | 6(3) | -4(3) | 0(3) |
| C(26) | 73(4) | 51(4) | 66(4) | -6(3) | -18(3) | -5(3) |
| C(27) | 80(4) | 79(5) | 58(4) | -7(3) | -33(3) | 18(4) |
| C(28) | 62(4) | 61(4) | 58(4) | -3(3) | -22(3) | 1(3) |
| C(29) | 84(4) | 68(4) | 61(4) | -14(3) | -33(3) | 7(4) |

|  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|
| O(30) | 147(5) | 119(4) | 129(4) | -39(3) | -53(3) | 77(4) |
| C(30) | 105(5) | 82(5) | 71(4) | -13(3) | -34(4) | 30(4) |
| C(31) | 112(6) | 53(4) | 80(5) | -1(3) | -4(4) | 1(4) |
| O(31) | 143(5) | 80(4) | 161(5) | -16(3) | 2(4) | -39(4) |
| O(32) | 85(4) | 122(4) | 108(4) | -13(3) | -36(3) | -12(3) |
| C(32) | 77(5) | 84(5) | 61(4) | -17(3) | -26(4) | 14(4) |
| O(33) | 129(4) | 81(3) | 61(3) | -12(2) | -31(3) | -8(3) |
| C(33) | 77(4) | 46(3) | 66(4) | -3(3) | -24(3) | -1(3) |
| O(34) | 146(4) | 127(4) | 57(3) | 7(3) | -32(3) | 17(3) |
| C(34) | 89(5) | 67(4) | 60(4) | 1(3) | -19(4) | 18(3) |
| N(50) | 41(2) | 45(3) | 54(3) | -10(2) | -12(2) | 1(2) |
| Fe(50) | 36(1) | 44(1) | 52(1) | -4(1) | -15(1) | -2(1) |
| Cr(50) | 60(1) | 58(1) | 72(1) | -21(1) | -32(1) | 11(1) |
| Fe(51) | 55(1) | 39(1) | 58(1) | -7(1) | -23(1) | -2(1) |
| C(51) | 53(4) | 62(4) | 81(4) | -18(3) | -35(3) | 3(3) |
| C(52) | 62(4) | 96(5) | 49(4) | -8(4) | -23(3) | 16(4) |
| C(53) | 66(4) | 62(4) | 67(4) | 14(3) | -13(3) | 1(3) |
| C(54) | 59(4) | 46(4) | 64(4) | -9(3) | -24(3) | 11(3) |
| C(55) | 34(3) | 68(4) | 61(4) | 6(3) | -15(3) | 3(3) |
| C(56) | 39(3) | 45(3) | 69(4) | -7(3) | -25(3) | 0(3) |
| C(57) | 39(3) | 71(4) | 75(4) | -11(3) | -9(3) | -5(3) |
| C(58) | 38(3) | 83(5) | 93(5) | -39(4) | -18(3) | 18(3) |
| C(59) | 52(4) | 49(4) | 99(5) | -8(3) | -35(3) | 7(3) |
| C(60) | 49(3) | 61(4) | 64(4) | 2(3) | -27(3) | 7(3) |
| C(61) | 41(3) | 59(4) | 62(4) | 0(3) | -19(3) | -1(3) |
| C(62) | 45(3) | 67(4) | 60(4) | -6(3) | -21(3) | 6(3) |
| C(63) | 54(3) | 49(4) | 56(4) | -5(3) | -24(3) | 6(3) |
| C(64) | 64(4) | 58(4) | 62(4) | 5(3) | -23(3) | -5(3) |
| C(65) | 68(4) | 45(4) | 105(5) | 2(4) | -41(4) | 1(3) |
| C(66) | 61(4) | 66(4) | 87(5) | -25(3) | -17(3) | 16(3) |
| C(67) | 51(3) | 55(4) | 81(4) | -5(3) | -23(3) | -3(3) |
| C(68) | 47(3) | 42(3) | 60(4) | -5(3) | -23(3) | -2(3) |
| C(69) | 81(4) | 38(3) | 70(4) | -6(3) | -41(3) | -1(3) |
| C(70) | 106(5) | 55(4) | 70(4) | -19(3) | -53(4) | 2(4) |
| C(71) | 87(5) | 52(4) | 112(6) | -1(4) | -59(4) | -12(4) |
| C(72) | 47(3) | 62(4) | 89(5) | 3(3) | -22(3) | -11(3) |
| C(73) | 40(3) | 51(4) | 57(3) | -6(3) | -19(2) | 8(3) |
| C(74) | 48(3) | 52(4) | 47(3) | -9(3) | -13(2) | 7(3) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(75) | 36(3) | 45(3) | 48(3) | -10(2) | -11(2) | 3(2) |
| C(76) | 65(4) | 52(4) | 48(3) | -10(3) | -2(3) | -2(3) |
| C(77) | 53(3) | 52(4) | 57(4) | -2(3) | -12(3) | -8(3) |
| C(78) | 61(4) | 45(3) | 59(4) | -1(3) | -5(3) | -3(3) |
| C(79) | 56(3) | 64(4) | 49(3) | -9(3) | -9(3) | -6(3) |
| O(80) | 186(6) | 93(4) | 147(5) | -71(3) | -107(4) | 52(4) |
| C(80) | 116(6) | 82(5) | 90(5) | -33(4) | -69(4) | 37(4) |
| O(81) | 68(3) | 121(4) | 141(4) | -14(3) | -41(3) | -15(3) |
| C(81) | 70(4) | 67(4) | 98(5) | -16(3) | -39(4) | 4(4) |
| O(82) | 60(3) | 165(5) | 100(4) | -11(3) | -7(3) | 11(3) |
| C(82) | 60(4) | 85(5) | 69(4) | -21(3) | -25(3) | 14(4) |
| C(83) | 90(5) | 79(5) | 83(5) | -28(4) | -43(4) | 8(4) |
| O(84) | 103(3) | 68(3) | 109(4) | 8(3) | -47(3) | -18(3) |
| C(84) | 60(4) | 54(4) | 81(5) | -20(3) | -30(3) | -3(3) |
| O(88) | 176(5) | 114(4) | 94(4) | 3(3) | -75(4) | -17(4) |

**Table 5**. Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters (Å$^2$x 10 $^3$) for str76m.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1) | 7866 | -256 | 1310 | 103 |
| H(2) | 6036 | 837 | 1051 | 103 |
| H(3) | 6159 | 2219 | 1586 | 83 |
| H(4) | 8079 | 2007 | 2139 | 84 |
| H(5) | 9137 | 466 | 1975 | 93 |
| H(7) | 6182 | 1217 | 3583 | 98 |
| H(8) | 7282 | -295 | 3361 | 128 |
| H(9) | 5958 | -1050 | 2750 | 137 |
| H(10) | 4120 | 36 | 2514 | 111 |
| H(11) | 4186 | 2229 | 3198 | 84 |
| H(12) | 2494 | 1311 | 2768 | 88 |
| H(14) | 2397 | 3442 | 3601 | 99 |
| H(15) | 486 | 4496 | 3412 | 124 |
| H(16) | -650 | 3844 | 2659 | 129 |
| H(17) | 518 | 2355 | 2368 | 109 |
| H(19) | 533 | 2397 | 4936 | 99 |
| H(20) | -1283 | 3525 | 4755 | 131 |
| H(21) | -2516 | 2926 | 4010 | 131 |
| H(22) | -1431 | 1427 | 3687 | 111 |
| H(23) | 613 | 389 | 3941 | 83 |
| H(24) | 1819 | 906 | 4877 | 77 |
| H(26) | 3674 | -73 | 5135 | 75 |
| H(27) | 1706 | -914 | 3879 | 85 |
| H(28) | 4994 | -1350 | 5033 | 71 |
| H(29) | 3102 | -2176 | 3816 | 82 |
| H(51) | 7520 | 5779 | 2328 | 74 |
| H(52) | 6137 | 4714 | 3160 | 82 |
| H(53) | 6210 | 3302 | 2599 | 80 |
| H(54) | 7612 | 3512 | 1434 | 67 |
| H(55) | 8425 | 5032 | 1259 | 66 |
| H(57) | 3471 | 4259 | 2287 | 74 |
| H(58) | 3789 | 5807 | 2544 | 84 |

|  |  |  |  |  |
|---|---|---|---|---|
| H(59) | 5152 | 6572 | 1500 | 77 |
| H(60) | 5637 | 5516 | 591 | 68 |
| H(61) | 5206 | 3801 | 497 | 64 |
| H(62) | 3315 | 3141 | 1537 | 67 |
| H(64) | 2742 | 1471 | 1477 | 72 |
| H(65) | 3240 | 359 | 612 | 84 |
| H(66) | 4652 | 1060 | -452 | 85 |
| H(67) | 5058 | 2605 | -236 | 73 |
| H(69) | 2382 | 3447 | -762 | 71 |
| H(70) | 2087 | 1911 | -1038 | 85 |
| H(71) | 710 | 1127 | -17 | 93 |
| H(72) | 80 | 2174 | 902 | 79 |
| H(73) | 737 | 3806 | 1055 | 59 |
| H(74) | 1905 | 4761 | -124 | 59 |
| H(76) | 2165 | 6334 | -76 | 67 |
| H(77) | 862 | 4890 | 1683 | 65 |
| H(78) | 2101 | 7530 | 512 | 68 |
| H(79) | 769 | 6136 | 2225 | 67 |

**Table 6**. Torsion angles [°] for str76m.

| | |
|---|---|
| C(30)-Cr(1)-N(1)-C(28) | -47(6) |
| C(32)-Cr(1)-N(1)-C(28) | -43.8(4) |
| C(33)-Cr(1)-N(1)-C(28) | -135.2(4) |
| C(34)-Cr(1)-N(1)-C(28) | 48.1(4) |
| C(31)-Cr(1)-N(1)-C(28) | 137.6(4) |
| C(30)-Cr(1)-N(1)-C(29) | 130(6) |
| C(32)-Cr(1)-N(1)-C(29) | 133.3(4) |
| C(33)-Cr(1)-N(1)-C(29) | 41.9(4) |
| C(34)-Cr(1)-N(1)-C(29) | -134.8(4) |
| C(31)-Cr(1)-N(1)-C(29) | -45.3(4) |
| C(8)-Fe(1)-C(1)-C(5) | -77.1(5) |
| C(4)-Fe(1)-C(1)-C(5) | 38.5(3) |
| C(3)-Fe(1)-C(1)-C(5) | 82.3(4) |
| C(10)-Fe(1)-C(1)-C(5) | -160.9(4) |
| C(9)-Fe(1)-C(1)-C(5) | -118.7(5) |
| C(7)-Fe(1)-C(1)-C(5) | -43.7(9) |
| C(2)-Fe(1)-C(1)-C(5) | 119.5(6) |
| C(6)-Fe(1)-C(1)-C(5) | 164.8(6) |
| C(8)-Fe(1)-C(1)-C(2) | 163.4(5) |
| C(4)-Fe(1)-C(1)-C(2) | -81.0(4) |
| C(3)-Fe(1)-C(1)-C(2) | -37.2(4) |
| C(10)-Fe(1)-C(1)-C(2) | 79.7(5) |
| C(5)-Fe(1)-C(1)-C(2) | -119.5(6) |
| C(9)-Fe(1)-C(1)-C(2) | 121.8(5) |
| C(7)-Fe(1)-C(1)-C(2) | -163.2(7) |
| C(6)-Fe(1)-C(1)-C(2) | 45.3(9) |
| C(5)-C(1)-C(2)-C(3) | -0.8(7) |
| Fe(1)-C(1)-C(2)-C(3) | 59.2(4) |
| C(5)-C(1)-C(2)-Fe(1) | -60.0(4) |
| C(8)-Fe(1)-C(2)-C(3) | -161.7(8) |
| C(1)-Fe(1)-C(2)-C(3) | -119.0(6) |
| C(4)-Fe(1)-C(2)-C(3) | -37.9(3) |
| C(10)-Fe(1)-C(2)-C(3) | 120.1(4) |
| C(5)-Fe(1)-C(2)-C(3) | -81.9(4) |
| C(9)-Fe(1)-C(2)-C(3) | 162.9(4) |
| C(7)-Fe(1)-C(2)-C(3) | 43.7(9) |
| C(6)-Fe(1)-C(2)-C(3) | 78.0(5) |
| C(8)-Fe(1)-C(2)-C(1) | -42.7(10) |
| C(4)-Fe(1)-C(2)-C(1) | 81.1(4) |
| C(3)-Fe(1)-C(2)-C(1) | 119.0(6) |
| C(10)-Fe(1)-C(2)-C(1) | -121.0(5) |
| C(5)-Fe(1)-C(2)-C(1) | 37.1(4) |
| C(9)-Fe(1)-C(2)-C(1) | -78.2(5) |
| C(7)-Fe(1)-C(2)-C(1) | 162.6(7) |
| C(6)-Fe(1)-C(2)-C(1) | -163.0(4) |
| C(1)-C(2)-C(3)-C(4) | 1.0(7) |
| Fe(1)-C(2)-C(3)-C(4) | 59.8(4) |
| C(1)-C(2)-C(3)-Fe(1) | -58.8(4) |
| C(8)-Fe(1)-C(3)-C(2) | 161.7(7) |
| C(1)-Fe(1)-C(3)-C(2) | 38.2(4) |
| C(4)-Fe(1)-C(3)-C(2) | 119.0(5) |
| C(10)-Fe(1)-C(3)-C(2) | -79.6(5) |
| C(5)-Fe(1)-C(3)-C(2) | 81.5(4) |
| C(9)-Fe(1)-C(3)-C(2) | -45.0(9) |
| C(7)-Fe(1)-C(3)-C(2) | -162.8(4) |
| C(6)-Fe(1)-C(3)-C(2) | -120.8(4) |
| C(8)-Fe(1)-C(3)-C(4) | 42.8(9) |
| C(1)-Fe(1)-C(3)-C(4) | -80.7(4) |
| C(10)-Fe(1)-C(3)-C(4) | 161.4(4) |
| C(5)-Fe(1)-C(3)-C(4) | -37.5(4) |
| C(9)-Fe(1)-C(3)-C(4) | -164.0(8) |
| C(7)-Fe(1)-C(3)-C(4) | 78.3(4) |
| C(2)-Fe(1)-C(3)-C(4) | -119.0(5) |
| C(6)-Fe(1)-C(3)-C(4) | 120.2(4) |
| C(2)-C(3)-C(4)-C(5) | -0.8(7) |
| Fe(1)-C(3)-C(4)-C(5) | 59.5(4) |
| C(2)-C(3)-C(4)-Fe(1) | -60.3(4) |
| C(8)-Fe(1)-C(4)-C(3) | -163.3(4) |
| C(1)-Fe(1)-C(4)-C(3) | 81.8(4) |
| C(10)-Fe(1)-C(4)-C(3) | -48.2(9) |
| C(5)-Fe(1)-C(4)-C(3) | 119.7(5) |
| C(9)-Fe(1)-C(4)-C(3) | 165.2(8) |
| C(7)-Fe(1)-C(4)-C(3) | -120.8(4) |
| C(2)-Fe(1)-C(4)-C(3) | 37.3(3) |
| C(6)-Fe(1)-C(4)-C(3) | -78.9(4) |
| C(8)-Fe(1)-C(4)-C(5) | 77.0(5) |
| C(1)-Fe(1)-C(4)-C(5) | -37.9(4) |
| C(3)-Fe(1)-C(4)-C(5) | -119.7(5) |
| C(10)-Fe(1)-C(4)-C(5) | -167.9(8) |
| C(9)-Fe(1)-C(4)-C(5) | 45.5(10) |
| C(7)-Fe(1)-C(4)-C(5) | 119.4(4) |
| C(2)-Fe(1)-C(4)-C(5) | -82.4(4) |
| C(6)-Fe(1)-C(4)-C(5) | 161.3(4) |
| C(2)-C(1)-C(5)-C(4) | 0.3(7) |
| Fe(1)-C(1)-C(5)-C(4) | -59.6(4) |
| C(2)-C(1)-C(5)-Fe(1) | 59.9(4) |
| C(3)-C(4)-C(5)-C(1) | 0.3(7) |
| Fe(1)-C(4)-C(5)-C(1) | 59.8(4) |
| C(3)-C(4)-C(5)-Fe(1) | -59.5(4) |
| C(8)-Fe(1)-C(5)-C(1) | 120.7(5) |
| C(4)-Fe(1)-C(5)-C(1) | -118.1(5) |
| C(3)-Fe(1)-C(5)-C(1) | -80.8(4) |
| C(10)-Fe(1)-C(5)-C(1) | 49.8(9) |
| C(9)-Fe(1)-C(5)-C(1) | 80.1(5) |
| C(7)-Fe(1)-C(5)-C(1) | 162.3(4) |
| C(2)-Fe(1)-C(5)-C(1) | -37.9(4) |
| C(6)-Fe(1)-C(5)-C(1) | -165.7(6) |
| C(8)-Fe(1)-C(5)-C(4) | -121.2(5) |
| C(1)-Fe(1)-C(5)-C(4) | 118.1(5) |
| C(3)-Fe(1)-C(5)-C(4) | 37.2(4) |
| C(10)-Fe(1)-C(5)-C(4) | 167.9(7) |
| C(9)-Fe(1)-C(5)-C(4) | -161.8(5) |
| C(7)-Fe(1)-C(5)-C(4) | -79.6(4) |
| C(2)-Fe(1)-C(5)-C(4) | 80.2(4) |
| C(6)-Fe(1)-C(5)-C(4) | -47.6(8) |
| C(8)-Fe(1)-C(6)-C(10) | -80.4(5) |
| C(1)-Fe(1)-C(6)-C(10) | 46.3(9) |
| C(4)-Fe(1)-C(6)-C(10) | 163.6(4) |
| C(3)-Fe(1)-C(6)-C(10) | 121.5(4) |
| C(5)-Fe(1)-C(6)-C(10) | -161.4(6) |
| C(9)-Fe(1)-C(6)-C(10) | -37.5(4) |

| | | | | | |
|---|---|---|---|---|---|
| C(7)-Fe(1)-C(6)-C(10) | -117.9(5) | C(9)-Fe(1)-C(7)-C(6) | -82.2(4) | C(2)-Fe(1)-C(9)-C(10) | -79.7(6) |
| C(2)-Fe(1)-C(6)-C(10) | 80.3(5) | C(2)-Fe(1)-C(7)-C(6) | 46.6(9) | C(6)-Fe(1)-C(9)-C(10) | 36.8(5) |
| C(8)-Fe(1)-C(6)-C(7) | 37.4(4) | C(6)-C(7)-C(8)-C(9) | -2.3(8) | C(7)-C(6)-C(10)-C(9) | 0.2(7) |
| C(1)-Fe(1)-C(6)-C(7) | 164.2(7) | Fe(1)-C(7)-C(8)-C(9) | -61.6(5) | C(11)-C(6)-C(10)-C(9) | -176.9(5) |
| C(4)-Fe(1)-C(6)-C(7) | -78.6(4) | C(6)-C(7)-C(8)-Fe(1) | 59.3(4) | Fe(1)-C(6)-C(10)-C(9) | 59.7(4) |
| C(3)-Fe(1)-C(6)-C(7) | -120.6(4) | C(1)-Fe(1)-C(8)-C(9) | -80.0(5) | C(7)-C(6)-C(10)-Fe(1) | -59.5(4) |
| C(10)-Fe(1)-C(6)-C(7) | 117.9(5) | C(4)-Fe(1)-C(8)-C(9) | -162.4(4) | C(11)-C(6)-C(10)-Fe(1) | 123.4(5) |
| C(5)-Fe(1)-C(6)-C(7) | -43.5(8) | C(3)-Fe(1)-C(8)-C(9) | 166.0(6) | C(8)-C(9)-C(10)-C(6) | -1.6(8) |
| C(9)-Fe(1)-C(6)-C(7) | 80.4(5) | C(10)-Fe(1)-C(8)-C(9) | 38.0(5) | Fe(1)-C(9)-C(10)-C(6) | -60.4(4) |
| C(2)-Fe(1)-C(6)-C(7) | -161.8(4) | C(5)-Fe(1)-C(8)-C(9) | -120.9(5) | C(8)-C(9)-C(10)-Fe(1) | 58.8(5) |
| C(8)-Fe(1)-C(6)-C(11) | 156.1(7) | C(7)-Fe(1)-C(8)-C(9) | 118.1(6) | C(8)-Fe(1)-C(10)-C(6) | 82.8(4) |
| C(1)-Fe(1)-C(6)-C(11) | -77.2(10) | C(2)-Fe(1)-C(8)-C(9) | -48.3(10) | C(1)-Fe(1)-C(10)-C(6) | -162.5(4) |
| C(4)-Fe(1)-C(6)-C(11) | 40.1(7) | C(6)-Fe(1)-C(8)-C(9) | 81.0(5) | C(4)-Fe(1)-C(10)-C(6) | -41.8(10) |
| C(3)-Fe(1)-C(6)-C(11) | -2.0(7) | C(1)-Fe(1)-C(8)-C(7) | 161.8(4) | C(3)-Fe(1)-C(10)-C(6) | -77.4(5) |
| C(10)-Fe(1)-C(6)-C(11) | -123.5(8) | C(4)-Fe(1)-C(8)-C(7) | 79.5(5) | C(5)-Fe(1)-C(10)-C(6) | 160.9(7) |
| C(5)-Fe(1)-C(6)-C(11) | 75.2(9) | C(3)-Fe(1)-C(8)-C(7) | 47.9(9) | C(9)-Fe(1)-C(10)-C(6) | 119.9(7) |
| C(9)-Fe(1)-C(6)-C(11) | -161.0(7) | C(10)-Fe(1)-C(8)-C(7) | -80.2(4) | C(7)-Fe(1)-C(10)-C(6) | 38.5(4) |
| C(7)-Fe(1)-C(6)-C(11) | 118.7(8) | C(5)-Fe(1)-C(8)-C(7) | 121.0(4) | C(2)-Fe(1)-C(10)-C(6) | -119.3(4) |
| C(2)-Fe(1)-C(6)-C(11) | -43.2(7) | C(9)-Fe(1)-C(8)-C(7) | -118.1(6) | C(8)-Fe(1)-C(10)-C(9) | -37.2(5) |
| C(10)-C(6)-C(7)-C(8) | 1.2(6) | C(2)-Fe(1)-C(8)-C(7) | -166.4(7) | C(1)-Fe(1)-C(10)-C(9) | 77.6(6) |
| C(11)-C(6)-C(7)-C(8) | 178.5(5) | C(6)-Fe(1)-C(8)-C(7) | -37.1(4) | C(4)-Fe(1)-C(10)-C(9) | -161.8(8) |
| Fe(1)-C(6)-C(7)-C(8) | -58.1(4) | C(7)-C(8)-C(9)-C(10) | 2.4(8) | C(3)-Fe(1)-C(10)-C(9) | 162.6(5) |
| C(10)-C(6)-C(7)-Fe(1) | 59.4(4) | Fe(1)-C(8)-C(9)-C(10) | -59.0(5) | C(5)-Fe(1)-C(10)-C(9) | 40.9(11) |
| C(11)-C(6)-C(7)-Fe(1) | -123.3(5) | C(7)-C(8)-C(9)-Fe(1) | 61.4(4) | C(7)-Fe(1)-C(10)-C(9) | -81.5(5) |
| C(1)-Fe(1)-C(7)-C(8) | -45.4(10) | C(1)-Fe(1)-C(9)-C(8) | 118.7(5) | C(2)-Fe(1)-C(10)-C(9) | 120.7(6) |
| C(4)-Fe(1)-C(7)-C(8) | -119.6(5) | C(4)-Fe(1)-C(9)-C(8) | 43.4(11) | C(6)-Fe(1)-C(10)-C(9) | -119.9(7) |
| C(3)-Fe(1)-C(7)-C(8) | -161.5(5) | C(3)-Fe(1)-C(9)-C(8) | -165.5(7) | C(10)-C(6)-C(11)-C(12) | 11.6(9) |
| C(10)-Fe(1)-C(7)-C(8) | 82.0(5) | C(10)-Fe(1)-C(9)-C(8) | -119.1(7) | C(7)-C(6)-C(11)-C(12) | -165.1(6) |
| C(5)-Fe(1)-C(7)-C(8) | -77.3(5) | C(5)-Fe(1)-C(9)-C(8) | 76.8(6) | Fe(1)-C(6)-C(11)-C(12) | 104.7(7) |
| C(9)-Fe(1)-C(7)-C(8) | 37.7(4) | C(7)-Fe(1)-C(9)-C(8) | -38.6(4) | C(6)-C(11)-C(12)-C(13) | 178.7(5) |
| C(2)-Fe(1)-C(7)-C(8) | 166.5(8) | C(2)-Fe(1)-C(9)-C(8) | 161.2(4) | C(11)-C(12)-C(13)-C(14) | -20.4(9) |
| C(6)-Fe(1)-C(7)-C(8) | 119.9(6) | C(6)-Fe(1)-C(9)-C(8) | -82.4(5) | C(11)-C(12)-C(13)-C(17) | 164.4(6) |
| C(8)-Fe(1)-C(7)-C(6) | -119.9(6) | C(8)-Fe(1)-C(9)-C(10) | 119.1(7) | C(11)-C(12)-C(13)-Fe(2) | -109.8(7) |
| C(1)-Fe(1)-C(7)-C(6) | -165.4(7) | C(1)-Fe(1)-C(9)-C(10) | -122.2(5) | C(22)-Fe(2)-C(13)-C(14) | -164.5(4) |
| C(4)-Fe(1)-C(7)-C(6) | 120.4(4) | C(4)-Fe(1)-C(9)-C(10) | 162.5(7) | C(21)-Fe(2)-C(13)-C(14) | 158.1(8) |
| C(3)-Fe(1)-C(7)-C(6) | 78.6(5) | C(3)-Fe(1)-C(9)-C(10) | -46.3(11) | C(17)-Fe(2)-C(13)-C(14) | 119.7(6) |
| C(10)-Fe(1)-C(7)-C(6) | -38.0(3) | C(5)-Fe(1)-C(9)-C(10) | -164.1(5) | C(16)-Fe(2)-C(13)-C(14) | 80.8(5) |
| C(5)-Fe(1)-C(7)-C(6) | 162.8(4) | C(7)-Fe(1)-C(9)-C(10) | 80.6(5) | C(15)-Fe(2)-C(13)-C(14) | 38.0(4) |

| | | | | | |
|---|---|---|---|---|---|
| C(20)-Fe(2)-C(13)-C(14) | -40.8(8) | C(19)-Fe(2)-C(14)-C(15) | -120.3(5) | C(19)-Fe(2)-C(16)-C(17) | 166.1(7) |
| C(19)-Fe(2)-C(13)-C(14) | -78.6(5) | C(13)-Fe(2)-C(14)-C(15) | 119.0(6) | C(13)-Fe(2)-C(16)-C(17) | 38.4(4) |
| C(18)-Fe(2)-C(13)-C(14) | -121.5(4) | C(18)-Fe(2)-C(14)-C(15) | -161.7(5) | C(18)-Fe(2)-C(16)-C(17) | -51.1(8) |
| C(22)-Fe(2)-C(13)-C(17) | 75.8(5) | C(13)-C(14)-C(15)-C(16) | 1.1(8) | C(14)-C(13)-C(17)-C(16) | 2.2(6) |
| C(21)-Fe(2)-C(13)-C(17) | 38.3(10) | Fe(2)-C(14)-C(15)-C(16) | -59.4(5) | C(12)-C(13)-C(17)-C(16) | 178.2(5) |
| C(16)-Fe(2)-C(13)-C(17) | -39.0(5) | C(13)-C(14)-C(15)-Fe(2) | 60.4(4) | Fe(2)-C(13)-C(17)-C(16) | 60.1(4) |
| C(14)-Fe(2)-C(13)-C(17) | -119.7(6) | C(22)-Fe(2)-C(15)-C(16) | -48.4(10) | C(14)-C(13)-C(17)-Fe(2) | -57.9(4) |
| C(15)-Fe(2)-C(13)-C(17) | -81.7(5) | C(21)-Fe(2)-C(15)-C(16) | -80.4(6) | C(12)-C(13)-C(17)-Fe(2) | 118.2(5) |
| C(20)-Fe(2)-C(13)-C(17) | -160.5(7) | C(17)-Fe(2)-C(15)-C(16) | 37.9(4) | C(15)-C(16)-C(17)-C(13) | -1.5(7) |
| C(19)-Fe(2)-C(13)-C(17) | 161.7(4) | C(14)-Fe(2)-C(15)-C(16) | 119.6(7) | Fe(2)-C(16)-C(17)-C(13) | -61.0(4) |
| C(18)-Fe(2)-C(13)-C(17) | 118.8(5) | C(20)-Fe(2)-C(15)-C(16) | -121.3(5) | C(15)-C(16)-C(17)-Fe(2) | 59.5(5) |
| C(22)-Fe(2)-C(13)-C(12) | -41.2(7) | C(19)-Fe(2)-C(15)-C(16) | -161.4(4) | C(22)-Fe(2)-C(17)-C(13) | -123.9(4) |
| C(21)-Fe(2)-C(13)-C(12) | -78.7(10) | C(13)-Fe(2)-C(15)-C(16) | 81.8(5) | C(21)-Fe(2)-C(17)-C(13) | -166.7(5) |
| C(17)-Fe(2)-C(13)-C(12) | -117.0(8) | C(18)-Fe(2)-C(15)-C(16) | 170.5(7) | C(16)-Fe(2)-C(17)-C(13) | 117.7(6) |
| C(16)-Fe(2)-C(13)-C(12) | -156.0(8) | C(22)-Fe(2)-C(15)-C(14) | -167.9(7) | C(14)-Fe(2)-C(17)-C(13) | 37.4(4) |
| C(14)-Fe(2)-C(13)-C(12) | 123.3(7) | C(21)-Fe(2)-C(15)-C(14) | 160.0(5) | C(15)-Fe(2)-C(17)-C(13) | 81.4(4) |
| C(15)-Fe(2)-C(13)-C(12) | 161.2(7) | C(17)-Fe(2)-C(15)-C(14) | -81.7(5) | C(20)-Fe(2)-C(17)-C(13) | 158.5(9) |
| C(20)-Fe(2)-C(13)-C(12) | 82.5(10) | C(16)-Fe(2)-C(15)-C(14) | -119.6(7) | C(19)-Fe(2)-C(17)-C(13) | -47.7(10) |
| C(19)-Fe(2)-C(13)-C(12) | 44.6(8) | C(20)-Fe(2)-C(15)-C(14) | 119.1(5) | C(18)-Fe(2)-C(17)-C(13) | -81.7(5) |
| C(18)-Fe(2)-C(13)-C(12) | 1.8(7) | C(19)-Fe(2)-C(15)-C(14) | 79.1(5) | C(22)-Fe(2)-C(17)-C(16) | 118.4(5) |
| C(17)-C(13)-C(14)-C(15) | -2.0(7) | C(13)-Fe(2)-C(15)-C(14) | -37.7(4) | C(21)-Fe(2)-C(17)-C(16) | 75.6(6) |
| C(12)-C(13)-C(14)-C(15) | -177.8(5) | C(18)-Fe(2)-C(15)-C(14) | 51.0(10) | C(14)-Fe(2)-C(17)-C(16) | -80.4(5) |
| Fe(2)-C(13)-C(14)-C(15) | -59.8(4) | C(14)-C(15)-C(16)-C(17) | 0.3(8) | C(15)-Fe(2)-C(17)-C(16) | -36.4(4) |
| C(17)-C(13)-C(14)-Fe(2) | 57.8(4) | Fe(2)-C(15)-C(16)-C(17) | -58.8(5) | C(20)-Fe(2)-C(17)-C(16) | 40.7(11) |
| C(12)-C(13)-C(14)-Fe(2) | -118.0(5) | C(14)-C(15)-C(16)-Fe(2) | 59.1(5) | C(19)-Fe(2)-C(17)-C(16) | -165.4(8) |
| C(22)-Fe(2)-C(14)-C(13) | 45.0(11) | C(22)-Fe(2)-C(16)-C(15) | 159.0(4) | C(13)-Fe(2)-C(17)-C(16) | -117.7(6) |
| C(21)-Fe(2)-C(14)-C(13) | -164.1(6) | C(21)-Fe(2)-C(16)-C(15) | 116.4(5) | C(18)-Fe(2)-C(17)-C(16) | 160.6(5) |
| C(17)-Fe(2)-C(14)-C(13) | -37.5(4) | C(17)-Fe(2)-C(16)-C(15) | -120.2(6) | C(22)-Fe(2)-C(18)-C(19) | -119.5(5) |
| C(16)-Fe(2)-C(14)-C(13) | -82.2(4) | C(14)-Fe(2)-C(16)-C(15) | -37.9(4) | C(21)-Fe(2)-C(18)-C(19) | -80.2(5) |
| C(15)-Fe(2)-C(14)-C(13) | -119.0(6) | C(20)-Fe(2)-C(16)-C(15) | 75.5(6) | C(17)-Fe(2)-C(18)-C(19) | 162.2(4) |
| C(20)-Fe(2)-C(14)-C(13) | 163.0(4) | C(19)-Fe(2)-C(16)-C(15) | 45.9(9) | C(16)-Fe(2)-C(18)-C(19) | -159.7(6) |
| C(19)-Fe(2)-C(14)-C(13) | 120.7(4) | C(13)-Fe(2)-C(16)-C(15) | -81.8(5) | C(14)-Fe(2)-C(18)-C(19) | 76.0(5) |
| C(18)-Fe(2)-C(14)-C(13) | 79.3(5) | C(18)-Fe(2)-C(16)-C(15) | -171.2(6) | C(15)-Fe(2)-C(18)-C(19) | 37.4(9) |
| C(22)-Fe(2)-C(14)-C(15) | 164.0(9) | C(22)-Fe(2)-C(16)-C(17) | -80.9(5) | C(20)-Fe(2)-C(18)-C(19) | -37.0(4) |
| C(21)-Fe(2)-C(14)-C(15) | -45.2(9) | C(21)-Fe(2)-C(16)-C(17) | -123.4(5) | C(13)-Fe(2)-C(18)-C(19) | 118.8(4) |
| C(17)-Fe(2)-C(14)-C(15) | 81.5(5) | C(14)-Fe(2)-C(16)-C(17) | 82.3(4) | C(21)-Fe(2)-C(18)-C(22) | 39.3(5) |
| C(16)-Fe(2)-C(14)-C(15) | 36.8(5) | C(15)-Fe(2)-C(16)-C(17) | 120.2(6) | C(17)-Fe(2)-C(18)-C(22) | -78.3(5) |
| C(20)-Fe(2)-C(14)-C(15) | -78.0(6) | C(20)-Fe(2)-C(16)-C(17) | -164.4(5) | C(16)-Fe(2)-C(18)-C(22) | -40.2(9) |

| | |
|---|---|
| C(14)-Fe(2)-C(18)-C(22) | -164.5(4) |
| C(15)-Fe(2)-C(18)-C(22) | 156.9(7) |
| C(20)-Fe(2)-C(18)-C(22) | 82.5(5) |
| C(19)-Fe(2)-C(18)-C(22) | 119.5(5) |
| C(13)-Fe(2)-C(18)-C(22) | -121.7(4) |
| C(22)-Fe(2)-C(18)-C(23) | 115.4(8) |
| C(21)-Fe(2)-C(18)-C(23) | 154.7(8) |
| C(17)-Fe(2)-C(18)-C(23) | 37.1(7) |
| C(16)-Fe(2)-C(18)-C(23) | 75.2(9) |
| C(14)-Fe(2)-C(18)-C(23) | -49.1(8) |
| C(15)-Fe(2)-C(18)-C(23) | -87.6(10) |
| C(20)-Fe(2)-C(18)-C(23) | -162.0(8) |
| C(19)-Fe(2)-C(18)-C(23) | -125.1(8) |
| C(13)-Fe(2)-C(18)-C(23) | -6.3(7) |
| C(22)-C(18)-C(19)-C(20) | 1.3(7) |
| C(23)-C(18)-C(19)-C(20) | 178.4(5) |
| Fe(2)-C(18)-C(19)-C(20) | 59.2(4) |
| C(22)-C(18)-C(19)-Fe(2) | -57.9(4) |
| C(23)-C(18)-C(19)-Fe(2) | 119.2(5) |
| C(22)-Fe(2)-C(19)-C(20) | -82.4(5) |
| C(21)-Fe(2)-C(19)-C(20) | -37.6(5) |
| C(17)-Fe(2)-C(19)-C(20) | -166.1(8) |
| C(16)-Fe(2)-C(19)-C(20) | 40.5(10) |
| C(14)-Fe(2)-C(19)-C(20) | 116.3(5) |
| C(15)-Fe(2)-C(19)-C(20) | 73.8(6) |
| C(13)-Fe(2)-C(19)-C(20) | 158.5(5) |
| C(18)-Fe(2)-C(19)-C(20) | -120.1(7) |
| C(22)-Fe(2)-C(19)-C(18) | 37.7(4) |
| C(21)-Fe(2)-C(19)-C(18) | 82.5(5) |
| C(17)-Fe(2)-C(19)-C(18) | -46.0(10) |
| C(16)-Fe(2)-C(19)-C(18) | 160.6(7) |
| C(14)-Fe(2)-C(19)-C(18) | -123.6(4) |
| C(15)-Fe(2)-C(19)-C(18) | -166.1(4) |
| C(20)-Fe(2)-C(19)-C(18) | 120.1(7) |
| C(13)-Fe(2)-C(19)-C(18) | -81.4(5) |
| C(18)-C(19)-C(20)-C(21) | -0.2(8) |
| Fe(2)-C(19)-C(20)-C(21) | 59.4(5) |
| C(18)-C(19)-C(20)-Fe(2) | -59.6(4) |
| C(22)-Fe(2)-C(20)-C(21) | -37.7(4) |
| C(17)-Fe(2)-C(20)-C(21) | 47.3(12) |
| C(16)-Fe(2)-C(20)-C(21) | 77.7(6) |
| C(14)-Fe(2)-C(20)-C(21) | 159.2(4) |
| C(15)-Fe(2)-C(20)-C(21) | 117.6(5) |
| C(19)-Fe(2)-C(20)-C(21) | -118.7(7) |
| C(13)-Fe(2)-C(20)-C(21) | -171.2(6) |
| C(18)-Fe(2)-C(20)-C(21) | -81.7(5) |
| C(22)-Fe(2)-C(20)-C(19) | 81.0(5) |
| C(21)-Fe(2)-C(20)-C(19) | 118.7(7) |
| C(17)-Fe(2)-C(20)-C(19) | 166.0(8) |
| C(16)-Fe(2)-C(20)-C(19) | -163.5(5) |
| C(14)-Fe(2)-C(20)-C(19) | -82.0(5) |
| C(15)-Fe(2)-C(20)-C(19) | -123.6(5) |
| C(13)-Fe(2)-C(20)-C(19) | -52.4(10) |
| C(18)-Fe(2)-C(20)-C(19) | 37.1(4) |
| C(19)-C(20)-C(21)-C(22) | -1.0(8) |
| Fe(2)-C(20)-C(21)-C(22) | 58.8(5) |
| C(19)-C(20)-C(21)-Fe(2) | -59.8(5) |
| C(22)-Fe(2)-C(21)-C(20) | 120.3(6) |
| C(17)-Fe(2)-C(21)-C(20) | -161.8(4) |
| C(16)-Fe(2)-C(21)-C(20) | -119.9(5) |
| C(14)-Fe(2)-C(21)-C(20) | -46.6(9) |
| C(15)-Fe(2)-C(21)-C(20) | -78.8(6) |
| C(19)-Fe(2)-C(21)-C(20) | 37.8(4) |
| C(13)-Fe(2)-C(21)-C(20) | 168.8(7) |
| C(18)-Fe(2)-C(21)-C(20) | 81.5(5) |
| C(17)-Fe(2)-C(21)-C(22) | 77.9(5) |
| C(16)-Fe(2)-C(21)-C(22) | 119.9(5) |
| C(14)-Fe(2)-C(21)-C(22) | -166.9(6) |
| C(15)-Fe(2)-C(21)-C(22) | 160.9(5) |
| C(20)-Fe(2)-C(21)-C(22) | -120.3(6) |
| C(19)-Fe(2)-C(21)-C(22) | -82.4(4) |
| C(13)-Fe(2)-C(21)-C(22) | 48.6(10) |
| C(18)-Fe(2)-C(21)-C(22) | -38.7(4) |
| C(19)-C(18)-C(22)-C(21) | -1.9(6) |
| C(23)-C(18)-C(22)-C(21) | -179.2(5) |
| Fe(2)-C(18)-C(22)-C(21) | -60.4(4) |
| C(19)-C(18)-C(22)-Fe(2) | 58.5(4) |
| C(23)-C(18)-C(22)-Fe(2) | -118.8(5) |
| C(20)-C(21)-C(22)-C(18) | 1.8(7) |
| Fe(2)-C(21)-C(22)-C(18) | 61.5(4) |
| C(20)-C(21)-C(22)-Fe(2) | -59.6(5) |
| C(21)-Fe(2)-C(22)-C(18) | -117.1(6) |
| C(17)-Fe(2)-C(22)-C(18) | 121.0(4) |
| C(16)-Fe(2)-C(22)-C(18) | 164.3(4) |
| C(14)-Fe(2)-C(22)-C(18) | 44.9(11) |
| C(15)-Fe(2)-C(22)-C(18) | -161.5(7) |
| C(20)-Fe(2)-C(22)-C(18) | -80.6(4) |
| C(19)-Fe(2)-C(22)-C(18) | -37.3(4) |
| C(13)-Fe(2)-C(22)-C(18) | 79.2(5) |
| C(17)-Fe(2)-C(22)-C(21) | -121.9(5) |
| C(16)-Fe(2)-C(22)-C(21) | -78.6(6) |
| C(14)-Fe(2)-C(22)-C(21) | 162.0(9) |
| C(15)-Fe(2)-C(22)-C(21) | -44.3(10) |
| C(20)-Fe(2)-C(22)-C(21) | 36.5(4) |
| C(19)-Fe(2)-C(22)-C(21) | 79.8(5) |
| C(13)-Fe(2)-C(22)-C(21) | -163.6(4) |
| C(18)-Fe(2)-C(22)-C(21) | 117.1(6) |
| C(19)-C(18)-C(23)-C(24) | 7.7(9) |
| C(22)-C(18)-C(23)-C(24) | -175.6(5) |
| Fe(2)-C(18)-C(23)-C(24) | 99.3(7) |
| C(18)-C(23)-C(24)-C(25) | 179.2(4) |
| C(23)-C(24)-C(25)-C(26) | 176.6(5) |
| C(23)-C(24)-C(25)-C(27) | -4.8(8) |
| C(27)-C(25)-C(26)-C(28) | 1.7(7) |
| C(24)-C(25)-C(26)-C(28) | -179.7(4) |
| C(26)-C(25)-C(27)-C(29) | -1.7(8) |
| C(24)-C(25)-C(27)-C(29) | 179.7(5) |
| C(29)-N(1)-C(28)-C(26) | -1.9(8) |
| Cr(1)-N(1)-C(28)-C(26) | 175.4(4) |
| C(25)-C(26)-C(28)-N(1) | 0.1(8) |
| C(28)-N(1)-C(29)-C(27) | 1.9(8) |
| Cr(1)-N(1)-C(29)-C(27) | -175.5(4) |
| C(25)-C(27)-C(29)-N(1) | -0.1(9) |
| C(32)-Cr(1)-C(30)-O(30) | -47(46) |

|  |  |  |  |  |  |
|---|---|---|---|---|---|
| C(33)-Cr(1)-C(30)-O(30) | 45(46) | C(54)-Fe(50)-C(51)-C(52) | -81.9(4) | C(60)-Fe(50)-C(53)-C(54) | 57.4(6) |
| C(34)-Cr(1)-C(30)-O(30) | -139(46) | C(60)-Fe(50)-C(51)-C(52) | 166.8(3) | C(51)-Fe(50)-C(53)-C(54) | -80.9(3) |
| C(31)-Cr(1)-C(30)-O(30) | 132(46) | C(55)-Fe(50)-C(51)-C(52) | -119.3(5) | C(55)-Fe(50)-C(53)-C(54) | -37.1(3) |
| N(1)-Cr(1)-C(30)-O(30) | -44(50) | C(56)-Fe(50)-C(51)-C(52) | -159.4(11) | C(56)-Fe(50)-C(53)-C(54) | 89.4(4) |
| C(30)-Cr(1)-C(31)-O(31) | -4(7) | C(57)-Fe(50)-C(51)-C(55) | 166.6(4) | C(57)-Fe(50)-C(53)-C(52) | -109.5(4) |
| C(32)-Cr(1)-C(31)-O(31) | 10(9) | C(58)-Fe(50)-C(51)-C(55) | -156.8(3) | C(58)-Fe(50)-C(53)-C(52) | -68.8(4) |
| C(33)-Cr(1)-C(31)-O(31) | 86(7) | C(59)-Fe(50)-C(51)-C(55) | -113.7(4) | C(59)-Fe(50)-C(53)-C(52) | -40.7(11) |
| C(34)-Cr(1)-C(31)-O(31) | -94(7) | C(53)-Fe(50)-C(51)-C(55) | 80.9(3) | C(54)-Fe(50)-C(53)-C(52) | 118.8(5) |
| N(1)-Cr(1)-C(31)-O(31) | 175(7) | C(52)-Fe(50)-C(51)-C(55) | 119.3(5) | C(60)-Fe(50)-C(53)-C(52) | 176.2(4) |
| C(30)-Cr(1)-C(32)-O(32) | 24(9) | C(54)-Fe(50)-C(51)-C(55) | 37.4(3) | C(51)-Fe(50)-C(53)-C(52) | 37.9(3) |
| C(33)-Cr(1)-C(32)-O(32) | -67(9) | C(60)-Fe(50)-C(51)-C(55) | -73.9(4) | C(55)-Fe(50)-C(53)-C(52) | 81.7(4) |
| C(34)-Cr(1)-C(32)-O(32) | 113(9) | C(56)-Fe(50)-C(51)-C(55) | -40.1(13) | C(56)-Fe(50)-C(53)-C(52) | -151.8(3) |
| C(31)-Cr(1)-C(32)-O(32) | 10(10) | C(55)-C(51)-C(52)-C(53) | 0.2(6) | C(52)-C(53)-C(54)-C(55) | 0.1(6) |
| N(1)-Cr(1)-C(32)-O(32) | -156(9) | Fe(50)-C(51)-C(52)-C(53) | 59.9(4) | Fe(50)-C(53)-C(54)-C(55) | 59.9(3) |
| C(30)-Cr(1)-C(33)-O(33) | 52(11) | C(55)-C(51)-C(52)-Fe(50) | -59.6(3) | C(52)-C(53)-C(54)-Fe(50) | -59.8(4) |
| C(32)-Cr(1)-C(33)-O(33) | 139(11) | C(57)-Fe(50)-C(52)-C(51) | -155.1(3) | C(57)-Fe(50)-C(54)-C(55) | 173.3(3) |
| C(34)-Cr(1)-C(33)-O(33) | -44(13) | C(58)-Fe(50)-C(52)-C(51) | -111.9(4) | C(58)-Fe(50)-C(54)-C(55) | -146.5(9) |
| C(31)-Cr(1)-C(33)-O(33) | -36(11) | C(59)-Fe(50)-C(52)-C(51) | -73.4(4) | C(59)-Fe(50)-C(54)-C(55) | 49.7(6) |
| N(1)-Cr(1)-C(33)-O(33) | -130(11) | C(53)-Fe(50)-C(52)-C(51) | 118.3(5) | C(53)-Fe(50)-C(54)-C(55) | -119.6(5) |
| C(30)-Cr(1)-C(34)-O(34) | -12(16) | C(54)-Fe(50)-C(52)-C(51) | 80.8(3) | C(52)-Fe(50)-C(54)-C(55) | -81.5(3) |
| C(32)-Cr(1)-C(34)-O(34) | -99(16) | C(60)-Fe(50)-C(52)-C(51) | -53.2(12) | C(60)-Fe(50)-C(54)-C(55) | 88.3(4) |
| C(33)-Cr(1)-C(34)-O(34) | 84(17) | C(55)-Fe(50)-C(52)-C(51) | 37.6(3) | C(51)-Fe(50)-C(54)-C(55) | -37.8(3) |
| C(31)-Cr(1)-C(34)-O(34) | 76(16) | C(56)-Fe(50)-C(52)-C(51) | 173.1(4) | C(56)-Fe(50)-C(54)-C(55) | 131.7(3) |
| N(1)-Cr(1)-C(34)-O(34) | 170(16) | C(57)-Fe(50)-C(52)-C(53) | 86.6(4) | C(57)-Fe(50)-C(54)-C(53) | -67.1(4) |
| C(78)-N(50)-Cr(50)-C(80) | 73(7) | C(58)-Fe(50)-C(52)-C(53) | 129.8(4) | C(58)-Fe(50)-C(54)-C(53) | -26.9(11) |
| C(79)-N(50)-Cr(50)-C(80) | -103(7) | C(59)-Fe(50)-C(52)-C(53) | 168.4(3) | C(59)-Fe(50)-C(54)-C(53) | 169.2(5) |
| C(78)-N(50)-Cr(50)-C(84) | 23.4(4) | C(54)-Fe(50)-C(52)-C(53) | -37.5(3) | C(52)-Fe(50)-C(54)-C(53) | 38.1(3) |
| C(79)-N(50)-Cr(50)-C(84) | -153.2(4) | C(60)-Fe(50)-C(52)-C(53) | -171.4(9) | C(60)-Fe(50)-C(54)-C(53) | -152.2(4) |
| C(78)-N(50)-Cr(50)-C(82) | 114.5(4) | C(51)-Fe(50)-C(52)-C(53) | -118.3(5) | C(51)-Fe(50)-C(54)-C(53) | 81.7(4) |
| C(79)-N(50)-Cr(50)-C(82) | -62.1(4) | C(55)-Fe(50)-C(52)-C(53) | -80.7(4) | C(55)-Fe(50)-C(54)-C(53) | 119.6(5) |
| C(78)-N(50)-Cr(50)-C(83) | -156.8(4) | C(56)-Fe(50)-C(52)-C(53) | 54.9(6) | C(56)-Fe(50)-C(54)-C(53) | -108.8(4) |
| C(79)-N(50)-Cr(50)-C(83) | 26.6(4) | C(51)-C(52)-C(53)-C(54) | -0.2(6) | C(53)-C(54)-C(55)-C(51) | 0.0(6) |
| C(78)-N(50)-Cr(50)-C(81) | -67.7(4) | Fe(50)-C(52)-C(53)-C(54) | 60.0(4) | Fe(50)-C(54)-C(55)-C(51) | 59.5(3) |
| C(79)-N(50)-Cr(50)-C(81) | 115.7(4) | C(51)-C(52)-C(53)-Fe(50) | -60.3(4) | C(53)-C(54)-C(55)-Fe(50) | -59.5(4) |
| C(57)-Fe(50)-C(51)-C(52) | 47.3(6) | C(57)-Fe(50)-C(53)-C(54) | 131.7(3) | C(52)-C(51)-C(55)-C(54) | -0.1(6) |
| C(58)-Fe(50)-C(51)-C(52) | 83.9(4) | C(58)-Fe(50)-C(53)-C(54) | 172.3(3) | Fe(50)-C(51)-C(55)-C(54) | -59.6(3) |
| C(59)-Fe(50)-C(51)-C(52) | 127.0(4) | C(59)-Fe(50)-C(53)-C(54) | -159.5(9) | C(52)-C(51)-C(55)-Fe(50) | 59.4(4) |
| C(53)-Fe(50)-C(51)-C(52) | -38.4(3) | C(52)-Fe(50)-C(53)-C(54) | -118.8(5) | C(57)-Fe(50)-C(55)-C(54) | -25.7(11) |

| | |
|---|---|
| C(58)-Fe(50)-C(55)-C(54) | 164.8(4) |
| C(59)-Fe(50)-C(55)-C(54) | -156.4(3) |
| C(53)-Fe(50)-C(55)-C(54) | 37.3(3) |
| C(52)-Fe(50)-C(55)-C(54) | 81.5(3) |
| C(60)-Fe(50)-C(55)-C(54) | -111.8(3) |
| C(51)-Fe(50)-C(55)-C(54) | 118.9(4) |
| C(56)-Fe(50)-C(55)-C(54) | -69.8(4) |
| C(57)-Fe(50)-C(55)-C(51) | -144.6(10) |
| C(58)-Fe(50)-C(55)-C(51) | 45.9(6) |
| C(59)-Fe(50)-C(55)-C(51) | 84.7(4) |
| C(53)-Fe(50)-C(55)-C(51) | -81.6(4) |
| C(52)-Fe(50)-C(55)-C(51) | -37.4(3) |
| C(54)-Fe(50)-C(55)-C(51) | -118.9(4) |
| C(60)-Fe(50)-C(55)-C(51) | 129.3(3) |
| C(56)-Fe(50)-C(55)-C(51) | 171.3(3) |
| C(58)-Fe(50)-C(56)-C(57) | -38.3(3) |
| C(59)-Fe(50)-C(56)-C(57) | -81.8(3) |
| C(53)-Fe(50)-C(56)-C(57) | 84.1(4) |
| C(52)-Fe(50)-C(56)-C(57) | 47.3(5) |
| C(54)-Fe(50)-C(56)-C(57) | 127.3(3) |
| C(60)-Fe(50)-C(56)-C(57) | -119.0(4) |
| C(51)-Fe(50)-C(56)-C(57) | -159.0(11) |
| C(55)-Fe(50)-C(56)-C(57) | 167.1(3) |
| C(57)-Fe(50)-C(56)-C(60) | 119.0(4) |
| C(58)-Fe(50)-C(56)-C(60) | 80.6(3) |
| C(59)-Fe(50)-C(56)-C(60) | 37.2(3) |
| C(53)-Fe(50)-C(56)-C(60) | -156.9(3) |
| C(52)-Fe(50)-C(56)-C(60) | 166.2(4) |
| C(54)-Fe(50)-C(56)-C(60) | -113.7(3) |
| C(51)-Fe(50)-C(56)-C(60) | -40.0(13) |
| C(55)-Fe(50)-C(56)-C(60) | -73.9(4) |
| C(57)-Fe(50)-C(56)-C(61) | -122.0(6) |
| C(58)-Fe(50)-C(56)-C(61) | -160.3(6) |
| C(59)-Fe(50)-C(56)-C(61) | 156.3(5) |
| C(53)-Fe(50)-C(56)-C(61) | -37.9(5) |
| C(52)-Fe(50)-C(56)-C(61) | -74.7(7) |
| C(54)-Fe(50)-C(56)-C(61) | 5.4(5) |
| C(60)-Fe(50)-C(56)-C(61) | 119.1(6) |
| C(51)-Fe(50)-C(56)-C(61) | 79.0(13) |
| C(55)-Fe(50)-C(56)-C(61) | 45.2(6) |
| C(60)-C(56)-C(57)-C(58) | 1.2(5) |
| C(61)-C(56)-C(57)-C(58) | -179.2(4) |
| Fe(50)-C(56)-C(57)-C(58) | 59.7(3) |
| C(60)-C(56)-C(57)-Fe(50) | -58.5(3) |
| C(61)-C(56)-C(57)-Fe(50) | 121.1(5) |
| C(58)-Fe(50)-C(57)-C(56) | 118.9(5) |
| C(59)-Fe(50)-C(57)-C(56) | 81.6(3) |
| C(53)-Fe(50)-C(57)-C(56) | -112.5(3) |
| C(52)-Fe(50)-C(57)-C(56) | -155.3(3) |
| C(54)-Fe(50)-C(57)-C(56) | -74.3(4) |
| C(60)-Fe(50)-C(57)-C(56) | 37.7(3) |
| C(51)-Fe(50)-C(57)-C(56) | 173.1(4) |
| C(55)-Fe(50)-C(57)-C(56) | -53.3(11) |
| C(59)-Fe(50)-C(57)-C(58) | -37.3(3) |
| C(53)-Fe(50)-C(57)-C(58) | 128.6(4) |
| C(52)-Fe(50)-C(57)-C(58) | 85.8(4) |
| C(54)-Fe(50)-C(57)-C(58) | 166.8(3) |
| C(60)-Fe(50)-C(57)-C(58) | -81.2(4) |
| C(51)-Fe(50)-C(57)-C(58) | 54.2(6) |
| C(55)-Fe(50)-C(57)-C(58) | -172.2(9) |
| C(56)-Fe(50)-C(57)-C(58) | -118.9(5) |
| C(56)-C(57)-C(58)-C(59) | -1.2(6) |
| Fe(50)-C(57)-C(58)-C(59) | 59.6(4) |
| C(56)-C(57)-C(58)-Fe(50) | -60.8(3) |
| C(57)-Fe(50)-C(58)-C(59) | -119.3(5) |
| C(53)-Fe(50)-C(58)-C(59) | 169.8(4) |
| C(52)-Fe(50)-C(58)-C(59) | 130.5(4) |
| C(54)-Fe(50)-C(58)-C(59) | -168.7(9) |
| C(60)-Fe(50)-C(58)-C(59) | -38.1(3) |
| C(51)-Fe(50)-C(58)-C(59) | 88.6(4) |
| C(55)-Fe(50)-C(58)-C(59) | 57.4(6) |
| C(56)-Fe(50)-C(58)-C(59) | -81.7(4) |
| C(59)-Fe(50)-C(58)-C(57) | 119.3(5) |
| C(53)-Fe(50)-C(58)-C(57) | -71.0(4) |
| C(52)-Fe(50)-C(58)-C(57) | -110.2(4) |
| C(54)-Fe(50)-C(58)-C(57) | -49.4(11) |
| C(60)-Fe(50)-C(58)-C(57) | 81.2(3) |
| C(51)-Fe(50)-C(58)-C(57) | -152.1(3) |
| C(55)-Fe(50)-C(58)-C(57) | 176.7(4) |
| C(56)-Fe(50)-C(58)-C(57) | 37.6(3) |
| C(57)-C(58)-C(59)-C(60) | 0.7(6) |
| Fe(50)-C(58)-C(59)-C(60) | 59.9(3) |
| C(57)-C(58)-C(59)-Fe(50) | -59.2(4) |
| C(57)-Fe(50)-C(59)-C(58) | 38.1(3) |
| C(53)-Fe(50)-C(59)-C(58) | -35.3(11) |
| C(52)-Fe(50)-C(59)-C(58) | -67.9(5) |
| C(54)-Fe(50)-C(59)-C(58) | 174.2(4) |
| C(60)-Fe(50)-C(59)-C(58) | 118.6(5) |
| C(51)-Fe(50)-C(59)-C(58) | -108.7(4) |
| C(55)-Fe(50)-C(59)-C(58) | -151.6(3) |
| C(56)-Fe(50)-C(59)-C(58) | 81.7(4) |
| C(57)-Fe(50)-C(59)-C(60) | -80.5(3) |
| C(58)-Fe(50)-C(59)-C(60) | -118.6(5) |
| C(53)-Fe(50)-C(59)-C(60) | -153.9(9) |
| C(52)-Fe(50)-C(59)-C(60) | 173.5(3) |
| C(54)-Fe(50)-C(59)-C(60) | 55.6(6) |
| C(51)-Fe(50)-C(59)-C(60) | 132.7(3) |
| C(55)-Fe(50)-C(59)-C(60) | 89.8(4) |
| C(56)-Fe(50)-C(59)-C(60) | -36.9(3) |
| C(57)-C(56)-C(60)-C(59) | -0.8(5) |
| C(61)-C(56)-C(60)-C(59) | 179.6(4) |
| Fe(50)-C(56)-C(60)-C(59) | -58.9(3) |
| C(57)-C(56)-C(60)-Fe(50) | 58.2(3) |
| C(61)-C(56)-C(60)-Fe(50) | -121.4(5) |
| C(58)-C(59)-C(60)-C(56) | 0.0(6) |
| Fe(50)-C(59)-C(60)-C(56) | 59.8(3) |
| C(58)-C(59)-C(60)-Fe(50) | -59.7(3) |
| C(57)-Fe(50)-C(60)-C(56) | -37.8(3) |
| C(58)-Fe(50)-C(60)-C(56) | -82.5(3) |
| C(59)-Fe(50)-C(60)-C(56) | -120.3(5) |
| C(53)-Fe(50)-C(60)-C(56) | 46.8(6) |
| C(52)-Fe(50)-C(60)-C(56) | -145.0(10) |
| C(54)-Fe(50)-C(60)-C(56) | 85.7(4) |
| C(51)-Fe(50)-C(60)-C(56) | 171.4(3) |

| | |
|---|---|
| C(55)-Fe(50)-C(60)-C(56) | 129.3(3) |
| C(57)-Fe(50)-C(60)-C(59) | 82.5(4) |
| C(58)-Fe(50)-C(60)-C(59) | 37.8(3) |
| C(53)-Fe(50)-C(60)-C(59) | 167.0(4) |
| C(52)-Fe(50)-C(60)-C(59) | -24.7(12) |
| C(54)-Fe(50)-C(60)-C(59) | -154.1(3) |
| C(51)-Fe(50)-C(60)-C(59) | -68.4(4) |
| C(55)-Fe(50)-C(60)-C(59) | -110.4(4) |
| C(56)-Fe(50)-C(60)-C(59) | 120.3(5) |
| C(57)-C(56)-C(61)-C(62) | 12.4(8) |
| C(60)-C(56)-C(61)-C(62) | -168.1(5) |
| Fe(50)-C(56)-C(61)-C(62) | 102.7(6) |
| C(56)-C(61)-C(62)-C(63) | 179.7(4) |
| C(61)-C(62)-C(63)-C(67) | -9.8(8) |
| C(61)-C(62)-C(63)-C(64) | 170.5(5) |
| C(61)-C(62)-C(63)-Fe(51) | -101.3(6) |
| C(71)-Fe(51)-C(63)-C(67) | 158.9(6) |
| C(66)-Fe(51)-C(63)-C(67) | 38.1(3) |
| C(64)-Fe(51)-C(63)-C(67) | 119.5(4) |
| C(70)-Fe(51)-C(63)-C(67) | -43.6(7) |
| C(69)-Fe(51)-C(63)-C(67) | -79.7(4) |
| C(65)-Fe(51)-C(63)-C(67) | 81.9(3) |
| C(72)-Fe(51)-C(63)-C(67) | -164.9(3) |
| C(68)-Fe(51)-C(63)-C(67) | -122.2(3) |
| C(71)-Fe(51)-C(63)-C(64) | 39.4(8) |
| C(66)-Fe(51)-C(63)-C(64) | -81.4(3) |
| C(70)-Fe(51)-C(63)-C(64) | -163.0(5) |
| C(67)-Fe(51)-C(63)-C(64) | -119.5(4) |
| C(69)-Fe(51)-C(63)-C(64) | 160.8(3) |
| C(65)-Fe(51)-C(63)-C(64) | -37.6(3) |
| C(72)-Fe(51)-C(63)-C(64) | 75.6(4) |
| C(68)-Fe(51)-C(63)-C(64) | 118.4(3) |
| C(71)-Fe(51)-C(63)-C(62) | -78.4(9) |
| C(66)-Fe(51)-C(63)-C(62) | 160.8(6) |
| C(64)-Fe(51)-C(63)-C(62) | -117.8(6) |
| C(70)-Fe(51)-C(63)-C(62) | 79.1(8) |
| C(67)-Fe(51)-C(63)-C(62) | 122.7(6) |
| C(69)-Fe(51)-C(63)-C(62) | 43.0(6) |
| C(65)-Fe(51)-C(63)-C(62) | -155.4(6) |
| C(72)-Fe(51)-C(63)-C(62) | -42.2(6) |
| C(68)-Fe(51)-C(63)-C(62) | 0.5(5) |
| C(67)-C(63)-C(64)-C(65) | 1.9(6) |
| C(62)-C(63)-C(64)-C(65) | -178.3(4) |
| Fe(51)-C(63)-C(64)-C(65) | 60.2(4) |
| C(67)-C(63)-C(64)-Fe(51) | -58.3(3) |
| C(62)-C(63)-C(64)-Fe(51) | 121.5(5) |
| C(71)-Fe(51)-C(64)-C(65) | 75.2(4) |
| C(66)-Fe(51)-C(64)-C(65) | -37.6(3) |
| C(70)-Fe(51)-C(64)-C(65) | 42.3(8) |
| C(67)-Fe(51)-C(64)-C(65) | -81.7(4) |
| C(69)-Fe(51)-C(64)-C(65) | -166.8(6) |
| C(72)-Fe(51)-C(64)-C(65) | 117.1(4) |
| C(68)-Fe(51)-C(64)-C(65) | 159.9(3) |
| C(63)-Fe(51)-C(64)-C(65) | -119.0(5) |
| C(71)-Fe(51)-C(64)-C(63) | -165.8(3) |
| C(66)-Fe(51)-C(64)-C(63) | 81.4(3) |
| C(70)-Fe(51)-C(64)-C(63) | 161.3(6) |
| C(67)-Fe(51)-C(64)-C(63) | 37.3(3) |
| C(69)-Fe(51)-C(64)-C(63) | -47.8(7) |
| C(65)-Fe(51)-C(64)-C(63) | 119.0(5) |
| C(72)-Fe(51)-C(64)-C(63) | -123.9(3) |
| C(68)-Fe(51)-C(64)-C(63) | -81.0(4) |
| C(63)-C(64)-C(65)-C(66) | -1.5(6) |
| Fe(51)-C(64)-C(65)-C(66) | 59.1(4) |
| C(63)-C(64)-C(65)-Fe(51) | -60.6(4) |
| C(71)-Fe(51)-C(65)-C(64) | -123.1(4) |
| C(66)-Fe(51)-C(65)-C(64) | 119.4(5) |
| C(70)-Fe(51)-C(65)-C(64) | -163.8(4) |
| C(67)-Fe(51)-C(65)-C(64) | 81.4(4) |
| C(69)-Fe(51)-C(65)-C(64) | 165.2(6) |
| C(72)-Fe(51)-C(65)-C(64) | -81.1(4) |
| C(68)-Fe(51)-C(65)-C(64) | -48.4(7) |
| C(63)-Fe(51)-C(65)-C(64) | 37.9(3) |
| C(71)-Fe(51)-C(65)-C(66) | 117.5(4) |
| C(64)-Fe(51)-C(65)-C(66) | -119.4(5) |
| C(70)-Fe(51)-C(65)-C(66) | 76.8(4) |
| C(67)-Fe(51)-C(65)-C(66) | -38.0(3) |
| C(69)-Fe(51)-C(65)-C(66) | 45.8(8) |
| C(72)-Fe(51)-C(65)-C(66) | 159.5(4) |
| C(68)-Fe(51)-C(65)-C(66) | -167.8(5) |
| C(63)-Fe(51)-C(65)-C(66) | -81.5(4) |
| C(64)-C(65)-C(66)-C(67) | 0.5(6) |
| Fe(51)-C(65)-C(66)-C(67) | 59.7(4) |
| C(64)-C(65)-C(66)-Fe(51) | -59.2(4) |
| C(71)-Fe(51)-C(66)-C(65) | -80.1(4) |
| C(64)-Fe(51)-C(66)-C(65) | 37.4(3) |
| C(70)-Fe(51)-C(66)-C(65) | -121.8(4) |
| C(67)-Fe(51)-C(66)-C(65) | 119.0(5) |
| C(69)-Fe(51)-C(66)-C(65) | -163.1(3) |
| C(72)-Fe(51)-C(66)-C(65) | -47.3(7) |
| C(68)-Fe(51)-C(66)-C(65) | 165.3(6) |
| C(63)-Fe(51)-C(66)-C(65) | 81.3(4) |
| C(71)-Fe(51)-C(66)-C(67) | 161.0(3) |
| C(64)-Fe(51)-C(66)-C(67) | -81.6(3) |
| C(70)-Fe(51)-C(66)-C(67) | 119.3(4) |
| C(69)-Fe(51)-C(66)-C(67) | 77.9(4) |
| C(65)-Fe(51)-C(66)-C(67) | -119.0(5) |
| C(72)-Fe(51)-C(66)-C(67) | -166.3(5) |
| C(68)-Fe(51)-C(66)-C(67) | 46.3(8) |
| C(63)-Fe(51)-C(66)-C(67) | -37.6(3) |
| C(64)-C(63)-C(67)-C(66) | -1.6(6) |
| C(62)-C(63)-C(67)-C(66) | 178.7(5) |
| Fe(51)-C(63)-C(67)-C(66) | -59.7(4) |
| C(64)-C(63)-C(67)-Fe(51) | 58.1(3) |
| C(62)-C(63)-C(67)-Fe(51) | -121.6(5) |
| C(65)-C(66)-C(67)-C(63) | 0.7(6) |
| Fe(51)-C(66)-C(67)-C(63) | 60.5(3) |
| C(65)-C(66)-C(67)-Fe(51) | -59.9(4) |
| C(71)-Fe(51)-C(67)-C(63) | -163.3(5) |
| C(66)-Fe(51)-C(67)-C(63) | -118.8(5) |
| C(64)-Fe(51)-C(67)-C(63) | -37.6(3) |
| C(70)-Fe(51)-C(67)-C(63) | 162.1(3) |
| C(69)-Fe(51)-C(67)-C(63) | 119.3(3) |
| C(65)-Fe(51)-C(67)-C(63) | -81.1(3) |

| | |
|---|---|
| C(72)-Fe(51)-C(67)-C(63) | 43.0(8) |
| C(68)-Fe(51)-C(67)-C(63) | 77.7(4) |
| C(71)-Fe(51)-C(67)-C(66) | -44.5(7) |
| C(64)-Fe(51)-C(67)-C(66) | 81.2(4) |
| C(70)-Fe(51)-C(67)-C(66) | -79.1(4) |
| C(69)-Fe(51)-C(67)-C(66) | -121.8(3) |
| C(65)-Fe(51)-C(67)-C(66) | 37.7(3) |
| C(72)-Fe(51)-C(67)-C(66) | 161.8(6) |
| C(68)-Fe(51)-C(67)-C(66) | -163.5(3) |
| C(63)-Fe(51)-C(67)-C(66) | 118.8(5) |
| C(71)-Fe(51)-C(68)-C(69) | -80.9(3) |
| C(66)-Fe(51)-C(68)-C(69) | 41.9(8) |
| C(64)-Fe(51)-C(68)-C(69) | 161.6(3) |
| C(70)-Fe(51)-C(68)-C(69) | -37.6(3) |
| C(67)-Fe(51)-C(68)-C(69) | 77.0(4) |
| C(65)-Fe(51)-C(68)-C(69) | -163.4(5) |
| C(72)-Fe(51)-C(68)-C(69) | -118.6(4) |
| C(63)-Fe(51)-C(68)-C(69) | 118.8(3) |
| C(71)-Fe(51)-C(68)-C(72) | 37.7(3) |
| C(66)-Fe(51)-C(68)-C(72) | 160.5(7) |
| C(64)-Fe(51)-C(68)-C(72) | -79.8(4) |
| C(70)-Fe(51)-C(68)-C(72) | 81.0(4) |
| C(67)-Fe(51)-C(68)-C(72) | -164.4(3) |
| C(69)-Fe(51)-C(68)-C(72) | 118.6(4) |
| C(65)-Fe(51)-C(68)-C(72) | -44.8(7) |
| C(63)-Fe(51)-C(68)-C(72) | -122.6(3) |
| C(71)-Fe(51)-C(68)-C(73) | 156.1(5) |
| C(66)-Fe(51)-C(68)-C(73) | -81.1(8) |
| C(64)-Fe(51)-C(68)-C(73) | 38.6(5) |
| C(70)-Fe(51)-C(68)-C(73) | -160.6(5) |
| C(67)-Fe(51)-C(68)-C(73) | -46.0(5) |
| C(69)-Fe(51)-C(68)-C(73) | -123.0(6) |
| C(65)-Fe(51)-C(68)-C(73) | 73.6(7) |
| C(72)-Fe(51)-C(68)-C(73) | 118.4(6) |
| C(63)-Fe(51)-C(68)-C(73) | -4.2(5) |
| C(72)-C(68)-C(69)-C(70) | 0.3(6) |
| C(73)-C(68)-C(69)-C(70) | 177.5(5) |
| Fe(51)-C(68)-C(69)-C(70) | 59.3(4) |
| C(72)-C(68)-C(69)-Fe(51) | -59.0(3) |
| C(73)-C(68)-C(69)-Fe(51) | 118.2(5) |
| C(71)-Fe(51)-C(69)-C(68) | 82.4(4) |
| C(66)-Fe(51)-C(69)-C(68) | -164.9(3) |
| C(64)-Fe(51)-C(69)-C(68) | -45.6(7) |
| C(70)-Fe(51)-C(69)-C(68) | 119.5(5) |
| C(67)-Fe(51)-C(69)-C(68) | -122.6(3) |
| C(65)-Fe(51)-C(69)-C(68) | 160.7(6) |
| C(72)-Fe(51)-C(69)-C(68) | 38.4(3) |
| C(63)-Fe(51)-C(69)-C(68) | -80.5(4) |
| C(71)-Fe(51)-C(69)-C(70) | -37.2(4) |
| C(66)-Fe(51)-C(69)-C(70) | 75.6(5) |
| C(64)-Fe(51)-C(69)-C(70) | -165.1(6) |
| C(67)-Fe(51)-C(69)-C(70) | 117.9(4) |
| C(65)-Fe(51)-C(69)-C(70) | 41.2(8) |
| C(72)-Fe(51)-C(69)-C(70) | -81.1(4) |
| C(68)-Fe(51)-C(69)-C(70) | -119.5(5) |
| C(63)-Fe(51)-C(69)-C(70) | 160.0(4) |
| C(68)-C(69)-C(70)-C(71) | -0.7(6) |
| Fe(51)-C(69)-C(70)-C(71) | 59.2(4) |
| C(68)-C(69)-C(70)-Fe(51) | -59.9(3) |
| C(66)-Fe(51)-C(70)-C(71) | 117.1(4) |
| C(64)-Fe(51)-C(70)-C(71) | 44.3(8) |
| C(67)-Fe(51)-C(70)-C(71) | 159.3(4) |
| C(69)-Fe(51)-C(70)-C(71) | -119.6(5) |
| C(65)-Fe(51)-C(70)-C(71) | 75.7(4) |
| C(72)-Fe(51)-C(70)-C(71) | -37.8(3) |
| C(68)-Fe(51)-C(70)-C(71) | -82.2(4) |
| C(63)-Fe(51)-C(70)-C(71) | -169.1(5) |
| C(71)-Fe(51)-C(70)-C(69) | 119.6(5) |
| C(66)-Fe(51)-C(70)-C(69) | -123.3(4) |
| C(64)-Fe(51)-C(70)-C(69) | 163.8(6) |
| C(67)-Fe(51)-C(70)-C(69) | -81.2(4) |
| C(65)-Fe(51)-C(70)-C(69) | -164.7(4) |
| C(72)-Fe(51)-C(70)-C(69) | 81.8(4) |
| C(68)-Fe(51)-C(70)-C(69) | 37.3(3) |
| C(63)-Fe(51)-C(70)-C(69) | -49.5(7) |
| C(69)-C(70)-C(71)-C(72) | 0.8(6) |
| Fe(51)-C(70)-C(71)-C(72) | 60.0(4) |
| C(69)-C(70)-C(71)-Fe(51) | -59.3(4) |
| C(66)-Fe(51)-C(71)-C(70) | -80.5(4) |
| C(64)-Fe(51)-C(71)-C(70) | -163.1(3) |
| C(67)-Fe(51)-C(71)-C(70) | -48.5(7) |
| C(69)-Fe(51)-C(71)-C(70) | 37.7(3) |
| C(65)-Fe(51)-C(71)-C(70) | -122.4(4) |
| C(72)-Fe(51)-C(71)-C(70) | 119.4(5) |
| C(68)-Fe(51)-C(71)-C(70) | 81.2(4) |
| C(63)-Fe(51)-C(71)-C(70) | 167.1(6) |
| C(66)-Fe(51)-C(71)-C(72) | 160.2(3) |
| C(64)-Fe(51)-C(71)-C(72) | 77.5(4) |
| C(70)-Fe(51)-C(71)-C(72) | -119.4(5) |
| C(67)-Fe(51)-C(71)-C(72) | -167.8(5) |
| C(69)-Fe(51)-C(71)-C(72) | -81.7(4) |
| C(65)-Fe(51)-C(71)-C(72) | 118.3(4) |
| C(68)-Fe(51)-C(71)-C(72) | -38.1(3) |
| C(63)-Fe(51)-C(71)-C(72) | 47.7(8) |
| C(70)-C(71)-C(72)-C(68) | -0.6(6) |
| Fe(51)-C(71)-C(72)-C(68) | 59.4(3) |
| C(70)-C(71)-C(72)-Fe(51) | -60.0(4) |
| C(69)-C(68)-C(72)-C(71) | 0.2(6) |
| C(73)-C(68)-C(72)-C(71) | -177.1(4) |
| Fe(51)-C(68)-C(72)-C(71) | -58.9(4) |
| C(69)-C(68)-C(72)-Fe(51) | 59.1(3) |
| C(73)-C(68)-C(72)-Fe(51) | -118.2(5) |
| C(66)-Fe(51)-C(72)-C(71) | -45.7(7) |
| C(64)-Fe(51)-C(72)-C(71) | -121.7(4) |
| C(70)-Fe(51)-C(72)-C(71) | 37.3(3) |
| C(67)-Fe(51)-C(72)-C(71) | 164.2(6) |
| C(69)-Fe(51)-C(72)-C(71) | 81.2(4) |
| C(65)-Fe(51)-C(72)-C(71) | -79.5(4) |
| C(68)-Fe(51)-C(72)-C(71) | 119.0(5) |
| C(63)-Fe(51)-C(72)-C(71) | -163.1(3) |
| C(71)-Fe(51)-C(72)-C(68) | -119.0(5) |
| C(66)-Fe(51)-C(72)-C(68) | -164.7(5) |
| C(64)-Fe(51)-C(72)-C(68) | 119.3(3) |
| C(70)-Fe(51)-C(72)-C(68) | -81.7(3) |

| | |
|---|---|
| C(67)-Fe(51)-C(72)-C(68) | 45.2(8) |
| C(69)-Fe(51)-C(72)-C(68) | -37.7(3) |
| C(65)-Fe(51)-C(72)-C(68) | 161.5(3) |
| C(63)-Fe(51)-C(72)-C(68) | 77.9(4) |
| C(69)-C(68)-C(73)-C(74) | 10.5(8) |
| C(72)-C(68)-C(73)-C(74) | -172.8(5) |
| Fe(51)-C(68)-C(73)-C(74) | 100.2(5) |
| C(68)-C(73)-C(74)-C(75) | -178.3(4) |
| C(73)-C(74)-C(75)-C(77) | 5.5(8) |
| C(73)-C(74)-C(75)-C(76) | -174.4(5) |
| C(77)-C(75)-C(76)-C(78) | -0.5(7) |
| C(74)-C(75)-C(76)-C(78) | 179.4(5) |
| C(76)-C(75)-C(77)-C(79) | 1.5(7) |
| C(74)-C(75)-C(77)-C(79) | -178.4(5) |
| C(79)-N(50)-C(78)-C(76) | 0.7(7) |
| Cr(50)-N(50)-C(78)-C(76) | -176.2(4) |
| C(75)-C(76)-C(78)-N(50) | -0.6(8) |
| C(78)-N(50)-C(79)-C(77) | 0.4(7) |
| Cr(50)-N(50)-C(79)-C(77) | 177.4(4) |
| C(75)-C(77)-C(79)-N(50) | -1.6(8) |
| C(84)-Cr(50)-C(80)-O(80) | -35(13) |
| C(82)-Cr(50)-C(80)-O(80) | -126(13) |
| C(83)-Cr(50)-C(80)-O(80) | 145(13) |
| C(81)-Cr(50)-C(80)-O(80) | 56(13) |
| N(50)-Cr(50)-C(80)-O(80) | -85(16) |
| C(80)-Cr(50)-C(81)-O(81) | 11(6) |
| C(84)-Cr(50)-C(81)-O(81) | 98(6) |
| C(82)-Cr(50)-C(81)-O(81) | -50(10) |
| C(83)-Cr(50)-C(81)-O(81) | -78(6) |
| N(50)-Cr(50)-C(81)-O(81) | -171(6) |
| C(80)-Cr(50)-C(82)-O(82) | -11(20) |
| C(84)-Cr(50)-C(82)-O(82) | -99(20) |
| C(83)-Cr(50)-C(82)-O(82) | 77(20) |
| C(81)-Cr(50)-C(82)-O(82) | 49(23) |
| N(50)-Cr(50)-C(82)-O(82) | 170(100) |
| C(80)-Cr(50)-C(83)-O(88) | 5(10) |
| C(84)-Cr(50)-C(83)-O(88) | 4(12) |
| C(82)-Cr(50)-C(83)-O(88) | -85(10) |
| C(81)-Cr(50)-C(83)-O(88) | 93(10) |
| N(50)-Cr(50)-C(83)-O(88) | -174(9) |
| C(80)-Cr(50)-C(84)-O(84) | 16(7) |
| C(82)-Cr(50)-C(84)-O(84) | 106(7) |
| C(83)-Cr(50)-C(84)-O(84) | 17(9) |
| C(81)-Cr(50)-C(84)-O(84) | -73(7) |
| N(50)-Cr(50)-C(84)-O(84) | -166(7) |

---

Symmetry transformations used to generate equivalent atoms:

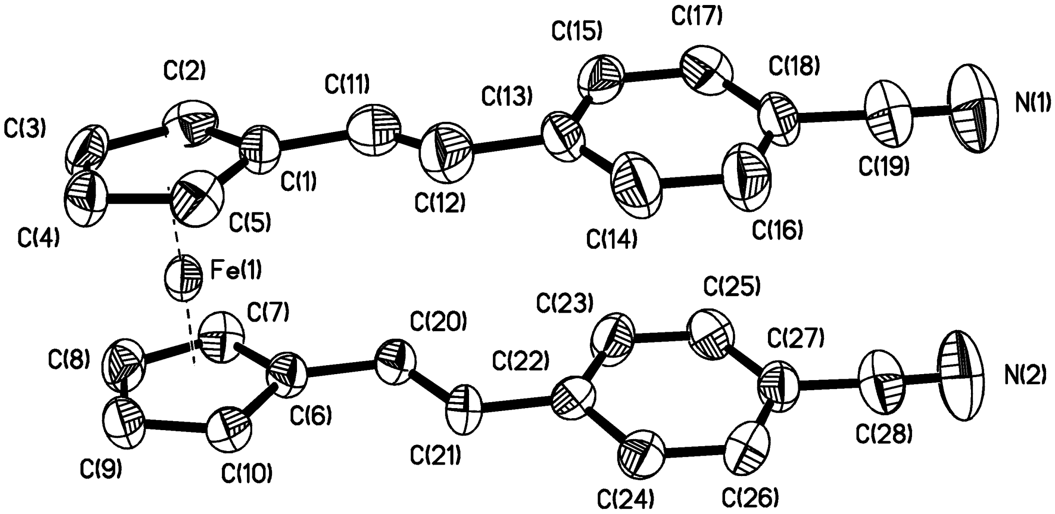

C(2)
C(3)
C(11)
C(13)
C(15)
C(17)
C(18)
N(1)
C(1)
C(12)
C(19)
C(4)
C(5)
C(14)
C(16)
Fe(1)
C(7)
C(20)
C(23)
C(25)
C(8)
C(27)
C(22)
N(2)
C(6)
C(28)
C(21)
C(9)
C(10)
C(24)
C(26)

**Table 1**. Crystal data and structure refinement for str94m.

| | | |
|---|---|---|
| Identification code | str94m | |
| Empirical formula | C28 H20 Fe N2 | |
| Formula weight | 440.31 | |
| Temperature | 293(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | P2(1) | |
| Unit cell dimensions | a = 6.2114(4) Å | $\alpha$= 90°. |
| | b = 14.0877(8) Å | $\beta$= 102.3550(10)°. |
| | c = 12.1250(7) Å | $\gamma$ = 90°. |
| Volume | 1036.42(11) Å$^3$ | |
| Z | 2 | |
| Density (calculated) | 1.411 Mg/m$^3$ | |
| Absorption coefficient | 0.746 mm$^{-1}$ | |
| F(000) | 456 | |
| Crystal size | 0.49 x 0.44 x 0.02 mm$^3$ | |
| Theta range for data collection | 1.72 to 30.53°. | |
| Index ranges | -8<=h<=8, -18<=k<=20, -16<=l<=17 | |
| Reflections collected | 8466 | |
| Independent reflections | 4917 [R(int) = 0.0313] | |
| Completeness to theta = 30.53° | 96.9 % | |
| Absorption correction | None | |
| Refinement method | Full-matrix least-squares on F$^2$ | |
| Data / restraints / parameters | 4917 / 1 / 281 | |
| Goodness-of-fit on F$^2$ | 0.876 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0422, wR2 = 0.0720 | |
| R indices (all data) | R1 = 0.0867, wR2 = 0.0805 | |
| Absolute structure parameter | 0.73(2) | |
| Largest diff. peak and hole | 0.428 and -0.246 e.Å$^{-3}$ | |

**Table 2.** Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) for str94m. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| Fe(1) | 577(1) | 6866(1) | 7293(1) | 34(1) |
| C(1) | 639(6) | 5666(2) | 6329(3) | 42(1) |
| N(1) | 6162(7) | 5542(3) | -108(3) | 94(1) |
| N(2) | 7749(6) | 8231(3) | 281(3) | 97(1) |
| C(2) | 1589(6) | 5487(2) | 7474(3) | 47(1) |
| C(3) | -10(7) | 5659(3) | 8120(3) | 47(1) |
| C(4) | -1942(6) | 5956(2) | 7391(3) | 47(1) |
| C(5) | -1561(5) | 5967(2) | 6282(3) | 44(1) |
| C(6) | 2317(5) | 7937(2) | 6743(3) | 39(1) |
| C(7) | 3280(5) | 7695(2) | 7876(3) | 44(1) |
| C(8) | 1688(6) | 7851(2) | 8527(3) | 49(1) |
| C(9) | -254(7) | 8177(3) | 7805(3) | 50(1) |
| C(10) | 120(6) | 8234(2) | 6696(3) | 41(1) |
| C(11) | 1833(7) | 5546(2) | 5411(3) | 55(1) |
| C(12) | 1058(7) | 5700(3) | 4367(3) | 58(1) |
| C(13) | 2246(6) | 5614(2) | 3424(3) | 48(1) |
| C(14) | 1213(6) | 5972(3) | 2389(3) | 60(1) |
| C(15) | 4248(7) | 5192(3) | 3514(3) | 52(1) |
| C(16) | 2202(6) | 5951(3) | 1479(3) | 60(1) |
| C(17) | 5294(6) | 5154(3) | 2594(3) | 51(1) |
| C(18) | 4246(7) | 5550(3) | 1580(3) | 45(1) |
| C(19) | 5298(7) | 5550(3) | 625(3) | 63(1) |
| C(20) | 3439(5) | 7882(2) | 5793(3) | 40(1) |
| C(21) | 2674(5) | 8232(2) | 4767(3) | 37(1) |
| C(22) | 3780(6) | 8191(2) | 3809(3) | 39(1) |
| C(23) | 5859(6) | 7820(2) | 3875(3) | 51(1) |
| C(24) | 2709(6) | 8574(2) | 2776(3) | 44(1) |
| C(25) | 6851(6) | 7827(3) | 2963(3) | 51(1) |
| C(26) | 3669(6) | 8577(3) | 1845(3) | 47(1) |
| C(27) | 5755(6) | 8204(3) | 1940(3) | 45(1) |
| C(28) | 6812(7) | 8230(3) | 995(3) | 60(1) |

**Table 3**. Bond lengths [Å] and angles [°] for str94m.

| | | | |
|---|---|---|---|
| Fe(1)-C(2) | 2.040(3) | C(22)-C(23) | 1.379(4) |
| Fe(1)-C(5) | 2.043(3) | C(22)-C(24) | 1.394(5) |
| Fe(1)-C(7) | 2.043(3) | C(23)-C(25) | 1.376(4) |
| Fe(1)-C(4) | 2.046(3) | C(24)-C(26) | 1.385(4) |
| Fe(1)-C(3) | 2.046(4) | C(25)-C(27) | 1.387(5) |
| Fe(1)-C(6) | 2.048(3) | C(26)-C(27) | 1.380(5) |
| Fe(1)-C(9) | 2.049(4) | C(27)-C(28) | 1.439(5) |
| Fe(1)-C(8) | 2.049(3) | C(2)-Fe(1)-C(5) | 67.65(14) |
| Fe(1)-C(10) | 2.056(3) | C(2)-Fe(1)-C(7) | 107.19(15) |
| Fe(1)-C(1) | 2.061(3) | C(5)-Fe(1)-C(7) | 160.45(11) |
| C(1)-C(2) | 1.411(5) | C(2)-Fe(1)-C(4) | 67.58(14) |
| C(1)-C(5) | 1.420(5) | C(5)-Fe(1)-C(4) | 40.50(12) |
| C(1)-C(11) | 1.473(5) | C(7)-Fe(1)-C(4) | 156.94(12) |
| N(1)-C(19) | 1.132(4) | C(2)-Fe(1)-C(3) | 40.40(14) |
| N(2)-C(28) | 1.141(4) | C(5)-Fe(1)-C(3) | 67.54(15) |
| C(2)-C(3) | 1.411(5) | C(7)-Fe(1)-C(3) | 121.64(16) |
| C(3)-C(4) | 1.394(5) | C(4)-Fe(1)-C(3) | 39.83(15) |
| C(4)-C(5) | 1.415(4) | C(2)-Fe(1)-C(6) | 124.36(14) |
| C(6)-C(10) | 1.416(4) | C(5)-Fe(1)-C(6) | 125.55(13) |
| C(6)-C(7) | 1.418(4) | C(7)-Fe(1)-C(6) | 40.54(13) |
| C(6)-C(20) | 1.471(4) | C(4)-Fe(1)-C(6) | 160.69(13) |
| C(7)-C(8) | 1.408(4) | C(3)-Fe(1)-C(6) | 158.92(15) |
| C(8)-C(9) | 1.407(5) | C(2)-Fe(1)-C(9) | 156.61(14) |
| C(9)-C(10) | 1.415(5) | C(5)-Fe(1)-C(9) | 124.55(16) |
| C(11)-C(12) | 1.273(5) | C(7)-Fe(1)-C(9) | 67.77(15) |
| C(12)-C(13) | 1.492(5) | C(4)-Fe(1)-C(9) | 107.59(14) |
| C(13)-C(15) | 1.362(5) | C(3)-Fe(1)-C(9) | 121.20(13) |
| C(13)-C(14) | 1.376(5) | C(6)-Fe(1)-C(9) | 67.64(14) |
| C(14)-C(16) | 1.373(4) | C(2)-Fe(1)-C(8) | 121.23(15) |
| C(15)-C(17) | 1.407(5) | C(5)-Fe(1)-C(8) | 158.80(13) |
| C(16)-C(18) | 1.371(5) | C(7)-Fe(1)-C(8) | 40.25(13) |
| C(17)-C(18) | 1.379(5) | C(4)-Fe(1)-C(8) | 121.63(13) |
| C(18)-C(19) | 1.447(5) | C(3)-Fe(1)-C(8) | 105.81(14) |
| C(20)-C(21) | 1.327(4) | C(6)-Fe(1)-C(8) | 67.68(13) |
| C(21)-C(22) | 1.473(4) | C(9)-Fe(1)-C(8) | 40.18(15) |

| | | | |
|---|---|---|---|
| C(2)-Fe(1)-C(10) | 161.17(12) | C(10)-C(6)-Fe(1) | 70.11(17) |
| C(5)-Fe(1)-C(10) | 110.27(14) | C(7)-C(6)-Fe(1) | 69.53(17) |
| C(7)-Fe(1)-C(10) | 68.15(14) | C(20)-C(6)-Fe(1) | 126.0(2) |
| C(4)-Fe(1)-C(10) | 123.93(14) | C(8)-C(7)-C(6) | 107.7(3) |
| C(3)-Fe(1)-C(10) | 157.78(13) | C(8)-C(7)-Fe(1) | 70.09(19) |
| C(6)-Fe(1)-C(10) | 40.37(12) | C(6)-C(7)-Fe(1) | 69.92(18) |
| C(9)-Fe(1)-C(10) | 40.33(14) | C(9)-C(8)-C(7) | 108.3(3) |
| C(8)-Fe(1)-C(10) | 67.82(14) | C(9)-C(8)-Fe(1) | 69.9(2) |
| C(2)-Fe(1)-C(1) | 40.23(13) | C(7)-C(8)-Fe(1) | 69.66(17) |
| C(5)-Fe(1)-C(1) | 40.48(13) | C(8)-C(9)-C(10) | 108.5(3) |
| C(7)-Fe(1)-C(1) | 123.47(13) | C(8)-C(9)-Fe(1) | 69.9(2) |
| C(4)-Fe(1)-C(1) | 68.04(13) | C(10)-C(9)-Fe(1) | 70.1(2) |
| C(3)-Fe(1)-C(1) | 67.84(15) | C(9)-C(10)-C(6) | 107.3(3) |
| C(6)-Fe(1)-C(1) | 110.14(12) | C(9)-C(10)-Fe(1) | 69.5(2) |
| C(9)-Fe(1)-C(1) | 161.41(16) | C(6)-C(10)-Fe(1) | 69.52(18) |
| C(8)-Fe(1)-C(1) | 157.75(14) | C(12)-C(11)-C(1) | 126.0(4) |
| C(10)-Fe(1)-C(1) | 125.92(14) | C(11)-C(12)-C(13) | 127.2(4) |
| C(2)-C(1)-C(5) | 106.8(3) | C(15)-C(13)-C(14) | 118.2(3) |
| C(2)-C(1)-C(11) | 123.4(3) | C(15)-C(13)-C(12) | 124.5(4) |
| C(5)-C(1)-C(11) | 129.7(3) | C(14)-C(13)-C(12) | 117.3(4) |
| C(2)-C(1)-Fe(1) | 69.09(19) | C(16)-C(14)-C(13) | 121.5(4) |
| C(5)-C(1)-Fe(1) | 69.09(18) | C(13)-C(15)-C(17) | 121.5(4) |
| C(11)-C(1)-Fe(1) | 126.6(2) | C(18)-C(16)-C(14) | 120.1(3) |
| C(1)-C(2)-C(3) | 108.6(3) | C(18)-C(17)-C(15) | 118.7(4) |
| C(1)-C(2)-Fe(1) | 70.7(2) | C(16)-C(18)-C(17) | 119.8(3) |
| C(3)-C(2)-Fe(1) | 70.0(2) | C(16)-C(18)-C(19) | 119.7(4) |
| C(4)-C(3)-C(2) | 108.2(3) | C(17)-C(18)-C(19) | 120.4(4) |
| C(4)-C(3)-Fe(1) | 70.1(2) | N(1)-C(19)-C(18) | 178.4(5) |
| C(2)-C(3)-Fe(1) | 69.6(2) | C(21)-C(20)-C(6) | 125.4(3) |
| C(3)-C(4)-C(5) | 108.0(3) | C(20)-C(21)-C(22) | 126.2(3) |
| C(3)-C(4)-Fe(1) | 70.1(2) | C(23)-C(22)-C(24) | 117.4(3) |
| C(5)-C(4)-Fe(1) | 69.64(17) | C(23)-C(22)-C(21) | 123.9(3) |
| C(4)-C(5)-C(1) | 108.3(3) | C(24)-C(22)-C(21) | 118.7(3) |
| C(4)-C(5)-Fe(1) | 69.86(18) | C(25)-C(23)-C(22) | 121.6(3) |
| C(1)-C(5)-Fe(1) | 70.43(19) | C(26)-C(24)-C(22) | 121.8(3) |
| C(10)-C(6)-C(7) | 108.3(3) | C(23)-C(25)-C(27) | 120.2(3) |
| C(10)-C(6)-C(20) | 126.7(3) | C(27)-C(26)-C(24) | 119.4(3) |
| C(7)-C(6)-C(20) | 125.0(3) | C(26)-C(27)-C(25) | 119.6(3) |

| | |
|---|---|
| C(26)-C(27)-C(28) | 120.3(4) |
| C(25)-C(27)-C(28) | 120.1(3) |
| N(2)-C(28)-C(27) | 176.4(5) |

Symmetry transformations used to generate equivalent atoms:

**Table 4**. Anisotropic displacement parameters ($Å^2$x $10^3$) for str94m. The anisotropic displacement factor exponent takes the form: $-2\pi^2[ h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12} ]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| Fe(1) | 39(1) | 37(1) | 29(1) | -1(1) | 14(1) | -3(1) |
| C(1) | 53(2) | 37(2) | 40(2) | -4(2) | 23(2) | -7(2) |
| N(1) | 97(3) | 134(4) | 64(2) | -14(2) | 48(2) | -7(3) |
| N(2) | 87(3) | 157(4) | 59(2) | -12(2) | 43(2) | -10(3) |
| C(2) | 45(2) | 39(2) | 55(2) | 6(2) | 8(2) | 3(2) |
| C(3) | 71(3) | 44(2) | 31(2) | 7(2) | 20(2) | -10(2) |
| C(4) | 47(2) | 48(2) | 51(2) | -1(2) | 27(2) | -7(2) |
| C(5) | 46(2) | 47(2) | 35(2) | -1(1) | 3(2) | -8(2) |
| C(6) | 42(2) | 37(2) | 42(2) | -1(1) | 18(2) | -4(2) |
| C(7) | 42(2) | 50(2) | 40(2) | -4(2) | 8(2) | -6(2) |
| C(8) | 70(2) | 50(2) | 32(2) | -6(2) | 17(2) | -9(2) |
| C(9) | 63(3) | 45(2) | 53(3) | -6(2) | 33(2) | -2(2) |
| C(10) | 49(2) | 34(2) | 43(2) | 0(2) | 17(2) | -1(2) |
| C(11) | 69(3) | 41(2) | 57(2) | -8(2) | 23(2) | -13(2) |
| C(12) | 70(3) | 57(2) | 50(2) | -5(2) | 19(2) | -7(2) |
| C(13) | 67(2) | 39(2) | 45(2) | -11(2) | 30(2) | -7(2) |
| C(14) | 65(3) | 71(3) | 49(2) | -6(2) | 24(2) | 11(2) |
| C(15) | 85(3) | 40(2) | 32(2) | 0(2) | 13(2) | -9(2) |
| C(16) | 70(3) | 75(3) | 36(2) | -2(2) | 14(2) | 9(2) |
| C(17) | 56(2) | 45(2) | 54(2) | -6(2) | 17(2) | 5(2) |
| C(18) | 57(2) | 48(2) | 36(2) | -9(2) | 20(2) | -3(2) |
| C(19) | 72(3) | 77(3) | 46(2) | -10(2) | 24(2) | 1(2) |
| C(20) | 43(2) | 38(2) | 42(2) | 1(1) | 18(2) | -3(2) |
| C(21) | 38(2) | 45(2) | 32(2) | 2(1) | 16(2) | -2(2) |
| C(22) | 45(2) | 33(2) | 42(2) | 3(1) | 14(2) | -2(2) |
| C(23) | 54(2) | 60(2) | 40(2) | 11(2) | 14(2) | 6(2) |
| C(24) | 46(2) | 45(2) | 45(2) | 7(2) | 15(2) | 6(2) |
| C(25) | 48(2) | 55(2) | 57(2) | 1(2) | 23(2) | 8(2) |
| C(26) | 52(2) | 51(2) | 36(2) | 9(2) | 10(2) | -2(2) |
| C(27) | 53(2) | 46(2) | 39(2) | -2(2) | 19(2) | -5(2) |
| C(28) | 65(3) | 75(3) | 43(2) | -12(2) | 16(2) | -9(2) |

**Table 5.** Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters ($Å^2$x $10^3$) for str94m.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(2) | 3030 | 5288 | 7757 | 56 |
| H(3) | 191 | 5587 | 8898 | 57 |
| H(4) | -3253 | 6118 | 7598 | 56 |
| H(5) | -2576 | 6142 | 5633 | 52 |
| H(7) | 4707 | 7473 | 8142 | 53 |
| H(8) | 1886 | 7755 | 9301 | 59 |
| H(9) | -1562 | 8329 | 8020 | 60 |
| H(10) | -889 | 8429 | 6054 | 49 |
| H(11) | 3286 | 5340 | 5613 | 66 |
| H(12) | -411 | 5886 | 4169 | 70 |
| H(14) | -186 | 6235 | 2305 | 72 |
| H(15) | 4940 | 4923 | 4199 | 62 |
| H(16) | 1484 | 6209 | 793 | 72 |
| H(17) | 6666 | 4867 | 2668 | 61 |
| H(20) | 4797 | 7577 | 5921 | 47 |
| H(21) | 1309 | 8531 | 4642 | 45 |
| H(23) | 6608 | 7558 | 4553 | 61 |
| H(24) | 1312 | 8835 | 2711 | 53 |
| H(25) | 8261 | 7578 | 3033 | 62 |
| H(26) | 2913 | 8827 | 1161 | 56 |

**Table 6.** Torsion angles [°] for str94m.

| | |
|---|---|
| C(5)-Fe(1)-C(1)-C(2) | -118.5(3) |
| C(7)-Fe(1)-C(1)-C(2) | 76.5(2) |
| C(4)-Fe(1)-C(1)-C(2) | -80.8(2) |
| C(3)-Fe(1)-C(1)-C(2) | -37.7(2) |
| C(6)-Fe(1)-C(1)-C(2) | 119.8(2) |
| C(9)-Fe(1)-C(1)-C(2) | -160.6(4) |
| C(8)-Fe(1)-C(1)-C(2) | 39.7(4) |
| C(10)-Fe(1)-C(1)-C(2) | 162.40(19) |
| C(2)-Fe(1)-C(1)-C(5) | 118.5(3) |
| C(7)-Fe(1)-C(1)-C(5) | -164.92(18) |
| C(4)-Fe(1)-C(1)-C(5) | 37.76(19) |
| C(3)-Fe(1)-C(1)-C(5) | 80.9(2) |
| C(6)-Fe(1)-C(1)-C(5) | -121.6(2) |
| C(9)-Fe(1)-C(1)-C(5) | -42.0(5) |
| C(8)-Fe(1)-C(1)-C(5) | 158.3(3) |
| C(10)-Fe(1)-C(1)-C(5) | -79.0(2) |
| C(2)-Fe(1)-C(1)-C(11) | -116.8(4) |
| C(5)-Fe(1)-C(1)-C(11) | 124.6(4) |
| C(7)-Fe(1)-C(1)-C(11) | -40.3(4) |
| C(4)-Fe(1)-C(1)-C(11) | 162.4(4) |
| C(3)-Fe(1)-C(1)-C(11) | -154.5(4) |
| C(6)-Fe(1)-C(1)-C(11) | 3.0(4) |
| C(9)-Fe(1)-C(1)-C(11) | 82.6(6) |
| C(8)-Fe(1)-C(1)-C(11) | -77.1(5) |
| C(10)-Fe(1)-C(1)-C(11) | 45.6(4) |
| C(5)-C(1)-C(2)-C(3) | 1.0(4) |
| C(11)-C(1)-C(2)-C(3) | -179.2(3) |
| Fe(1)-C(1)-C(2)-C(3) | 60.0(3) |
| C(5)-C(1)-C(2)-Fe(1) | -59.0(2) |
| C(11)-C(1)-C(2)-Fe(1) | 120.8(3) |
| C(5)-Fe(1)-C(2)-C(1) | 38.07(19) |
| C(7)-Fe(1)-C(2)-C(1) | -121.9(2) |
| C(4)-Fe(1)-C(2)-C(1) | 82.0(2) |
| C(3)-Fe(1)-C(2)-C(1) | 119.2(3) |
| C(6)-Fe(1)-C(2)-C(1) | -80.7(2) |
| C(9)-Fe(1)-C(2)-C(1) | 164.5(4) |
| C(8)-Fe(1)-C(2)-C(1) | -163.56(19) |
| C(10)-Fe(1)-C(2)-C(1) | -49.3(6) |
| C(5)-Fe(1)-C(2)-C(3) | -81.1(2) |
| C(7)-Fe(1)-C(2)-C(3) | 118.9(2) |
| C(4)-Fe(1)-C(2)-C(3) | -37.2(2) |
| C(6)-Fe(1)-C(2)-C(3) | 160.2(2) |
| C(9)-Fe(1)-C(2)-C(3) | 45.3(5) |
| C(8)-Fe(1)-C(2)-C(3) | 77.2(3) |
| C(10)-Fe(1)-C(2)-C(3) | -168.5(4) |
| C(1)-Fe(1)-C(2)-C(3) | -119.2(3) |
| C(1)-C(2)-C(3)-C(4) | -0.7(4) |
| Fe(1)-C(2)-C(3)-C(4) | 59.6(3) |
| C(1)-C(2)-C(3)-Fe(1) | -60.4(3) |
| C(2)-Fe(1)-C(3)-C(4) | -119.3(3) |
| C(5)-Fe(1)-C(3)-C(4) | -37.9(2) |
| C(7)-Fe(1)-C(3)-C(4) | 161.53(19) |
| C(6)-Fe(1)-C(3)-C(4) | -170.5(3) |
| C(9)-Fe(1)-C(3)-C(4) | 79.9(3) |
| C(8)-Fe(1)-C(3)-C(4) | 120.8(2) |
| C(10)-Fe(1)-C(3)-C(4) | 50.9(5) |
| C(1)-Fe(1)-C(3)-C(4) | -81.8(2) |
| C(5)-Fe(1)-C(3)-C(2) | 81.4(2) |
| C(7)-Fe(1)-C(3)-C(2) | -79.1(3) |
| C(4)-Fe(1)-C(3)-C(2) | 119.3(3) |
| C(6)-Fe(1)-C(3)-C(2) | -51.2(5) |
| C(9)-Fe(1)-C(3)-C(2) | -160.7(2) |
| C(8)-Fe(1)-C(3)-C(2) | -119.9(2) |
| C(10)-Fe(1)-C(3)-C(2) | 170.2(4) |
| C(1)-Fe(1)-C(3)-C(2) | 37.5(2) |
| C(2)-C(3)-C(4)-C(5) | 0.2(4) |
| Fe(1)-C(3)-C(4)-C(5) | 59.5(2) |
| C(2)-C(3)-C(4)-Fe(1) | -59.3(3) |
| C(2)-Fe(1)-C(4)-C(3) | 37.7(2) |
| C(5)-Fe(1)-C(4)-C(3) | 119.0(3) |
| C(7)-Fe(1)-C(4)-C(3) | -43.5(4) |
| C(6)-Fe(1)-C(4)-C(3) | 169.7(4) |
| C(9)-Fe(1)-C(4)-C(3) | -117.9(2) |
| C(8)-Fe(1)-C(4)-C(3) | -76.2(3) |

| | |
|---|---|
| C(10)-Fe(1)-C(4)-C(3) | -159.3(2) |
| C(1)-Fe(1)-C(4)-C(3) | 81.3(2) |
| C(2)-Fe(1)-C(4)-C(5) | -81.4(2) |
| C(7)-Fe(1)-C(4)-C(5) | -162.5(3) |
| C(3)-Fe(1)-C(4)-C(5) | -119.0(3) |
| C(6)-Fe(1)-C(4)-C(5) | 50.6(5) |
| C(9)-Fe(1)-C(4)-C(5) | 123.0(2) |
| C(8)-Fe(1)-C(4)-C(5) | 164.8(2) |
| C(10)-Fe(1)-C(4)-C(5) | 81.7(2) |
| C(1)-Fe(1)-C(4)-C(5) | -37.75(19) |
| C(3)-C(4)-C(5)-C(1) | 0.4(4) |
| Fe(1)-C(4)-C(5)-C(1) | 60.2(2) |
| C(3)-C(4)-C(5)-Fe(1) | -59.8(3) |
| C(2)-C(1)-C(5)-C(4) | -0.8(4) |
| C(11)-C(1)-C(5)-C(4) | 179.3(3) |
| Fe(1)-C(1)-C(5)-C(4) | -59.9(2) |
| C(2)-C(1)-C(5)-Fe(1) | 59.0(2) |
| C(11)-C(1)-C(5)-Fe(1) | -120.8(4) |
| C(2)-Fe(1)-C(5)-C(4) | 81.2(2) |
| C(7)-Fe(1)-C(5)-C(4) | 159.4(4) |
| C(3)-Fe(1)-C(5)-C(4) | 37.3(2) |
| C(6)-Fe(1)-C(5)-C(4) | -161.69(19) |
| C(9)-Fe(1)-C(5)-C(4) | -76.0(2) |
| C(8)-Fe(1)-C(5)-C(4) | -38.2(5) |
| C(10)-Fe(1)-C(5)-C(4) | -118.9(2) |
| C(1)-Fe(1)-C(5)-C(4) | 119.0(3) |
| C(2)-Fe(1)-C(5)-C(1) | -37.84(18) |
| C(7)-Fe(1)-C(5)-C(1) | 40.4(5) |
| C(4)-Fe(1)-C(5)-C(1) | -119.0(3) |
| C(3)-Fe(1)-C(5)-C(1) | -81.7(2) |
| C(6)-Fe(1)-C(5)-C(1) | 79.3(2) |
| C(9)-Fe(1)-C(5)-C(1) | 165.0(2) |
| C(8)-Fe(1)-C(5)-C(1) | -157.2(3) |
| C(10)-Fe(1)-C(5)-C(1) | 122.1(2) |
| C(2)-Fe(1)-C(6)-C(10) | 165.0(2) |
| C(5)-Fe(1)-C(6)-C(10) | 79.4(2) |
| C(7)-Fe(1)-C(6)-C(10) | -119.4(3) |
| C(4)-Fe(1)-C(6)-C(10) | 41.3(5) |
| C(3)-Fe(1)-C(6)-C(10) | -157.3(4) |
| C(9)-Fe(1)-C(6)-C(10) | -37.9(2) |
| C(8)-Fe(1)-C(6)-C(10) | -81.5(2) |
| C(1)-Fe(1)-C(6)-C(10) | 122.2(2) |
| C(2)-Fe(1)-C(6)-C(7) | -75.6(2) |
| C(5)-Fe(1)-C(6)-C(7) | -161.15(19) |
| C(4)-Fe(1)-C(6)-C(7) | 160.7(4) |
| C(3)-Fe(1)-C(6)-C(7) | -37.9(5) |
| C(9)-Fe(1)-C(6)-C(7) | 81.5(2) |
| C(8)-Fe(1)-C(6)-C(7) | 37.9(2) |
| C(10)-Fe(1)-C(6)-C(7) | 119.4(3) |
| C(1)-Fe(1)-C(6)-C(7) | -118.4(2) |
| C(2)-Fe(1)-C(6)-C(20) | 43.5(4) |
| C(5)-Fe(1)-C(6)-C(20) | -42.0(4) |
| C(7)-Fe(1)-C(6)-C(20) | 119.1(4) |
| C(4)-Fe(1)-C(6)-C(20) | -80.1(5) |
| C(3)-Fe(1)-C(6)-C(20) | 81.2(5) |
| C(9)-Fe(1)-C(6)-C(20) | -159.4(4) |
| C(8)-Fe(1)-C(6)-C(20) | 157.0(3) |
| C(10)-Fe(1)-C(6)-C(20) | -121.5(4) |
| C(1)-Fe(1)-C(6)-C(20) | 0.8(3) |
| C(10)-C(6)-C(7)-C(8) | -0.6(4) |
| C(20)-C(6)-C(7)-C(8) | 179.5(3) |
| Fe(1)-C(6)-C(7)-C(8) | -60.2(2) |
| C(10)-C(6)-C(7)-Fe(1) | 59.6(2) |
| C(20)-C(6)-C(7)-Fe(1) | -120.3(3) |
| C(2)-Fe(1)-C(7)-C(8) | -118.3(2) |
| C(5)-Fe(1)-C(7)-C(8) | 170.2(4) |
| C(4)-Fe(1)-C(7)-C(8) | -45.4(4) |
| C(3)-Fe(1)-C(7)-C(8) | -76.6(2) |
| C(6)-Fe(1)-C(7)-C(8) | 118.5(3) |
| C(9)-Fe(1)-C(7)-C(8) | 37.4(2) |
| C(10)-Fe(1)-C(7)-C(8) | 81.0(2) |
| C(1)-Fe(1)-C(7)-C(8) | -159.4(2) |
| C(2)-Fe(1)-C(7)-C(6) | 123.2(2) |
| C(5)-Fe(1)-C(7)-C(6) | 51.8(5) |
| C(4)-Fe(1)-C(7)-C(6) | -163.8(3) |
| C(3)-Fe(1)-C(7)-C(6) | 164.97(19) |

| | |
|---|---|
| C(9)-Fe(1)-C(7)-C(6) | -81.1(2) |
| C(8)-Fe(1)-C(7)-C(6) | -118.5(3) |
| C(10)-Fe(1)-C(7)-C(6) | -37.45(18) |
| C(1)-Fe(1)-C(7)-C(6) | 82.1(2) |
| C(6)-C(7)-C(8)-C(9) | 0.6(4) |
| Fe(1)-C(7)-C(8)-C(9) | -59.5(3) |
| C(6)-C(7)-C(8)-Fe(1) | 60.1(2) |
| C(2)-Fe(1)-C(8)-C(9) | -161.0(2) |
| C(5)-Fe(1)-C(8)-C(9) | -51.5(5) |
| C(7)-Fe(1)-C(8)-C(9) | 119.4(3) |
| C(4)-Fe(1)-C(8)-C(9) | -79.7(2) |
| C(3)-Fe(1)-C(8)-C(9) | -119.9(2) |
| C(6)-Fe(1)-C(8)-C(9) | 81.3(2) |
| C(10)-Fe(1)-C(8)-C(9) | 37.52(19) |
| C(1)-Fe(1)-C(8)-C(9) | 170.1(3) |
| C(2)-Fe(1)-C(8)-C(7) | 79.5(2) |
| C(5)-Fe(1)-C(8)-C(7) | -171.0(3) |
| C(4)-Fe(1)-C(8)-C(7) | 160.9(2) |
| C(3)-Fe(1)-C(8)-C(7) | 120.6(2) |
| C(6)-Fe(1)-C(8)-C(7) | -38.14(19) |
| C(9)-Fe(1)-C(8)-C(7) | -119.4(3) |
| C(10)-Fe(1)-C(8)-C(7) | -81.9(2) |
| C(1)-Fe(1)-C(8)-C(7) | 50.7(4) |
| C(7)-C(8)-C(9)-C(10) | -0.5(4) |
| Fe(1)-C(8)-C(9)-C(10) | -59.8(3) |
| C(7)-C(8)-C(9)-Fe(1) | 59.3(2) |
| C(2)-Fe(1)-C(9)-C(8) | 44.5(5) |
| C(5)-Fe(1)-C(9)-C(8) | 159.89(18) |
| C(7)-Fe(1)-C(9)-C(8) | -37.43(19) |
| C(4)-Fe(1)-C(9)-C(8) | 118.5(2) |
| C(3)-Fe(1)-C(9)-C(8) | 77.1(2) |
| C(6)-Fe(1)-C(9)-C(8) | -81.4(2) |
| C(10)-Fe(1)-C(9)-C(8) | -119.4(3) |
| C(1)-Fe(1)-C(9)-C(8) | -168.2(4) |
| C(2)-Fe(1)-C(9)-C(10) | 163.9(3) |
| C(5)-Fe(1)-C(9)-C(10) | -80.7(2) |
| C(7)-Fe(1)-C(9)-C(10) | 82.0(2) |
| C(4)-Fe(1)-C(9)-C(10) | -122.1(2) |
| C(3)-Fe(1)-C(9)-C(10) | -163.5(2) |
| C(6)-Fe(1)-C(9)-C(10) | 38.0(2) |
| C(8)-Fe(1)-C(9)-C(10) | 119.4(3) |
| C(1)-Fe(1)-C(9)-C(10) | -48.9(5) |
| C(8)-C(9)-C(10)-C(6) | 0.1(4) |
| Fe(1)-C(9)-C(10)-C(6) | -59.5(2) |
| C(8)-C(9)-C(10)-Fe(1) | 59.6(3) |
| C(7)-C(6)-C(10)-C(9) | 0.3(4) |
| C(20)-C(6)-C(10)-C(9) | -179.8(3) |
| Fe(1)-C(6)-C(10)-C(9) | 59.5(2) |
| C(7)-C(6)-C(10)-Fe(1) | -59.3(2) |
| C(20)-C(6)-C(10)-Fe(1) | 120.6(3) |
| C(2)-Fe(1)-C(10)-C(9) | -160.0(4) |
| C(5)-Fe(1)-C(10)-C(9) | 120.0(2) |
| C(7)-Fe(1)-C(10)-C(9) | -80.9(3) |
| C(4)-Fe(1)-C(10)-C(9) | 76.7(3) |
| C(3)-Fe(1)-C(10)-C(9) | 39.9(5) |
| C(6)-Fe(1)-C(10)-C(9) | -118.5(3) |
| C(8)-Fe(1)-C(10)-C(9) | -37.4(2) |
| C(1)-Fe(1)-C(10)-C(9) | 162.8(2) |
| C(2)-Fe(1)-C(10)-C(6) | -41.5(6) |
| C(5)-Fe(1)-C(10)-C(6) | -121.5(2) |
| C(7)-Fe(1)-C(10)-C(6) | 37.60(19) |
| C(4)-Fe(1)-C(10)-C(6) | -164.74(19) |
| C(3)-Fe(1)-C(10)-C(6) | 158.5(4) |
| C(9)-Fe(1)-C(10)-C(6) | 118.5(3) |
| C(8)-Fe(1)-C(10)-C(6) | 81.2(2) |
| C(1)-Fe(1)-C(10)-C(6) | -78.7(2) |
| C(2)-C(1)-C(11)-C(12) | -179.8(4) |
| C(5)-C(1)-C(11)-C(12) | 0.0(6) |
| Fe(1)-C(1)-C(11)-C(12) | -92.3(5) |
| C(1)-C(11)-C(12)-C(13) | 177.9(3) |
| C(11)-C(12)-C(13)-C(15) | 12.5(6) |
| C(11)-C(12)-C(13)-C(14) | -168.9(4) |
| C(15)-C(13)-C(14)-C(16) | -3.1(6) |
| C(12)-C(13)-C(14)-C(16) | 178.1(3) |
| C(14)-C(13)-C(15)-C(17) | 2.6(5) |
| C(12)-C(13)-C(15)-C(17) | -178.7(3) |

| | |
|---|---|
| C(13)-C(14)-C(16)-C(18) | 1.3(6) |
| C(13)-C(15)-C(17)-C(18) | -0.4(6) |
| C(14)-C(16)-C(18)-C(17) | 1.0(6) |
| C(14)-C(16)-C(18)-C(19) | -178.5(4) |
| C(15)-C(17)-C(18)-C(16) | -1.5(6) |
| C(15)-C(17)-C(18)-C(19) | 178.1(3) |
| C(16)-C(18)-C(19)-N(1) | 175(100) |
| C(17)-C(18)-C(19)-N(1) | -4(18) |
| C(10)-C(6)-C(20)-C(21) | 10.4(5) |
| C(7)-C(6)-C(20)-C(21) | -169.7(3) |
| Fe(1)-C(6)-C(20)-C(21) | 101.3(4) |
| C(6)-C(20)-C(21)-C(22) | 179.4(3) |
| C(20)-C(21)-C(22)-C(23) | -3.7(5) |
| C(20)-C(21)-C(22)-C(24) | 178.3(3) |
| C(24)-C(22)-C(23)-C(25) | 0.2(5) |
| C(21)-C(22)-C(23)-C(25) | -177.8(3) |
| C(23)-C(22)-C(24)-C(26) | 0.7(5) |
| C(21)-C(22)-C(24)-C(26) | 178.8(3) |
| C(22)-C(23)-C(25)-C(27) | -0.7(6) |
| C(22)-C(24)-C(26)-C(27) | -1.0(5) |
| C(24)-C(26)-C(27)-C(25) | 0.5(5) |
| C(24)-C(26)-C(27)-C(28) | -177.8(3) |
| C(23)-C(25)-C(27)-C(26) | 0.3(6) |
| C(23)-C(25)-C(27)-C(28) | 178.6(3) |
| C(26)-C(27)-C(28)-N(2) | 175(7) |
| C(25)-C(27)-C(28)-N(2) | -3(8) |

Symmetry transformations used to generate equivalent atoms:

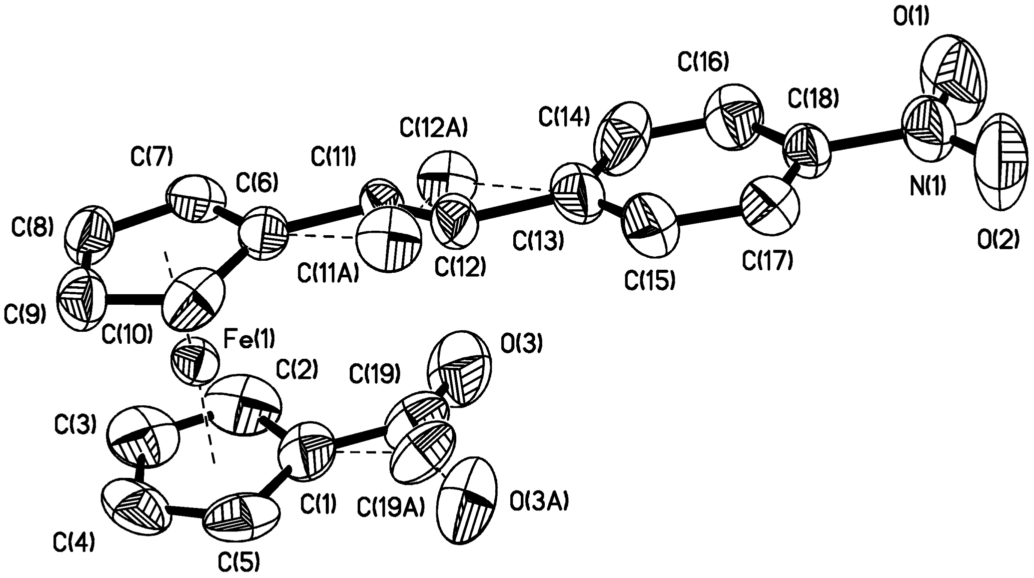

O(1)
C(16)
C(18)
C(14)
C(12A)
C(11)
C(7)
C(6)
C(8)
N(1)
O(2)
C(13)
C(17)
C(15)
C(11A)
C(12)
C(9)
C(10)
Fe(1)
O(3)
C(2)
C(19)
C(3)
C(1)
C(19A)
O(3A)
C(4)
C(5)

**Table 1**. Crystal data and structure refinement for str99m.

| | | |
|---|---|---|
| Identification code | str99m | |
| Empirical formula | C19 H15 Fe N O3 | |
| Formula weight | 361.17 | |
| Temperature | 293(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | P2(1)/n | |
| Unit cell dimensions | a = 7.6532(5) Å | $\alpha$= 90°. |
| | b = 7.6518(5) Å | $\beta$= 91.328(2)°. |
| | c = 26.6880(17) Å | $\gamma$ = 90°. |
| Volume | 1562.45(18) Å$^3$ | |
| Z | 4 | |
| Density (calculated) | 1.535 Mg/m$^3$ | |
| Absorption coefficient | 0.982 mm$^{-1}$ | |
| F(000) | 744 | |
| Crystal size | 0.28 x 0.23 x 0.16 mm$^3$ | |
| Theta range for data collection | 1.53 to 30.55°. | |
| Index ranges | -9<=h<=10, -10<=k<=10, -37<=l<=25 | |
| Reflections collected | 12775 | |
| Independent reflections | 4766 [R(int) = 0.0617] | |
| Completeness to theta = 30.55° | 99.5 % | |
| Absorption correction | None | |
| Refinement method | Full-matrix least-squares on F$^2$ | |
| Data / restraints / parameters | 4766 / 0 / 245 | |
| Goodness-of-fit on F$^2$ | 0.868 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0454, wR2 = 0.0850 | |
| R indices (all data) | R1 = 0.1366, wR2 = 0.1027 | |
| Largest diff. peak and hole | 0.529 and -0.261 e.Å$^{-3}$ | |

**Table 2**. Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters (Å$^2$x $10^3$) for str99m. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| Fe(1) | 268(1) | 9261(1) | 1737(1) | 37(1) |
| N(1) | 4433(4) | 5838(4) | -1409(1) | 61(1) |
| O(1) | 5561(4) | 6790(4) | -1570(1) | 96(1) |
| C(1) | -861(4) | 10702(5) | 1184(1) | 60(1) |
| C(2) | -30(5) | 11803(4) | 1542(2) | 74(1) |
| O(2) | 3707(4) | 4711(4) | -1656(1) | 95(1) |
| C(3) | -778(5) | 11515(5) | 1999(2) | 74(1) |
| O(3A) | -1600(13) | 9078(13) | 405(3) | 95(4) |
| O(3) | 918(6) | 11532(7) | 490(2) | 98(2) |
| C(4) | -2084(4) | 10235(5) | 1943(2) | 71(1) |
| C(5) | -2144(4) | 9722(4) | 1438(2) | 65(1) |
| C(6) | 2150(4) | 7613(4) | 1468(1) | 50(1) |
| C(7) | 2864(4) | 8788(4) | 1824(1) | 53(1) |
| C(8) | 2030(4) | 8546(4) | 2277(1) | 52(1) |
| C(9) | 763(4) | 7260(4) | 2215(1) | 50(1) |
| C(10) | 817(4) | 6671(4) | 1713(1) | 50(1) |
| C(11) | 2809(6) | 7633(7) | 954(2) | 44(2) |
| C(11A) | 2071(19) | 6784(19) | 901(6) | 62(4) |
| C(12) | 2369(6) | 6396(7) | 623(2) | 48(2) |
| C(12A) | 3264(17) | 7504(17) | 672(6) | 55(4) |
| C(13) | 2997(4) | 6382(5) | 98(1) | 60(1) |
| C(14) | 4241(5) | 7505(4) | -105(1) | 69(1) |
| C(15) | 2305(4) | 5107(5) | -199(1) | 63(1) |
| C(16) | 4739(4) | 7347(4) | -601(1) | 59(1) |
| C(17) | 2745(4) | 4945(4) | -693(1) | 54(1) |
| C(18) | 3950(4) | 6067(4) | -888(1) | 45(1) |
| C(19A) | -780(30) | 10050(30) | 629(8) | 61(4) |
| C(19) | -189(15) | 10673(17) | 674(5) | 66(2) |

**Table 3**. Bond lengths [Å] and angles [°] for str99m.

| | |
|---|---|
| Fe(1)-C(1) | 2.020(3) |
| Fe(1)-C(9) | 2.022(3) |
| Fe(1)-C(2) | 2.025(3) |
| Fe(1)-C(5) | 2.026(3) |
| Fe(1)-C(8) | 2.026(3) |
| Fe(1)-C(10) | 2.028(3) |
| Fe(1)-C(7) | 2.028(3) |
| Fe(1)-C(3) | 2.032(3) |
| Fe(1)-C(4) | 2.036(3) |
| Fe(1)-C(6) | 2.057(3) |
| N(1)-O(2) | 1.212(3) |
| N(1)-O(1) | 1.216(3) |
| N(1)-C(18) | 1.458(4) |
| C(1)-C(2) | 1.414(5) |
| C(1)-C(5) | 1.419(5) |
| C(1)-C(19) | 1.466(13) |
| C(1)-C(19A) | 1.57(2) |
| C(2)-C(3) | 1.378(5) |
| C(3)-C(4) | 1.405(5) |
| O(3A)-C(19A) | 1.135(18) |
| O(3A)-C(19) | 1.771(12) |
| O(3)-C(19) | 1.188(10) |
| O(3)-C(19A) | 1.77(2) |
| C(4)-C(5) | 1.405(5) |
| C(6)-C(7) | 1.409(4) |
| C(6)-C(10) | 1.421(4) |
| C(6)-C(11) | 1.472(7) |
| C(6)-C(11A) | 1.640(17) |
| C(7)-C(8) | 1.393(4) |
| C(8)-C(9) | 1.388(4) |
| C(9)-C(10) | 1.414(4) |
| C(11)-C(12A) | 0.843(13) |
| C(11)-C(11A) | 0.870(12) |
| C(11)-C(12) | 1.333(12) |
| C(11A)-C(12) | 0.836(14) |
| C(11A)-C(12A) | 1.24(3) |
| C(12)-C(12A) | 1.096(12) |
| C(12)-C(13) | 1.492(6) |
| C(12A)-C(13) | 1.764(15) |
| C(13)-C(15) | 1.355(5) |
| C(13)-C(14) | 1.400(5) |
| C(14)-C(16) | 1.391(4) |
| C(15)-C(17) | 1.376(4) |
| C(16)-C(18) | 1.374(4) |
| C(17)-C(18) | 1.371(4) |
| C(19A)-C(19) | 0.666(15) |
| C(1)-Fe(1)-C(9) | 160.78(14) |
| C(1)-Fe(1)-C(2) | 40.90(14) |
| C(9)-Fe(1)-C(2) | 155.21(15) |
| C(1)-Fe(1)-C(5) | 41.07(14) |
| C(9)-Fe(1)-C(5) | 122.44(14) |
| C(2)-Fe(1)-C(5) | 68.58(14) |
| C(1)-Fe(1)-C(8) | 158.98(14) |
| C(9)-Fe(1)-C(8) | 40.12(11) |
| C(2)-Fe(1)-C(8) | 120.79(15) |
| C(5)-Fe(1)-C(8) | 155.98(15) |
| C(1)-Fe(1)-C(10) | 126.54(13) |
| C(9)-Fe(1)-C(10) | 40.88(11) |
| C(2)-Fe(1)-C(10) | 162.34(15) |
| C(5)-Fe(1)-C(10) | 110.20(13) |
| C(8)-Fe(1)-C(10) | 67.88(12) |
| C(1)-Fe(1)-C(7) | 125.60(14) |
| C(9)-Fe(1)-C(7) | 67.91(12) |
| C(2)-Fe(1)-C(7) | 107.77(14) |
| C(5)-Fe(1)-C(7) | 163.30(14) |
| C(8)-Fe(1)-C(7) | 40.19(11) |
| C(10)-Fe(1)-C(7) | 68.02(12) |
| C(1)-Fe(1)-C(3) | 67.85(15) |
| C(9)-Fe(1)-C(3) | 119.71(15) |
| C(2)-Fe(1)-C(3) | 39.69(14) |

| | | | |
|---|---|---|---|
| C(5)-Fe(1)-C(3) | 67.99(14) | C(2)-C(3)-Fe(1) | 69.89(19) |
| C(8)-Fe(1)-C(3) | 104.25(14) | C(4)-C(3)-Fe(1) | 69.94(19) |
| C(10)-Fe(1)-C(3) | 157.56(16) | C(19A)-O(3A)-C(19) | 7.9(16) |
| C(7)-Fe(1)-C(3) | 120.35(14) | C(19)-O(3)-C(19A) | 12.8(12) |
| C(1)-Fe(1)-C(4) | 68.39(14) | C(3)-C(4)-C(5) | 107.7(3) |
| C(9)-Fe(1)-C(4) | 105.13(14) | C(3)-C(4)-Fe(1) | 69.65(18) |
| C(2)-Fe(1)-C(4) | 67.85(15) | C(5)-C(4)-Fe(1) | 69.37(18) |
| C(5)-Fe(1)-C(4) | 40.48(14) | C(4)-C(5)-C(1) | 107.6(3) |
| C(8)-Fe(1)-C(4) | 119.03(14) | C(4)-C(5)-Fe(1) | 70.16(19) |
| C(10)-Fe(1)-C(4) | 123.48(15) | C(1)-C(5)-Fe(1) | 69.27(17) |
| C(7)-Fe(1)-C(4) | 154.82(15) | C(7)-C(6)-C(10) | 106.5(3) |
| C(3)-Fe(1)-C(4) | 40.41(14) | C(7)-C(6)-C(11) | 119.1(4) |
| C(1)-Fe(1)-C(6) | 111.72(12) | C(10)-C(6)-C(11) | 134.4(4) |
| C(9)-Fe(1)-C(6) | 68.50(12) | C(7)-C(6)-C(11A) | 150.9(6) |
| C(2)-Fe(1)-C(6) | 125.06(14) | C(10)-C(6)-C(11A) | 102.5(6) |
| C(5)-Fe(1)-C(6) | 127.44(13) | C(11)-C(6)-C(11A) | 31.9(4) |
| C(8)-Fe(1)-C(6) | 67.84(11) | C(7)-C(6)-Fe(1) | 68.71(16) |
| C(10)-Fe(1)-C(6) | 40.71(12) | C(10)-C(6)-Fe(1) | 68.54(15) |
| C(7)-Fe(1)-C(6) | 40.36(11) | C(11)-C(6)-Fe(1) | 125.3(2) |
| C(3)-Fe(1)-C(6) | 157.72(15) | C(11A)-C(6)-Fe(1) | 123.3(5) |
| C(4)-Fe(1)-C(6) | 161.75(15) | C(8)-C(7)-C(6) | 108.8(3) |
| O(2)-N(1)-O(1) | 123.7(3) | C(8)-C(7)-Fe(1) | 69.82(16) |
| O(2)-N(1)-C(18) | 118.8(3) | C(6)-C(7)-Fe(1) | 70.92(16) |
| O(1)-N(1)-C(18) | 117.6(3) | C(9)-C(8)-C(7) | 108.9(3) |
| C(2)-C(1)-C(5) | 107.3(3) | C(9)-C(8)-Fe(1) | 69.81(16) |
| C(2)-C(1)-C(19) | 118.3(7) | C(7)-C(8)-Fe(1) | 69.99(17) |
| C(5)-C(1)-C(19) | 134.1(6) | C(8)-C(9)-C(10) | 107.7(3) |
| C(2)-C(1)-C(19A) | 143.3(10) | C(8)-C(9)-Fe(1) | 70.07(17) |
| C(5)-C(1)-C(19A) | 109.0(10) | C(10)-C(9)-Fe(1) | 69.76(16) |
| C(19)-C(1)-C(19A) | 25.1(6) | C(9)-C(10)-C(6) | 108.1(3) |
| C(2)-C(1)-Fe(1) | 69.74(19) | C(9)-C(10)-Fe(1) | 69.36(17) |
| C(5)-C(1)-Fe(1) | 69.65(18) | C(6)-C(10)-Fe(1) | 70.74(16) |
| C(19)-C(1)-Fe(1) | 121.1(5) | C(12A)-C(11)-C(11A) | 93(2) |
| C(19A)-C(1)-Fe(1) | 119.3(7) | C(12A)-C(11)-C(12) | 55.1(11) |
| C(3)-C(2)-C(1) | 108.3(3) | C(11A)-C(11)-C(12) | 37.7(13) |
| C(3)-C(2)-Fe(1) | 70.4(2) | C(12A)-C(11)-C(6) | 171.4(10) |
| C(1)-C(2)-Fe(1) | 69.36(18) | C(11A)-C(11)-C(6) | 84.8(14) |
| C(2)-C(3)-C(4) | 109.1(3) | C(12)-C(11)-C(6) | 121.6(5) |

| | |
|---|---|
| C(12)-C(11A)-C(11) | 103(2) |
| C(12)-C(11A)-C(12A) | 60.0(14) |
| C(11)-C(11A)-C(12A) | 42.8(11) |
| C(12)-C(11A)-C(6) | 162.0(17) |
| C(11)-C(11A)-C(6) | 63.3(13) |
| C(12A)-C(11A)-C(6) | 105.7(14) |
| C(11A)-C(12)-C(12A) | 78.6(17) |
| C(11A)-C(12)-C(11) | 39.6(12) |
| C(12A)-C(12)-C(11) | 39.1(9) |
| C(11A)-C(12)-C(13) | 159.6(13) |
| C(12A)-C(12)-C(13) | 84.5(10) |
| C(11)-C(12)-C(13) | 123.1(5) |
| C(11)-C(12A)-C(11A) | 44.5(13) |
| C(11)-C(12A)-C(12) | 85.8(17) |
| C(11A)-C(12A)-C(12) | 41.4(8) |
| C(11)-C(12A)-C(13) | 142.3(16) |
| C(11A)-C(12A)-C(13) | 98.1(13) |
| C(12)-C(12A)-C(13) | 57.3(8) |
| C(15)-C(13)-C(14) | 118.4(3) |
| C(15)-C(13)-C(12) | 115.0(4) |
| C(14)-C(13)-C(12) | 126.5(4) |
| C(15)-C(13)-C(12A) | 153.2(6) |
| C(14)-C(13)-C(12A) | 88.3(6) |
| C(12)-C(13)-C(12A) | 38.2(4) |
| C(16)-C(14)-C(13) | 121.2(3) |
| C(13)-C(15)-C(17) | 121.6(3) |
| C(18)-C(16)-C(14) | 117.7(3) |
| C(18)-C(17)-C(15) | 119.2(3) |
| C(17)-C(18)-C(16) | 121.8(3) |
| C(17)-C(18)-N(1) | 118.2(3) |
| C(16)-C(18)-N(1) | 119.9(3) |
| C(19)-C(19A)-O(3A) | 158(4) |
| C(19)-C(19A)-C(1) | 69(3) |
| O(3A)-C(19A)-C(1) | 132(2) |
| C(19)-C(19A)-O(3) | 23(2) |
| O(3A)-C(19A)-O(3) | 135.2(19) |
| C(1)-C(19A)-O(3) | 92.2(11) |
| C(19A)-C(19)-O(3) | 144(4) |
| C(19A)-C(19)-C(1) | 86(3) |
| O(3)-C(19)-C(1) | 130.2(12) |
| C(19A)-C(19)-O(3A) | 14(3) |
| O(3)-C(19)-O(3A) | 130.3(11) |
| C(1)-C(19)-O(3A) | 99.4(7) |

Symmetry transformations used to generate equivalent atoms:

**Table 4**. Anisotropic displacement parameters (Å$^2$x 10$^3$) for str99m. The anisotropic displacement factor exponent takes the form: $-2\pi^2$[ $h^2 a^{*2}U^{11}$ + ... + 2 h k a* b* $U^{12}$ ]

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| Fe(1) | 39(1) | 36(1) | 37(1) | -2(1) | 3(1) | 6(1) |
| N(1) | 68(2) | 76(2) | 38(2) | 7(2) | 9(1) | 13(2) |
| O(1) | 111(2) | 120(2) | 57(2) | 19(2) | 33(2) | -15(2) |
| C(1) | 69(2) | 55(2) | 57(2) | 13(2) | -2(2) | 27(2) |
| C(2) | 72(2) | 35(2) | 114(3) | 8(2) | 5(2) | 13(2) |
| O(2) | 119(2) | 119(3) | 47(2) | -27(2) | 9(2) | -14(2) |
| C(3) | 74(2) | 59(2) | 89(3) | -30(2) | 2(2) | 24(2) |
| O(3A) | 125(7) | 105(8) | 54(5) | -8(5) | -12(5) | 1(6) |
| O(3) | 106(4) | 117(4) | 72(3) | 42(3) | 4(3) | -11(3) |
| C(4) | 52(2) | 76(3) | 86(3) | -7(2) | 21(2) | 23(2) |
| C(5) | 44(2) | 59(2) | 92(3) | -12(2) | -15(2) | 17(2) |
| C(6) | 54(2) | 59(2) | 38(2) | 1(2) | 2(2) | 28(2) |
| C(7) | 37(2) | 64(2) | 60(2) | 5(2) | 4(2) | 6(1) |
| C(8) | 59(2) | 60(2) | 36(2) | -3(1) | -5(2) | 4(2) |
| C(9) | 59(2) | 53(2) | 39(2) | 10(2) | 6(1) | 2(2) |
| C(10) | 64(2) | 34(2) | 51(2) | -6(1) | -15(2) | 10(1) |
| C(11) | 47(3) | 54(3) | 31(3) | 1(2) | 7(2) | 19(2) |
| C(12) | 54(3) | 56(3) | 33(3) | -5(2) | 3(2) | 24(2) |
| C(13) | 69(2) | 69(2) | 43(2) | 10(2) | 11(2) | 38(2) |
| C(14) | 104(3) | 52(2) | 51(2) | -14(2) | -19(2) | 23(2) |
| C(15) | 57(2) | 88(3) | 45(2) | 5(2) | 12(2) | 11(2) |
| C(16) | 74(2) | 52(2) | 53(2) | 7(2) | 4(2) | 7(2) |
| C(17) | 48(2) | 68(2) | 47(2) | 0(2) | 3(2) | 5(2) |
| C(18) | 49(2) | 55(2) | 32(2) | 5(1) | 6(1) | 13(1) |
| C(19A) | 74(13) | 44(10) | 64(10) | 17(9) | -27(9) | 3(7) |
| C(19) | 71(7) | 58(6) | 69(5) | 19(6) | -17(5) | 9(4) |

**Table 5**. Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters (Å$^2$x 10 $^3$) for str99m.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(2) | 867 | 12588 | 1479 | 88 |
| H(3) | -468 | 12078 | 2297 | 89 |
| H(4) | -2783 | 9805 | 2196 | 85 |
| H(5) | -2889 | 8891 | 1295 | 78 |
| H(7) | 3748 | 9592 | 1766 | 64 |
| H(8) | 2281 | 9147 | 2573 | 62 |
| H(9) | 14 | 6859 | 2459 | 60 |
| H(10) | 104 | 5815 | 1569 | 60 |
| H(14) | 4743 | 8372 | 96 | 83 |
| H(15) | 1515 | 4323 | -64 | 76 |
| H(16) | 5577 | 8083 | -734 | 71 |
| H(17) | 2231 | 4083 | -894 | 65 |

**Table 6**. Torsion angles [°] for str99m.

| | |
|---|---|
| C(9)-Fe(1)-C(1)-C(2) | 154.2(3) |
| C(5)-Fe(1)-C(1)-C(2) | 118.4(3) |
| C(8)-Fe(1)-C(1)-C(2) | -34.5(4) |
| C(10)-Fe(1)-C(1)-C(2) | -162.9(2) |
| C(7)-Fe(1)-C(1)-C(2) | -75.3(2) |
| C(3)-Fe(1)-C(1)-C(2) | 36.97(19) |
| C(4)-Fe(1)-C(1)-C(2) | 80.7(2) |
| C(6)-Fe(1)-C(1)-C(2) | -119.0(2) |
| C(9)-Fe(1)-C(1)-C(5) | 35.8(5) |
| C(2)-Fe(1)-C(1)-C(5) | -118.4(3) |
| C(8)-Fe(1)-C(1)-C(5) | -152.9(3) |
| C(10)-Fe(1)-C(1)-C(5) | 78.7(2) |
| C(7)-Fe(1)-C(1)-C(5) | 166.3(2) |
| C(3)-Fe(1)-C(1)-C(5) | -81.4(2) |
| C(4)-Fe(1)-C(1)-C(5) | -37.7(2) |
| C(6)-Fe(1)-C(1)-C(5) | 122.6(2) |
| C(9)-Fe(1)-C(1)-C(19) | -94.2(8) |
| C(2)-Fe(1)-C(1)-C(19) | 111.6(8) |
| C(5)-Fe(1)-C(1)-C(19) | -130.0(8) |
| C(8)-Fe(1)-C(1)-C(19) | 77.1(8) |
| C(10)-Fe(1)-C(1)-C(19) | -51.4(7) |
| C(7)-Fe(1)-C(1)-C(19) | 36.2(7) |
| C(3)-Fe(1)-C(1)-C(19) | 148.5(7) |
| C(4)-Fe(1)-C(1)-C(19) | -167.8(7) |
| C(6)-Fe(1)-C(1)-C(19) | -7.4(7) |
| C(9)-Fe(1)-C(1)-C(19A) | -65.2(12) |
| C(2)-Fe(1)-C(1)-C(19A) | 140.6(12) |
| C(5)-Fe(1)-C(1)-C(19A) | -101.0(11) |
| C(8)-Fe(1)-C(1)-C(19A) | 106.1(11) |
| C(10)-Fe(1)-C(1)-C(19A) | -22.3(11) |
| C(7)-Fe(1)-C(1)-C(19A) | 65.3(11) |
| C(3)-Fe(1)-C(1)-C(19A) | 177.6(11) |
| C(4)-Fe(1)-C(1)-C(19A) | -138.7(11) |
| C(6)-Fe(1)-C(1)-C(19A) | 21.6(11) |
| C(5)-C(1)-C(2)-C(3) | -0.1(4) |
| C(19)-C(1)-C(2)-C(3) | -175.2(5) |
| C(19A)-C(1)-C(2)-C(3) | -172.1(12) |
| Fe(1)-C(1)-C(2)-C(3) | -59.9(2) |
| C(5)-C(1)-C(2)-Fe(1) | 59.8(2) |
| C(19)-C(1)-C(2)-Fe(1) | -115.3(5) |
| C(19A)-C(1)-C(2)-Fe(1) | -112.2(13) |
| C(1)-Fe(1)-C(2)-C(3) | 119.3(3) |
| C(9)-Fe(1)-C(2)-C(3) | -40.7(4) |
| C(5)-Fe(1)-C(2)-C(3) | 80.9(2) |
| C(8)-Fe(1)-C(2)-C(3) | -74.4(2) |
| C(10)-Fe(1)-C(2)-C(3) | 170.4(4) |
| C(7)-Fe(1)-C(2)-C(3) | -116.4(2) |
| C(4)-Fe(1)-C(2)-C(3) | 37.2(2) |
| C(6)-Fe(1)-C(2)-C(3) | -157.6(2) |
| C(9)-Fe(1)-C(2)-C(1) | -160.0(3) |
| C(5)-Fe(1)-C(2)-C(1) | -38.4(2) |
| C(8)-Fe(1)-C(2)-C(1) | 166.34(19) |
| C(10)-Fe(1)-C(2)-C(1) | 51.1(5) |
| C(7)-Fe(1)-C(2)-C(1) | 124.3(2) |
| C(3)-Fe(1)-C(2)-C(1) | -119.3(3) |
| C(4)-Fe(1)-C(2)-C(1) | -82.1(2) |
| C(6)-Fe(1)-C(2)-C(1) | 83.1(2) |
| C(1)-C(2)-C(3)-C(4) | 0.1(4) |
| Fe(1)-C(2)-C(3)-C(4) | -59.1(2) |
| C(1)-C(2)-C(3)-Fe(1) | 59.3(2) |
| C(1)-Fe(1)-C(3)-C(2) | -38.1(2) |
| C(9)-Fe(1)-C(3)-C(2) | 161.6(2) |
| C(5)-Fe(1)-C(3)-C(2) | -82.6(2) |
| C(8)-Fe(1)-C(3)-C(2) | 121.4(2) |
| C(10)-Fe(1)-C(3)-C(2) | -172.4(3) |
| C(7)-Fe(1)-C(3)-C(2) | 81.3(3) |
| C(4)-Fe(1)-C(3)-C(2) | -120.3(3) |
| C(6)-Fe(1)-C(3)-C(2) | 55.4(5) |
| C(1)-Fe(1)-C(3)-C(4) | 82.2(2) |
| C(9)-Fe(1)-C(3)-C(4) | -78.1(3) |
| C(2)-Fe(1)-C(3)-C(4) | 120.3(3) |
| C(5)-Fe(1)-C(3)-C(4) | 37.7(2) |
| C(8)-Fe(1)-C(3)-C(4) | -118.3(2) |

| | | | |
|---|---|---|---|
| C(10)-Fe(1)-C(3)-C(4) | -52.1(4) | C(3)-Fe(1)-C(5)-C(4) | -37.7(2) |
| C(7)-Fe(1)-C(3)-C(4) | -158.4(2) | C(6)-Fe(1)-C(5)-C(4) | 161.0(2) |
| C(6)-Fe(1)-C(3)-C(4) | 175.7(3) | C(9)-Fe(1)-C(5)-C(1) | -166.80(19) |
| C(2)-C(3)-C(4)-C(5) | -0.1(4) | C(2)-Fe(1)-C(5)-C(1) | 38.2(2) |
| Fe(1)-C(3)-C(4)-C(5) | -59.2(2) | C(8)-Fe(1)-C(5)-C(1) | 156.3(3) |
| C(2)-C(3)-C(4)-Fe(1) | 59.1(2) | C(10)-Fe(1)-C(5)-C(1) | -122.9(2) |
| C(1)-Fe(1)-C(4)-C(3) | -80.8(3) | C(7)-Fe(1)-C(5)-C(1) | -42.2(6) |
| C(9)-Fe(1)-C(4)-C(3) | 118.3(2) | C(3)-Fe(1)-C(5)-C(1) | 81.1(2) |
| C(2)-Fe(1)-C(4)-C(3) | -36.5(2) | C(4)-Fe(1)-C(5)-C(1) | 118.8(3) |
| C(5)-Fe(1)-C(4)-C(3) | -119.1(3) | C(6)-Fe(1)-C(5)-C(1) | -80.3(2) |
| C(8)-Fe(1)-C(4)-C(3) | 77.4(3) | C(1)-Fe(1)-C(6)-C(7) | 119.9(2) |
| C(10)-Fe(1)-C(4)-C(3) | 158.8(2) | C(9)-Fe(1)-C(6)-C(7) | -80.76(19) |
| C(7)-Fe(1)-C(4)-C(3) | 48.2(5) | C(2)-Fe(1)-C(6)-C(7) | 75.5(2) |
| C(6)-Fe(1)-C(4)-C(3) | -174.8(4) | C(5)-Fe(1)-C(6)-C(7) | 164.1(2) |
| C(1)-Fe(1)-C(4)-C(5) | 38.3(2) | C(8)-Fe(1)-C(6)-C(7) | -37.39(18) |
| C(9)-Fe(1)-C(4)-C(5) | -122.6(2) | C(10)-Fe(1)-C(6)-C(7) | -118.8(2) |
| C(2)-Fe(1)-C(4)-C(5) | 82.5(2) | C(3)-Fe(1)-C(6)-C(7) | 35.6(4) |
| C(8)-Fe(1)-C(4)-C(5) | -163.5(2) | C(4)-Fe(1)-C(6)-C(7) | -153.4(4) |
| C(10)-Fe(1)-C(4)-C(5) | -82.1(3) | C(1)-Fe(1)-C(6)-C(10) | -121.31(19) |
| C(7)-Fe(1)-C(4)-C(5) | 167.3(3) | C(9)-Fe(1)-C(6)-C(10) | 38.00(16) |
| C(3)-Fe(1)-C(4)-C(5) | 119.1(3) | C(2)-Fe(1)-C(6)-C(10) | -165.7(2) |
| C(6)-Fe(1)-C(4)-C(5) | -55.7(5) | C(5)-Fe(1)-C(6)-C(10) | -77.1(2) |
| C(3)-C(4)-C(5)-C(1) | 0.0(4) | C(8)-Fe(1)-C(6)-C(10) | 81.36(18) |
| Fe(1)-C(4)-C(5)-C(1) | -59.4(2) | C(7)-Fe(1)-C(6)-C(10) | 118.8(2) |
| C(3)-C(4)-C(5)-Fe(1) | 59.3(2) | C(3)-Fe(1)-C(6)-C(10) | 154.3(4) |
| C(2)-C(1)-C(5)-C(4) | 0.1(3) | C(4)-Fe(1)-C(6)-C(10) | -34.6(5) |
| C(19)-C(1)-C(5)-C(4) | 174.0(6) | C(1)-Fe(1)-C(6)-C(11) | 8.6(4) |
| C(19A)-C(1)-C(5)-C(4) | 175.0(8) | C(9)-Fe(1)-C(6)-C(11) | 168.0(4) |
| Fe(1)-C(1)-C(5)-C(4) | 59.9(2) | C(2)-Fe(1)-C(6)-C(11) | -35.8(4) |
| C(2)-C(1)-C(5)-Fe(1) | -59.8(2) | C(5)-Fe(1)-C(6)-C(11) | 52.8(4) |
| C(19)-C(1)-C(5)-Fe(1) | 114.1(7) | C(8)-Fe(1)-C(6)-C(11) | -148.7(4) |
| C(19A)-C(1)-C(5)-Fe(1) | 115.1(8) | C(10)-Fe(1)-C(6)-C(11) | 130.0(4) |
| C(1)-Fe(1)-C(5)-C(4) | -118.8(3) | C(7)-Fe(1)-C(6)-C(11) | -111.3(5) |
| C(9)-Fe(1)-C(5)-C(4) | 74.4(3) | C(3)-Fe(1)-C(6)-C(11) | -75.7(5) |
| C(2)-Fe(1)-C(5)-C(4) | -80.5(2) | C(4)-Fe(1)-C(6)-C(11) | 95.3(6) |
| C(8)-Fe(1)-C(5)-C(4) | 37.5(4) | C(1)-Fe(1)-C(6)-C(11A) | -30.1(7) |
| C(10)-Fe(1)-C(5)-C(4) | 118.3(2) | C(9)-Fe(1)-C(6)-C(11A) | 129.2(7) |
| C(7)-Fe(1)-C(5)-C(4) | -161.0(4) | C(2)-Fe(1)-C(6)-C(11A) | -74.5(7) |

| | | | |
|---|---|---|---|
| C(5)-Fe(1)-C(6)-C(11A) | 14.1(7) | C(4)-Fe(1)-C(8)-C(9) | 78.7(2) |
| C(8)-Fe(1)-C(6)-C(11A) | 172.6(7) | C(6)-Fe(1)-C(8)-C(9) | -82.48(19) |
| C(10)-Fe(1)-C(6)-C(11A) | 91.2(7) | C(1)-Fe(1)-C(8)-C(7) | -55.5(4) |
| C(7)-Fe(1)-C(6)-C(11A) | -150.0(7) | C(9)-Fe(1)-C(8)-C(7) | 120.0(3) |
| C(3)-Fe(1)-C(6)-C(11A) | -114.5(7) | C(2)-Fe(1)-C(8)-C(7) | -81.1(2) |
| C(4)-Fe(1)-C(6)-C(11A) | 56.6(8) | C(5)-Fe(1)-C(8)-C(7) | 171.9(3) |
| C(10)-C(6)-C(7)-C(8) | 1.5(3) | C(10)-Fe(1)-C(8)-C(7) | 81.7(2) |
| C(11)-C(6)-C(7)-C(8) | 179.3(3) | C(3)-Fe(1)-C(8)-C(7) | -120.5(2) |
| C(11A)-C(6)-C(7)-C(8) | -179.5(10) | C(4)-Fe(1)-C(8)-C(7) | -161.2(2) |
| Fe(1)-C(6)-C(7)-C(8) | 59.8(2) | C(6)-Fe(1)-C(8)-C(7) | 37.55(18) |
| C(10)-C(6)-C(7)-Fe(1) | -58.33(18) | C(7)-C(8)-C(9)-C(10) | 0.6(3) |
| C(11)-C(6)-C(7)-Fe(1) | 119.5(3) | Fe(1)-C(8)-C(9)-C(10) | 59.9(2) |
| C(11A)-C(6)-C(7)-Fe(1) | 120.7(10) | C(7)-C(8)-C(9)-Fe(1) | -59.3(2) |
| C(1)-Fe(1)-C(7)-C(8) | 158.7(2) | C(1)-Fe(1)-C(9)-C(8) | 175.2(3) |
| C(9)-Fe(1)-C(7)-C(8) | -37.02(18) | C(2)-Fe(1)-C(9)-C(8) | -47.6(4) |
| C(2)-Fe(1)-C(7)-C(8) | 117.0(2) | C(5)-Fe(1)-C(9)-C(8) | -157.71(19) |
| C(5)-Fe(1)-C(7)-C(8) | -168.4(4) | C(10)-Fe(1)-C(9)-C(8) | 118.5(3) |
| C(10)-Fe(1)-C(7)-C(8) | -81.3(2) | C(7)-Fe(1)-C(9)-C(8) | 37.08(18) |
| C(3)-Fe(1)-C(7)-C(8) | 75.4(2) | C(3)-Fe(1)-C(9)-C(8) | -76.3(2) |
| C(4)-Fe(1)-C(7)-C(8) | 41.4(4) | C(4)-Fe(1)-C(9)-C(8) | -117.3(2) |
| C(6)-Fe(1)-C(7)-C(8) | -119.4(3) | C(6)-Fe(1)-C(9)-C(8) | 80.70(19) |
| C(1)-Fe(1)-C(7)-C(6) | -82.0(2) | C(1)-Fe(1)-C(9)-C(10) | 56.6(4) |
| C(9)-Fe(1)-C(7)-C(6) | 82.34(19) | C(2)-Fe(1)-C(9)-C(10) | -166.1(3) |
| C(2)-Fe(1)-C(7)-C(6) | -123.7(2) | C(5)-Fe(1)-C(9)-C(10) | 83.7(2) |
| C(5)-Fe(1)-C(7)-C(6) | -49.1(5) | C(8)-Fe(1)-C(9)-C(10) | -118.5(3) |
| C(8)-Fe(1)-C(7)-C(6) | 119.4(3) | C(7)-Fe(1)-C(9)-C(10) | -81.47(19) |
| C(10)-Fe(1)-C(7)-C(6) | 38.07(17) | C(3)-Fe(1)-C(9)-C(10) | 165.19(19) |
| C(3)-Fe(1)-C(7)-C(6) | -165.2(2) | C(4)-Fe(1)-C(9)-C(10) | 124.1(2) |
| C(4)-Fe(1)-C(7)-C(6) | 160.7(3) | C(6)-Fe(1)-C(9)-C(10) | -37.85(18) |
| C(6)-C(7)-C(8)-C(9) | -1.3(3) | C(8)-C(9)-C(10)-C(6) | 0.3(3) |
| Fe(1)-C(7)-C(8)-C(9) | 59.2(2) | Fe(1)-C(9)-C(10)-C(6) | 60.38(19) |
| C(6)-C(7)-C(8)-Fe(1) | -60.5(2) | C(8)-C(9)-C(10)-Fe(1) | -60.1(2) |
| C(1)-Fe(1)-C(8)-C(9) | -175.6(3) | C(7)-C(6)-C(10)-C(9) | -1.1(3) |
| C(2)-Fe(1)-C(8)-C(9) | 158.88(19) | C(11)-C(6)-C(10)-C(9) | -178.4(3) |
| C(5)-Fe(1)-C(8)-C(9) | 51.8(4) | C(11A)-C(6)-C(10)-C(9) | 179.4(5) |
| C(10)-Fe(1)-C(8)-C(9) | -38.36(18) | Fe(1)-C(6)-C(10)-C(9) | -59.5(2) |
| C(7)-Fe(1)-C(8)-C(9) | -120.0(3) | C(7)-C(6)-C(10)-Fe(1) | 58.43(19) |
| C(3)-Fe(1)-C(8)-C(9) | 119.5(2) | C(11)-C(6)-C(10)-Fe(1) | -118.9(4) |

| | |
|---|---|
| C(11A)-C(6)-C(10)-Fe(1) | -121.1(5) |
| C(1)-Fe(1)-C(10)-C(9) | -159.98(18) |
| C(2)-Fe(1)-C(10)-C(9) | 160.7(4) |
| C(5)-Fe(1)-C(10)-C(9) | -116.6(2) |
| C(8)-Fe(1)-C(10)-C(9) | 37.67(17) |
| C(7)-Fe(1)-C(10)-C(9) | 81.18(19) |
| C(3)-Fe(1)-C(10)-C(9) | -35.6(4) |
| C(4)-Fe(1)-C(10)-C(9) | -73.4(2) |
| C(6)-Fe(1)-C(10)-C(9) | 118.9(2) |
| C(1)-Fe(1)-C(10)-C(6) | 81.1(2) |
| C(9)-Fe(1)-C(10)-C(6) | -118.9(2) |
| C(2)-Fe(1)-C(10)-C(6) | 41.7(5) |
| C(5)-Fe(1)-C(10)-C(6) | 124.43(19) |
| C(8)-Fe(1)-C(10)-C(6) | -81.27(18) |
| C(7)-Fe(1)-C(10)-C(6) | -37.75(17) |
| C(3)-Fe(1)-C(10)-C(6) | -154.5(3) |
| C(4)-Fe(1)-C(10)-C(6) | 167.68(19) |
| C(7)-C(6)-C(11)-C(12A) | 106(9) |
| C(10)-C(6)-C(11)-C(12A) | -77(9) |
| C(11A)-C(6)-C(11)-C(12A) | -73(9) |
| Fe(1)-C(6)-C(11)-C(12A) | -171(9) |
| C(7)-C(6)-C(11)-C(11A) | 178.9(9) |
| C(10)-C(6)-C(11)-C(11A) | -4.1(11) |
| Fe(1)-C(6)-C(11)-C(11A) | -97.8(10) |
| C(7)-C(6)-C(11)-C(12) | 170.2(3) |
| C(10)-C(6)-C(11)-C(12) | -12.7(6) |
| C(11A)-C(6)-C(11)-C(12) | -8.6(9) |
| Fe(1)-C(6)-C(11)-C(12) | -106.4(4) |
| C(12A)-C(11)-C(11A)-C(12) | 3.8(16) |
| C(6)-C(11)-C(11A)-C(12) | -167.9(12) |
| C(12)-C(11)-C(11A)-C(12A) | -3.8(16) |
| C(6)-C(11)-C(11A)-C(12A) | -171.7(9) |
| C(12A)-C(11)-C(11A)-C(6) | 171.7(9) |
| C(12)-C(11)-C(11A)-C(6) | 167.9(12) |
| C(7)-C(6)-C(11A)-C(12) | 39(6) |
| C(10)-C(6)-C(11A)-C(12) | -142(5) |
| C(11)-C(6)-C(11A)-C(12) | 41(5) |
| Fe(1)-C(6)-C(11A)-C(12) | 146(5) |
| C(7)-C(6)-C(11A)-C(11) | -2.1(17) |
| C(10)-C(6)-C(11A)-C(11) | 177.0(8) |
| Fe(1)-C(6)-C(11A)-C(11) | 104.6(9) |
| C(7)-C(6)-C(11A)-C(12A) | 3.8(17) |
| C(10)-C(6)-C(11A)-C(12A) | -177.2(9) |
| C(11)-C(6)-C(11A)-C(12A) | 5.8(7) |
| Fe(1)-C(6)-C(11A)-C(12A) | 110.4(9) |
| C(11)-C(11A)-C(12)-C(12A) | -3.0(12) |
| C(6)-C(11A)-C(12)-C(12A) | -40(5) |
| C(12A)-C(11A)-C(12)-C(11) | 3.0(12) |
| C(6)-C(11A)-C(12)-C(11) | -37(4) |
| C(11)-C(11A)-C(12)-C(13) | -38(4) |
| C(12A)-C(11A)-C(12)-C(13) | -35(3) |
| C(6)-C(11A)-C(12)-C(13) | -75(6) |
| C(12A)-C(11)-C(12)-C(11A) | -175.4(19) |
| C(6)-C(11)-C(12)-C(11A) | 14.2(14) |
| C(11A)-C(11)-C(12)-C(12A) | 175.4(19) |
| C(6)-C(11)-C(12)-C(12A) | -170.5(11) |
| C(12A)-C(11)-C(12)-C(13) | -10.1(10) |
| C(11A)-C(11)-C(12)-C(13) | 165.3(16) |
| C(6)-C(11)-C(12)-C(13) | 179.4(3) |
| C(12)-C(11)-C(12A)-C(11A) | 2.8(12) |
| C(6)-C(11)-C(12A)-C(11A) | 73(9) |
| C(11A)-C(11)-C(12A)-C(12) | -2.8(12) |
| C(6)-C(11)-C(12A)-C(12) | 70(9) |
| C(11A)-C(11)-C(12A)-C(13) | 9(2) |
| C(12)-C(11)-C(12A)-C(13) | 11.7(12) |
| C(6)-C(11)-C(12A)-C(13) | 82(9) |
| C(12)-C(11A)-C(12A)-C(11) | -175.7(18) |
| C(6)-C(11A)-C(12A)-C(11) | -7.7(9) |
| C(11)-C(11A)-C(12A)-C(12) | 175.7(18) |
| C(6)-C(11A)-C(12A)-C(12) | 168.0(14) |
| C(12)-C(11A)-C(12A)-C(13) | 9.8(9) |
| C(11)-C(11A)-C(12A)-C(13) | -174.5(13) |
| C(6)-C(11A)-C(12A)-C(13) | 177.8(6) |
| C(11A)-C(12)-C(12A)-C(11) | 3.0(12) |
| C(13)-C(12)-C(12A)-C(11) | 171.5(9) |
| C(11)-C(12)-C(12A)-C(11A) | -3.0(12) |

| | |
|---|---|
| C(13)-C(12)-C(12A)-C(11A) | 168.5(10) |
| C(11A)-C(12)-C(12A)-C(13) | -168.5(10) |
| C(11)-C(12)-C(12A)-C(13) | -171.5(8) |
| C(11A)-C(12)-C(13)-C(15) | -147(3) |
| C(12A)-C(12)-C(13)-C(15) | 178.8(7) |
| C(11)-C(12)-C(13)-C(15) | -174.8(3) |
| C(11A)-C(12)-C(13)-C(14) | 35(4) |
| C(12A)-C(12)-C(13)-C(14) | 0.8(7) |
| C(11)-C(12)-C(13)-C(14) | 7.2(6) |
| C(11A)-C(12)-C(13)-C(12A) | 34(3) |
| C(11)-C(12)-C(13)-C(12A) | 6.4(6) |
| C(11)-C(12A)-C(13)-C(15) | -16(3) |
| C(11A)-C(12A)-C(13)-C(15) | -10.1(15) |
| C(12)-C(12A)-C(13)-C(15) | -2.5(13) |
| C(11)-C(12A)-C(13)-C(14) | 166.7(18) |
| C(11A)-C(12A)-C(13)-C(14) | 173.0(8) |
| C(12)-C(12A)-C(13)-C(14) | -179.3(6) |
| C(11)-C(12A)-C(13)-C(12) | -13.9(14) |
| C(11A)-C(12A)-C(13)-C(12) | -7.7(7) |
| C(15)-C(13)-C(14)-C(16) | 1.2(5) |
| C(12)-C(13)-C(14)-C(16) | 179.1(3) |
| C(12A)-C(13)-C(14)-C(16) | 179.6(4) |
| C(14)-C(13)-C(15)-C(17) | -2.7(5) |
| C(12)-C(13)-C(15)-C(17) | 179.2(3) |
| C(12A)-C(13)-C(15)-C(17) | -179.1(9) |
| C(13)-C(14)-C(16)-C(18) | 0.9(5) |
| C(13)-C(15)-C(17)-C(18) | 1.9(5) |
| C(15)-C(17)-C(18)-C(16) | 0.3(5) |
| C(15)-C(17)-C(18)-N(1) | 178.2(3) |
| C(14)-C(16)-C(18)-C(17) | -1.7(4) |
| C(14)-C(16)-C(18)-N(1) | -179.6(3) |
| O(2)-N(1)-C(18)-C(17) | 2.8(4) |
| O(1)-N(1)-C(18)-C(17) | -176.7(3) |
| O(2)-N(1)-C(18)-C(16) | -179.3(3) |
| O(1)-N(1)-C(18)-C(16) | 1.2(4) |
| C(19)-O(3A)-C(19A)-C(1) | 168(12) |
| C(19)-O(3A)-C(19A)-O(3) | -4(8) |
| C(2)-C(1)-C(19A)-C(19) | -6(3) |
| C(5)-C(1)-C(19A)-C(19) | -178(2) |
| Fe(1)-C(1)-C(19A)-C(19) | -101(2) |
| C(2)-C(1)-C(19A)-O(3A) | 178.2(12) |
| C(5)-C(1)-C(19A)-O(3A) | 6(2) |
| C(19)-C(1)-C(19A)-O(3A) | -175(4) |
| Fe(1)-C(1)-C(19A)-O(3A) | 83(2) |
| C(2)-C(1)-C(19A)-O(3) | -6.9(17) |
| C(5)-C(1)-C(19A)-O(3) | -178.8(5) |
| C(19)-C(1)-C(19A)-O(3) | -0.6(18) |
| Fe(1)-C(1)-C(19A)-O(3) | -102.0(8) |
| C(19)-O(3)-C(19A)-O(3A) | 176(7) |
| C(19)-O(3)-C(19A)-C(1) | 1(4) |
| O(3A)-C(19A)-C(19)-O(3) | -8(14) |
| C(1)-C(19A)-C(19)-O(3) | -179(5) |
| O(3A)-C(19A)-C(19)-C(1) | 171(9) |
| O(3)-C(19A)-C(19)-C(1) | 179(5) |
| C(1)-C(19A)-C(19)-O(3A) | -171(9) |
| O(3)-C(19A)-C(19)-O(3A) | 8(14) |
| C(19A)-O(3)-C(19)-C(1) | -178(6) |
| C(19A)-O(3)-C(19)-O(3A) | -2(4) |
| C(2)-C(1)-C(19)-C(19A) | 176(2) |
| C(5)-C(1)-C(19)-C(19A) | 2(3) |
| Fe(1)-C(1)-C(19)-C(19A) | 93(3) |
| C(2)-C(1)-C(19)-O(3) | -5.5(13) |
| C(5)-C(1)-C(19)-O(3) | -178.9(7) |
| C(19A)-C(1)-C(19)-O(3) | 179(3) |
| Fe(1)-C(1)-C(19)-O(3) | -87.7(12) |
| C(2)-C(1)-C(19)-O(3A) | 177.9(4) |
| C(5)-C(1)-C(19)-O(3A) | 4.5(10) |
| C(19A)-C(1)-C(19)-O(3A) | 2(2) |
| Fe(1)-C(1)-C(19)-O(3A) | 95.6(6) |
| C(19A)-O(3A)-C(19)-O(3) | 174(11) |
| C(19A)-O(3A)-C(19)-C(1) | -9(9) |

Symmetry transformations used to generate equivalent atoms:

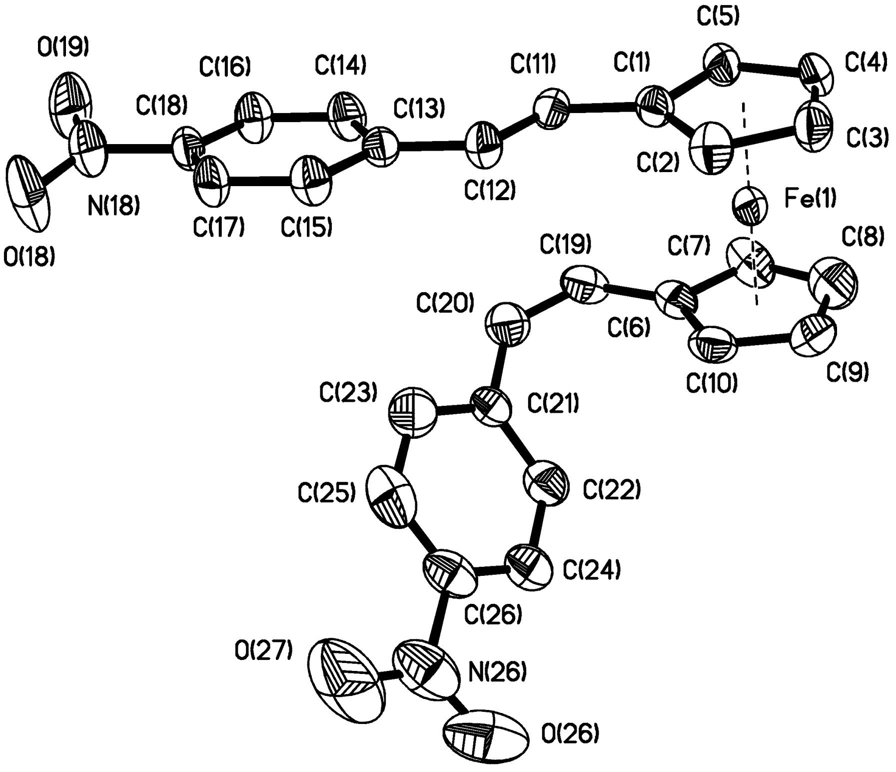

O(19)
C(16)
C(14)
C(11)
C(1)
C(5)
C(4)
C(18)
C(13)
C(3)
C(2)
C(12)
Fe(1)
N(18)
C(17)
C(15)
O(18)
C(19)
C(7)
C(8)
C(20)
C(6)
C(10)
C(9)
C(23)
C(21)
C(25)
C(22)
C(24)
C(26)
O(27)
N(26)
O(26)

**Table 1**.Crystal data and structure refinement for str100m.

| | | |
|---|---|---|
| Identification code | str100m | |
| Empirical formula | C26 H20 Fe N2 O4 | |
| Formula weight | 480.29 | |
| Temperature | 293(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Triclinic | |
| Space group | P-1 | |
| Unit cell dimensions | a = 7.5874(17) Å | $\alpha$= 100.919(5)°. |
| | b = 10.569(2) Å | $\beta$= 103.232(5)°. |
| | c = 14.416(3) Å | $\gamma$ = 101.555(6)°. |
| Volume | 1068.5(4) Å$^3$ | |
| Z | 2 | |
| Density (calculated) | 1.493 Mg/m$^3$ | |
| Absorption coefficient | 0.743 mm$^{-1}$ | |
| F(000) | 496 | |
| Crystal size | 0.26 x 0.11 x 0.10 mm$^3$ | |
| Theta range for data collection | 1.50 to 30.59°. | |
| Index ranges | -8<=h<=10, -15<=k<=14, -20<=l<=15 | |
| Reflections collected | 9110 | |
| Independent reflections | 6400 [R(int) = 0.0553] | |
| Completeness to theta = 30.59° | 97.5 % | |
| Refinement method | Full-matrix least-squares on F$^2$ | |
| Data / restraints / parameters | 6400 / 0 / 298 | |
| Goodness-of-fit on F$^2$ | 0.844 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0572, wR2 = 0.0943 | |
| R indices (all data) | R1 = 0.1695, wR2 = 0.1191 | |
| Largest diff. peak and hole | 0.758 and -0.599 e.Å$^{-3}$ | |

**Table 2**. Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters (Å$^2$x $10^3$) for str100m. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| Fe(1) | -60(1) | 4340(1) | 2386(1) | 30(1) |
| C(1) | -349(5) | 2774(3) | 1214(2) | 33(1) |
| C(2) | -1955(5) | 2621(3) | 1571(2) | 40(1) |
| C(3) | -2718(5) | 3712(3) | 1474(2) | 42(1) |
| C(4) | -1585(5) | 4566(3) | 1087(2) | 41(1) |
| C(5) | -119(5) | 4014(3) | 937(2) | 37(1) |
| C(6) | 2342(5) | 4504(3) | 3455(2) | 38(1) |
| C(7) | 2284(6) | 5767(3) | 3237(3) | 52(1) |
| C(8) | 693(6) | 6108(4) | 3426(3) | 60(1) |
| C(9) | -261(6) | 5082(4) | 3760(2) | 56(1) |
| C(10) | 735(5) | 4083(3) | 3766(2) | 43(1) |
| C(11) | 898(5) | 1902(3) | 1157(2) | 33(1) |
| C(12) | 660(5) | 729(3) | 1374(2) | 35(1) |
| C(13) | 1871(4) | -169(3) | 1309(2) | 31(1) |
| C(14) | 3559(5) | 156(3) | 1075(2) | 38(1) |
| C(15) | 1323(5) | -1438(3) | 1469(2) | 36(1) |
| C(16) | 4663(5) | -727(3) | 1004(2) | 39(1) |
| C(17) | 2424(5) | -2324(3) | 1399(2) | 38(1) |
| C(18) | 4048(5) | -1960(3) | 1161(2) | 33(1) |
| N(18) | 5226(5) | -2906(3) | 1077(2) | 49(1) |
| O(18) | 4855(4) | -3894(3) | 1390(2) | 78(1) |
| O(19) | 6482(4) | -2668(2) | 690(2) | 65(1) |
| C(19) | 3756(5) | 3834(3) | 3272(2) | 45(1) |
| C(20) | 4261(5) | 2808(4) | 3575(2) | 50(1) |
| C(21) | 3600(5) | 2121(3) | 4278(2) | 40(1) |
| C(22) | 3431(5) | 2826(3) | 5155(2) | 46(1) |
| C(23) | 3236(5) | 740(4) | 4102(3) | 56(1) |
| C(24) | 2910(5) | 2192(4) | 5845(3) | 49(1) |
| C(25) | 2710(6) | 97(4) | 4779(3) | 60(1) |
| N(26) | 2061(5) | 149(4) | 6372(3) | 71(1) |
| C(26) | 2571(5) | 830(4) | 5635(3) | 48(1) |
| O(26) | 1791(5) | 818(4) | 7093(3) | 98(1) |
| O(27) | 1958(6) | -1030(4) | 6236(3) | 121(1) |

**Table 3**. Bond lengths [Å] and angles [°] for str100m.

| | |
|---|---|
| Fe(1)-C(2) | 2.030(3) |
| Fe(1)-C(10) | 2.029(3) |
| Fe(1)-C(7) | 2.041(4) |
| Fe(1)-C(3) | 2.038(3) |
| Fe(1)-C(9) | 2.038(3) |
| Fe(1)-C(5) | 2.040(3) |
| Fe(1)-C(8) | 2.045(4) |
| Fe(1)-C(4) | 2.048(3) |
| Fe(1)-C(6) | 2.053(3) |
| Fe(1)-C(1) | 2.066(3) |
| C(1)-C(2) | 1.420(4) |
| C(1)-C(5) | 1.430(4) |
| C(1)-C(11) | 1.452(4) |
| C(2)-C(3) | 1.406(4) |
| C(3)-C(4) | 1.402(5) |
| C(4)-C(5) | 1.396(4) |
| C(6)-C(10) | 1.413(5) |
| C(6)-C(7) | 1.435(4) |
| C(6)-C(19) | 1.443(5) |
| C(7)-C(8) | 1.395(5) |
| C(8)-C(9) | 1.405(5) |
| C(9)-C(10) | 1.416(5) |
| C(11)-C(12) | 1.323(4) |
| C(12)-C(13) | 1.452(4) |
| C(13)-C(14) | 1.391(4) |
| C(13)-C(15) | 1.401(4) |
| C(14)-C(16) | 1.379(4) |
| C(15)-C(17) | 1.380(4) |
| C(16)-C(18) | 1.372(4) |
| C(17)-C(18) | 1.355(4) |
| C(18)-N(18) | 1.475(4) |
| N(18)-O(19) | 1.218(4) |
| N(18)-O(18) | 1.221(3) |
| C(19)-C(20) | 1.335(4) |
| C(20)-C(21) | 1.474(5) |
| C(21)-C(22) | 1.388(4) |
| C(21)-C(23) | 1.391(5) |
| C(22)-C(24) | 1.385(4) |
| C(23)-C(25) | 1.377(5) |
| C(24)-C(26) | 1.372(5) |
| C(25)-C(26) | 1.365(5) |
| N(26)-O(26) | 1.225(4) |
| N(26)-O(27) | 1.208(4) |
| N(26)-C(26) | 1.470(5) |
| C(2)-Fe(1)-C(10) | 105.89(14) |
| C(2)-Fe(1)-C(7) | 165.77(13) |
| C(10)-Fe(1)-C(7) | 68.28(14) |
| C(2)-Fe(1)-C(3) | 40.44(12) |
| C(10)-Fe(1)-C(3) | 125.46(14) |
| C(7)-Fe(1)-C(3) | 153.46(13) |
| C(2)-Fe(1)-C(9) | 117.26(16) |
| C(10)-Fe(1)-C(9) | 40.76(13) |
| C(7)-Fe(1)-C(9) | 67.45(17) |
| C(3)-Fe(1)-C(9) | 106.91(15) |
| C(2)-Fe(1)-C(5) | 68.27(13) |
| C(10)-Fe(1)-C(5) | 153.91(12) |
| C(7)-Fe(1)-C(5) | 110.88(15) |
| C(3)-Fe(1)-C(5) | 67.48(14) |
| C(9)-Fe(1)-C(5) | 164.93(13) |
| C(2)-Fe(1)-C(8) | 151.64(16) |
| C(10)-Fe(1)-C(8) | 68.39(15) |
| C(7)-Fe(1)-C(8) | 39.93(15) |
| C(3)-Fe(1)-C(8) | 118.90(15) |
| C(9)-Fe(1)-C(8) | 40.26(15) |
| C(5)-Fe(1)-C(8) | 128.85(14) |
| C(2)-Fe(1)-C(4) | 67.99(13) |
| C(10)-Fe(1)-C(4) | 163.46(14) |
| C(7)-Fe(1)-C(4) | 121.16(14) |
| C(3)-Fe(1)-C(4) | 40.13(13) |
| C(9)-Fe(1)-C(4) | 126.95(14) |
| C(5)-Fe(1)-C(4) | 39.92(12) |
| C(8)-Fe(1)-C(4) | 109.22(14) |
| C(2)-Fe(1)-C(6) | 126.30(12) |

| | |
|---|---|
| C(10)-Fe(1)-C(6) | 40.49(13) |
| C(7)-Fe(1)-C(6) | 41.02(12) |
| C(3)-Fe(1)-C(6) | 163.32(12) |
| C(9)-Fe(1)-C(6) | 68.08(15) |
| C(5)-Fe(1)-C(6) | 121.28(14) |
| C(8)-Fe(1)-C(6) | 68.31(14) |
| C(4)-Fe(1)-C(6) | 155.32(14) |
| C(2)-Fe(1)-C(1) | 40.56(12) |
| C(10)-Fe(1)-C(1) | 118.27(13) |
| C(7)-Fe(1)-C(1) | 129.54(16) |
| C(3)-Fe(1)-C(1) | 67.77(13) |
| C(9)-Fe(1)-C(1) | 151.87(15) |
| C(5)-Fe(1)-C(1) | 40.75(11) |
| C(8)-Fe(1)-C(1) | 166.82(16) |
| C(4)-Fe(1)-C(1) | 67.81(12) |
| C(6)-Fe(1)-C(1) | 108.66(13) |
| C(2)-C(1)-C(5) | 106.5(3) |
| C(2)-C(1)-C(11) | 128.6(3) |
| C(5)-C(1)-C(11) | 124.9(3) |
| C(2)-C(1)-Fe(1) | 68.34(17) |
| C(5)-C(1)-Fe(1) | 68.64(17) |
| C(11)-C(1)-Fe(1) | 126.2(2) |
| C(3)-C(2)-C(1) | 108.1(3) |
| C(3)-C(2)-Fe(1) | 70.10(18) |
| C(1)-C(2)-Fe(1) | 71.09(17) |
| C(2)-C(3)-C(4) | 108.6(3) |
| C(2)-C(3)-Fe(1) | 69.47(19) |
| C(4)-C(3)-Fe(1) | 70.31(19) |
| C(5)-C(4)-C(3) | 108.1(3) |
| C(5)-C(4)-Fe(1) | 69.74(17) |
| C(3)-C(4)-Fe(1) | 69.56(18) |
| C(4)-C(5)-C(1) | 108.6(3) |
| C(4)-C(5)-Fe(1) | 70.34(18) |
| C(1)-C(5)-Fe(1) | 70.61(17) |
| C(10)-C(6)-C(7) | 106.7(3) |
| C(10)-C(6)-C(19) | 130.8(3) |
| C(7)-C(6)-C(19) | 122.2(3) |
| C(10)-C(6)-Fe(1) | 68.85(19) |
| C(7)-C(6)-Fe(1) | 69.07(19) |
| C(19)-C(6)-Fe(1) | 122.6(2) |
| C(8)-C(7)-C(6) | 108.8(3) |
| C(8)-C(7)-Fe(1) | 70.2(2) |
| C(6)-C(7)-Fe(1) | 69.91(18) |
| C(7)-C(8)-C(9) | 107.9(3) |
| C(7)-C(8)-Fe(1) | 69.9(2) |
| C(9)-C(8)-Fe(1) | 69.6(2) |
| C(8)-C(9)-C(10) | 108.5(4) |
| C(8)-C(9)-Fe(1) | 70.1(2) |
| C(10)-C(9)-Fe(1) | 69.26(19) |
| C(6)-C(10)-C(9) | 108.1(3) |
| C(6)-C(10)-Fe(1) | 70.66(18) |
| C(9)-C(10)-Fe(1) | 69.98(19) |
| C(12)-C(11)-C(1) | 125.5(3) |
| C(11)-C(12)-C(13) | 126.4(3) |
| C(14)-C(13)-C(15) | 117.5(3) |
| C(14)-C(13)-C(12) | 123.2(3) |
| C(15)-C(13)-C(12) | 119.3(3) |
| C(16)-C(14)-C(13) | 121.7(3) |
| C(17)-C(15)-C(13) | 120.9(3) |
| C(18)-C(16)-C(14) | 118.2(3) |
| C(18)-C(17)-C(15) | 119.2(3) |
| C(17)-C(18)-C(16) | 122.5(3) |
| C(17)-C(18)-N(18) | 119.5(3) |
| C(16)-C(18)-N(18) | 118.0(3) |
| O(19)-N(18)-O(18) | 124.2(3) |
| O(19)-N(18)-C(18) | 118.4(3) |
| O(18)-N(18)-C(18) | 117.4(3) |
| C(20)-C(19)-C(6) | 131.3(3) |
| C(19)-C(20)-C(21) | 128.1(3) |
| C(22)-C(21)-C(23) | 118.1(3) |
| C(22)-C(21)-C(20) | 121.4(3) |
| C(23)-C(21)-C(20) | 120.3(3) |
| C(24)-C(22)-C(21) | 121.8(3) |
| C(25)-C(23)-C(21) | 120.6(4) |
| C(26)-C(24)-C(22) | 117.6(3) |
| C(26)-C(25)-C(23) | 119.3(3) |

|  |  |
|---|---|
| O(26)-N(26)-O(27) | 124.0(4) |
| O(26)-N(26)-C(26) | 117.9(4) |
| O(27)-N(26)-C(26) | 118.1(4) |
| C(25)-C(26)-C(24) | 122.5(3) |
| C(25)-C(26)-N(26) | 119.4(4) |
| C(24)-C(26)-N(26) | 118.1(4) |

**Table 4**. Anisotropic displacement parameters (Å$^2$x 10$^3$) for str100m. The anisotropic displacement factor exponent takes the form: $-2\pi^2$[ $h^2$ $a^{*2}U^{11}$ + ... + 2 h k a* b* $U^{12}$ ]

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| Fe(1) | 35(1) | 26(1) | 32(1) | 9(1) | 10(1) | 11(1) |
| C(1) | 38(2) | 25(2) | 33(2) | 7(1) | 7(2) | 9(1) |
| C(2) | 35(2) | 32(2) | 49(2) | 8(2) | 11(2) | 7(2) |
| C(3) | 36(2) | 45(2) | 48(2) | 8(2) | 9(2) | 21(2) |
| C(4) | 49(2) | 41(2) | 37(2) | 12(2) | 5(2) | 28(2) |
| C(5) | 45(2) | 36(2) | 40(2) | 17(2) | 16(2) | 19(2) |
| C(6) | 39(2) | 37(2) | 33(2) | 11(2) | 3(2) | 8(2) |
| C(7) | 49(3) | 36(2) | 56(2) | 14(2) | -6(2) | 2(2) |
| C(8) | 77(3) | 38(2) | 51(2) | -1(2) | -1(2) | 16(2) |
| C(9) | 65(3) | 73(3) | 35(2) | 7(2) | 16(2) | 35(2) |
| C(10) | 49(2) | 54(2) | 33(2) | 20(2) | 15(2) | 15(2) |
| C(11) | 38(2) | 31(2) | 34(2) | 8(1) | 14(2) | 14(2) |
| C(12) | 33(2) | 35(2) | 43(2) | 11(2) | 13(2) | 15(2) |
| C(13) | 32(2) | 28(2) | 31(2) | 6(1) | 5(1) | 10(1) |
| C(14) | 39(2) | 27(2) | 52(2) | 16(2) | 15(2) | 8(2) |
| C(15) | 33(2) | 33(2) | 49(2) | 16(2) | 16(2) | 10(2) |
| C(16) | 30(2) | 35(2) | 58(2) | 15(2) | 18(2) | 10(2) |
| C(17) | 43(2) | 24(2) | 51(2) | 13(2) | 16(2) | 12(2) |
| C(18) | 35(2) | 29(2) | 39(2) | 9(1) | 8(2) | 16(2) |
| N(18) | 45(2) | 44(2) | 68(2) | 19(2) | 17(2) | 25(2) |
| O(18) | 81(2) | 61(2) | 130(3) | 57(2) | 49(2) | 47(2) |
| O(19) | 53(2) | 61(2) | 100(2) | 26(2) | 38(2) | 35(2) |
| C(19) | 39(2) | 61(2) | 38(2) | 22(2) | 11(2) | 12(2) |
| C(20) | 41(2) | 70(3) | 45(2) | 18(2) | 12(2) | 26(2) |
| C(21) | 38(2) | 47(2) | 33(2) | 12(2) | 2(2) | 17(2) |
| C(22) | 47(2) | 44(2) | 43(2) | 13(2) | 5(2) | 12(2) |
| C(23) | 60(3) | 55(2) | 46(2) | 6(2) | 4(2) | 21(2) |
| C(24) | 49(3) | 56(2) | 44(2) | 16(2) | 6(2) | 18(2) |
| C(25) | 56(3) | 44(2) | 75(3) | 20(2) | 3(2) | 12(2) |
| N(26) | 52(3) | 80(3) | 86(3) | 47(3) | 16(2) | 8(2) |
| C(26) | 33(2) | 58(2) | 50(2) | 26(2) | 4(2) | 6(2) |
| O(26) | 100(3) | 124(3) | 77(2) | 52(2) | 34(2) | 10(2) |
| O(27) | 126(4) | 90(3) | 175(4) | 87(3) | 60(3) | 21(2) |

**Table 5**. Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters (Å$^2$x 10 $^3$) for str100m.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(2) | -2422 | 1920 | 1825 | 47 |
| H(3) | -3793 | 3846 | 1640 | 51 |
| H(4) | -1778 | 5363 | 952 | 49 |
| H(5) | 847 | 4390 | 698 | 45 |
| H(7) | 3161 | 6275 | 3008 | 62 |
| H(8) | 329 | 6878 | 3345 | 72 |
| H(9) | -1360 | 5062 | 3945 | 67 |
| H(10) | 391 | 3287 | 3944 | 52 |
| H(11) | 1951 | 2192 | 952 | 40 |
| H(12) | -385 | 452 | 1589 | 42 |
| H(14) | 3952 | 992 | 964 | 46 |
| H(15) | 201 | -1686 | 1626 | 43 |
| H(16) | 5794 | -494 | 854 | 47 |
| H(17) | 2057 | -3162 | 1512 | 45 |
| H(19) | 4433 | 4178 | 2874 | 54 |
| H(20) | 5140 | 2487 | 3309 | 60 |
| H(22) | 3675 | 3749 | 5284 | 55 |
| H(23) | 3350 | 248 | 3521 | 67 |
| H(24) | 2795 | 2673 | 6429 | 59 |
| H(25) | 2452 | -827 | 4655 | 72 |

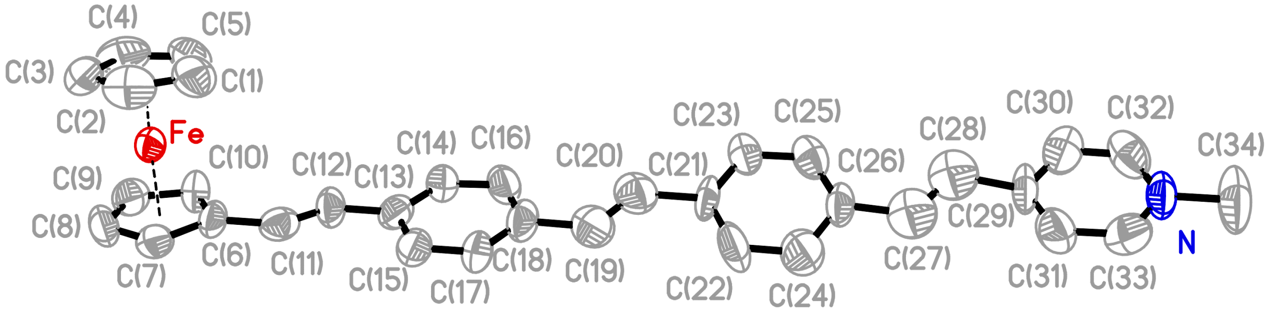
**Table 6**. Torsion angles [°] for str100m.

| | |
|---|---|
| C(10)-Fe(1)-C(1)-C(2) | 81.4(2) |
| C(7)-Fe(1)-C(1)-C(2) | 165.57(19) |
| C(3)-Fe(1)-C(1)-C(2) | -38.10(18) |
| C(9)-Fe(1)-C(1)-C(2) | 46.3(4) |
| C(5)-Fe(1)-C(1)-C(2) | -118.9(3) |
| C(8)-Fe(1)-C(1)-C(2) | -161.1(6) |
| C(4)-Fe(1)-C(1)-C(2) | -81.6(2) |
| C(6)-Fe(1)-C(1)-C(2) | 124.49(19) |
| C(2)-Fe(1)-C(1)-C(5) | 118.9(3) |
| C(10)-Fe(1)-C(1)-C(5) | -159.72(19) |
| C(7)-Fe(1)-C(1)-C(5) | -75.5(2) |
| C(3)-Fe(1)-C(1)-C(5) | 80.8(2) |
| C(9)-Fe(1)-C(1)-C(5) | 165.2(3) |
| C(8)-Fe(1)-C(1)-C(5) | -42.2(7) |
| C(4)-Fe(1)-C(1)-C(5) | 37.3(2) |
| C(6)-Fe(1)-C(1)-C(5) | -116.6(2) |
| C(2)-Fe(1)-C(1)-C(11) | -122.8(3) |
| C(10)-Fe(1)-C(1)-C(11) | -41.4(3) |
| C(7)-Fe(1)-C(1)-C(11) | 42.8(3) |
| C(3)-Fe(1)-C(1)-C(11) | -160.9(3) |
| C(9)-Fe(1)-C(1)-C(11) | -76.5(4) |
| C(5)-Fe(1)-C(1)-C(11) | 118.3(4) |
| C(8)-Fe(1)-C(1)-C(11) | 76.1(7) |
| C(4)-Fe(1)-C(1)-C(11) | 155.6(3) |
| C(6)-Fe(1)-C(1)-C(11) | 1.7(3) |
| C(5)-C(1)-C(2)-C(3) | 2.4(3) |
| C(11)-C(1)-C(2)-C(3) | -179.7(3) |
| Fe(1)-C(1)-C(2)-C(3) | 60.6(2) |
| C(5)-C(1)-C(2)-Fe(1) | -58.2(2) |
| C(11)-C(1)-C(2)-Fe(1) | 119.7(3) |
| C(10)-Fe(1)-C(2)-C(3) | 126.6(2) |
| C(7)-Fe(1)-C(2)-C(3) | -169.7(6) |
| C(9)-Fe(1)-C(2)-C(3) | 84.2(2) |
| C(5)-Fe(1)-C(2)-C(3) | -80.3(2) |
| C(8)-Fe(1)-C(2)-C(3) | 52.8(4) |
| C(4)-Fe(1)-C(2)-C(3) | -37.16(19) |
| C(6)-Fe(1)-C(2)-C(3) | 166.05(19) |
| C(1)-Fe(1)-C(2)-C(3) | -118.3(3) |
| C(10)-Fe(1)-C(2)-C(1) | -115.13(19) |
| C(7)-Fe(1)-C(2)-C(1) | -51.4(7) |
| C(3)-Fe(1)-C(2)-C(1) | 118.3(3) |
| C(9)-Fe(1)-C(2)-C(1) | -157.46(18) |
| C(5)-Fe(1)-C(2)-C(1) | 37.96(17) |
| C(8)-Fe(1)-C(2)-C(1) | 171.1(3) |
| C(4)-Fe(1)-C(2)-C(1) | 81.1(2) |
| C(6)-Fe(1)-C(2)-C(1) | -75.7(2) |
| C(1)-C(2)-C(3)-C(4) | -1.6(4) |
| Fe(1)-C(2)-C(3)-C(4) | 59.6(2) |
| C(1)-C(2)-C(3)-Fe(1) | -61.2(2) |
| C(10)-Fe(1)-C(3)-C(2) | -71.5(2) |
| C(7)-Fe(1)-C(3)-C(2) | 174.4(3) |
| C(9)-Fe(1)-C(3)-C(2) | -112.4(2) |
| C(5)-Fe(1)-C(3)-C(2) | 82.5(2) |
| C(8)-Fe(1)-C(3)-C(2) | -154.4(2) |
| C(4)-Fe(1)-C(3)-C(2) | 119.7(3) |
| C(6)-Fe(1)-C(3)-C(2) | -42.6(5) |
| C(1)-Fe(1)-C(3)-C(2) | 38.22(18) |
| C(2)-Fe(1)-C(3)-C(4) | -119.7(3) |
| C(10)-Fe(1)-C(3)-C(4) | 168.83(18) |
| C(7)-Fe(1)-C(3)-C(4) | 54.7(4) |
| C(9)-Fe(1)-C(3)-C(4) | 127.9(2) |
| C(5)-Fe(1)-C(3)-C(4) | -37.23(17) |
| C(8)-Fe(1)-C(3)-C(4) | 85.9(2) |
| C(6)-Fe(1)-C(3)-C(4) | -162.3(4) |
| C(1)-Fe(1)-C(3)-C(4) | -81.47(19) |
| C(2)-C(3)-C(4)-C(5) | 0.2(4) |
| Fe(1)-C(3)-C(4)-C(5) | 59.3(2) |
| C(2)-C(3)-C(4)-Fe(1) | -59.1(2) |
| C(2)-Fe(1)-C(4)-C(5) | -82.0(2) |
| C(10)-Fe(1)-C(4)-C(5) | -153.1(4) |
| C(7)-Fe(1)-C(4)-C(5) | 85.8(2) |
| C(3)-Fe(1)-C(4)-C(5) | -119.4(3) |
| C(9)-Fe(1)-C(4)-C(5) | 169.7(2) |

| | | | |
|---|---|---|---|
| C(8)-Fe(1)-C(4)-C(5) | 128.2(2) | C(9)-Fe(1)-C(6)-C(10) | 38.2(2) |
| C(6)-Fe(1)-C(4)-C(5) | 48.5(4) | C(5)-Fe(1)-C(6)-C(10) | -155.06(19) |
| C(1)-Fe(1)-C(4)-C(5) | -38.06(19) | C(8)-Fe(1)-C(6)-C(10) | 81.7(2) |
| C(2)-Fe(1)-C(4)-C(3) | 37.43(18) | C(4)-Fe(1)-C(6)-C(10) | 170.7(3) |
| C(10)-Fe(1)-C(4)-C(3) | -33.7(5) | C(1)-Fe(1)-C(6)-C(10) | -112.0(2) |
| C(7)-Fe(1)-C(4)-C(3) | -154.8(2) | C(2)-Fe(1)-C(6)-C(7) | 171.2(2) |
| C(9)-Fe(1)-C(4)-C(3) | -70.9(2) | C(10)-Fe(1)-C(6)-C(7) | -118.5(3) |
| C(5)-Fe(1)-C(4)-C(3) | 119.4(3) | C(3)-Fe(1)-C(6)-C(7) | -155.8(4) |
| C(8)-Fe(1)-C(4)-C(3) | -112.4(2) | C(9)-Fe(1)-C(6)-C(7) | -80.4(2) |
| C(6)-Fe(1)-C(4)-C(3) | 167.9(3) | C(5)-Fe(1)-C(6)-C(7) | 86.4(2) |
| C(1)-Fe(1)-C(4)-C(3) | 81.4(2) | C(8)-Fe(1)-C(6)-C(7) | -36.9(2) |
| C(3)-C(4)-C(5)-C(1) | 1.3(4) | C(4)-Fe(1)-C(6)-C(7) | 52.2(4) |
| Fe(1)-C(4)-C(5)-C(1) | 60.5(2) | C(1)-Fe(1)-C(6)-C(7) | 129.5(2) |
| C(3)-C(4)-C(5)-Fe(1) | -59.2(2) | C(2)-Fe(1)-C(6)-C(19) | 55.5(3) |
| C(2)-C(1)-C(5)-C(4) | -2.3(4) | C(10)-Fe(1)-C(6)-C(19) | 125.8(4) |
| C(11)-C(1)-C(5)-C(4) | 179.7(3) | C(7)-Fe(1)-C(6)-C(19) | -115.7(4) |
| Fe(1)-C(1)-C(5)-C(4) | -60.3(2) | C(3)-Fe(1)-C(6)-C(19) | 88.5(5) |
| C(2)-C(1)-C(5)-Fe(1) | 58.1(2) | C(9)-Fe(1)-C(6)-C(19) | 163.9(3) |
| C(11)-C(1)-C(5)-Fe(1) | -120.0(3) | C(5)-Fe(1)-C(6)-C(19) | -29.3(3) |
| C(2)-Fe(1)-C(5)-C(4) | 81.2(2) | C(8)-Fe(1)-C(6)-C(19) | -152.5(3) |
| C(10)-Fe(1)-C(5)-C(4) | 163.0(3) | C(4)-Fe(1)-C(6)-C(19) | -63.5(4) |
| C(7)-Fe(1)-C(5)-C(4) | -114.0(2) | C(1)-Fe(1)-C(6)-C(19) | 13.8(3) |
| C(3)-Fe(1)-C(5)-C(4) | 37.42(19) | C(10)-C(6)-C(7)-C(8) | 0.8(4) |
| C(9)-Fe(1)-C(5)-C(4) | -33.3(7) | C(19)-C(6)-C(7)-C(8) | 175.7(3) |
| C(8)-Fe(1)-C(5)-C(4) | -72.3(3) | Fe(1)-C(6)-C(7)-C(8) | 59.6(3) |
| C(6)-Fe(1)-C(5)-C(4) | -158.54(19) | C(10)-C(6)-C(7)-Fe(1) | -58.8(2) |
| C(1)-Fe(1)-C(5)-C(4) | 119.0(3) | C(19)-C(6)-C(7)-Fe(1) | 116.1(3) |
| C(2)-Fe(1)-C(5)-C(1) | -37.79(19) | C(2)-Fe(1)-C(7)-C(8) | -150.0(6) |
| C(10)-Fe(1)-C(5)-C(1) | 43.9(4) | C(10)-Fe(1)-C(7)-C(8) | -81.9(2) |
| C(7)-Fe(1)-C(5)-C(1) | 127.0(2) | C(3)-Fe(1)-C(7)-C(8) | 45.0(4) |
| C(3)-Fe(1)-C(5)-C(1) | -81.6(2) | C(9)-Fe(1)-C(7)-C(8) | -37.7(2) |
| C(9)-Fe(1)-C(5)-C(1) | -152.4(6) | C(5)-Fe(1)-C(7)-C(8) | 126.2(2) |
| C(8)-Fe(1)-C(5)-C(1) | 168.7(2) | C(4)-Fe(1)-C(7)-C(8) | 82.9(3) |
| C(4)-Fe(1)-C(5)-C(1) | -119.0(3) | C(6)-Fe(1)-C(7)-C(8) | -119.7(3) |
| C(6)-Fe(1)-C(5)-C(1) | 82.4(2) | C(1)-Fe(1)-C(7)-C(8) | 168.7(2) |
| C(2)-Fe(1)-C(6)-C(10) | -70.3(2) | C(2)-Fe(1)-C(7)-C(6) | -30.3(7) |
| C(7)-Fe(1)-C(6)-C(10) | 118.5(3) | C(10)-Fe(1)-C(7)-C(6) | 37.9(2) |
| C(3)-Fe(1)-C(6)-C(10) | -37.3(5) | C(3)-Fe(1)-C(7)-C(6) | 164.8(3) |

| | | | |
|---|---|---|---|
| C(9)-Fe(1)-C(7)-C(6) | 82.0(2) | C(5)-Fe(1)-C(9)-C(10) | -169.1(5) |
| C(5)-Fe(1)-C(7)-C(6) | -114.1(2) | C(8)-Fe(1)-C(9)-C(10) | -119.8(3) |
| C(8)-Fe(1)-C(7)-C(6) | 119.7(3) | C(4)-Fe(1)-C(9)-C(10) | 164.7(2) |
| C(4)-Fe(1)-C(7)-C(6) | -157.33(19) | C(6)-Fe(1)-C(9)-C(10) | -37.9(2) |
| C(1)-Fe(1)-C(7)-C(6) | -71.5(3) | C(1)-Fe(1)-C(9)-C(10) | 50.9(4) |
| C(6)-C(7)-C(8)-C(9) | 0.0(4) | C(7)-C(6)-C(10)-C(9) | -1.3(4) |
| Fe(1)-C(7)-C(8)-C(9) | 59.4(3) | C(19)-C(6)-C(10)-C(9) | -175.6(3) |
| C(6)-C(7)-C(8)-Fe(1) | -59.5(2) | Fe(1)-C(6)-C(10)-C(9) | -60.2(2) |
| C(2)-Fe(1)-C(8)-C(7) | 165.0(3) | C(7)-C(6)-C(10)-Fe(1) | 58.9(2) |
| C(10)-Fe(1)-C(8)-C(7) | 81.5(2) | C(19)-C(6)-C(10)-Fe(1) | -115.4(4) |
| C(3)-Fe(1)-C(8)-C(7) | -158.8(2) | C(8)-C(9)-C(10)-C(6) | 1.3(4) |
| C(9)-Fe(1)-C(8)-C(7) | 119.1(3) | Fe(1)-C(9)-C(10)-C(6) | 60.7(2) |
| C(5)-Fe(1)-C(8)-C(7) | -75.6(3) | C(8)-C(9)-C(10)-Fe(1) | -59.4(2) |
| C(4)-Fe(1)-C(8)-C(7) | -115.9(2) | C(2)-Fe(1)-C(10)-C(6) | 127.9(2) |
| C(6)-Fe(1)-C(8)-C(7) | 37.8(2) | C(7)-Fe(1)-C(10)-C(6) | -38.4(2) |
| C(1)-Fe(1)-C(8)-C(7) | -41.3(7) | C(3)-Fe(1)-C(10)-C(6) | 167.67(18) |
| C(2)-Fe(1)-C(8)-C(9) | 45.9(4) | C(9)-Fe(1)-C(10)-C(6) | -118.6(3) |
| C(10)-Fe(1)-C(8)-C(9) | -37.5(2) | C(5)-Fe(1)-C(10)-C(6) | 55.0(4) |
| C(7)-Fe(1)-C(8)-C(9) | -119.1(3) | C(8)-Fe(1)-C(10)-C(6) | -81.5(2) |
| C(3)-Fe(1)-C(8)-C(9) | 82.1(3) | C(4)-Fe(1)-C(10)-C(6) | -166.3(4) |
| C(5)-Fe(1)-C(8)-C(9) | 165.3(2) | C(1)-Fe(1)-C(10)-C(6) | 86.0(2) |
| C(4)-Fe(1)-C(8)-C(9) | 125.0(2) | C(2)-Fe(1)-C(10)-C(9) | -113.5(2) |
| C(6)-Fe(1)-C(8)-C(9) | -81.3(2) | C(7)-Fe(1)-C(10)-C(9) | 80.2(3) |
| C(1)-Fe(1)-C(8)-C(9) | -160.4(6) | C(3)-Fe(1)-C(10)-C(9) | -73.8(3) |
| C(7)-C(8)-C(9)-C(10) | -0.8(4) | C(5)-Fe(1)-C(10)-C(9) | 173.6(3) |
| Fe(1)-C(8)-C(9)-C(10) | 58.8(2) | C(8)-Fe(1)-C(10)-C(9) | 37.1(2) |
| C(7)-C(8)-C(9)-Fe(1) | -59.6(3) | C(4)-Fe(1)-C(10)-C(9) | -47.7(6) |
| C(2)-Fe(1)-C(9)-C(8) | -157.4(2) | C(6)-Fe(1)-C(10)-C(9) | 118.6(3) |
| C(10)-Fe(1)-C(9)-C(8) | 119.8(3) | C(1)-Fe(1)-C(10)-C(9) | -155.5(2) |
| C(7)-Fe(1)-C(9)-C(8) | 37.4(2) | C(2)-C(1)-C(11)-C(12) | 5.2(5) |
| C(3)-Fe(1)-C(9)-C(8) | -115.0(2) | C(5)-C(1)-C(11)-C(12) | -177.2(3) |
| C(5)-Fe(1)-C(9)-C(8) | -49.3(7) | Fe(1)-C(1)-C(11)-C(12) | 95.2(4) |
| C(4)-Fe(1)-C(9)-C(8) | -75.5(3) | C(1)-C(11)-C(12)-C(13) | 179.0(3) |
| C(6)-Fe(1)-C(9)-C(8) | 81.9(2) | C(11)-C(12)-C(13)-C(14) | 5.3(5) |
| C(1)-Fe(1)-C(9)-C(8) | 170.7(3) | C(11)-C(12)-C(13)-C(15) | -173.5(3) |
| C(2)-Fe(1)-C(9)-C(10) | 82.8(3) | C(15)-C(13)-C(14)-C(16) | -0.1(5) |
| C(7)-Fe(1)-C(9)-C(10) | -82.4(2) | C(12)-C(13)-C(14)-C(16) | -179.0(3) |
| C(3)-Fe(1)-C(9)-C(10) | 125.2(2) | C(14)-C(13)-C(15)-C(17) | 0.1(5) |

| | |
|---|---|
| C(12)-C(13)-C(15)-C(17) | 179.0(3) |
| C(13)-C(14)-C(16)-C(18) | 0.7(5) |
| C(13)-C(15)-C(17)-C(18) | -0.6(5) |
| C(15)-C(17)-C(18)-C(16) | 1.2(5) |
| C(15)-C(17)-C(18)-N(18) | -179.5(3) |
| C(14)-C(16)-C(18)-C(17) | -1.2(5) |
| C(14)-C(16)-C(18)-N(18) | 179.5(3) |
| C(17)-C(18)-N(18)-O(19) | 166.5(3) |
| C(16)-C(18)-N(18)-O(19) | -14.1(5) |
| C(17)-C(18)-N(18)-O(18) | -12.5(5) |
| C(16)-C(18)-N(18)-O(18) | 166.9(3) |
| C(10)-C(6)-C(19)-C(20) | -20.2(6) |
| C(7)-C(6)-C(19)-C(20) | 166.2(4) |
| Fe(1)-C(6)-C(19)-C(20) | -109.4(4) |
| C(6)-C(19)-C(20)-C(21) | -6.1(6) |
| C(19)-C(20)-C(21)-C(22) | -44.6(6) |
| C(19)-C(20)-C(21)-C(23) | 139.4(4) |
| C(23)-C(21)-C(22)-C(24) | -0.2(5) |
| C(20)-C(21)-C(22)-C(24) | -176.4(3) |
| C(22)-C(21)-C(23)-C(25) | 0.5(5) |
| C(20)-C(21)-C(23)-C(25) | 176.7(3) |
| C(21)-C(22)-C(24)-C(26) | 0.3(5) |
| C(21)-C(23)-C(25)-C(26) | -0.8(6) |
| C(23)-C(25)-C(26)-C(24) | 1.0(6) |
| C(23)-C(25)-C(26)-N(26) | -178.3(3) |
| C(22)-C(24)-C(26)-C(25) | -0.7(6) |
| C(22)-C(24)-C(26)-N(26) | 178.6(3) |
| O(26)-N(26)-C(26)-C(25) | -173.9(4) |
| O(27)-N(26)-C(26)-C(25) | 7.0(6) |
| O(26)-N(26)-C(26)-C(24) | 6.8(6) |
| O(27)-N(26)-C(26)-C(24) | -172.2(4) |


C(4)
C(5)
C(3)
C(1)
C(2)
Fe
C(10)
C(9)
C(8)
C(7)
C(6)
C(11)
C(12)
C(13)
C(14)
C(15)
C(16)
C(17)
C(18)
C(19)
C(20)
C(21)
C(22)
C(23)
C(24)
C(25)
C(26)
C(27)
C(28)
C(29)
C(30)
C(31)
C(32)
C(33)
C(34)
N

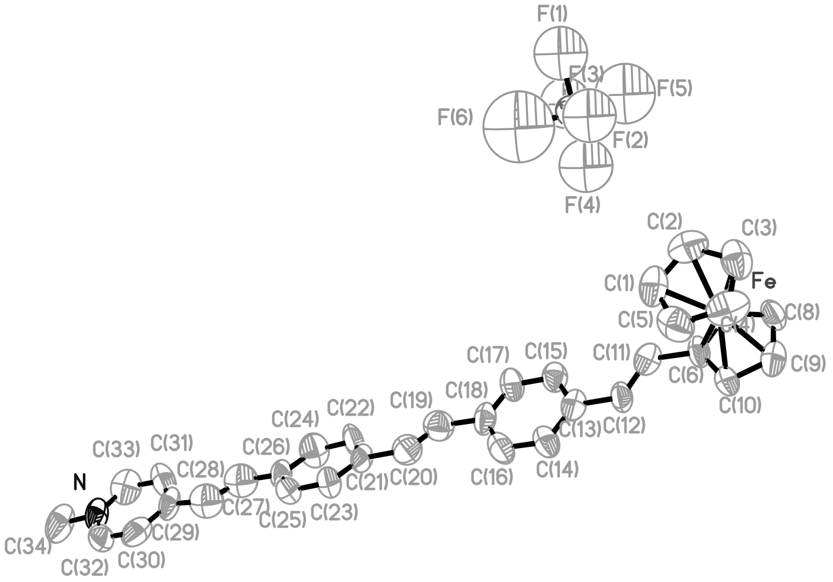

F(1)
F(3)
F(5)
F(6)
F(2)
F(4)
C(2)
C(3)
Fe
C(1)
C(5)
C(8)
C(9)
C(11)
C(6)
C(10)
C(17)
C(15)
C(18)
C(19)
C(12)
C(13)
C(24)
C(22)
C(14)
C(16)
C(20)
C(21)
C(26)
C(33)
C(31)
C(28)
N
C(27)
C(25)
C(23)
C(29)
C(34)
C(32)
C(30)

Table 1. Crystal data and structure refinement for str62m.

| | | |
|---|---|---|
| Identification code | str62m | |
| Empirical formula | C34 H30 F6 Fe N P | |
| Formula weight | 653.41 | |
| Temperature | 293(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | P2(1)/c | |
| Unit cell dimensions | a = 14.1378(9) Å | $\alpha$= 90°. |
| | b = 17.6844(11) Å | $\beta$= 110.748(2)°. |
| | c = 12.6401(8) Å | $\gamma$ = 90°. |
| Volume | 2955.3(3) Å$^3$ | |
| Z | 4 | |
| Density (calculated) | 1.469 Mg/m$^3$ | |
| Absorption coefficient | 0.628 mm$^{-1}$ | |
| F(000) | 1344 | |
| Crystal size | 0.014 x 0.016 x 0.062 mm$^3$ | |
| Theta range for data collection | 1.54 to 23.58°. | |
| Index ranges | -12<=h<=12, -17<=k<=17, -11<=l<=14 | |
| Reflections collected | 11043 | |
| Independent reflections | 3103 [R(int) = 0.0769] | |
| Completeness to theta = 23.58° | 70.3 % | |
| Absorption correction | None | |
| Refinement method | Full-matrix least-squares on F$^2$ | |
| Data / restraints / parameters | 3103 / 0 / 348 | |
| Goodness-of-fit on F$^2$ | 1.232 | |
| Final R indices [I>2sigma(I)] | R1 = 0.1035, wR2 = 0.3046 | |
| R indices (all data) | R1 = 0.1573, wR2 = 0.3432 | |
| Largest diff. peak and hole | 0.913 and -0.679 e.Å$^{-3}$ | |

Table 2. Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) for str62m. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| Fe | 4123(1) | 2859(1) | 5461(1) | 54(1) |
| N | 9048(10) | 5366(10) | -8013(9) | 83(4) |
| P(1) | -82(4) | 2676(3) | 944(4) | 95(2) |
| C(1) | 3450(15) | 2410(9) | 3863(12) | 87(5) |
| F(1) | -1274(13) | 2505(10) | 253(14) | 205(6) |
| C(2) | 2705(13) | 2577(8) | 4304(15) | 91(5) |
| F(2) | -55(11) | 1852(9) | 1341(12) | 195(6) |
| C(3) | 2932(13) | 2183(8) | 5375(13) | 85(5) |
| F(3) | -238(11) | 3501(9) | 605(12) | 196(5) |
| C(4) | 3798(13) | 1746(8) | 5516(15) | 90(5) |
| F(4) | 1006(14) | 2797(8) | 1551(15) | 214(6) |
| C(5) | 4116(13) | 1894(10) | 4577(16) | 91(5) |
| F(5) | -395(16) | 2925(11) | 1868(18) | 265(9) |
| C(6) | 5103(10) | 3694(7) | 5380(9) | 61(4) |
| F(6) | 140(20) | 2490(16) | -130(30) | 374(14) |
| C(7) | 4337(10) | 4002(7) | 5731(10) | 64(4) |
| C(8) | 4357(10) | 3631(8) | 6699(11) | 68(4) |
| C(9) | 5149(11) | 3110(8) | 6972(10) | 71(4) |
| C(10) | 5596(10) | 3130(8) | 6160(10) | 64(4) |
| C(11) | 5287(11) | 3927(7) | 4318(10) | 64(4) |
| C(12) | 6029(10) | 3677(7) | 4027(10) | 64(4) |
| C(13) | 6239(10) | 3895(7) | 3016(10) | 63(4) |
| C(14) | 6914(10) | 3498(8) | 2686(11) | 69(4) |
| C(15) | 5776(10) | 4519(7) | 2352(10) | 66(4) |
| C(16) | 7089(11) | 3676(8) | 1705(12) | 77(4) |
| C(17) | 5973(11) | 4719(8) | 1412(10) | 72(4) |
| C(18) | 6615(11) | 4315(9) | 1068(10) | 72(4) |
| C(19) | 6821(11) | 4556(9) | 12(12) | 84(4) |
| C(20) | 7240(11) | 4178(9) | -504(12) | 84(4) |
| C(21) | 7485(10) | 4404(8) | -1550(9) | 63(4) |
| C(22) | 7296(12) | 5120(9) | -2001(11) | 90(5) |
| C(23) | 7859(10) | 3885(8) | -2058(11) | 72(4) |
| C(24) | 7563(12) | 5324(9) | -2942(13) | 96(5) |
| C(25) | 8098(9) | 4073(9) | -3003(11) | 73(4) |
| C(26) | 7943(10) | 4781(9) | -3465(9) | 66(4) |

| | | | | |
|---|---|---|---|---|
| C(27) | 8167(13) | 5049(10) | -4477(15) | 109(5) |
| C(28) | 8499(14) | 4634(10) | -5076(15) | 111(5) |
| C(29) | 8671(13) | 4977(12) | -6088(10) | 84(5) |
| C(30) | 9170(11) | 4509(10) | -6560(13) | 86(5) |
| C(31) | 8323(13) | 5634(10) | -6627(15) | 96(5) |
| C(32) | 9383(11) | 4711(11) | -7486(14) | 88(5) |
| C(33) | 8536(14) | 5830(9) | -7621(14) | 99(5) |
| C(34) | 9329(13) | 5564(12) | -8989(12) | 135(8) |

Table 3. Bond lengths [Å] and angles [°] for str62m.

| | | | |
|---|---|---|---|
| Fe-C(9) | 1.997(13) | C(18)-C(19) | 1.525(18) |
| Fe-C(10) | 2.012(13) | C(19)-C(20) | 1.223(17) |
| Fe-C(8) | 2.014(12) | C(20)-C(21) | 1.535(18) |
| Fe-C(4) | 2.027(14) | C(21)-C(23) | 1.332(17) |
| Fe-C(3) | 2.036(14) | C(21)-C(22) | 1.375(18) |
| Fe-C(5) | 2.037(14) | C(22)-C(24) | 1.416(19) |
| Fe-C(6) | 2.053(11) | C(23)-C(25) | 1.392(17) |
| Fe-C(7) | 2.056(12) | C(24)-C(26) | 1.377(18) |
| Fe-C(1) | 2.062(14) | C(25)-C(26) | 1.366(18) |
| Fe-C(2) | 2.081(15) | C(26)-C(27) | 1.500(19) |
| N-C(33) | 1.304(19) | C(27)-C(28) | 1.26(2) |
| N-C(32) | 1.337(19) | C(28)-C(29) | 1.51(2) |
| N-C(34) | 1.466(17) | C(29)-C(31) | 1.35(2) |
| P(1)-F(5) | 1.46(2) | C(29)-C(30) | 1.36(2) |
| P(1)-F(4) | 1.471(18) | C(30)-C(32) | 1.355(19) |
| P(1)-F(3) | 1.515(16) | C(31)-C(33) | 1.43(2) |
| P(1)-F(6) | 1.53(3) | C(9)-Fe-C(10) | 40.4(5) |
| P(1)-F(2) | 1.537(16) | C(9)-Fe-C(8) | 40.7(5) |
| P(1)-F(1) | 1.628(18) | C(10)-Fe-C(8) | 68.8(5) |
| C(1)-C(2) | 1.39(2) | C(9)-Fe-C(4) | 106.2(6) |
| C(1)-C(5) | 1.39(2) | C(10)-Fe-C(4) | 115.4(6) |
| C(2)-C(3) | 1.45(2) | C(8)-Fe-C(4) | 127.4(7) |
| C(3)-C(4) | 1.40(2) | C(9)-Fe-C(3) | 119.2(6) |
| C(4)-C(5) | 1.44(2) | C(10)-Fe-C(3) | 150.7(6) |
| C(6)-C(10) | 1.403(16) | C(8)-Fe-C(3) | 110.1(6) |
| C(6)-C(7) | 1.417(16) | C(4)-Fe-C(3) | 40.5(6) |
| C(6)-C(11) | 1.512(16) | C(9)-Fe-C(5) | 124.8(7) |
| C(7)-C(8) | 1.380(16) | C(10)-Fe-C(5) | 104.1(6) |
| C(8)-C(9) | 1.396(17) | C(8)-Fe-C(5) | 164.0(7) |
| C(9)-C(10) | 1.383(17) | C(4)-Fe-C(5) | 41.4(6) |
| C(11)-C(12) | 1.305(16) | C(3)-Fe-C(5) | 68.7(6) |
| C(12)-C(13) | 1.462(16) | C(9)-Fe-C(6) | 67.3(5) |
| C(13)-C(14) | 1.365(17) | C(10)-Fe-C(6) | 40.4(5) |
| C(13)-C(15) | 1.400(16) | C(8)-Fe-C(6) | 67.9(5) |
| C(14)-C(16) | 1.383(17) | C(4)-Fe-C(6) | 149.9(7) |
| C(15)-C(17) | 1.361(16) | C(3)-Fe-C(6) | 168.5(7) |
| C(16)-C(18) | 1.411(18) | C(5)-Fe-C(6) | 116.5(6) |
| C(17)-C(18) | 1.343(18) | C(9)-Fe-C(7) | 66.9(5) |

| | | | |
|---|---|---|---|
| C(10)-Fe-C(7) | 67.9(5) | F(2)-P(1)-F(1) | 84.3(8) |
| C(8)-Fe-C(7) | 39.6(5) | C(2)-C(1)-C(5) | 108.4(14) |
| C(4)-Fe-C(7) | 166.2(7) | C(2)-C(1)-Fe | 71.2(9) |
| C(3)-Fe-C(7) | 131.0(6) | C(5)-C(1)-Fe | 69.2(8) |
| C(5)-Fe-C(7) | 152.4(7) | C(1)-C(2)-C(3) | 108.9(14) |
| C(6)-Fe-C(7) | 40.3(5) | C(1)-C(2)-Fe | 69.7(9) |
| C(9)-Fe-C(1) | 161.6(7) | C(3)-C(2)-Fe | 67.7(8) |
| C(10)-Fe-C(1) | 124.6(7) | C(4)-C(3)-C(2) | 106.1(14) |
| C(8)-Fe-C(1) | 156.0(7) | C(4)-C(3)-Fe | 69.4(8) |
| C(4)-Fe-C(1) | 68.2(6) | C(2)-C(3)-Fe | 71.0(8) |
| C(3)-Fe-C(1) | 68.7(6) | C(3)-C(4)-C(5) | 108.0(13) |
| C(5)-Fe-C(1) | 39.6(6) | C(3)-C(4)-Fe | 70.1(8) |
| C(6)-Fe-C(1) | 108.2(6) | C(5)-C(4)-Fe | 69.7(8) |
| C(7)-Fe-C(1) | 122.1(6) | C(1)-C(5)-C(4) | 108.5(14) |
| C(9)-Fe-C(2) | 156.7(7) | C(1)-C(5)-Fe | 71.1(9) |
| C(10)-Fe-C(2) | 162.9(7) | C(4)-C(5)-Fe | 68.9(8) |
| C(8)-Fe-C(2) | 124.1(7) | C(10)-C(6)-C(7) | 107.3(10) |
| C(4)-Fe-C(2) | 67.5(6) | C(10)-C(6)-C(11) | 128.2(12) |
| C(3)-Fe-C(2) | 41.3(6) | C(7)-C(6)-C(11) | 124.4(12) |
| C(5)-Fe-C(2) | 66.3(6) | C(10)-C(6)-Fe | 68.2(7) |
| C(6)-Fe-C(2) | 129.5(6) | C(7)-C(6)-Fe | 69.9(7) |
| C(7)-Fe-C(2) | 113.6(6) | C(11)-C(6)-Fe | 124.9(8) |
| C(1)-Fe-C(2) | 39.1(6) | C(8)-C(7)-C(6) | 108.5(12) |
| C(33)-N-C(32) | 120.2(13) | C(8)-C(7)-Fe | 68.5(7) |
| C(33)-N-C(34) | 121.4(17) | C(6)-C(7)-Fe | 69.7(7) |
| C(32)-N-C(34) | 118.2(17) | C(7)-C(8)-C(9) | 107.2(12) |
| F(5)-P(1)-F(4) | 95.5(11) | C(7)-C(8)-Fe | 71.8(7) |
| F(5)-P(1)-F(3) | 83.1(9) | C(9)-C(8)-Fe | 69.0(7) |
| F(4)-P(1)-F(3) | 91.6(8) | C(10)-C(9)-C(8) | 109.7(12) |
| F(5)-P(1)-F(6) | 172.1(15) | C(10)-C(9)-Fe | 70.4(7) |
| F(4)-P(1)-F(6) | 89.5(13) | C(8)-C(9)-Fe | 70.3(8) |
| F(3)-P(1)-F(6) | 90.7(12) | C(9)-C(10)-C(6) | 107.2(12) |
| F(5)-P(1)-F(2) | 90.2(10) | C(9)-C(10)-Fe | 69.2(7) |
| F(4)-P(1)-F(2) | 93.9(8) | C(6)-C(10)-Fe | 71.4(7) |
| F(3)-P(1)-F(2) | 171.8(9) | C(12)-C(11)-C(6) | 124.5(12) |
| F(6)-P(1)-F(2) | 95.5(12) | C(11)-C(12)-C(13) | 126.0(13) |
| F(5)-P(1)-F(1) | 86.3(10) | C(14)-C(13)-C(15) | 116.8(12) |
| F(4)-P(1)-F(1) | 177.4(9) | C(14)-C(13)-C(12) | 120.8(13) |
| F(3)-P(1)-F(1) | 90.4(8) | C(15)-C(13)-C(12) | 122.4(13) |
| F(6)-P(1)-F(1) | 88.9(13) | C(13)-C(14)-C(16) | 121.5(14) |

| | |
|---|---|
| C(17)-C(15)-C(13) | 122.1(13) |
| C(14)-C(16)-C(18) | 119.7(13) |
| C(18)-C(17)-C(15) | 121.0(13) |
| C(17)-C(18)-C(16) | 118.7(12) |
| C(17)-C(18)-C(19) | 119.7(14) |
| C(16)-C(18)-C(19) | 121.6(14) |
| C(20)-C(19)-C(18) | 126.3(16) |
| C(19)-C(20)-C(21) | 128.0(16) |
| C(23)-C(21)-C(22) | 119.1(11) |
| C(23)-C(21)-C(20) | 119.0(13) |
| C(22)-C(21)-C(20) | 121.9(14) |
| C(21)-C(22)-C(24) | 120.8(14) |
| C(21)-C(23)-C(25) | 120.5(13) |
| C(26)-C(24)-C(22) | 119.4(14) |
| C(26)-C(25)-C(23) | 122.3(13) |
| C(25)-C(26)-C(24) | 117.7(12) |
| C(25)-C(26)-C(27) | 127.1(14) |
| C(24)-C(26)-C(27) | 115.2(14) |
| C(28)-C(27)-C(26) | 124.5(17) |
| C(27)-C(28)-C(29) | 118.8(18) |
| C(31)-C(29)-C(30) | 117.2(13) |
| C(31)-C(29)-C(28) | 129.3(18) |
| C(30)-C(29)-C(28) | 113.1(18) |
| C(32)-C(30)-C(29) | 122.0(16) |
| C(29)-C(31)-C(33) | 119.9(15) |
| N-C(32)-C(30) | 120.7(15) |
| N-C(33)-C(31) | 119.8(16) |

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (Å$^2$x 10$^3$) for str62m. The anisotropic displacement factor exponent takes the form: $-2\pi^2[ h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12} ]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| Fe | 66(2) | 50(1) | 55(1) | 5(1) | 33(1) | 0(1) |
| N | 89(10) | 118(12) | 51(7) | -6(8) | 38(7) | -40(9) |
| P(1) | 89(4) | 93(3) | 109(4) | 21(3) | 43(3) | 17(2) |
| C(1) | 117(15) | 84(11) | 59(9) | -10(8) | 31(10) | -14(10) |
| C(2) | 76(11) | 78(10) | 101(13) | -3(10) | 10(11) | 6(9) |
| C(3) | 105(13) | 81(11) | 82(11) | -14(9) | 50(10) | -35(10) |
| C(4) | 90(12) | 48(9) | 117(14) | 12(8) | 16(11) | 7(9) |
| C(5) | 86(12) | 90(12) | 106(13) | -45(10) | 43(11) | -14(10) |
| C(6) | 73(9) | 72(9) | 47(8) | -2(7) | 34(7) | -20(7) |
| C(7) | 83(10) | 51(8) | 63(9) | -2(6) | 30(8) | -9(7) |
| C(8) | 72(10) | 83(10) | 62(9) | -9(7) | 41(8) | 2(8) |
| C(9) | 92(11) | 72(9) | 49(8) | 1(6) | 24(8) | -16(9) |
| C(10) | 65(9) | 82(9) | 57(8) | 8(7) | 36(7) | 1(7) |
| C(11) | 82(10) | 48(8) | 57(8) | 5(6) | 18(8) | -6(7) |
| C(12) | 73(10) | 82(9) | 45(7) | 2(6) | 32(7) | -7(8) |
| C(13) | 74(10) | 63(9) | 50(8) | -2(7) | 20(7) | -24(7) |
| C(14) | 77(10) | 73(9) | 71(9) | -10(7) | 42(8) | -14(8) |
| C(15) | 73(9) | 71(9) | 58(8) | -3(7) | 27(7) | -16(7) |
| C(16) | 76(10) | 92(11) | 79(10) | -28(9) | 46(9) | -20(9) |
| C(17) | 95(11) | 74(9) | 61(9) | 8(7) | 45(9) | -10(8) |
| C(18) | 81(11) | 95(11) | 42(8) | -1(7) | 25(8) | -28(9) |
| C(19) | 81(11) | 84(11) | 87(11) | -9(8) | 31(9) | -2(9) |
| C(20) | 73(11) | 95(11) | 81(11) | -20(9) | 24(9) | -17(9) |
| C(21) | 65(9) | 93(11) | 38(7) | 17(7) | 26(7) | -17(8) |
| C(22) | 118(13) | 107(13) | 65(9) | -3(9) | 60(9) | 23(10) |
| C(23) | 87(11) | 80(10) | 60(9) | -3(7) | 38(8) | 1(8) |
| C(24) | 128(14) | 79(11) | 87(11) | 14(9) | 47(11) | 19(10) |
| C(25) | 64(9) | 94(11) | 65(9) | -11(8) | 30(8) | 3(8) |
| C(26) | 75(10) | 88(11) | 40(7) | 8(7) | 27(7) | -9(8) |
| C(29) | 80(12) | 141(16) | 38(8) | -7(9) | 30(8) | -52(11) |
| C(30) | 69(11) | 113(13) | 66(10) | 13(9) | 11(9) | -23(9) |
| C(31) | 113(14) | 104(13) | 96(12) | -26(11) | 67(11) | -19(11) |
| C(32) | 61(10) | 129(15) | 79(11) | -31(11) | 33(9) | -15(10) |
| C(33) | 120(15) | 77(11) | 99(13) | -4(9) | 38(12) | -28(10) |
| C(34) | 115(14) | 240(20) | 63(10) | 0(12) | 44(10) | -73(15) |

Table 5. Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters ($Å^2$x $10^3$) for str62m.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1) | 3496 | 2610 | 3203 | 104 |
| H(2) | 2150 | 2889 | 3969 | 109 |
| H(3) | 2576 | 2215 | 5868 | 102 |
| H(4) | 4110 | 1418 | 6114 | 108 |
| H(5) | 4674 | 1681 | 4464 | 110 |
| H(7) | 3895 | 4390 | 5371 | 77 |
| H(8) | 3923 | 3712 | 7095 | 81 |
| H(9) | 5347 | 2796 | 7605 | 85 |
| H(10) | 6125 | 2826 | 6136 | 77 |
| H(11) | 4842 | 4273 | 3840 | 77 |
| H(12) | 6464 | 3327 | 4507 | 77 |
| H(14) | 7266 | 3098 | 3130 | 83 |
| H(15) | 5319 | 4806 | 2561 | 79 |
| H(16) | 7516 | 3377 | 1467 | 92 |
| H(17) | 5657 | 5142 | 1000 | 86 |
| H(19) | 6608 | 5037 | -268 | 100 |
| H(20) | 7434 | 3693 | -227 | 101 |
| H(22) | 6990 | 5474 | -1684 | 108 |
| H(23) | 7961 | 3394 | -1779 | 87 |
| H(24) | 7482 | 5819 | -3205 | 115 |
| H(25) | 8374 | 3704 | -3331 | 87 |
| H(30) | 9372 | 4035 | -6240 | 103 |
| H(31) | 7945 | 5959 | -6355 | 115 |
| H(32) | 9767 | 4390 | -7757 | 105 |
| H(33) | 8309 | 6288 | -7984 | 118 |
| H(34A) | 8856 | 5926 | -9451 | 203 |
| H(34B) | 9319 | 5118 | -9425 | 203 |
| H(34C) | 9997 | 5778 | -8729 | 203 |

Table 6. Torsion angles [°] for str62m.

| | | | |
|---|---|---|---|
| C(9)-Fe-C(1)-C(2) | 156.3(16) | C(9)-Fe-C(3)-C(4) | -80.6(11) |
| C(10)-Fe-C(1)-C(2) | -172.7(9) | C(10)-Fe-C(3)-C(4) | -42.4(15) |
| C(8)-Fe-C(1)-C(2) | -54.7(18) | C(8)-Fe-C(3)-C(4) | -124.6(10) |
| C(4)-Fe-C(1)-C(2) | 80.7(10) | C(5)-Fe-C(3)-C(4) | 38.4(9) |
| C(3)-Fe-C(1)-C(2) | 37.1(9) | C(6)-Fe-C(3)-C(4) | 158(2) |
| C(5)-Fe-C(1)-C(2) | 119.0(14) | C(7)-Fe-C(3)-C(4) | -164.4(9) |
| C(6)-Fe-C(1)-C(2) | -131.1(10) | C(1)-Fe-C(3)-C(4) | 81.0(10) |
| C(7)-Fe-C(1)-C(2) | -88.9(11) | C(2)-Fe-C(3)-C(4) | 116.2(13) |
| C(9)-Fe-C(1)-C(5) | 37(2) | C(9)-Fe-C(3)-C(2) | 163.2(10) |
| C(10)-Fe-C(1)-C(5) | 68.2(12) | C(10)-Fe-C(3)-C(2) | -158.6(11) |
| C(8)-Fe-C(1)-C(5) | -173.8(13) | C(8)-Fe-C(3)-C(2) | 119.2(10) |
| C(4)-Fe-C(1)-C(5) | -38.3(10) | C(4)-Fe-C(3)-C(2) | -116.2(13) |
| C(3)-Fe-C(1)-C(5) | -82.0(10) | C(5)-Fe-C(3)-C(2) | -77.8(10) |
| C(6)-Fe-C(1)-C(5) | 109.9(11) | C(6)-Fe-C(3)-C(2) | 41(3) |
| C(7)-Fe-C(1)-C(5) | 152.1(10) | C(7)-Fe-C(3)-C(2) | 79.4(11) |
| C(2)-Fe-C(1)-C(5) | -119.0(14) | C(1)-Fe-C(3)-C(2) | -35.2(9) |
| C(5)-C(1)-C(2)-C(3) | 3.2(17) | C(2)-C(3)-C(4)-C(5) | 2.4(16) |
| Fe-C(1)-C(2)-C(3) | -56.3(10) | Fe-C(3)-C(4)-C(5) | -59.6(10) |
| C(5)-C(1)-C(2)-Fe | 59.5(10) | C(2)-C(3)-C(4)-Fe | 62.0(9) |
| C(9)-Fe-C(2)-C(1) | -161.4(13) | C(9)-Fe-C(4)-C(3) | 116.3(10) |
| C(10)-Fe-C(2)-C(1) | 21(2) | C(10)-Fe-C(4)-C(3) | 158.5(8) |
| C(8)-Fe-C(2)-C(1) | 156.4(9) | C(8)-Fe-C(4)-C(3) | 76.7(11) |
| C(4)-Fe-C(2)-C(1) | -82.7(10) | C(5)-Fe-C(4)-C(3) | -119.0(13) |
| C(3)-Fe-C(2)-C(1) | -121.7(13) | C(6)-Fe-C(4)-C(3) | -171.2(9) |
| C(5)-Fe-C(2)-C(1) | -37.5(9) | C(7)-Fe-C(4)-C(3) | 58(3) |
| C(6)-Fe-C(2)-C(1) | 68.2(12) | C(1)-Fe-C(4)-C(3) | -82.3(10) |
| C(7)-Fe-C(2)-C(1) | 112.3(10) | C(2)-Fe-C(4)-C(3) | -39.9(9) |
| C(9)-Fe-C(2)-C(3) | -39.7(19) | C(9)-Fe-C(4)-C(5) | -124.7(10) |
| C(10)-Fe-C(2)-C(3) | 142.5(18) | C(10)-Fe-C(4)-C(5) | -82.5(10) |
| C(8)-Fe-C(2)-C(3) | -81.9(11) | C(8)-Fe-C(4)-C(5) | -164.3(9) |
| C(4)-Fe-C(2)-C(3) | 39.1(9) | C(3)-Fe-C(4)-C(5) | 119.0(13) |
| C(5)-Fe-C(2)-C(3) | 84.2(10) | C(6)-Fe-C(4)-C(5) | -52.2(15) |
| C(6)-Fe-C(2)-C(3) | -170.1(9) | C(7)-Fe-C(4)-C(5) | 177(2) |
| C(7)-Fe-C(2)-C(3) | -126.0(9) | C(1)-Fe-C(4)-C(5) | 36.7(9) |
| C(1)-Fe-C(2)-C(3) | 121.7(13) | C(2)-Fe-C(4)-C(5) | 79.1(10) |
| C(1)-C(2)-C(3)-C(4) | -3.4(16) | C(2)-C(1)-C(5)-C(4) | -1.7(17) |
| Fe-C(2)-C(3)-C(4) | -61.0(10) | Fe-C(1)-C(5)-C(4) | 59.0(10) |
| C(1)-C(2)-C(3)-Fe | 57.5(11) | C(2)-C(1)-C(5)-Fe | -60.7(11) |

|  |  |  |  |
|---|---|---|---|
| C(3)-C(4)-C(5)-C(1) | -0.5(17) | C(5)-Fe-C(6)-C(11) | 41.9(14) |
| Fe-C(4)-C(5)-C(1) | -60.4(11) | C(7)-Fe-C(6)-C(11) | -118.6(15) |
| C(3)-C(4)-C(5)-Fe | 59.9(10) | C(1)-Fe-C(6)-C(11) | -0.2(14) |
| C(9)-Fe-C(5)-C(1) | -166.6(9) | C(2)-Fe-C(6)-C(11) | -38.3(15) |
| C(10)-Fe-C(5)-C(1) | -128.0(10) | C(10)-C(6)-C(7)-C(8) | -0.5(14) |
| C(8)-Fe-C(5)-C(1) | 170.8(19) | C(11)-C(6)-C(7)-C(8) | 176.9(10) |
| C(4)-Fe-C(5)-C(1) | 119.4(14) | Fe-C(6)-C(7)-C(8) | 57.7(9) |
| C(3)-Fe-C(5)-C(1) | 81.9(10) | C(10)-C(6)-C(7)-Fe | -58.1(8) |
| C(6)-Fe-C(5)-C(1) | -86.9(11) | C(11)-C(6)-C(7)-Fe | 119.2(11) |
| C(7)-Fe-C(5)-C(1) | -59.0(16) | C(9)-Fe-C(7)-C(8) | -39.0(8) |
| C(2)-Fe-C(5)-C(1) | 37.1(10) | C(10)-Fe-C(7)-C(8) | -82.9(8) |
| C(9)-Fe-C(5)-C(4) | 74.0(11) | C(4)-Fe-C(7)-C(8) | 24(3) |
| C(10)-Fe-C(5)-C(4) | 112.5(10) | C(3)-Fe-C(7)-C(8) | 70.4(11) |
| C(8)-Fe-C(5)-C(4) | 51(2) | C(5)-Fe-C(7)-C(8) | -160.8(13) |
| C(3)-Fe-C(5)-C(4) | -37.5(9) | C(6)-Fe-C(7)-C(8) | -120.5(11) |
| C(6)-Fe-C(5)-C(4) | 153.7(9) | C(1)-Fe-C(7)-C(8) | 159.1(9) |
| C(7)-Fe-C(5)-C(4) | -178.4(11) | C(2)-Fe-C(7)-C(8) | 115.5(10) |
| C(1)-Fe-C(5)-C(4) | -119.4(14) | C(9)-Fe-C(7)-C(6) | 81.5(8) |
| C(2)-Fe-C(5)-C(4) | -82.4(10) | C(10)-Fe-C(7)-C(6) | 37.6(7) |
| C(9)-Fe-C(6)-C(10) | 38.5(8) | C(8)-Fe-C(7)-C(6) | 120.5(11) |
| C(8)-Fe-C(6)-C(10) | 82.8(8) | C(4)-Fe-C(7)-C(6) | 144(2) |
| C(4)-Fe-C(6)-C(10) | -44.6(14) | C(3)-Fe-C(7)-C(6) | -169.0(8) |
| C(3)-Fe-C(6)-C(10) | 165(2) | C(5)-Fe-C(7)-C(6) | -40.2(16) |
| C(5)-Fe-C(6)-C(10) | -80.3(10) | C(1)-Fe-C(7)-C(6) | -80.4(10) |
| C(7)-Fe-C(6)-C(10) | 119.2(10) | C(2)-Fe-C(7)-C(6) | -123.9(9) |
| C(1)-Fe-C(6)-C(10) | -122.4(9) | C(6)-C(7)-C(8)-C(9) | 1.8(14) |
| C(2)-Fe-C(6)-C(10) | -160.5(9) | Fe-C(7)-C(8)-C(9) | 60.2(9) |
| C(9)-Fe-C(6)-C(7) | -80.6(8) | C(6)-C(7)-C(8)-Fe | -58.4(8) |
| C(10)-Fe-C(6)-C(7) | -119.2(10) | C(9)-Fe-C(8)-C(7) | 117.4(11) |
| C(8)-Fe-C(6)-C(7) | -36.4(7) | C(10)-Fe-C(8)-C(7) | 80.6(8) |
| C(4)-Fe-C(6)-C(7) | -163.8(11) | C(4)-Fe-C(8)-C(7) | -173.1(9) |
| C(3)-Fe-C(6)-C(7) | 46(3) | C(3)-Fe-C(8)-C(7) | -130.8(9) |
| C(5)-Fe-C(6)-C(7) | 160.5(9) | C(5)-Fe-C(8)-C(7) | 146(2) |
| C(1)-Fe-C(6)-C(7) | 118.4(9) | C(6)-Fe-C(8)-C(7) | 37.0(8) |
| C(2)-Fe-C(6)-C(7) | 80.3(10) | C(1)-Fe-C(8)-C(7) | -48.2(18) |
| C(9)-Fe-C(6)-C(11) | 160.8(14) | C(2)-Fe-C(8)-C(7) | -86.7(10) |
| C(10)-Fe-C(6)-C(11) | 122.2(15) | C(10)-Fe-C(8)-C(9) | -36.8(7) |
| C(8)-Fe-C(6)-C(11) | -155.0(14) | C(4)-Fe-C(8)-C(9) | 69.5(11) |
| C(4)-Fe-C(6)-C(11) | 77.6(17) | C(3)-Fe-C(8)-C(9) | 111.8(9) |
| C(3)-Fe-C(6)-C(11) | -73(3) | C(5)-Fe-C(8)-C(9) | 29(2) |

| | | | |
|---|---|---|---|
| C(6)-Fe-C(8)-C(9) | -80.4(8) | C(8)-Fe-C(10)-C(6) | -80.4(8) |
| C(7)-Fe-C(8)-C(9) | -117.4(11) | C(4)-Fe-C(10)-C(6) | 157.1(9) |
| C(1)-Fe-C(8)-C(9) | -165.6(14) | C(3)-Fe-C(10)-C(6) | -173.9(10) |
| C(2)-Fe-C(8)-C(9) | 155.9(9) | C(5)-Fe-C(10)-C(6) | 114.6(9) |
| C(7)-C(8)-C(9)-C(10) | -2.5(15) | C(7)-Fe-C(10)-C(6) | -37.6(7) |
| Fe-C(8)-C(9)-C(10) | 59.5(9) | C(1)-Fe-C(10)-C(6) | 77.0(10) |
| C(7)-C(8)-C(9)-Fe | -62.0(9) | C(2)-Fe-C(10)-C(6) | 61(2) |
| C(8)-Fe-C(9)-C(10) | -120.5(11) | C(10)-C(6)-C(11)-C(12) | -7(2) |
| C(4)-Fe-C(9)-C(10) | 110.3(10) | C(7)-C(6)-C(11)-C(12) | 175.8(12) |
| C(3)-Fe-C(9)-C(10) | 152.1(9) | Fe-C(6)-C(11)-C(12) | -95.9(15) |
| C(5)-Fe-C(9)-C(10) | 68.8(10) | C(6)-C(11)-C(12)-C(13) | -179.2(11) |
| C(6)-Fe-C(9)-C(10) | -38.5(7) | C(11)-C(12)-C(13)-C(14) | -167.7(13) |
| C(7)-Fe-C(9)-C(10) | -82.5(8) | C(11)-C(12)-C(13)-C(15) | 13(2) |
| C(1)-Fe-C(9)-C(10) | 41(2) | C(15)-C(13)-C(14)-C(16) | -3.7(18) |
| C(2)-Fe-C(9)-C(10) | -179.0(13) | C(12)-C(13)-C(14)-C(16) | 177.1(11) |
| C(10)-Fe-C(9)-C(8) | 120.5(11) | C(14)-C(13)-C(15)-C(17) | 0.9(18) |
| C(4)-Fe-C(9)-C(8) | -129.2(9) | C(12)-C(13)-C(15)-C(17) | -179.9(11) |
| C(3)-Fe-C(9)-C(8) | -87.4(10) | C(13)-C(14)-C(16)-C(18) | 4.5(19) |
| C(5)-Fe-C(9)-C(8) | -170.6(9) | C(13)-C(15)-C(17)-C(18) | 1(2) |
| C(6)-Fe-C(9)-C(8) | 82.0(8) | C(15)-C(17)-C(18)-C(16) | 0(2) |
| C(7)-Fe-C(9)-C(8) | 38.0(8) | C(15)-C(17)-C(18)-C(19) | -179.9(11) |
| C(1)-Fe-C(9)-C(8) | 161.3(16) | C(14)-C(16)-C(18)-C(17) | -2.5(19) |
| C(2)-Fe-C(9)-C(8) | -58.5(17) | C(14)-C(16)-C(18)-C(19) | 177.1(11) |
| C(8)-C(9)-C(10)-C(6) | 2.2(14) | C(17)-C(18)-C(19)-C(20) | -166.4(15) |
| Fe-C(9)-C(10)-C(6) | 61.7(9) | C(16)-C(18)-C(19)-C(20) | 14(2) |
| C(8)-C(9)-C(10)-Fe | -59.4(9) | C(18)-C(19)-C(20)-C(21) | -178.4(11) |
| C(7)-C(6)-C(10)-C(9) | -1.1(14) | C(19)-C(20)-C(21)-C(23) | -173.6(15) |
| C(11)-C(6)-C(10)-C(9) | -178.3(11) | C(19)-C(20)-C(21)-C(22) | 4(2) |
| Fe-C(6)-C(10)-C(9) | -60.3(9) | C(23)-C(21)-C(22)-C(24) | -5(2) |
| C(7)-C(6)-C(10)-Fe | 59.2(8) | C(20)-C(21)-C(22)-C(24) | 177.7(13) |
| C(11)-C(6)-C(10)-Fe | -118.0(12) | C(22)-C(21)-C(23)-C(25) | 3(2) |
| C(8)-Fe-C(10)-C(9) | 37.1(8) | C(20)-C(21)-C(23)-C(25) | -179.4(11) |
| C(4)-Fe-C(10)-C(9) | -85.4(10) | C(21)-C(22)-C(24)-C(26) | 5(2) |
| C(3)-Fe-C(10)-C(9) | -56.4(15) | C(21)-C(23)-C(25)-C(26) | -2(2) |
| C(5)-Fe-C(10)-C(9) | -127.9(10) | C(23)-C(25)-C(26)-C(24) | 2(2) |
| C(6)-Fe-C(10)-C(9) | 117.5(11) | C(23)-C(25)-C(26)-C(27) | -179.9(13) |
| C(7)-Fe-C(10)-C(9) | 79.9(8) | C(22)-C(24)-C(26)-C(25) | -4(2) |
| C(1)-Fe-C(10)-C(9) | -165.5(9) | C(22)-C(24)-C(26)-C(27) | 178.0(14) |
| C(2)-Fe-C(10)-C(9) | 178.7(17) | C(25)-C(26)-C(27)-C(28) | 3(3) |
| C(9)-Fe-C(10)-C(6) | -117.5(11) | C(24)-C(26)-C(27)-C(28) | -178.6(18) |

| | |
|---|---|
| C(26)-C(27)-C(28)-C(29) | 178.7(13) |
| C(27)-C(28)-C(29)-C(31) | -16(3) |
| C(27)-C(28)-C(29)-C(30) | 170.6(17) |
| C(31)-C(29)-C(30)-C(32) | 5(2) |
| C(28)-C(29)-C(30)-C(32) | 179.1(13) |
| C(30)-C(29)-C(31)-C(33) | -3(2) |
| C(28)-C(29)-C(31)-C(33) | -176.5(14) |
| C(33)-N-C(32)-C(30) | 2(2) |
| C(34)-N-C(32)-C(30) | 178.2(12) |
| C(29)-C(30)-C(32)-N | -4(2) |
| C(32)-N-C(33)-C(31) | -1(2) |
| C(34)-N-C(33)-C(31) | -176.6(13) |
| C(29)-C(31)-C(33)-N | 1(2) |

---

Symmetry transformations used to generate equivalent atoms:

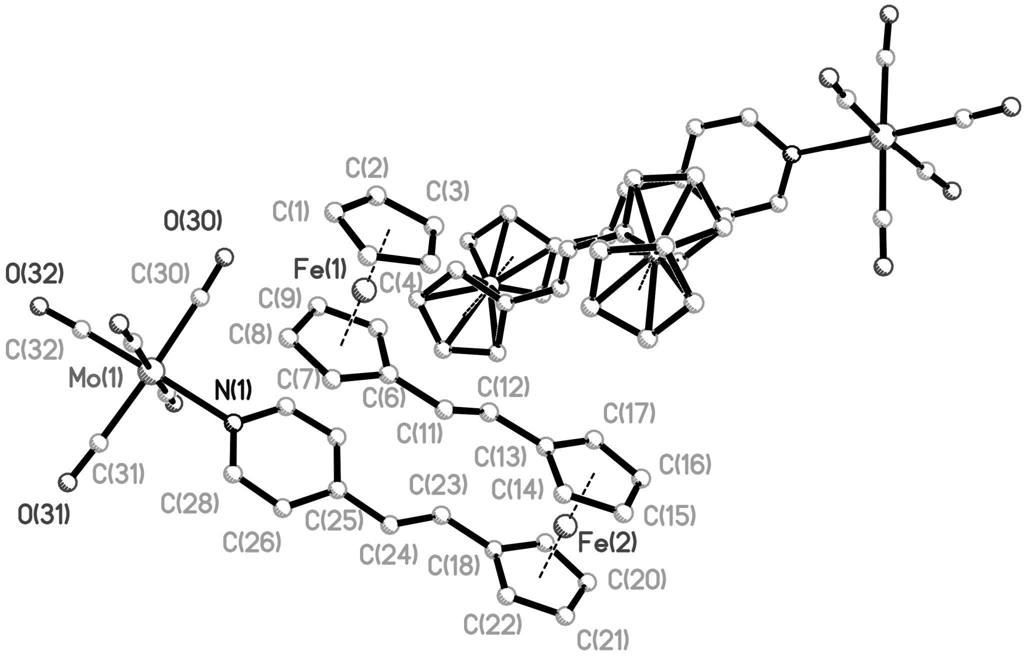

C(2)
C(3)
C(1)
O(30)
O(32)
C(30)
Fe(1)
C(4)
C(9)
C(8)
C(32)
Mo(1)
N(1)
C(7)
C(6)
C(12)
C(17)
C(11)
C(13)
C(16)
C(31)
C(23)
C(14)
C(28)
C(15)
O(31)
C(25)
Fe(2)
C(26)
C(24)
C(18)
C(20)
C(22)
C(21)

**Table 1**. Crystal data and structure refinement for str105m.

| | | |
|---|---|---|
| Identification code | str105m | |
| Empirical formula | C34 H25 Fe2 Mo N O5 | |
| Formula weight | 735.19 | |
| Temperature | 293(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Triclinic | |
| Space group | -1 | |
| Unit cell dimensions | a = 10.4088(11) Å | $\alpha$= 83.278(2)°. |
| | b = 15.1733(15) Å | $\beta$= 77.073(2)°. |
| | c = 20.490(2) Å | $\gamma$ = 85.000(2)°. |
| Volume | 3126.1(6) Å$^3$ | |
| Z | 4 | |
| Density (calculated) | 1.562 Mg/m$^3$ | |
| Absorption coefficient | 1.352 mm$^{-1}$ | |
| F(000) | 1480 | |
| Crystal size | 0.30 x 0.16 x 0.12 mm$^3$ | |
| Theta range for data collection | 1.02 to 30.51°. | |
| Index ranges | -10<=h<=14, -21<=k<=21, -27<=l<=29 | |
| Reflections collected | 26545 | |
| Independent reflections | 18642 [R(int) = 0.0565] | |
| Completeness to theta = 30.51° | 97.6 % | |
| Absorption correction | SADABS | |
| Refinement method | Full-matrix least-squares on F$^2$ | |
| Data / restraints / parameters | 18642 / 0 / 775 | |
| Goodness-of-fit on F$^2$ | 0.794 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0467, wR2 = 0.0819 | |
| R indices (all data) | R1 = 0.2101, wR2 = 0.1201 | |
| Largest diff. peak and hole | 0.426 and -0.603 e.Å$^{-3}$ | |

**Table 2**. Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters (Å$^2$x $10^3$) for str105m. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| Mo(1) | 8720(1) | 1830(1) | 3042(1) | 61(1) |
| Fe(1) | 4126(1) | 5106(1) | 3161(1) | 41(1) |
| N(1) | 8554(3) | 3055(2) | 3617(2) | 49(1) |
| C(1) | 2622(5) | 4742(3) | 2767(3) | 64(1) |
| Fe(2) | 7385(1) | 7939(1) | 4785(1) | 50(1) |
| C(2) | 3398(5) | 5344(4) | 2309(3) | 72(2) |
| C(3) | 3366(5) | 6134(3) | 2604(3) | 63(1) |
| C(4) | 2564(4) | 6028(3) | 3251(2) | 55(1) |
| C(5) | 2109(4) | 5169(3) | 3357(3) | 58(1) |
| C(6) | 5451(4) | 5404(3) | 3710(2) | 49(1) |
| C(7) | 4861(4) | 4591(3) | 3971(2) | 56(1) |
| C(8) | 5143(5) | 3994(3) | 3478(3) | 64(1) |
| C(9) | 5899(5) | 4427(4) | 2890(3) | 72(2) |
| C(10) | 6083(4) | 5294(3) | 3031(3) | 61(1) |
| C(11) | 5376(4) | 6185(3) | 4075(2) | 56(1) |
| C(12) | 6101(5) | 6856(3) | 3881(2) | 56(1) |
| C(13) | 6071(4) | 7656(3) | 4225(2) | 51(1) |
| C(14) | 5419(5) | 7820(3) | 4886(3) | 64(1) |
| C(15) | 5657(5) | 8687(4) | 4993(3) | 77(2) |
| C(16) | 6477(5) | 9063(3) | 4401(3) | 74(2) |
| C(17) | 6725(5) | 8427(3) | 3941(3) | 63(1) |
| C(18) | 8795(4) | 6908(3) | 4793(2) | 50(1) |
| C(19) | 9380(5) | 7734(3) | 4539(3) | 67(2) |
| C(20) | 9047(6) | 8317(4) | 5033(4) | 87(2) |
| C(21) | 8235(6) | 7887(4) | 5605(3) | 77(2) |
| C(22) | 8077(5) | 7018(3) | 5459(2) | 58(1) |
| C(23) | 8870(4) | 6138(3) | 4425(2) | 51(1) |
| C(24) | 8457(4) | 5343(3) | 4673(2) | 49(1) |
| C(25) | 8490(4) | 4579(3) | 4304(2) | 42(1) |
| C(26) | 8153(4) | 3753(3) | 4640(2) | 54(1) |
| C(27) | 8851(4) | 4606(3) | 3612(2) | 53(1) |
| C(28) | 8197(4) | 3033(3) | 4283(3) | 58(1) |
| C(29) | 8871(4) | 3849(3) | 3294(2) | 56(1) |

| | | | | |
|---|---|---|---|---|
| O(30) | 8514(6) | 3000(3) | 1665(2) | 135(2) |
| C(30) | 8570(6) | 2607(4) | 2157(3) | 88(2) |
| O(31) | 9017(4) | 532(3) | 4332(2) | 102(1) |
| C(31) | 8900(5) | 1012(4) | 3880(3) | 68(2) |
| O(32) | 9037(5) | 127(3) | 2295(2) | 133(2) |
| C(32) | 8926(6) | 769(4) | 2559(3) | 92(2) |
| C(33) | 10720(6) | 1945(4) | 2780(3) | 76(2) |
| O(33) | 11813(4) | 1999(4) | 2620(2) | 123(2) |
| O(34) | 5638(4) | 1565(3) | 3341(2) | 112(2) |
| C(34) | 6725(6) | 1688(4) | 3251(3) | 79(2) |
| Mo(50) | 4470(1) | 13051(1) | 731(1) | 61(1) |
| N(50) | 5911(4) | 11827(2) | 586(2) | 51(1) |
| Fe(51) | 3522(1) | 9300(1) | 2637(1) | 56(1) |
| C(51) | 2335(7) | 9651(4) | 3506(3) | 100(2) |
| Fe(52) | 9882(1) | 7179(1) | 1348(1) | 66(1) |
| C(52) | 3351(6) | 9055(5) | 3648(3) | 93(2) |
| C(53) | 3277(5) | 8277(4) | 3375(3) | 75(2) |
| C(54) | 2208(5) | 8383(4) | 3061(3) | 77(2) |
| C(55) | 1605(5) | 9240(4) | 3134(3) | 82(2) |
| C(56) | 5225(5) | 9021(4) | 1936(3) | 67(2) |
| C(57) | 5269(5) | 9814(4) | 2205(3) | 93(2) |
| C(58) | 4232(8) | 10411(4) | 2069(4) | 124(3) |
| C(59) | 3508(7) | 9985(5) | 1733(4) | 108(3) |
| C(60) | 4114(6) | 9138(4) | 1635(3) | 84(2) |
| C(61) | 6103(5) | 8225(4) | 1925(3) | 75(2) |
| C(62) | 7225(6) | 8131(4) | 2065(2) | 77(2) |
| C(63) | 8142(5) | 7316(4) | 2043(3) | 63(1) |
| C(64) | 8157(5) | 6586(4) | 1684(3) | 84(2) |
| C(65) | 9232(7) | 5984(5) | 1779(4) | 100(2) |
| C(66) | 9862(6) | 6357(5) | 2199(4) | 109(3) |
| C(67) | 9232(6) | 7188(5) | 2355(3) | 93(2) |
| C(68) | 10149(5) | 8311(4) | 694(3) | 74(2) |
| C(69) | 10084(6) | 7580(4) | 351(3) | 94(2) |
| C(70) | 11089(8) | 6935(5) | 448(4) | 117(3) |
| C(71) | 11783(6) | 7261(5) | 863(4) | 117(3) |
| C(72) | 11219(5) | 8110(5) | 1025(3) | 98(2) |
| C(73) | 9326(5) | 9145(4) | 749(3) | 77(2) |
| C(74) | 8402(5) | 9412(4) | 432(3) | 71(2) |

|  |  |  |  |  |
|---|---|---|---|---|
| C(75) | 7572(5) | 10243(3) | 490(2) | 59(1) |
| C(76) | 6566(5) | 10428(3) | 147(3) | 71(2) |
| C(77) | 7742(5) | 10909(4) | 862(3) | 80(2) |
| C(78) | 5793(5) | 11196(3) | 208(2) | 66(1) |
| C(79) | 6929(6) | 11670(4) | 888(3) | 78(2) |
| O(80) | 2377(5) | 14652(3) | 945(2) | 138(2) |
| C(80) | 3146(7) | 14072(4) | 874(3) | 92(2) |
| O(81) | 6625(5) | 14445(3) | 636(2) | 127(2) |
| C(81) | 5911(6) | 13926(4) | 646(3) | 81(2) |
| C(82) | 4586(6) | 13275(4) | -277(3) | 81(2) |
| O(82) | 4626(4) | 13430(3) | -838(2) | 110(2) |
| O(83) | 4471(4) | 12801(3) | 2289(2) | 96(1) |
| C(83) | 4439(5) | 12875(3) | 1735(3) | 68(2) |
| O(84) | 1967(4) | 11913(3) | 946(2) | 112(2) |
| C(84) | 2905(6) | 12289(4) | 857(3) | 78(2) |

**Table 3**. Bond lengths [Å] and angles [°] for str105m.

| | |
|---|---|
| Mo(1)-C(32) | 1.959(6) |
| Mo(1)-C(31) | 2.032(6) |
| Mo(1)-C(33) | 2.048(6) |
| Mo(1)-C(34) | 2.049(7) |
| Mo(1)-C(30) | 2.072(7) |
| Mo(1)-N(1) | 2.288(4) |
| Fe(1)-C(7) | 2.027(4) |
| Fe(1)-C(9) | 2.030(5) |
| Fe(1)-C(8) | 2.032(5) |
| Fe(1)-C(3) | 2.033(5) |
| Fe(1)-C(10) | 2.035(4) |
| Fe(1)-C(2) | 2.037(5) |
| Fe(1)-C(4) | 2.040(4) |
| Fe(1)-C(5) | 2.043(4) |
| Fe(1)-C(1) | 2.057(4) |
| Fe(1)-C(6) | 2.073(4) |
| N(1)-C(28) | 1.329(5) |
| N(1)-C(29) | 1.336(5) |
| C(1)-C(2) | 1.398(6) |
| C(1)-C(5) | 1.415(6) |
| Fe(2)-C(15) | 2.030(5) |
| Fe(2)-C(19) | 2.030(5) |
| Fe(2)-C(14) | 2.032(5) |
| Fe(2)-C(16) | 2.039(5) |
| Fe(2)-C(17) | 2.039(5) |
| Fe(2)-C(22) | 2.048(5) |
| Fe(2)-C(18) | 2.051(4) |
| Fe(2)-C(20) | 2.052(5) |
| Fe(2)-C(21) | 2.056(5) |
| Fe(2)-C(13) | 2.071(4) |
| C(2)-C(3) | 1.398(7) |
| C(3)-C(4) | 1.400(6) |
| C(4)-C(5) | 1.401(6) |
| C(6)-C(7) | 1.420(6) |
| C(6)-C(10) | 1.422(6) |
| C(6)-C(11) | 1.459(6) |
| C(7)-C(8) | 1.399(6) |
| C(8)-C(9) | 1.409(7) |
| C(9)-C(10) | 1.417(6) |
| C(11)-C(12) | 1.293(6) |
| C(12)-C(13) | 1.469(6) |
| C(13)-C(17) | 1.404(6) |
| C(13)-C(14) | 1.412(6) |
| C(14)-C(15) | 1.410(6) |
| C(15)-C(16) | 1.408(7) |
| C(16)-C(17) | 1.395(6) |
| C(18)-C(22) | 1.423(6) |
| C(18)-C(19) | 1.431(6) |
| C(18)-C(23) | 1.451(6) |
| C(19)-C(20) | 1.388(7) |
| C(20)-C(21) | 1.409(7) |
| C(21)-C(22) | 1.415(6) |
| C(23)-C(24) | 1.321(6) |
| C(24)-C(25) | 1.449(6) |
| C(25)-C(27) | 1.380(6) |
| C(25)-C(26) | 1.391(6) |
| C(26)-C(28) | 1.376(6) |
| C(27)-C(29) | 1.381(6) |
| O(30)-C(30) | 1.121(6) |
| O(31)-C(31) | 1.131(5) |
| O(32)-C(32) | 1.155(6) |
| C(33)-O(33) | 1.118(6) |
| O(34)-C(34) | 1.134(6) |
| Mo(50)-C(80) | 1.984(7) |
| Mo(50)-C(84) | 2.032(7) |
| Mo(50)-C(82) | 2.032(6) |
| Mo(50)-C(83) | 2.035(6) |
| Mo(50)-C(81) | 2.053(7) |
| Mo(50)-N(50) | 2.288(4) |
| N(50)-C(78) | 1.330(5) |
| N(50)-C(79) | 1.334(6) |
| Fe(51)-C(57) | 2.016(5) |
| Fe(51)-C(59) | 2.017(7) |

| | |
|---|---|
| Fe(51)-C(54) | 2.019(5) |
| Fe(51)-C(51) | 2.025(6) |
| Fe(51)-C(53) | 2.026(5) |
| Fe(51)-C(58) | 2.029(6) |
| Fe(51)-C(55) | 2.031(5) |
| Fe(51)-C(52) | 2.031(6) |
| Fe(51)-C(60) | 2.046(6) |
| Fe(51)-C(56) | 2.063(5) |
| C(51)-C(52) | 1.390(8) |
| C(51)-C(55) | 1.414(8) |
| Fe(52)-C(71) | 2.013(6) |
| Fe(52)-C(66) | 2.018(6) |
| Fe(52)-C(72) | 2.021(6) |
| Fe(52)-C(64) | 2.022(5) |
| Fe(52)-C(67) | 2.024(6) |
| Fe(52)-C(65) | 2.024(6) |
| Fe(52)-C(69) | 2.032(5) |
| Fe(52)-C(70) | 2.039(6) |
| Fe(52)-C(63) | 2.049(5) |
| Fe(52)-C(68) | 2.050(5) |
| C(52)-C(53) | 1.379(7) |
| C(53)-C(54) | 1.393(7) |
| C(54)-C(55) | 1.402(7) |
| C(56)-C(57) | 1.389(7) |
| C(56)-C(60) | 1.417(7) |
| C(56)-C(61) | 1.450(7) |
| C(57)-C(58) | 1.403(8) |
| C(58)-C(59) | 1.371(9) |
| C(59)-C(60) | 1.398(8) |
| C(61)-C(62) | 1.256(7) |
| C(62)-C(63) | 1.493(7) |
| C(63)-C(64) | 1.397(7) |
| C(63)-C(67) | 1.411(7) |
| C(64)-C(65) | 1.415(8) |
| C(65)-C(66) | 1.386(9) |
| C(66)-C(67) | 1.407(9) |
| C(68)-C(69) | 1.396(8) |
| C(68)-C(72) | 1.423(8) |
| C(68)-C(73) | 1.465(7) |
| C(69)-C(70) | 1.400(8) |
| C(70)-C(71) | 1.387(9) |
| C(71)-C(72) | 1.413(9) |
| C(73)-C(74) | 1.290(7) |
| C(74)-C(75) | 1.466(7) |
| C(75)-C(76) | 1.379(7) |
| C(75)-C(77) | 1.380(7) |
| C(76)-C(78) | 1.358(6) |
| C(77)-C(79) | 1.370(7) |
| O(80)-C(80) | 1.137(6) |
| O(81)-C(81) | 1.124(6) |
| C(82)-O(82) | 1.138(5) |
| O(83)-C(83) | 1.136(5) |
| O(84)-C(84) | 1.142(6) |
| C(32)-Mo(1)-C(31) | 87.8(2) |
| C(32)-Mo(1)-C(33) | 90.0(2) |
| C(31)-Mo(1)-C(33) | 91.1(2) |
| C(32)-Mo(1)-C(34) | 87.3(2) |
| C(31)-Mo(1)-C(34) | 90.7(2) |
| C(33)-Mo(1)-C(34) | 176.7(2) |
| C(32)-Mo(1)-C(30) | 89.2(2) |
| C(31)-Mo(1)-C(30) | 176.9(2) |
| C(33)-Mo(1)-C(30) | 88.2(2) |
| C(34)-Mo(1)-C(30) | 89.8(2) |
| C(32)-Mo(1)-N(1) | 177.85(19) |
| C(31)-Mo(1)-N(1) | 91.02(17) |
| C(33)-Mo(1)-N(1) | 88.26(18) |
| C(34)-Mo(1)-N(1) | 94.53(18) |
| C(30)-Mo(1)-N(1) | 91.99(19) |
| C(7)-Fe(1)-C(9) | 68.0(2) |
| C(7)-Fe(1)-C(8) | 40.32(17) |
| C(9)-Fe(1)-C(8) | 40.59(19) |
| C(7)-Fe(1)-C(3) | 152.2(2) |
| C(9)-Fe(1)-C(3) | 126.3(2) |
| C(8)-Fe(1)-C(3) | 165.0(2) |
| C(7)-Fe(1)-C(10) | 67.70(19) |
| C(9)-Fe(1)-C(10) | 40.79(18) |

| | |
|---|---|
| C(8)-Fe(1)-C(10) | 68.2(2) |
| C(3)-Fe(1)-C(10) | 106.4(2) |
| C(7)-Fe(1)-C(2) | 167.6(2) |
| C(9)-Fe(1)-C(2) | 105.6(2) |
| C(8)-Fe(1)-C(2) | 128.1(2) |
| C(3)-Fe(1)-C(2) | 40.18(19) |
| C(10)-Fe(1)-C(2) | 115.0(2) |
| C(7)-Fe(1)-C(4) | 121.28(19) |
| C(9)-Fe(1)-C(4) | 165.4(2) |
| C(8)-Fe(1)-C(4) | 153.7(2) |
| C(3)-Fe(1)-C(4) | 40.21(17) |
| C(10)-Fe(1)-C(4) | 129.0(2) |
| C(2)-Fe(1)-C(4) | 67.4(2) |
| C(7)-Fe(1)-C(5) | 112.63(19) |
| C(9)-Fe(1)-C(5) | 150.8(2) |
| C(8)-Fe(1)-C(5) | 120.1(2) |
| C(3)-Fe(1)-C(5) | 67.60(19) |
| C(10)-Fe(1)-C(5) | 168.4(2) |
| C(2)-Fe(1)-C(5) | 67.4(2) |
| C(4)-Fe(1)-C(5) | 40.15(17) |
| C(7)-Fe(1)-C(1) | 132.0(2) |
| C(9)-Fe(1)-C(1) | 115.9(2) |
| C(8)-Fe(1)-C(1) | 109.2(2) |
| C(3)-Fe(1)-C(1) | 67.6(2) |
| C(10)-Fe(1)-C(1) | 148.1(2) |
| C(2)-Fe(1)-C(1) | 39.95(19) |
| C(4)-Fe(1)-C(1) | 67.62(19) |
| C(5)-Fe(1)-C(1) | 40.37(17) |
| C(7)-Fe(1)-C(6) | 40.52(17) |
| C(9)-Fe(1)-C(6) | 68.66(19) |
| C(8)-Fe(1)-C(6) | 68.46(18) |
| C(3)-Fe(1)-C(6) | 117.1(2) |
| C(10)-Fe(1)-C(6) | 40.50(17) |
| C(2)-Fe(1)-C(6) | 148.7(2) |
| C(4)-Fe(1)-C(6) | 110.19(19) |
| C(5)-Fe(1)-C(6) | 132.2(2) |
| C(1)-Fe(1)-C(6) | 170.6(2) |
| C(28)-N(1)-C(29) | 115.1(4) |
| C(28)-N(1)-Mo(1) | 123.8(3) |
| C(29)-N(1)-Mo(1) | 121.0(3) |
| C(2)-C(1)-C(5) | 107.1(4) |
| C(2)-C(1)-Fe(1) | 69.3(3) |
| C(5)-C(1)-Fe(1) | 69.3(3) |
| C(15)-Fe(2)-C(19) | 154.9(2) |
| C(15)-Fe(2)-C(14) | 40.64(18) |
| C(19)-Fe(2)-C(14) | 163.0(2) |
| C(15)-Fe(2)-C(16) | 40.5(2) |
| C(19)-Fe(2)-C(16) | 120.4(2) |
| C(14)-Fe(2)-C(16) | 68.1(2) |
| C(15)-Fe(2)-C(17) | 67.3(2) |
| C(19)-Fe(2)-C(17) | 108.9(2) |
| C(14)-Fe(2)-C(17) | 67.2(2) |
| C(16)-Fe(2)-C(17) | 40.01(19) |
| C(15)-Fe(2)-C(22) | 124.9(2) |
| C(19)-Fe(2)-C(22) | 68.0(2) |
| C(14)-Fe(2)-C(22) | 109.1(2) |
| C(16)-Fe(2)-C(22) | 160.7(2) |
| C(17)-Fe(2)-C(22) | 158.2(2) |
| C(15)-Fe(2)-C(18) | 162.1(2) |
| C(19)-Fe(2)-C(18) | 41.06(17) |
| C(14)-Fe(2)-C(18) | 125.83(19) |
| C(16)-Fe(2)-C(18) | 156.5(2) |
| C(17)-Fe(2)-C(18) | 122.7(2) |
| C(22)-Fe(2)-C(18) | 40.62(17) |
| C(15)-Fe(2)-C(20) | 120.4(2) |
| C(19)-Fe(2)-C(20) | 39.8(2) |
| C(14)-Fe(2)-C(20) | 156.2(3) |
| C(16)-Fe(2)-C(20) | 106.8(2) |
| C(17)-Fe(2)-C(20) | 124.8(2) |
| C(22)-Fe(2)-C(20) | 67.6(2) |
| C(18)-Fe(2)-C(20) | 68.1(2) |
| C(15)-Fe(2)-C(21) | 107.3(2) |
| C(19)-Fe(2)-C(21) | 67.5(2) |
| C(14)-Fe(2)-C(21) | 122.0(2) |
| C(16)-Fe(2)-C(21) | 123.7(2) |
| C(17)-Fe(2)-C(21) | 160.3(2) |

| | |
|---|---|
| C(22)-Fe(2)-C(21) | 40.35(17) |
| C(18)-Fe(2)-C(21) | 68.2(2) |
| C(20)-Fe(2)-C(21) | 40.1(2) |
| C(15)-Fe(2)-C(13) | 68.0(2) |
| C(19)-Fe(2)-C(13) | 126.1(2) |
| C(14)-Fe(2)-C(13) | 40.25(17) |
| C(16)-Fe(2)-C(13) | 67.87(19) |
| C(17)-Fe(2)-C(13) | 39.95(17) |
| C(22)-Fe(2)-C(13) | 123.15(18) |
| C(18)-Fe(2)-C(13) | 109.18(18) |
| C(20)-Fe(2)-C(13) | 161.4(2) |
| C(21)-Fe(2)-C(13) | 157.7(2) |
| C(3)-C(2)-C(1) | 108.9(5) |
| C(3)-C(2)-Fe(1) | 69.8(3) |
| C(1)-C(2)-Fe(1) | 70.8(3) |
| C(2)-C(3)-C(4) | 107.9(4) |
| C(2)-C(3)-Fe(1) | 70.1(3) |
| C(4)-C(3)-Fe(1) | 70.2(3) |
| C(3)-C(4)-C(5) | 108.1(4) |
| C(3)-C(4)-Fe(1) | 69.6(3) |
| C(5)-C(4)-Fe(1) | 70.0(3) |
| C(4)-C(5)-C(1) | 108.1(4) |
| C(4)-C(5)-Fe(1) | 69.8(3) |
| C(1)-C(5)-Fe(1) | 70.3(3) |
| C(7)-C(6)-C(10) | 105.5(4) |
| C(7)-C(6)-C(11) | 125.9(5) |
| C(10)-C(6)-C(11) | 128.6(4) |
| C(7)-C(6)-Fe(1) | 68.0(2) |
| C(10)-C(6)-Fe(1) | 68.3(2) |
| C(11)-C(6)-Fe(1) | 126.8(3) |
| C(8)-C(7)-C(6) | 110.0(4) |
| C(8)-C(7)-Fe(1) | 70.0(3) |
| C(6)-C(7)-Fe(1) | 71.5(3) |
| C(7)-C(8)-C(9) | 107.8(5) |
| C(7)-C(8)-Fe(1) | 69.7(3) |
| C(9)-C(8)-Fe(1) | 69.6(3) |
| C(8)-C(9)-C(10) | 107.6(5) |
| C(8)-C(9)-Fe(1) | 69.8(3) |
| C(10)-C(9)-Fe(1) | 69.8(3) |
| C(9)-C(10)-C(6) | 109.2(4) |
| C(9)-C(10)-Fe(1) | 69.4(3) |
| C(6)-C(10)-Fe(1) | 71.2(2) |
| C(12)-C(11)-C(6) | 125.3(5) |
| C(11)-C(12)-C(13) | 127.7(5) |
| C(17)-C(13)-C(14) | 106.2(4) |
| C(17)-C(13)-C(12) | 124.9(5) |
| C(14)-C(13)-C(12) | 128.9(4) |
| C(17)-C(13)-Fe(2) | 68.8(3) |
| C(14)-C(13)-Fe(2) | 68.4(3) |
| C(12)-C(13)-Fe(2) | 127.2(3) |
| C(15)-C(14)-C(13) | 108.7(5) |
| C(15)-C(14)-Fe(2) | 69.6(3) |
| C(13)-C(14)-Fe(2) | 71.4(3) |
| C(16)-C(15)-C(14) | 107.8(5) |
| C(16)-C(15)-Fe(2) | 70.1(3) |
| C(14)-C(15)-Fe(2) | 69.8(3) |
| C(17)-C(16)-C(15) | 107.2(5) |
| C(17)-C(16)-Fe(2) | 70.0(3) |
| C(15)-C(16)-Fe(2) | 69.4(3) |
| C(16)-C(17)-C(13) | 110.1(5) |
| C(16)-C(17)-Fe(2) | 70.0(3) |
| C(13)-C(17)-Fe(2) | 71.2(3) |
| C(22)-C(18)-C(19) | 106.1(4) |
| C(22)-C(18)-C(23) | 127.5(4) |
| C(19)-C(18)-C(23) | 126.3(5) |
| C(22)-C(18)-Fe(2) | 69.6(3) |
| C(19)-C(18)-Fe(2) | 68.7(3) |
| C(23)-C(18)-Fe(2) | 123.9(3) |
| C(20)-C(19)-C(18) | 109.1(5) |
| C(20)-C(19)-Fe(2) | 71.0(3) |
| C(18)-C(19)-Fe(2) | 70.3(3) |
| C(19)-C(20)-C(21) | 108.4(5) |
| C(19)-C(20)-Fe(2) | 69.3(3) |
| C(21)-C(20)-Fe(2) | 70.1(3) |
| C(20)-C(21)-C(22) | 107.8(5) |
| C(20)-C(21)-Fe(2) | 69.8(3) |

| | |
|---|---|
| C(22)-C(21)-Fe(2) | 69.5(3) |
| C(21)-C(22)-C(18) | 108.5(5) |
| C(21)-C(22)-Fe(2) | 70.1(3) |
| C(18)-C(22)-Fe(2) | 69.8(3) |
| C(24)-C(23)-C(18) | 126.7(4) |
| C(23)-C(24)-C(25) | 127.0(4) |
| C(27)-C(25)-C(26) | 115.3(4) |
| C(27)-C(25)-C(24) | 123.8(4) |
| C(26)-C(25)-C(24) | 120.9(4) |
| C(28)-C(26)-C(25) | 120.2(4) |
| C(25)-C(27)-C(29) | 120.7(4) |
| N(1)-C(28)-C(26) | 124.7(4) |
| N(1)-C(29)-C(27) | 124.0(4) |
| O(30)-C(30)-Mo(1) | 177.2(6) |
| O(31)-C(31)-Mo(1) | 177.4(5) |
| O(32)-C(32)-Mo(1) | 177.8(6) |
| O(33)-C(33)-Mo(1) | 178.1(5) |
| O(34)-C(34)-Mo(1) | 175.5(5) |
| C(80)-Mo(50)-C(84) | 86.2(3) |
| C(80)-Mo(50)-C(82) | 89.8(2) |
| C(84)-Mo(50)-C(82) | 91.8(2) |
| C(80)-Mo(50)-C(83) | 90.2(2) |
| C(84)-Mo(50)-C(83) | 91.4(2) |
| C(82)-Mo(50)-C(83) | 176.7(2) |
| C(80)-Mo(50)-C(81) | 88.0(3) |
| C(84)-Mo(50)-C(81) | 173.9(2) |
| C(82)-Mo(50)-C(81) | 89.7(2) |
| C(83)-Mo(50)-C(81) | 87.1(2) |
| C(80)-Mo(50)-N(50) | 177.1(2) |
| C(84)-Mo(50)-N(50) | 91.01(18) |
| C(82)-Mo(50)-N(50) | 90.88(18) |
| C(83)-Mo(50)-N(50) | 89.26(18) |
| C(81)-Mo(50)-N(50) | 94.86(19) |
| C(78)-N(50)-C(79) | 113.8(4) |
| C(78)-N(50)-Mo(50) | 123.3(3) |
| C(79)-N(50)-Mo(50) | 122.9(3) |
| C(57)-Fe(51)-C(59) | 67.5(3) |
| C(57)-Fe(51)-C(54) | 159.2(2) |
| C(59)-Fe(51)-C(54) | 122.4(3) |
| C(57)-Fe(51)-C(51) | 124.8(3) |
| C(59)-Fe(51)-C(51) | 123.1(3) |
| C(54)-Fe(51)-C(51) | 67.6(3) |
| C(57)-Fe(51)-C(53) | 124.5(3) |
| C(59)-Fe(51)-C(53) | 158.7(3) |
| C(54)-Fe(51)-C(53) | 40.3(2) |
| C(51)-Fe(51)-C(53) | 67.3(2) |
| C(57)-Fe(51)-C(58) | 40.6(2) |
| C(59)-Fe(51)-C(58) | 39.6(3) |
| C(54)-Fe(51)-C(58) | 157.9(3) |
| C(51)-Fe(51)-C(58) | 109.1(3) |
| C(53)-Fe(51)-C(58) | 160.6(3) |
| C(57)-Fe(51)-C(55) | 159.6(3) |
| C(59)-Fe(51)-C(55) | 106.5(3) |
| C(54)-Fe(51)-C(55) | 40.5(2) |
| C(51)-Fe(51)-C(55) | 40.8(2) |
| C(53)-Fe(51)-C(55) | 68.2(2) |
| C(58)-Fe(51)-C(55) | 122.5(3) |
| C(57)-Fe(51)-C(52) | 110.2(3) |
| C(59)-Fe(51)-C(52) | 159.4(3) |
| C(54)-Fe(51)-C(52) | 67.3(2) |
| C(51)-Fe(51)-C(52) | 40.1(2) |
| C(53)-Fe(51)-C(52) | 39.7(2) |
| C(58)-Fe(51)-C(52) | 125.2(3) |
| C(55)-Fe(51)-C(52) | 68.2(3) |
| C(57)-Fe(51)-C(60) | 66.7(3) |
| C(59)-Fe(51)-C(60) | 40.2(2) |
| C(54)-Fe(51)-C(60) | 107.9(2) |
| C(51)-Fe(51)-C(60) | 158.7(3) |
| C(53)-Fe(51)-C(60) | 123.7(3) |
| C(58)-Fe(51)-C(60) | 66.8(3) |
| C(55)-Fe(51)-C(60) | 122.1(3) |
| C(52)-Fe(51)-C(60) | 159.5(3) |
| C(57)-Fe(51)-C(56) | 39.8(2) |
| C(59)-Fe(51)-C(56) | 68.2(2) |
| C(54)-Fe(51)-C(56) | 123.1(2) |
| C(51)-Fe(51)-C(56) | 159.7(3) |

| | |
|---|---|
| C(53)-Fe(51)-C(56) | 108.6(2) |
| C(58)-Fe(51)-C(56) | 67.8(2) |
| C(55)-Fe(51)-C(56) | 158.2(3) |
| C(52)-Fe(51)-C(56) | 124.1(2) |
| C(60)-Fe(51)-C(56) | 40.3(2) |
| C(52)-C(51)-C(55) | 108.6(6) |
| C(52)-C(51)-Fe(51) | 70.2(3) |
| C(55)-C(51)-Fe(51) | 69.8(3) |
| C(71)-Fe(52)-C(66) | 107.1(3) |
| C(71)-Fe(52)-C(72) | 41.0(2) |
| C(66)-Fe(52)-C(72) | 122.1(3) |
| C(71)-Fe(52)-C(64) | 155.5(3) |
| C(66)-Fe(52)-C(64) | 67.4(3) |
| C(72)-Fe(52)-C(64) | 162.2(3) |
| C(71)-Fe(52)-C(67) | 124.4(3) |
| C(66)-Fe(52)-C(67) | 40.7(2) |
| C(72)-Fe(52)-C(67) | 108.3(3) |
| C(64)-Fe(52)-C(67) | 68.2(2) |
| C(71)-Fe(52)-C(65) | 119.3(3) |
| C(66)-Fe(52)-C(65) | 40.1(3) |
| C(72)-Fe(52)-C(65) | 155.8(3) |
| C(64)-Fe(52)-C(65) | 40.9(2) |
| C(67)-Fe(52)-C(65) | 68.9(3) |
| C(71)-Fe(52)-C(69) | 67.3(3) |
| C(66)-Fe(52)-C(69) | 159.2(3) |
| C(72)-Fe(52)-C(69) | 67.8(3) |
| C(64)-Fe(52)-C(69) | 108.8(3) |
| C(67)-Fe(52)-C(69) | 158.9(3) |
| C(65)-Fe(52)-C(69) | 123.5(3) |
| C(71)-Fe(52)-C(70) | 40.0(3) |
| C(66)-Fe(52)-C(70) | 122.7(3) |
| C(72)-Fe(52)-C(70) | 68.4(3) |
| C(64)-Fe(52)-C(70) | 121.2(3) |
| C(67)-Fe(52)-C(70) | 159.7(3) |
| C(65)-Fe(52)-C(70) | 105.5(3) |
| C(69)-Fe(52)-C(70) | 40.2(2) |
| C(71)-Fe(52)-C(63) | 162.1(3) |
| C(66)-Fe(52)-C(63) | 67.6(2) |
| C(72)-Fe(52)-C(63) | 126.0(3) |
| C(64)-Fe(52)-C(63) | 40.1(2) |
| C(67)-Fe(52)-C(63) | 40.5(2) |
| C(65)-Fe(52)-C(63) | 68.5(2) |
| C(69)-Fe(52)-C(63) | 123.7(2) |
| C(70)-Fe(52)-C(63) | 157.3(3) |
| C(71)-Fe(52)-C(68) | 68.4(2) |
| C(66)-Fe(52)-C(68) | 158.8(3) |
| C(72)-Fe(52)-C(68) | 40.9(2) |
| C(64)-Fe(52)-C(68) | 125.3(2) |
| C(67)-Fe(52)-C(68) | 123.4(3) |
| C(65)-Fe(52)-C(68) | 160.5(3) |
| C(69)-Fe(52)-C(68) | 40.0(2) |
| C(70)-Fe(52)-C(68) | 68.1(3) |
| C(63)-Fe(52)-C(68) | 110.0(2) |
| C(53)-C(52)-C(51) | 108.3(6) |
| C(53)-C(52)-Fe(51) | 69.9(3) |
| C(51)-C(52)-Fe(51) | 69.7(4) |
| C(52)-C(53)-C(54) | 108.1(5) |
| C(52)-C(53)-Fe(51) | 70.3(3) |
| C(54)-C(53)-Fe(51) | 69.6(3) |
| C(53)-C(54)-C(55) | 108.9(6) |
| C(53)-C(54)-Fe(51) | 70.1(3) |
| C(55)-C(54)-Fe(51) | 70.2(3) |
| C(54)-C(55)-C(51) | 106.0(5) |
| C(54)-C(55)-Fe(51) | 69.3(3) |
| C(51)-C(55)-Fe(51) | 69.4(3) |
| C(57)-C(56)-C(60) | 105.5(5) |
| C(57)-C(56)-C(61) | 130.3(6) |
| C(60)-C(56)-C(61) | 124.2(6) |
| C(57)-C(56)-Fe(51) | 68.3(3) |
| C(60)-C(56)-Fe(51) | 69.2(3) |
| C(61)-C(56)-Fe(51) | 128.1(4) |
| C(56)-C(57)-C(58) | 109.7(7) |
| C(56)-C(57)-Fe(51) | 71.9(3) |
| C(58)-C(57)-Fe(51) | 70.2(3) |
| C(59)-C(58)-C(57) | 107.7(7) |
| C(59)-C(58)-Fe(51) | 69.7(4) |

| | |
|---|---|
| C(57)-C(58)-Fe(51) | 69.2(3) |
| C(58)-C(59)-C(60) | 108.2(7) |
| C(58)-C(59)-Fe(51) | 70.7(5) |
| C(60)-C(59)-Fe(51) | 71.0(4) |
| C(59)-C(60)-C(56) | 108.8(6) |
| C(59)-C(60)-Fe(51) | 68.8(4) |
| C(56)-C(60)-Fe(51) | 70.5(3) |
| C(62)-C(61)-C(56) | 127.6(6) |
| C(61)-C(62)-C(63) | 127.7(6) |
| C(64)-C(63)-C(67) | 107.7(5) |
| C(64)-C(63)-C(62) | 127.9(5) |
| C(67)-C(63)-C(62) | 124.3(6) |
| C(64)-C(63)-Fe(52) | 68.9(3) |
| C(67)-C(63)-Fe(52) | 68.8(3) |
| C(62)-C(63)-Fe(52) | 124.3(3) |
| C(63)-C(64)-C(65) | 109.1(6) |
| C(63)-C(64)-Fe(52) | 71.0(3) |
| C(65)-C(64)-Fe(52) | 69.6(3) |
| C(66)-C(65)-C(64) | 106.3(7) |
| C(66)-C(65)-Fe(52) | 69.7(4) |
| C(64)-C(65)-Fe(52) | 69.5(3) |
| C(65)-C(66)-C(67) | 110.1(6) |
| C(65)-C(66)-Fe(52) | 70.2(4) |
| C(67)-C(66)-Fe(52) | 69.9(3) |
| C(66)-C(67)-C(63) | 106.8(6) |
| C(66)-C(67)-Fe(52) | 69.4(4) |
| C(63)-C(67)-Fe(52) | 70.7(3) |
| C(69)-C(68)-C(72) | 106.6(6) |
| C(69)-C(68)-C(73) | 130.8(6) |
| C(72)-C(68)-C(73) | 122.6(7) |
| C(69)-C(68)-Fe(52) | 69.3(3) |
| C(72)-C(68)-Fe(52) | 68.5(3) |
| C(73)-C(68)-Fe(52) | 126.2(3) |
| C(68)-C(69)-C(70) | 109.9(7) |
| C(68)-C(69)-Fe(52) | 70.7(3) |
| C(70)-C(69)-Fe(52) | 70.2(4) |
| C(71)-C(70)-C(69) | 107.1(7) |
| C(71)-C(70)-Fe(52) | 69.0(4) |
| C(69)-C(70)-Fe(52) | 69.6(3) |
| C(70)-C(71)-C(72) | 109.1(7) |
| C(70)-C(71)-Fe(52) | 71.0(4) |
| C(72)-C(71)-Fe(52) | 69.8(3) |
| C(71)-C(72)-C(68) | 107.2(7) |
| C(71)-C(72)-Fe(52) | 69.2(4) |
| C(68)-C(72)-Fe(52) | 70.6(3) |
| C(74)-C(73)-C(68) | 127.0(6) |
| C(73)-C(74)-C(75) | 127.0(6) |
| C(76)-C(75)-C(77) | 114.5(5) |
| C(76)-C(75)-C(74) | 121.2(5) |
| C(77)-C(75)-C(74) | 124.2(6) |
| C(78)-C(76)-C(75) | 120.9(5) |
| C(79)-C(77)-C(75) | 120.8(5) |
| N(50)-C(78)-C(76) | 125.3(5) |
| N(50)-C(79)-C(77) | 124.6(5) |
| O(80)-C(80)-Mo(50) | 178.6(6) |
| O(81)-C(81)-Mo(50) | 174.2(6) |
| O(82)-C(82)-Mo(50) | 177.4(5) |
| O(83)-C(83)-Mo(50) | 176.7(5) |
| O(84)-C(84)-Mo(50) | 175.0(5) |

Symmetry transformations used to generate equivalent atoms:

**Table 4**. Anisotropic displacement parameters ($Å^2$x $10^3$) for str105m. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + \ldots\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| Mo(1) | 64(1) | 56(1) | 75(1) | -19(1) | -35(1) | 11(1) |
| Fe(1) | 33(1) | 45(1) | 50(1) | -4(1) | -16(1) | -3(1) |
| N(1) | 46(2) | 46(2) | 58(3) | -8(2) | -16(2) | 1(2) |
| C(1) | 49(3) | 64(4) | 95(4) | -27(3) | -40(3) | 3(3) |
| Fe(2) | 58(1) | 37(1) | 62(1) | -5(1) | -29(1) | -3(1) |
| C(2) | 60(4) | 101(5) | 59(4) | -11(3) | -22(3) | 2(3) |
| C(3) | 65(3) | 59(4) | 62(4) | 15(3) | -19(3) | -4(3) |
| C(4) | 54(3) | 51(3) | 62(3) | -7(2) | -22(3) | 13(3) |
| C(5) | 35(3) | 65(4) | 75(4) | 10(3) | -24(2) | -7(3) |
| C(6) | 40(3) | 47(3) | 69(4) | -10(3) | -27(2) | 0(2) |
| C(7) | 45(3) | 63(3) | 64(3) | -1(3) | -30(2) | 5(3) |
| C(8) | 57(3) | 51(3) | 94(4) | -10(3) | -39(3) | 10(3) |
| C(9) | 42(3) | 89(4) | 90(4) | -35(4) | -17(3) | 6(3) |
| C(10) | 34(3) | 76(4) | 74(4) | -13(3) | -11(3) | -9(3) |
| C(11) | 38(3) | 68(4) | 66(3) | 1(3) | -23(2) | -5(3) |
| C(12) | 43(3) | 63(3) | 68(3) | -5(3) | -26(2) | 5(3) |
| C(13) | 46(3) | 51(3) | 60(3) | -6(3) | -23(2) | 4(2) |
| C(14) | 55(3) | 60(4) | 81(4) | -7(3) | -20(3) | -7(3) |
| C(15) | 74(4) | 61(4) | 101(5) | -27(3) | -30(3) | 11(3) |
| C(16) | 76(4) | 40(3) | 115(5) | 7(3) | -49(4) | -1(3) |
| C(17) | 65(4) | 53(3) | 74(4) | 6(3) | -28(3) | -2(3) |
| C(18) | 42(3) | 42(3) | 71(4) | 1(3) | -24(2) | -3(2) |
| C(19) | 51(3) | 64(4) | 94(4) | 13(3) | -35(3) | -17(3) |
| C(20) | 105(5) | 52(4) | 132(6) | -3(4) | -83(4) | -17(4) |
| C(21) | 113(5) | 51(3) | 92(5) | -18(3) | -68(4) | 2(3) |
| C(22) | 72(3) | 47(3) | 66(4) | -8(3) | -34(3) | -3(3) |
| C(23) | 34(3) | 56(3) | 63(3) | -3(3) | -14(2) | 7(2) |
| C(24) | 50(3) | 50(3) | 48(3) | -4(2) | -15(2) | 5(2) |
| C(25) | 30(2) | 43(3) | 54(3) | -6(2) | -12(2) | 0(2) |
| C(26) | 61(3) | 53(3) | 47(3) | -2(3) | -10(2) | 1(3) |
| C(27) | 49(3) | 55(3) | 55(3) | 1(3) | -10(2) | -12(2) |
| C(28) | 59(3) | 48(3) | 66(4) | -3(3) | -12(3) | -1(3) |
| C(29) | 58(3) | 64(4) | 48(3) | -11(3) | -13(2) | -1(3) |

|  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|
| O(30) | 206(6) | 117(4) | 104(4) | 8(3) | -89(4) | -16(4) |
| C(30) | 103(5) | 78(5) | 98(5) | -34(4) | -47(4) | 4(4) |
| O(31) | 123(4) | 72(3) | 126(4) | 16(3) | -67(3) | -23(3) |
| C(31) | 77(4) | 51(4) | 89(4) | -12(3) | -45(3) | 0(3) |
| O(32) | 188(5) | 93(3) | 159(4) | -74(3) | -114(4) | 54(3) |
| C(32) | 111(5) | 86(5) | 98(5) | -35(4) | -67(4) | 30(4) |
| C(33) | 71(4) | 91(4) | 66(4) | -14(3) | -20(3) | 10(4) |
| O(33) | 61(3) | 177(5) | 117(4) | -14(3) | -1(3) | 11(3) |
| O(34) | 74(3) | 123(4) | 147(4) | -6(3) | -44(3) | -13(3) |
| C(34) | 80(4) | 71(4) | 97(5) | -15(3) | -41(4) | 2(4) |
| Mo(50) | 76(1) | 56(1) | 51(1) | -6(1) | -19(1) | 17(1) |
| N(50) | 62(3) | 48(2) | 45(2) | -6(2) | -16(2) | 6(2) |
| Fe(51) | 42(1) | 46(1) | 74(1) | -1(1) | -6(1) | 9(1) |
| C(51) | 111(6) | 79(5) | 92(5) | -17(4) | 5(4) | 38(4) |
| Fe(52) | 42(1) | 74(1) | 63(1) | 21(1) | 3(1) | 21(1) |
| C(52) | 97(5) | 103(6) | 79(4) | -13(4) | -27(4) | 14(4) |
| C(53) | 62(4) | 65(4) | 88(4) | 11(3) | -12(3) | 14(3) |
| C(54) | 53(4) | 71(4) | 100(5) | 13(3) | -11(3) | -1(3) |
| C(55) | 44(3) | 84(5) | 98(5) | 18(4) | 3(3) | 19(3) |
| C(56) | 45(3) | 70(4) | 74(4) | 6(3) | 2(3) | 9(3) |
| C(57) | 52(4) | 69(4) | 143(6) | -9(4) | 11(4) | -10(3) |
| C(58) | 91(6) | 50(4) | 185(9) | 29(5) | 42(5) | 8(4) |
| C(59) | 68(5) | 115(7) | 113(6) | 44(5) | 5(4) | 19(5) |
| C(60) | 71(4) | 96(5) | 78(4) | 2(3) | -13(3) | 21(4) |
| C(61) | 45(3) | 84(4) | 88(4) | 4(3) | -8(3) | 5(3) |
| C(62) | 65(4) | 100(5) | 55(4) | 6(3) | 7(3) | -9(4) |
| C(63) | 44(3) | 78(4) | 53(3) | 19(3) | -2(2) | 10(3) |
| C(64) | 49(4) | 98(5) | 94(5) | 18(4) | -9(3) | -4(3) |
| C(65) | 77(5) | 87(5) | 111(6) | 32(4) | 4(4) | 13(4) |
| C(66) | 58(4) | 140(7) | 93(6) | 73(5) | 7(4) | 26(5) |
| C(67) | 62(4) | 145(6) | 61(4) | 18(4) | -7(3) | 3(4) |
| C(68) | 58(4) | 70(4) | 70(4) | 20(3) | 10(3) | 17(3) |
| C(69) | 112(5) | 91(5) | 54(4) | 9(3) | 14(3) | 30(4) |
| C(70) | 112(7) | 100(6) | 93(6) | 17(4) | 38(5) | 47(5) |
| C(71) | 44(4) | 117(7) | 139(8) | 57(5) | 34(4) | 36(4) |
| C(72) | 46(4) | 108(5) | 119(5) | 30(4) | 2(3) | 4(4) |
| C(73) | 68(4) | 90(5) | 60(4) | 17(3) | -3(3) | 3(3) |
| C(74) | 81(4) | 69(4) | 53(3) | 6(3) | -3(3) | 7(3) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(75) | 74(4) | 45(3) | 48(3) | -1(3) | 2(3) | 5(3) |
| C(76) | 77(4) | 55(4) | 82(4) | -15(3) | -21(3) | 6(3) |
| C(77) | 87(4) | 89(4) | 69(4) | -8(3) | -42(3) | 30(4) |
| C(78) | 72(4) | 63(4) | 70(4) | -14(3) | -26(3) | 5(3) |
| C(79) | 101(5) | 72(4) | 72(4) | -21(3) | -43(3) | 10(4) |
| O(80) | 163(5) | 120(4) | 135(4) | -48(3) | -65(3) | 95(4) |
| C(80) | 121(5) | 90(5) | 69(4) | -21(3) | -39(4) | 35(4) |
| O(81) | 148(5) | 77(3) | 146(4) | -14(3) | -1(3) | -33(3) |
| C(81) | 102(5) | 47(4) | 83(4) | 5(3) | -6(4) | 5(3) |
| C(82) | 100(5) | 79(4) | 58(4) | -7(3) | -20(3) | 24(3) |
| O(82) | 132(4) | 134(4) | 62(3) | 2(3) | -34(3) | 22(3) |
| O(83) | 148(4) | 91(3) | 56(3) | -5(2) | -35(3) | -13(3) |
| C(83) | 85(4) | 53(3) | 65(4) | -12(3) | -13(3) | -4(3) |
| O(84) | 88(3) | 132(4) | 125(4) | -10(3) | -39(3) | -14(3) |
| C(84) | 78(4) | 94(5) | 65(4) | -18(3) | -23(3) | 17(4) |

**Table 5**. Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters (Å$^2$x $10^3$) for str105m.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1) | 2472 | 4169 | 2697 | 77 |
| H(2) | 3860 | 5237 | 1879 | 87 |
| H(3) | 3801 | 6640 | 2405 | 75 |
| H(4) | 2367 | 6453 | 3557 | 66 |
| H(5) | 1566 | 4922 | 3748 | 69 |
| H(7) | 4362 | 4472 | 4405 | 67 |
| H(8) | 4878 | 3416 | 3530 | 77 |
| H(9) | 6219 | 4188 | 2483 | 86 |
| H(10) | 6544 | 5722 | 2728 | 73 |
| H(11) | 4757 | 6200 | 4479 | 67 |
| H(12) | 6713 | 6830 | 3475 | 68 |
| H(14) | 4916 | 7421 | 5199 | 77 |
| H(15) | 5330 | 8962 | 5384 | 92 |
| H(16) | 6794 | 9628 | 4330 | 89 |
| H(17) | 7247 | 8503 | 3508 | 76 |
| H(19) | 9901 | 7860 | 4111 | 81 |
| H(20) | 9313 | 8893 | 4994 | 105 |
| H(21) | 7868 | 8130 | 6006 | 93 |
| H(22) | 7587 | 6592 | 5749 | 70 |
| H(23) | 9246 | 6211 | 3967 | 61 |
| H(24) | 8109 | 5266 | 5133 | 59 |
| H(26) | 7898 | 3687 | 5107 | 65 |
| H(27) | 9083 | 5139 | 3357 | 64 |
| H(28) | 7959 | 2493 | 4525 | 70 |
| H(29) | 9121 | 3896 | 2827 | 67 |
| H(51) | 2163 | 10225 | 3634 | 120 |
| H(52) | 3974 | 9162 | 3887 | 111 |
| H(53) | 3842 | 7770 | 3396 | 90 |
| H(54) | 1938 | 7956 | 2839 | 93 |
| H(55) | 875 | 9487 | 2971 | 98 |
| H(57) | 5892 | 9931 | 2441 | 112 |
| H(58) | 4067 | 10991 | 2185 | 149 |
| H(59) | 2744 | 10219 | 1596 | 130 |

| | | | | |
|---|---|---|---|---|
| H(60) | 3835 | 8719 | 1408 | 101 |
| H(61) | 5801 | 7724 | 1800 | 90 |
| H(62) | 7519 | 8629 | 2199 | 93 |
| H(64) | 7556 | 6508 | 1424 | 100 |
| H(65) | 9469 | 5445 | 1596 | 120 |
| H(66) | 10594 | 6096 | 2354 | 131 |
| H(67) | 9485 | 7578 | 2615 | 112 |
| H(69) | 9465 | 7528 | 95 | 113 |
| H(70) | 11259 | 6391 | 269 | 140 |
| H(71) | 12503 | 6967 | 1011 | 140 |
| H(72) | 11496 | 8471 | 1298 | 117 |
| H(73) | 9488 | 9521 | 1045 | 92 |
| H(74) | 8245 | 9037 | 134 | 85 |
| H(76) | 6415 | 10023 | -131 | 85 |
| H(77) | 8418 | 10840 | 1097 | 96 |
| H(78) | 5127 | 11287 | -33 | 80 |
| H(79) | 7099 | 12107 | 1134 | 93 |

**Table 6**. Torsion angles [°] for str105m.

| | |
|---|---|
| C(32)-Mo(1)-N(1)-C(28) | -78(6) |
| C(31)-Mo(1)-N(1)-C(28) | -21.3(4) |
| C(33)-Mo(1)-N(1)-C(28) | -112.4(4) |
| C(34)-Mo(1)-N(1)-C(28) | 69.4(4) |
| C(30)-Mo(1)-N(1)-C(28) | 159.4(4) |
| C(32)-Mo(1)-N(1)-C(29) | 100(6) |
| C(31)-Mo(1)-N(1)-C(29) | 155.9(4) |
| C(33)-Mo(1)-N(1)-C(29) | 64.8(4) |
| C(34)-Mo(1)-N(1)-C(29) | -113.3(4) |
| C(30)-Mo(1)-N(1)-C(29) | -23.4(4) |
| C(7)-Fe(1)-C(1)-C(2) | -166.3(3) |
| C(9)-Fe(1)-C(1)-C(2) | -83.4(4) |
| C(8)-Fe(1)-C(1)-C(2) | -127.0(3) |
| C(3)-Fe(1)-C(1)-C(2) | 37.4(3) |
| C(10)-Fe(1)-C(1)-C(2) | -47.8(5) |
| C(4)-Fe(1)-C(1)-C(2) | 81.0(3) |
| C(5)-Fe(1)-C(1)-C(2) | 118.7(4) |
| C(6)-Fe(1)-C(1)-C(2) | 159.4(11) |
| C(7)-Fe(1)-C(1)-C(5) | 75.0(4) |
| C(9)-Fe(1)-C(1)-C(5) | 157.9(3) |
| C(8)-Fe(1)-C(1)-C(5) | 114.3(3) |
| C(3)-Fe(1)-C(1)-C(5) | -81.3(3) |
| C(10)-Fe(1)-C(1)-C(5) | -166.4(4) |
| C(2)-Fe(1)-C(1)-C(5) | -118.7(4) |
| C(4)-Fe(1)-C(1)-C(5) | -37.6(3) |
| C(6)-Fe(1)-C(1)-C(5) | 40.7(13) |
| C(5)-C(1)-C(2)-C(3) | -0.4(6) |
| Fe(1)-C(1)-C(2)-C(3) | -59.6(4) |
| C(5)-C(1)-C(2)-Fe(1) | 59.2(3) |
| C(7)-Fe(1)-C(2)-C(3) | 174.3(8) |
| C(9)-Fe(1)-C(2)-C(3) | -128.5(3) |
| C(8)-Fe(1)-C(2)-C(3) | -167.0(3) |
| C(10)-Fe(1)-C(2)-C(3) | -86.0(3) |
| C(4)-Fe(1)-C(2)-C(3) | 37.9(3) |
| C(5)-Fe(1)-C(2)-C(3) | 81.6(3) |
| C(1)-Fe(1)-C(2)-C(3) | 119.6(4) |
| C(6)-Fe(1)-C(2)-C(3) | -54.1(5) |
| C(7)-Fe(1)-C(2)-C(1) | 54.7(10) |
| C(9)-Fe(1)-C(2)-C(1) | 111.9(3) |
| C(8)-Fe(1)-C(2)-C(1) | 73.4(4) |
| C(3)-Fe(1)-C(2)-C(1) | -119.6(4) |
| C(10)-Fe(1)-C(2)-C(1) | 154.4(3) |
| C(4)-Fe(1)-C(2)-C(1) | -81.7(3) |
| C(5)-Fe(1)-C(2)-C(1) | -38.0(3) |
| C(6)-Fe(1)-C(2)-C(1) | -173.6(3) |
| C(1)-C(2)-C(3)-C(4) | -0.1(6) |
| Fe(1)-C(2)-C(3)-C(4) | -60.3(3) |
| C(1)-C(2)-C(3)-Fe(1) | 60.2(4) |
| C(7)-Fe(1)-C(3)-C(2) | -177.4(4) |
| C(9)-Fe(1)-C(3)-C(2) | 69.3(4) |
| C(8)-Fe(1)-C(3)-C(2) | 43.2(9) |
| C(10)-Fe(1)-C(3)-C(2) | 109.5(3) |
| C(4)-Fe(1)-C(3)-C(2) | -118.5(4) |
| C(5)-Fe(1)-C(3)-C(2) | -81.0(3) |
| C(1)-Fe(1)-C(3)-C(2) | -37.2(3) |
| C(6)-Fe(1)-C(3)-C(2) | 151.8(3) |
| C(7)-Fe(1)-C(3)-C(4) | -58.8(5) |
| C(9)-Fe(1)-C(3)-C(4) | -172.2(3) |
| C(8)-Fe(1)-C(3)-C(4) | 161.7(7) |
| C(10)-Fe(1)-C(3)-C(4) | -132.0(3) |
| C(2)-Fe(1)-C(3)-C(4) | 118.5(4) |
| C(5)-Fe(1)-C(3)-C(4) | 37.5(3) |
| C(1)-Fe(1)-C(3)-C(4) | 81.4(3) |
| C(6)-Fe(1)-C(3)-C(4) | -89.7(3) |
| C(2)-C(3)-C(4)-C(5) | 0.5(5) |
| Fe(1)-C(3)-C(4)-C(5) | -59.7(3) |
| C(2)-C(3)-C(4)-Fe(1) | 60.2(3) |
| C(7)-Fe(1)-C(4)-C(3) | 152.1(3) |
| C(9)-Fe(1)-C(4)-C(3) | 25.8(9) |
| C(8)-Fe(1)-C(4)-C(3) | -169.4(4) |
| C(10)-Fe(1)-C(4)-C(3) | 66.7(4) |
| C(2)-Fe(1)-C(4)-C(3) | -37.9(3) |
| C(5)-Fe(1)-C(4)-C(3) | -119.1(4) |
| C(1)-Fe(1)-C(4)-C(3) | -81.3(3) |

| | |
|---|---|
| C(6)-Fe(1)-C(4)-C(3) | 108.5(3) |
| C(7)-Fe(1)-C(4)-C(5) | -88.7(3) |
| C(9)-Fe(1)-C(4)-C(5) | 144.9(8) |
| C(8)-Fe(1)-C(4)-C(5) | -50.3(5) |
| C(3)-Fe(1)-C(4)-C(5) | 119.1(4) |
| C(10)-Fe(1)-C(4)-C(5) | -174.2(3) |
| C(2)-Fe(1)-C(4)-C(5) | 81.2(3) |
| C(1)-Fe(1)-C(4)-C(5) | 37.8(3) |
| C(6)-Fe(1)-C(4)-C(5) | -132.3(3) |
| C(3)-C(4)-C(5)-C(1) | -0.7(5) |
| Fe(1)-C(4)-C(5)-C(1) | -60.2(3) |
| C(3)-C(4)-C(5)-Fe(1) | 59.5(3) |
| C(2)-C(1)-C(5)-C(4) | 0.7(5) |
| Fe(1)-C(1)-C(5)-C(4) | 59.9(3) |
| C(2)-C(1)-C(5)-Fe(1) | -59.2(3) |
| C(7)-Fe(1)-C(5)-C(4) | 112.2(3) |
| C(9)-Fe(1)-C(5)-C(4) | -162.8(4) |
| C(8)-Fe(1)-C(5)-C(4) | 156.7(3) |
| C(3)-Fe(1)-C(5)-C(4) | -37.6(3) |
| C(10)-Fe(1)-C(5)-C(4) | 23.0(11) |
| C(2)-Fe(1)-C(5)-C(4) | -81.2(3) |
| C(1)-Fe(1)-C(5)-C(4) | -118.8(4) |
| C(6)-Fe(1)-C(5)-C(4) | 69.4(4) |
| C(7)-Fe(1)-C(5)-C(1) | -128.9(3) |
| C(9)-Fe(1)-C(5)-C(1) | -43.9(6) |
| C(8)-Fe(1)-C(5)-C(1) | -84.4(4) |
| C(3)-Fe(1)-C(5)-C(1) | 81.3(3) |
| C(10)-Fe(1)-C(5)-C(1) | 141.8(10) |
| C(2)-Fe(1)-C(5)-C(1) | 37.6(3) |
| C(4)-Fe(1)-C(5)-C(1) | 118.8(4) |
| C(6)-Fe(1)-C(5)-C(1) | -171.7(3) |
| C(9)-Fe(1)-C(6)-C(7) | -80.6(3) |
| C(8)-Fe(1)-C(6)-C(7) | -36.9(3) |
| C(3)-Fe(1)-C(6)-C(7) | 158.4(3) |
| C(10)-Fe(1)-C(6)-C(7) | -118.1(4) |
| C(2)-Fe(1)-C(6)-C(7) | -165.7(4) |
| C(4)-Fe(1)-C(6)-C(7) | 114.9(3) |
| C(5)-Fe(1)-C(6)-C(7) | 74.9(4) |
| C(1)-Fe(1)-C(6)-C(7) | 40.2(12) |
| C(7)-Fe(1)-C(6)-C(10) | 118.1(4) |
| C(9)-Fe(1)-C(6)-C(10) | 37.4(3) |
| C(8)-Fe(1)-C(6)-C(10) | 81.2(3) |
| C(3)-Fe(1)-C(6)-C(10) | -83.6(3) |
| C(2)-Fe(1)-C(6)-C(10) | -47.6(5) |
| C(4)-Fe(1)-C(6)-C(10) | -127.0(3) |
| C(5)-Fe(1)-C(6)-C(10) | -167.0(3) |
| C(1)-Fe(1)-C(6)-C(10) | 158.2(11) |
| C(7)-Fe(1)-C(6)-C(11) | -119.2(6) |
| C(9)-Fe(1)-C(6)-C(11) | 160.1(5) |
| C(8)-Fe(1)-C(6)-C(11) | -156.1(5) |
| C(3)-Fe(1)-C(6)-C(11) | 39.1(5) |
| C(10)-Fe(1)-C(6)-C(11) | 122.7(6) |
| C(2)-Fe(1)-C(6)-C(11) | 75.1(6) |
| C(4)-Fe(1)-C(6)-C(11) | -4.3(5) |
| C(5)-Fe(1)-C(6)-C(11) | -44.3(5) |
| C(1)-Fe(1)-C(6)-C(11) | -79.1(13) |
| C(10)-C(6)-C(7)-C(8) | 1.3(5) |
| C(11)-C(6)-C(7)-C(8) | -180.0(4) |
| Fe(1)-C(6)-C(7)-C(8) | 59.6(3) |
| C(10)-C(6)-C(7)-Fe(1) | -58.3(3) |
| C(11)-C(6)-C(7)-Fe(1) | 120.4(4) |
| C(9)-Fe(1)-C(7)-C(8) | -37.9(3) |
| C(3)-Fe(1)-C(7)-C(8) | -165.0(4) |
| C(10)-Fe(1)-C(7)-C(8) | -82.1(3) |
| C(2)-Fe(1)-C(7)-C(8) | 23.0(10) |
| C(4)-Fe(1)-C(7)-C(8) | 154.8(3) |
| C(5)-Fe(1)-C(7)-C(8) | 110.5(3) |
| C(1)-Fe(1)-C(7)-C(8) | 67.8(4) |
| C(6)-Fe(1)-C(7)-C(8) | -120.4(4) |
| C(9)-Fe(1)-C(7)-C(6) | 82.5(3) |
| C(8)-Fe(1)-C(7)-C(6) | 120.4(4) |
| C(3)-Fe(1)-C(7)-C(6) | -44.6(5) |
| C(10)-Fe(1)-C(7)-C(6) | 38.3(3) |
| C(2)-Fe(1)-C(7)-C(6) | 143.3(9) |
| C(4)-Fe(1)-C(7)-C(6) | -84.9(3) |
| C(5)-Fe(1)-C(7)-C(6) | -129.2(3) |

| | | | |
|---|---|---|---|
| C(1)-Fe(1)-C(7)-C(6) | -171.9(3) | C(6)-Fe(1)-C(9)-C(10) | -37.2(3) |
| C(6)-C(7)-C(8)-C(9) | -1.1(5) | C(8)-C(9)-C(10)-C(6) | 0.4(6) |
| Fe(1)-C(7)-C(8)-C(9) | 59.4(3) | Fe(1)-C(9)-C(10)-C(6) | 60.3(3) |
| C(6)-C(7)-C(8)-Fe(1) | -60.5(3) | C(8)-C(9)-C(10)-Fe(1) | -59.8(3) |
| C(9)-Fe(1)-C(8)-C(7) | 119.0(4) | C(7)-C(6)-C(10)-C(9) | -1.1(5) |
| C(3)-Fe(1)-C(8)-C(7) | 152.0(7) | C(11)-C(6)-C(10)-C(9) | -179.7(4) |
| C(10)-Fe(1)-C(8)-C(7) | 80.8(3) | Fe(1)-C(6)-C(10)-C(9) | -59.2(3) |
| C(2)-Fe(1)-C(8)-C(7) | -173.9(3) | C(7)-C(6)-C(10)-Fe(1) | 58.1(3) |
| C(4)-Fe(1)-C(8)-C(7) | -55.2(5) | C(11)-C(6)-C(10)-Fe(1) | -120.5(5) |
| C(5)-Fe(1)-C(8)-C(7) | -90.2(3) | C(7)-Fe(1)-C(10)-C(9) | 81.7(3) |
| C(1)-Fe(1)-C(8)-C(7) | -133.2(3) | C(8)-Fe(1)-C(10)-C(9) | 38.0(3) |
| C(6)-Fe(1)-C(8)-C(7) | 37.1(3) | C(3)-Fe(1)-C(10)-C(9) | -127.2(3) |
| C(7)-Fe(1)-C(8)-C(9) | -119.0(4) | C(2)-Fe(1)-C(10)-C(9) | -85.1(4) |
| C(3)-Fe(1)-C(8)-C(9) | 33.1(9) | C(4)-Fe(1)-C(10)-C(9) | -165.4(3) |
| C(10)-Fe(1)-C(8)-C(9) | -38.2(3) | C(5)-Fe(1)-C(10)-C(9) | 175.7(9) |
| C(2)-Fe(1)-C(8)-C(9) | 67.1(4) | C(1)-Fe(1)-C(10)-C(9) | -53.5(5) |
| C(4)-Fe(1)-C(8)-C(9) | -174.2(4) | C(6)-Fe(1)-C(10)-C(9) | 120.0(4) |
| C(5)-Fe(1)-C(8)-C(9) | 150.8(3) | C(7)-Fe(1)-C(10)-C(6) | -38.3(3) |
| C(1)-Fe(1)-C(8)-C(9) | 107.8(3) | C(9)-Fe(1)-C(10)-C(6) | -120.0(4) |
| C(6)-Fe(1)-C(8)-C(9) | -81.9(3) | C(8)-Fe(1)-C(10)-C(6) | -82.0(3) |
| C(7)-C(8)-C(9)-C(10) | 0.4(5) | C(3)-Fe(1)-C(10)-C(6) | 112.8(3) |
| Fe(1)-C(8)-C(9)-C(10) | 59.8(3) | C(2)-Fe(1)-C(10)-C(6) | 155.0(3) |
| C(7)-C(8)-C(9)-Fe(1) | -59.5(3) | C(4)-Fe(1)-C(10)-C(6) | 74.7(4) |
| C(7)-Fe(1)-C(9)-C(8) | 37.6(3) | C(5)-Fe(1)-C(10)-C(6) | 55.8(11) |
| C(3)-Fe(1)-C(9)-C(8) | -169.9(3) | C(1)-Fe(1)-C(10)-C(6) | -173.4(4) |
| C(10)-Fe(1)-C(9)-C(8) | 118.6(5) | C(7)-C(6)-C(11)-C(12) | 166.8(5) |
| C(2)-Fe(1)-C(9)-C(8) | -131.1(3) | C(10)-C(6)-C(11)-C(12) | -14.8(8) |
| C(4)-Fe(1)-C(9)-C(8) | 169.7(7) | Fe(1)-C(6)-C(11)-C(12) | -105.2(5) |
| C(5)-Fe(1)-C(9)-C(8) | -59.7(6) | C(6)-C(11)-C(12)-C(13) | -179.9(4) |
| C(1)-Fe(1)-C(9)-C(8) | -89.6(4) | C(11)-C(12)-C(13)-C(17) | -168.9(5) |
| C(6)-Fe(1)-C(9)-C(8) | 81.4(3) | C(11)-C(12)-C(13)-C(14) | 11.4(8) |
| C(7)-Fe(1)-C(9)-C(10) | -80.9(3) | C(11)-C(12)-C(13)-Fe(2) | 102.4(5) |
| C(8)-Fe(1)-C(9)-C(10) | -118.6(5) | C(15)-Fe(2)-C(13)-C(17) | 80.5(3) |
| C(3)-Fe(1)-C(9)-C(10) | 71.5(4) | C(19)-Fe(2)-C(13)-C(17) | -75.6(4) |
| C(2)-Fe(1)-C(9)-C(10) | 110.3(3) | C(14)-Fe(2)-C(13)-C(17) | 118.4(4) |
| C(4)-Fe(1)-C(9)-C(10) | 51.1(9) | C(16)-Fe(2)-C(13)-C(17) | 36.7(3) |
| C(5)-Fe(1)-C(9)-C(10) | -178.2(4) | C(22)-Fe(2)-C(13)-C(17) | -161.2(3) |
| C(1)-Fe(1)-C(9)-C(10) | 151.8(3) | C(18)-Fe(2)-C(13)-C(17) | -118.3(3) |

| | |
|---|---|
| C(20)-Fe(2)-C(13)-C(17) | -40.1(8) |
| C(21)-Fe(2)-C(13)-C(17) | 162.5(5) |
| C(15)-Fe(2)-C(13)-C(14) | -37.9(3) |
| C(19)-Fe(2)-C(13)-C(14) | 166.0(3) |
| C(16)-Fe(2)-C(13)-C(14) | -81.7(3) |
| C(17)-Fe(2)-C(13)-C(14) | -118.4(4) |
| C(22)-Fe(2)-C(13)-C(14) | 80.4(3) |
| C(18)-Fe(2)-C(13)-C(14) | 123.3(3) |
| C(20)-Fe(2)-C(13)-C(14) | -158.5(6) |
| C(21)-Fe(2)-C(13)-C(14) | 44.1(6) |
| C(15)-Fe(2)-C(13)-C(12) | -161.0(5) |
| C(19)-Fe(2)-C(13)-C(12) | 42.9(5) |
| C(14)-Fe(2)-C(13)-C(12) | -123.1(6) |
| C(16)-Fe(2)-C(13)-C(12) | 155.1(5) |
| C(17)-Fe(2)-C(13)-C(12) | 118.5(6) |
| C(22)-Fe(2)-C(13)-C(12) | -42.7(5) |
| C(18)-Fe(2)-C(13)-C(12) | 0.1(5) |
| C(20)-Fe(2)-C(13)-C(12) | 78.3(8) |
| C(21)-Fe(2)-C(13)-C(12) | -79.0(7) |
| C(17)-C(13)-C(14)-C(15) | 1.2(5) |
| C(12)-C(13)-C(14)-C(15) | -179.1(4) |
| Fe(2)-C(13)-C(14)-C(15) | 59.8(4) |
| C(17)-C(13)-C(14)-Fe(2) | -58.7(3) |
| C(12)-C(13)-C(14)-Fe(2) | 121.0(5) |
| C(19)-Fe(2)-C(14)-C(15) | -161.1(7) |
| C(16)-Fe(2)-C(14)-C(15) | -37.9(3) |
| C(17)-Fe(2)-C(14)-C(15) | -81.3(3) |
| C(22)-Fe(2)-C(14)-C(15) | 121.8(3) |
| C(18)-Fe(2)-C(14)-C(15) | 164.0(3) |
| C(20)-Fe(2)-C(14)-C(15) | 44.1(7) |
| C(21)-Fe(2)-C(14)-C(15) | 79.1(4) |
| C(13)-Fe(2)-C(14)-C(15) | -119.1(4) |
| C(15)-Fe(2)-C(14)-C(13) | 119.1(4) |
| C(19)-Fe(2)-C(14)-C(13) | -42.0(8) |
| C(16)-Fe(2)-C(14)-C(13) | 81.2(3) |
| C(17)-Fe(2)-C(14)-C(13) | 37.8(3) |
| C(22)-Fe(2)-C(14)-C(13) | -119.1(3) |
| C(18)-Fe(2)-C(14)-C(13) | -76.9(3) |
| C(20)-Fe(2)-C(14)-C(13) | 163.2(5) |
| C(21)-Fe(2)-C(14)-C(13) | -161.8(3) |
| C(13)-C(14)-C(15)-C(16) | -0.9(6) |
| Fe(2)-C(14)-C(15)-C(16) | 60.0(4) |
| C(13)-C(14)-C(15)-Fe(2) | -60.9(3) |
| C(19)-Fe(2)-C(15)-C(16) | 48.4(7) |
| C(14)-Fe(2)-C(15)-C(16) | -118.7(5) |
| C(17)-Fe(2)-C(15)-C(16) | -37.9(3) |
| C(22)-Fe(2)-C(15)-C(16) | 162.8(3) |
| C(18)-Fe(2)-C(15)-C(16) | -165.6(6) |
| C(20)-Fe(2)-C(15)-C(16) | 80.2(4) |
| C(21)-Fe(2)-C(15)-C(16) | 122.0(4) |
| C(13)-Fe(2)-C(15)-C(16) | -81.2(3) |
| C(19)-Fe(2)-C(15)-C(14) | 167.1(5) |
| C(16)-Fe(2)-C(15)-C(14) | 118.7(5) |
| C(17)-Fe(2)-C(15)-C(14) | 80.8(3) |
| C(22)-Fe(2)-C(15)-C(14) | -78.4(4) |
| C(18)-Fe(2)-C(15)-C(14) | -46.8(8) |
| C(20)-Fe(2)-C(15)-C(14) | -161.0(3) |
| C(21)-Fe(2)-C(15)-C(14) | -119.3(3) |
| C(13)-Fe(2)-C(15)-C(14) | 37.5(3) |
| C(14)-C(15)-C(16)-C(17) | 0.3(6) |
| Fe(2)-C(15)-C(16)-C(17) | 60.1(4) |
| C(14)-C(15)-C(16)-Fe(2) | -59.8(4) |
| C(15)-Fe(2)-C(16)-C(17) | -118.2(5) |
| C(19)-Fe(2)-C(16)-C(17) | 83.4(4) |
| C(14)-Fe(2)-C(16)-C(17) | -80.2(3) |
| C(22)-Fe(2)-C(16)-C(17) | -165.4(5) |
| C(18)-Fe(2)-C(16)-C(17) | 50.8(6) |
| C(20)-Fe(2)-C(16)-C(17) | 124.5(4) |
| C(21)-Fe(2)-C(16)-C(17) | 165.1(3) |
| C(13)-Fe(2)-C(16)-C(17) | -36.6(3) |
| C(19)-Fe(2)-C(16)-C(15) | -158.5(3) |
| C(14)-Fe(2)-C(16)-C(15) | 38.0(3) |
| C(17)-Fe(2)-C(16)-C(15) | 118.2(5) |
| C(22)-Fe(2)-C(16)-C(15) | -47.2(7) |
| C(18)-Fe(2)-C(16)-C(15) | 169.0(4) |
| C(20)-Fe(2)-C(16)-C(15) | -117.4(4) |

| | | | |
|---|---|---|---|
| C(21)-Fe(2)-C(16)-C(15) | -76.7(4) | C(22)-Fe(2)-C(18)-C(19) | -117.6(4) |
| C(13)-Fe(2)-C(16)-C(15) | 81.6(3) | C(20)-Fe(2)-C(18)-C(19) | -36.9(3) |
| C(15)-C(16)-C(17)-C(13) | 0.4(6) | C(21)-Fe(2)-C(18)-C(19) | -80.2(3) |
| Fe(2)-C(16)-C(17)-C(13) | 60.1(3) | C(13)-Fe(2)-C(18)-C(19) | 123.5(3) |
| C(15)-C(16)-C(17)-Fe(2) | -59.7(4) | C(15)-Fe(2)-C(18)-C(23) | 80.9(8) |
| C(14)-C(13)-C(17)-C(16) | -1.0(6) | C(19)-Fe(2)-C(18)-C(23) | -120.2(5) |
| C(12)-C(13)-C(17)-C(16) | 179.3(4) | C(14)-Fe(2)-C(18)-C(23) | 45.0(5) |
| Fe(2)-C(13)-C(17)-C(16) | -59.4(4) | C(16)-Fe(2)-C(18)-C(23) | -75.2(6) |
| C(14)-C(13)-C(17)-Fe(2) | 58.4(3) | C(17)-Fe(2)-C(18)-C(23) | -38.9(5) |
| C(12)-C(13)-C(17)-Fe(2) | -121.3(4) | C(22)-Fe(2)-C(18)-C(23) | 122.2(5) |
| C(15)-Fe(2)-C(17)-C(16) | 38.4(3) | C(20)-Fe(2)-C(18)-C(23) | -157.1(5) |
| C(19)-Fe(2)-C(17)-C(16) | -115.1(3) | C(21)-Fe(2)-C(18)-C(23) | 159.5(5) |
| C(14)-Fe(2)-C(17)-C(16) | 82.6(3) | C(13)-Fe(2)-C(18)-C(23) | 3.2(4) |
| C(22)-Fe(2)-C(17)-C(16) | 167.0(5) | C(22)-C(18)-C(19)-C(20) | 0.8(5) |
| C(18)-Fe(2)-C(17)-C(16) | -158.4(3) | C(23)-C(18)-C(19)-C(20) | 177.7(4) |
| C(20)-Fe(2)-C(17)-C(16) | -73.8(4) | Fe(2)-C(18)-C(19)-C(20) | 60.6(4) |
| C(21)-Fe(2)-C(17)-C(16) | -39.5(8) | C(22)-C(18)-C(19)-Fe(2) | -59.8(3) |
| C(13)-Fe(2)-C(17)-C(16) | 120.7(4) | C(23)-C(18)-C(19)-Fe(2) | 117.1(4) |
| C(15)-Fe(2)-C(17)-C(13) | -82.3(3) | C(15)-Fe(2)-C(19)-C(20) | 45.4(7) |
| C(19)-Fe(2)-C(17)-C(13) | 124.2(3) | C(14)-Fe(2)-C(19)-C(20) | -164.5(7) |
| C(14)-Fe(2)-C(17)-C(13) | -38.1(3) | C(16)-Fe(2)-C(19)-C(20) | 79.6(4) |
| C(16)-Fe(2)-C(17)-C(13) | -120.7(4) | C(17)-Fe(2)-C(19)-C(20) | 122.1(4) |
| C(22)-Fe(2)-C(17)-C(13) | 46.4(7) | C(22)-Fe(2)-C(19)-C(20) | -81.0(3) |
| C(18)-Fe(2)-C(17)-C(13) | 80.9(3) | C(18)-Fe(2)-C(19)-C(20) | -119.5(5) |
| C(20)-Fe(2)-C(17)-C(13) | 165.5(3) | C(21)-Fe(2)-C(19)-C(20) | -37.3(3) |
| C(21)-Fe(2)-C(17)-C(13) | -160.1(6) | C(13)-Fe(2)-C(19)-C(20) | 163.2(3) |
| C(15)-Fe(2)-C(18)-C(22) | -41.3(8) | C(15)-Fe(2)-C(19)-C(18) | 164.9(5) |
| C(19)-Fe(2)-C(18)-C(22) | 117.6(4) | C(14)-Fe(2)-C(19)-C(18) | -45.0(8) |
| C(14)-Fe(2)-C(18)-C(22) | -77.1(3) | C(16)-Fe(2)-C(19)-C(18) | -160.9(3) |
| C(16)-Fe(2)-C(18)-C(22) | 162.6(5) | C(17)-Fe(2)-C(19)-C(18) | -118.4(3) |
| C(17)-Fe(2)-C(18)-C(22) | -161.1(3) | C(22)-Fe(2)-C(19)-C(18) | 38.5(3) |
| C(20)-Fe(2)-C(18)-C(22) | 80.7(3) | C(20)-Fe(2)-C(19)-C(18) | 119.5(5) |
| C(21)-Fe(2)-C(18)-C(22) | 37.4(3) | C(21)-Fe(2)-C(19)-C(18) | 82.2(3) |
| C(13)-Fe(2)-C(18)-C(22) | -118.9(3) | C(13)-Fe(2)-C(19)-C(18) | -77.4(3) |
| C(15)-Fe(2)-C(18)-C(19) | -158.9(6) | C(18)-C(19)-C(20)-C(21) | -0.8(6) |
| C(14)-Fe(2)-C(18)-C(19) | 165.2(3) | Fe(2)-C(19)-C(20)-C(21) | 59.3(4) |
| C(16)-Fe(2)-C(18)-C(19) | 45.0(6) | C(18)-C(19)-C(20)-Fe(2) | -60.1(3) |
| C(17)-Fe(2)-C(18)-C(19) | 81.3(3) | C(15)-Fe(2)-C(20)-C(19) | -159.5(3) |

| | |
|---|---|
| C(14)-Fe(2)-C(20)-C(19) | 168.8(5) |
| C(16)-Fe(2)-C(20)-C(19) | -117.5(4) |
| C(17)-Fe(2)-C(20)-C(19) | -77.4(4) |
| C(22)-Fe(2)-C(20)-C(19) | 82.1(3) |
| C(18)-Fe(2)-C(20)-C(19) | 38.0(3) |
| C(21)-Fe(2)-C(20)-C(19) | 119.8(5) |
| C(13)-Fe(2)-C(20)-C(19) | -47.1(8) |
| C(15)-Fe(2)-C(20)-C(21) | 80.7(4) |
| C(19)-Fe(2)-C(20)-C(21) | -119.8(5) |
| C(14)-Fe(2)-C(20)-C(21) | 49.0(7) |
| C(16)-Fe(2)-C(20)-C(21) | 122.7(4) |
| C(17)-Fe(2)-C(20)-C(21) | 162.9(3) |
| C(22)-Fe(2)-C(20)-C(21) | -37.7(3) |
| C(18)-Fe(2)-C(20)-C(21) | -81.7(3) |
| C(13)-Fe(2)-C(20)-C(21) | -166.9(5) |
| C(19)-C(20)-C(21)-C(22) | 0.5(6) |
| Fe(2)-C(20)-C(21)-C(22) | 59.3(4) |
| C(19)-C(20)-C(21)-Fe(2) | -58.8(4) |
| C(15)-Fe(2)-C(21)-C(20) | -116.9(4) |
| C(19)-Fe(2)-C(21)-C(20) | 36.9(3) |
| C(14)-Fe(2)-C(21)-C(20) | -159.0(3) |
| C(16)-Fe(2)-C(21)-C(20) | -75.5(4) |
| C(17)-Fe(2)-C(21)-C(20) | -46.1(8) |
| C(22)-Fe(2)-C(21)-C(20) | 119.1(5) |
| C(18)-Fe(2)-C(21)-C(20) | 81.4(4) |
| C(13)-Fe(2)-C(21)-C(20) | 169.0(5) |
| C(15)-Fe(2)-C(21)-C(22) | 124.0(4) |
| C(19)-Fe(2)-C(21)-C(22) | -82.1(3) |
| C(14)-Fe(2)-C(21)-C(22) | 81.9(4) |
| C(16)-Fe(2)-C(21)-C(22) | 165.5(3) |
| C(17)-Fe(2)-C(21)-C(22) | -165.1(6) |
| C(18)-Fe(2)-C(21)-C(22) | -37.6(3) |
| C(20)-Fe(2)-C(21)-C(22) | -119.1(5) |
| C(13)-Fe(2)-C(21)-C(22) | 49.9(7) |
| C(20)-C(21)-C(22)-C(18) | 0.0(6) |
| Fe(2)-C(21)-C(22)-C(18) | 59.5(3) |
| C(20)-C(21)-C(22)-Fe(2) | -59.5(4) |
| C(19)-C(18)-C(22)-C(21) | -0.5(5) |
| C(23)-C(18)-C(22)-C(21) | -177.3(4) |
| Fe(2)-C(18)-C(22)-C(21) | -59.7(3) |
| C(19)-C(18)-C(22)-Fe(2) | 59.2(3) |
| C(23)-C(18)-C(22)-Fe(2) | -117.6(5) |
| C(15)-Fe(2)-C(22)-C(21) | -74.8(4) |
| C(19)-Fe(2)-C(22)-C(21) | 80.6(4) |
| C(14)-Fe(2)-C(22)-C(21) | -117.3(4) |
| C(16)-Fe(2)-C(22)-C(21) | -39.3(8) |
| C(17)-Fe(2)-C(22)-C(21) | 166.6(5) |
| C(18)-Fe(2)-C(22)-C(21) | 119.5(5) |
| C(20)-Fe(2)-C(22)-C(21) | 37.5(4) |
| C(13)-Fe(2)-C(22)-C(21) | -159.7(3) |
| C(15)-Fe(2)-C(22)-C(18) | 165.7(3) |
| C(19)-Fe(2)-C(22)-C(18) | -38.9(3) |
| C(14)-Fe(2)-C(22)-C(18) | 123.2(3) |
| C(16)-Fe(2)-C(22)-C(18) | -158.8(6) |
| C(17)-Fe(2)-C(22)-C(18) | 47.1(6) |
| C(20)-Fe(2)-C(22)-C(18) | -82.0(3) |
| C(21)-Fe(2)-C(22)-C(18) | -119.5(5) |
| C(13)-Fe(2)-C(22)-C(18) | 80.9(3) |
| C(22)-C(18)-C(23)-C(24) | -11.6(8) |
| C(19)-C(18)-C(23)-C(24) | 172.2(5) |
| Fe(2)-C(18)-C(23)-C(24) | -100.7(5) |
| C(18)-C(23)-C(24)-C(25) | 177.9(4) |
| C(23)-C(24)-C(25)-C(27) | -6.7(7) |
| C(23)-C(24)-C(25)-C(26) | 173.0(4) |
| C(27)-C(25)-C(26)-C(28) | 0.1(6) |
| C(24)-C(25)-C(26)-C(28) | -179.6(4) |
| C(26)-C(25)-C(27)-C(29) | -0.4(6) |
| C(24)-C(25)-C(27)-C(29) | 179.4(4) |
| C(29)-N(1)-C(28)-C(26) | -0.7(7) |
| Mo(1)-N(1)-C(28)-C(26) | 176.7(3) |
| C(25)-C(26)-C(28)-N(1) | 0.4(7) |
| C(28)-N(1)-C(29)-C(27) | 0.5(7) |
| Mo(1)-N(1)-C(29)-C(27) | -177.0(3) |
| C(25)-C(27)-C(29)-N(1) | 0.1(7) |
| C(32)-Mo(1)-C(30)-O(30) | -22(13) |
| C(31)-Mo(1)-C(30)-O(30) | -10(16) |

| | |
|---|---|
| C(33)-Mo(1)-C(30)-O(30) | 68(13) |
| C(34)-Mo(1)-C(30)-O(30) | -109(13) |
| N(1)-Mo(1)-C(30)-O(30) | 157(13) |
| C(32)-Mo(1)-C(31)-O(31) | 14(11) |
| C(33)-Mo(1)-C(31)-O(31) | -76(11) |
| C(34)-Mo(1)-C(31)-O(31) | 101(11) |
| C(30)-Mo(1)-C(31)-O(31) | 2(14) |
| N(1)-Mo(1)-C(31)-O(31) | -164(11) |
| C(31)-Mo(1)-C(32)-O(32) | 18(14) |
| C(33)-Mo(1)-C(32)-O(32) | 109(14) |
| C(34)-Mo(1)-C(32)-O(32) | -73(14) |
| C(30)-Mo(1)-C(32)-O(32) | -162(14) |
| N(1)-Mo(1)-C(32)-O(32) | 75(17) |
| C(32)-Mo(1)-C(33)-O(33) | 33(19) |
| C(31)-Mo(1)-C(33)-O(33) | 121(19) |
| C(34)-Mo(1)-C(33)-O(33) | -1(22) |
| C(30)-Mo(1)-C(33)-O(33) | -56(19) |
| N(1)-Mo(1)-C(33)-O(33) | -148(19) |
| C(32)-Mo(1)-C(34)-O(34) | -5(7) |
| C(31)-Mo(1)-C(34)-O(34) | -93(7) |
| C(33)-Mo(1)-C(34)-O(34) | 29(10) |
| C(30)-Mo(1)-C(34)-O(34) | 84(7) |
| N(1)-Mo(1)-C(34)-O(34) | 176(100) |
| C(80)-Mo(50)-N(50)-C(78) | 56(4) |
| C(84)-Mo(50)-N(50)-C(78) | 43.6(4) |
| C(82)-Mo(50)-N(50)-C(78) | -48.2(4) |
| C(83)-Mo(50)-N(50)-C(78) | 135.0(4) |
| C(81)-Mo(50)-N(50)-C(78) | -138.0(4) |
| C(80)-Mo(50)-N(50)-C(79) | -122(4) |
| C(84)-Mo(50)-N(50)-C(79) | -134.4(4) |
| C(82)-Mo(50)-N(50)-C(79) | 133.7(4) |
| C(83)-Mo(50)-N(50)-C(79) | -43.0(4) |
| C(81)-Mo(50)-N(50)-C(79) | 44.0(4) |
| C(57)-Fe(51)-C(51)-C(52) | -80.0(5) |
| C(59)-Fe(51)-C(51)-C(52) | -164.0(4) |
| C(54)-Fe(51)-C(51)-C(52) | 80.9(4) |
| C(53)-Fe(51)-C(51)-C(52) | 37.1(4) |
| C(58)-Fe(51)-C(51)-C(52) | -122.4(5) |
| C(55)-Fe(51)-C(51)-C(52) | 119.6(6) |
| C(60)-Fe(51)-C(51)-C(52) | 162.8(6) |
| C(56)-Fe(51)-C(51)-C(52) | -45.0(9) |
| C(57)-Fe(51)-C(51)-C(55) | 160.4(4) |
| C(59)-Fe(51)-C(51)-C(55) | 76.3(5) |
| C(54)-Fe(51)-C(51)-C(55) | -38.7(3) |
| C(53)-Fe(51)-C(51)-C(55) | -82.5(4) |
| C(58)-Fe(51)-C(51)-C(55) | 118.0(4) |
| C(52)-Fe(51)-C(51)-C(55) | -119.6(6) |
| C(60)-Fe(51)-C(51)-C(55) | 43.1(9) |
| C(56)-Fe(51)-C(51)-C(55) | -164.6(6) |
| C(55)-C(51)-C(52)-C(53) | -0.1(7) |
| Fe(51)-C(51)-C(52)-C(53) | -59.5(4) |
| C(55)-C(51)-C(52)-Fe(51) | 59.4(4) |
| C(57)-Fe(51)-C(52)-C(53) | -120.0(4) |
| C(59)-Fe(51)-C(52)-C(53) | 160.4(7) |
| C(54)-Fe(51)-C(52)-C(53) | 37.8(3) |
| C(51)-Fe(51)-C(52)-C(53) | 119.4(6) |
| C(58)-Fe(51)-C(52)-C(53) | -163.1(4) |
| C(55)-Fe(51)-C(52)-C(53) | 81.7(4) |
| C(60)-Fe(51)-C(52)-C(53) | -42.7(9) |
| C(56)-Fe(51)-C(52)-C(53) | -77.7(4) |
| C(57)-Fe(51)-C(52)-C(51) | 120.5(5) |
| C(59)-Fe(51)-C(52)-C(51) | 41.0(10) |
| C(54)-Fe(51)-C(52)-C(51) | -81.6(4) |
| C(53)-Fe(51)-C(52)-C(51) | -119.4(6) |
| C(58)-Fe(51)-C(52)-C(51) | 77.5(5) |
| C(55)-Fe(51)-C(52)-C(51) | -37.7(4) |
| C(60)-Fe(51)-C(52)-C(51) | -162.1(7) |
| C(56)-Fe(51)-C(52)-C(51) | 162.8(4) |
| C(51)-C(52)-C(53)-C(54) | -0.2(7) |
| Fe(51)-C(52)-C(53)-C(54) | -59.6(4) |
| C(51)-C(52)-C(53)-Fe(51) | 59.4(4) |
| C(57)-Fe(51)-C(53)-C(52) | 80.2(4) |
| C(59)-Fe(51)-C(53)-C(52) | -161.1(6) |
| C(54)-Fe(51)-C(53)-C(52) | -119.0(5) |
| C(51)-Fe(51)-C(53)-C(52) | -37.4(4) |
| C(58)-Fe(51)-C(53)-C(52) | 45.5(9) |

|  |  |  |  |
|---|---|---|---|
| C(55)-Fe(51)-C(53)-C(52) | -81.7(4) | C(51)-Fe(51)-C(55)-C(54) | -117.2(5) |
| C(60)-Fe(51)-C(53)-C(52) | 163.4(4) | C(53)-Fe(51)-C(55)-C(54) | -37.2(4) |
| C(56)-Fe(51)-C(53)-C(52) | 121.4(4) | C(58)-Fe(51)-C(55)-C(54) | 161.1(5) |
| C(57)-Fe(51)-C(53)-C(54) | -160.8(4) | C(52)-Fe(51)-C(55)-C(54) | -80.1(4) |
| C(59)-Fe(51)-C(53)-C(54) | -42.1(8) | C(60)-Fe(51)-C(55)-C(54) | 79.9(4) |
| C(51)-Fe(51)-C(53)-C(54) | 81.6(4) | C(56)-Fe(51)-C(55)-C(54) | 48.5(8) |
| C(58)-Fe(51)-C(53)-C(54) | 164.6(7) | C(57)-Fe(51)-C(55)-C(51) | -52.4(9) |
| C(55)-Fe(51)-C(53)-C(54) | 37.4(4) | C(59)-Fe(51)-C(55)-C(51) | -121.9(4) |
| C(52)-Fe(51)-C(53)-C(54) | 119.0(5) | C(54)-Fe(51)-C(55)-C(51) | 117.2(5) |
| C(60)-Fe(51)-C(53)-C(54) | -77.6(4) | C(53)-Fe(51)-C(55)-C(51) | 80.0(4) |
| C(56)-Fe(51)-C(53)-C(54) | -119.6(4) | C(58)-Fe(51)-C(55)-C(51) | -81.7(5) |
| C(52)-C(53)-C(54)-C(55) | 0.4(6) | C(52)-Fe(51)-C(55)-C(51) | 37.1(4) |
| Fe(51)-C(53)-C(54)-C(55) | -59.7(4) | C(60)-Fe(51)-C(55)-C(51) | -162.9(4) |
| C(52)-C(53)-C(54)-Fe(51) | 60.0(4) | C(56)-Fe(51)-C(55)-C(51) | 165.7(5) |
| C(57)-Fe(51)-C(54)-C(53) | 50.0(9) | C(59)-Fe(51)-C(56)-C(57) | 80.5(4) |
| C(59)-Fe(51)-C(54)-C(53) | 163.2(4) | C(54)-Fe(51)-C(56)-C(57) | -164.1(4) |
| C(51)-Fe(51)-C(54)-C(53) | -80.8(4) | C(51)-Fe(51)-C(56)-C(57) | -47.5(8) |
| C(58)-Fe(51)-C(54)-C(53) | -166.4(7) | C(53)-Fe(51)-C(56)-C(57) | -122.0(4) |
| C(55)-Fe(51)-C(54)-C(53) | -119.8(5) | C(58)-Fe(51)-C(56)-C(57) | 37.6(4) |
| C(52)-Fe(51)-C(54)-C(53) | -37.3(3) | C(55)-Fe(51)-C(56)-C(57) | 160.4(6) |
| C(60)-Fe(51)-C(54)-C(53) | 121.4(4) | C(52)-Fe(51)-C(56)-C(57) | -80.8(5) |
| C(56)-Fe(51)-C(54)-C(53) | 79.6(4) | C(60)-Fe(51)-C(56)-C(57) | 117.4(5) |
| C(57)-Fe(51)-C(54)-C(55) | 169.8(7) | C(57)-Fe(51)-C(56)-C(60) | -117.4(5) |
| C(59)-Fe(51)-C(54)-C(55) | -77.0(5) | C(59)-Fe(51)-C(56)-C(60) | -36.9(4) |
| C(51)-Fe(51)-C(54)-C(55) | 39.0(4) | C(54)-Fe(51)-C(56)-C(60) | 78.5(4) |
| C(53)-Fe(51)-C(54)-C(55) | 119.8(5) | C(51)-Fe(51)-C(56)-C(60) | -164.8(6) |
| C(58)-Fe(51)-C(54)-C(55) | -46.6(9) | C(53)-Fe(51)-C(56)-C(60) | 120.6(4) |
| C(52)-Fe(51)-C(54)-C(55) | 82.5(4) | C(58)-Fe(51)-C(56)-C(60) | -79.8(4) |
| C(60)-Fe(51)-C(54)-C(55) | -118.8(4) | C(55)-Fe(51)-C(56)-C(60) | 43.0(8) |
| C(56)-Fe(51)-C(54)-C(55) | -160.6(4) | C(52)-Fe(51)-C(56)-C(60) | 161.9(4) |
| C(53)-C(54)-C(55)-C(51) | -0.4(6) | C(57)-Fe(51)-C(56)-C(61) | 124.8(7) |
| Fe(51)-C(54)-C(55)-C(51) | -60.0(4) | C(59)-Fe(51)-C(56)-C(61) | -154.7(7) |
| C(53)-C(54)-C(55)-Fe(51) | 59.6(4) | C(54)-Fe(51)-C(56)-C(61) | -39.3(7) |
| C(52)-C(51)-C(55)-C(54) | 0.3(7) | C(51)-Fe(51)-C(56)-C(61) | 77.4(9) |
| Fe(51)-C(51)-C(55)-C(54) | 59.9(4) | C(53)-Fe(51)-C(56)-C(61) | 2.9(6) |
| C(52)-C(51)-C(55)-Fe(51) | -59.7(4) | C(58)-Fe(51)-C(56)-C(61) | 162.5(7) |
| C(57)-Fe(51)-C(55)-C(54) | -169.6(7) | C(55)-Fe(51)-C(56)-C(61) | -74.8(8) |
| C(59)-Fe(51)-C(55)-C(54) | 120.9(4) | C(52)-Fe(51)-C(56)-C(61) | 44.1(7) |

| | | | |
|---|---|---|---|
| C(60)-Fe(51)-C(56)-C(61) | -117.8(7) | C(52)-Fe(51)-C(58)-C(57) | 80.0(5) |
| C(60)-C(56)-C(57)-C(58) | -0.8(6) | C(60)-Fe(51)-C(58)-C(57) | -80.8(4) |
| C(61)-C(56)-C(57)-C(58) | 177.5(5) | C(56)-Fe(51)-C(58)-C(57) | -36.9(4) |
| Fe(51)-C(56)-C(57)-C(58) | -60.3(4) | C(57)-C(58)-C(59)-C(60) | -2.4(8) |
| C(60)-C(56)-C(57)-Fe(51) | 59.5(4) | Fe(51)-C(58)-C(59)-C(60) | -61.4(5) |
| C(61)-C(56)-C(57)-Fe(51) | -122.2(6) | C(57)-C(58)-C(59)-Fe(51) | 59.0(5) |
| C(59)-Fe(51)-C(57)-C(56) | -82.6(4) | C(57)-Fe(51)-C(59)-C(58) | -38.0(4) |
| C(54)-Fe(51)-C(57)-C(56) | 40.3(9) | C(54)-Fe(51)-C(59)-C(58) | 162.7(4) |
| C(51)-Fe(51)-C(57)-C(56) | 161.9(4) | C(51)-Fe(51)-C(59)-C(58) | 79.9(5) |
| C(53)-Fe(51)-C(57)-C(56) | 77.2(5) | C(53)-Fe(51)-C(59)-C(58) | -166.5(5) |
| C(58)-Fe(51)-C(57)-C(56) | -119.7(7) | C(55)-Fe(51)-C(59)-C(58) | 121.4(5) |
| C(55)-Fe(51)-C(57)-C(56) | -159.0(7) | C(52)-Fe(51)-C(59)-C(58) | 49.6(10) |
| C(52)-Fe(51)-C(57)-C(56) | 119.4(4) | C(60)-Fe(51)-C(59)-C(58) | -118.1(6) |
| C(60)-Fe(51)-C(57)-C(56) | -38.7(4) | C(56)-Fe(51)-C(59)-C(58) | -81.1(4) |
| C(59)-Fe(51)-C(57)-C(58) | 37.1(5) | C(57)-Fe(51)-C(59)-C(60) | 80.1(4) |
| C(54)-Fe(51)-C(57)-C(58) | 160.0(7) | C(54)-Fe(51)-C(59)-C(60) | -79.3(5) |
| C(51)-Fe(51)-C(57)-C(58) | -78.4(6) | C(51)-Fe(51)-C(59)-C(60) | -162.0(4) |
| C(53)-Fe(51)-C(57)-C(58) | -163.1(5) | C(53)-Fe(51)-C(59)-C(60) | -48.4(8) |
| C(55)-Fe(51)-C(57)-C(58) | -39.3(10) | C(58)-Fe(51)-C(59)-C(60) | 118.1(6) |
| C(52)-Fe(51)-C(57)-C(58) | -120.9(5) | C(55)-Fe(51)-C(59)-C(60) | -120.6(4) |
| C(60)-Fe(51)-C(57)-C(58) | 80.9(5) | C(52)-Fe(51)-C(59)-C(60) | 167.7(7) |
| C(56)-Fe(51)-C(57)-C(58) | 119.7(7) | C(56)-Fe(51)-C(59)-C(60) | 37.0(4) |
| C(56)-C(57)-C(58)-C(59) | 2.0(8) | C(58)-C(59)-C(60)-C(56) | 1.9(8) |
| Fe(51)-C(57)-C(58)-C(59) | -59.4(5) | Fe(51)-C(59)-C(60)-C(56) | -59.3(4) |
| C(56)-C(57)-C(58)-Fe(51) | 61.4(4) | C(58)-C(59)-C(60)-Fe(51) | 61.2(5) |
| C(57)-Fe(51)-C(58)-C(59) | 119.1(7) | C(57)-C(56)-C(60)-C(59) | -0.7(6) |
| C(54)-Fe(51)-C(58)-C(59) | -42.0(10) | C(61)-C(56)-C(60)-C(59) | -179.2(5) |
| C(51)-Fe(51)-C(58)-C(59) | -119.2(5) | Fe(51)-C(56)-C(60)-C(59) | 58.2(4) |
| C(53)-Fe(51)-C(58)-C(59) | 165.2(6) | C(57)-C(56)-C(60)-Fe(51) | -58.9(4) |
| C(55)-Fe(51)-C(58)-C(59) | -76.0(5) | C(61)-C(56)-C(60)-Fe(51) | 122.6(5) |
| C(52)-Fe(51)-C(58)-C(59) | -160.9(4) | C(57)-Fe(51)-C(60)-C(59) | -82.1(4) |
| C(60)-Fe(51)-C(58)-C(59) | 38.3(4) | C(54)-Fe(51)-C(60)-C(59) | 119.3(4) |
| C(56)-Fe(51)-C(58)-C(59) | 82.2(5) | C(51)-Fe(51)-C(60)-C(59) | 45.3(9) |
| C(59)-Fe(51)-C(58)-C(57) | -119.1(7) | C(53)-Fe(51)-C(60)-C(59) | 160.9(4) |
| C(54)-Fe(51)-C(58)-C(57) | -161.2(6) | C(58)-Fe(51)-C(60)-C(59) | -37.7(4) |
| C(51)-Fe(51)-C(58)-C(57) | 121.7(5) | C(55)-Fe(51)-C(60)-C(59) | 77.1(5) |
| C(53)-Fe(51)-C(58)-C(57) | 46.1(10) | C(52)-Fe(51)-C(60)-C(59) | -167.7(7) |
| C(55)-Fe(51)-C(58)-C(57) | 164.9(4) | C(56)-Fe(51)-C(60)-C(59) | -120.3(6) |

| | |
|---|---|
| C(57)-Fe(51)-C(60)-C(56) | 38.2(3) |
| C(59)-Fe(51)-C(60)-C(56) | 120.3(6) |
| C(54)-Fe(51)-C(60)-C(56) | -120.3(4) |
| C(51)-Fe(51)-C(60)-C(56) | 165.6(7) |
| C(53)-Fe(51)-C(60)-C(56) | -78.7(4) |
| C(58)-Fe(51)-C(60)-C(56) | 82.6(4) |
| C(55)-Fe(51)-C(60)-C(56) | -162.6(3) |
| C(52)-Fe(51)-C(60)-C(56) | -47.3(9) |
| C(57)-C(56)-C(61)-C(62) | -12.5(10) |
| C(60)-C(56)-C(61)-C(62) | 165.5(6) |
| Fe(51)-C(56)-C(61)-C(62) | -105.2(7) |
| C(56)-C(61)-C(62)-C(63) | -178.8(5) |
| C(61)-C(62)-C(63)-C(64) | 20.9(9) |
| C(61)-C(62)-C(63)-C(67) | -164.1(6) |
| C(61)-C(62)-C(63)-Fe(52) | 109.6(6) |
| C(71)-Fe(52)-C(63)-C(64) | -157.1(8) |
| C(66)-Fe(52)-C(63)-C(64) | -81.1(4) |
| C(72)-Fe(52)-C(63)-C(64) | 164.7(4) |
| C(67)-Fe(52)-C(63)-C(64) | -119.9(5) |
| C(65)-Fe(52)-C(63)-C(64) | -37.7(4) |
| C(69)-Fe(52)-C(63)-C(64) | 79.1(4) |
| C(70)-Fe(52)-C(63)-C(64) | 40.8(8) |
| C(68)-Fe(52)-C(63)-C(64) | 121.6(4) |
| C(71)-Fe(52)-C(63)-C(67) | -37.2(10) |
| C(66)-Fe(52)-C(63)-C(67) | 38.9(4) |
| C(72)-Fe(52)-C(63)-C(67) | -75.4(5) |
| C(64)-Fe(52)-C(63)-C(67) | 119.9(5) |
| C(65)-Fe(52)-C(63)-C(67) | 82.2(4) |
| C(69)-Fe(52)-C(63)-C(67) | -161.0(4) |
| C(70)-Fe(52)-C(63)-C(67) | 160.7(7) |
| C(68)-Fe(52)-C(63)-C(67) | -118.5(4) |
| C(71)-Fe(52)-C(63)-C(62) | 80.7(10) |
| C(66)-Fe(52)-C(63)-C(62) | 156.7(7) |
| C(72)-Fe(52)-C(63)-C(62) | 42.5(6) |
| C(64)-Fe(52)-C(63)-C(62) | -122.2(7) |
| C(67)-Fe(52)-C(63)-C(62) | 117.9(7) |
| C(65)-Fe(52)-C(63)-C(62) | -159.9(6) |
| C(69)-Fe(52)-C(63)-C(62) | -43.1(6) |
| C(70)-Fe(52)-C(63)-C(62) | -81.4(9) |
| C(68)-Fe(52)-C(63)-C(62) | -0.6(6) |
| C(67)-C(63)-C(64)-C(65) | 1.4(6) |
| C(62)-C(63)-C(64)-C(65) | 177.1(5) |
| Fe(52)-C(63)-C(64)-C(65) | 59.4(4) |
| C(67)-C(63)-C(64)-Fe(52) | -58.0(4) |
| C(62)-C(63)-C(64)-Fe(52) | 117.7(5) |
| C(71)-Fe(52)-C(64)-C(63) | 163.3(7) |
| C(66)-Fe(52)-C(64)-C(63) | 81.5(4) |
| C(72)-Fe(52)-C(64)-C(63) | -44.5(10) |
| C(67)-Fe(52)-C(64)-C(63) | 37.4(3) |
| C(65)-Fe(52)-C(64)-C(63) | 119.9(6) |
| C(69)-Fe(52)-C(64)-C(63) | -120.3(4) |
| C(70)-Fe(52)-C(64)-C(63) | -162.9(4) |
| C(68)-Fe(52)-C(64)-C(63) | -78.9(4) |
| C(71)-Fe(52)-C(64)-C(65) | 43.4(9) |
| C(66)-Fe(52)-C(64)-C(65) | -38.3(4) |
| C(72)-Fe(52)-C(64)-C(65) | -164.3(8) |
| C(67)-Fe(52)-C(64)-C(65) | -82.5(4) |
| C(69)-Fe(52)-C(64)-C(65) | 119.8(5) |
| C(70)-Fe(52)-C(64)-C(65) | 77.3(5) |
| C(63)-Fe(52)-C(64)-C(65) | -119.9(6) |
| C(68)-Fe(52)-C(64)-C(65) | 161.2(4) |
| C(63)-C(64)-C(65)-C(66) | 0.1(7) |
| Fe(52)-C(64)-C(65)-C(66) | 60.3(5) |
| C(63)-C(64)-C(65)-Fe(52) | -60.2(4) |
| C(71)-Fe(52)-C(65)-C(66) | 81.8(5) |
| C(72)-Fe(52)-C(65)-C(66) | 51.1(9) |
| C(64)-Fe(52)-C(65)-C(66) | -117.3(6) |
| C(67)-Fe(52)-C(65)-C(66) | -36.7(4) |
| C(69)-Fe(52)-C(65)-C(66) | 162.7(4) |
| C(70)-Fe(52)-C(65)-C(66) | 122.7(5) |
| C(63)-Fe(52)-C(65)-C(66) | -80.4(4) |
| C(68)-Fe(52)-C(65)-C(66) | -169.5(6) |
| C(71)-Fe(52)-C(65)-C(64) | -160.9(5) |
| C(66)-Fe(52)-C(65)-C(64) | 117.3(6) |
| C(72)-Fe(52)-C(65)-C(64) | 168.4(6) |
| C(67)-Fe(52)-C(65)-C(64) | 80.6(4) |

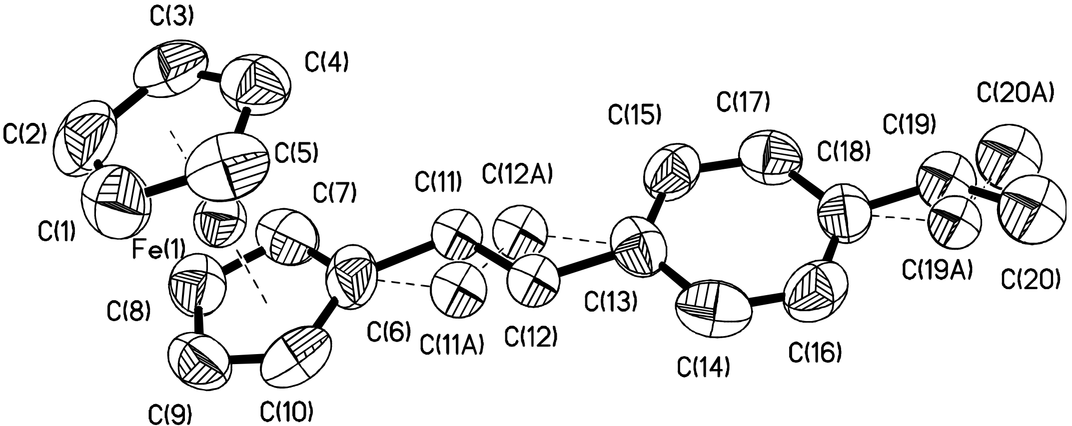
| | |
|---|---|
| C(69)-Fe(52)-C(65)-C(64) | -80.1(5) |
| C(70)-Fe(52)-C(65)-C(64) | -120.0(5) |
| C(63)-Fe(52)-C(65)-C(64) | 36.9(4) |
| C(68)-Fe(52)-C(65)-C(64) | -52.2(9) |
| C(64)-C(65)-C(66)-C(67) | -1.6(7) |
| Fe(52)-C(65)-C(66)-C(67) | 58.6(4) |
| C(64)-C(65)-C(66)-Fe(52) | -60.1(4) |
| C(71)-Fe(52)-C(66)-C(65) | -115.4(5) |
| C(72)-Fe(52)-C(66)-C(65) | -157.8(4) |
| C(64)-Fe(52)-C(66)-C(65) | 39.1(4) |
| C(67)-Fe(52)-C(66)-C(65) | 121.4(6) |
| C(69)-Fe(52)-C(66)-C(65) | -44.5(9) |
| C(70)-Fe(52)-C(66)-C(65) | -74.4(5) |
| C(63)-Fe(52)-C(66)-C(65) | 82.7(4) |
| C(68)-Fe(52)-C(66)-C(65) | 170.3(5) |
| C(71)-Fe(52)-C(66)-C(67) | 123.2(5) |
| C(72)-Fe(52)-C(66)-C(67) | 80.8(4) |
| C(64)-Fe(52)-C(66)-C(67) | -82.3(4) |
| C(65)-Fe(52)-C(66)-C(67) | -121.4(6) |
| C(69)-Fe(52)-C(66)-C(67) | -165.9(7) |
| C(70)-Fe(52)-C(66)-C(67) | 164.2(4) |
| C(63)-Fe(52)-C(66)-C(67) | -38.7(4) |
| C(68)-Fe(52)-C(66)-C(67) | 48.9(8) |
| C(65)-C(66)-C(67)-C(63) | 2.4(7) |
| Fe(52)-C(66)-C(67)-C(63) | 61.2(4) |
| C(65)-C(66)-C(67)-Fe(52) | -58.8(5) |
| C(64)-C(63)-C(67)-C(66) | -2.3(6) |
| C(62)-C(63)-C(67)-C(66) | -178.2(4) |
| Fe(52)-C(63)-C(67)-C(66) | -60.3(4) |
| C(64)-C(63)-C(67)-Fe(52) | 58.1(4) |
| C(62)-C(63)-C(67)-Fe(52) | -117.8(5) |
| C(71)-Fe(52)-C(67)-C(66) | -75.7(5) |
| C(72)-Fe(52)-C(67)-C(66) | -118.2(4) |
| C(64)-Fe(52)-C(67)-C(66) | 80.3(4) |
| C(65)-Fe(52)-C(67)-C(66) | 36.1(4) |
| C(69)-Fe(52)-C(67)-C(66) | 166.1(7) |
| C(70)-Fe(52)-C(67)-C(66) | -41.2(11) |
| C(63)-Fe(52)-C(67)-C(66) | 117.3(6) |
| C(68)-Fe(52)-C(67)-C(66) | -160.9(4) |
| C(71)-Fe(52)-C(67)-C(63) | 167.0(4) |
| C(66)-Fe(52)-C(67)-C(63) | -117.3(6) |
| C(72)-Fe(52)-C(67)-C(63) | 124.5(4) |
| C(64)-Fe(52)-C(67)-C(63) | -37.0(3) |
| C(65)-Fe(52)-C(67)-C(63) | -81.2(4) |
| C(69)-Fe(52)-C(67)-C(63) | 48.8(9) |
| C(70)-Fe(52)-C(67)-C(63) | -158.5(8) |
| C(68)-Fe(52)-C(67)-C(63) | 81.8(4) |
| C(71)-Fe(52)-C(68)-C(69) | 80.0(4) |
| C(66)-Fe(52)-C(68)-C(69) | 161.6(6) |
| C(72)-Fe(52)-C(68)-C(69) | 118.6(5) |
| C(64)-Fe(52)-C(68)-C(69) | -76.7(4) |
| C(67)-Fe(52)-C(68)-C(69) | -162.2(4) |
| C(65)-Fe(52)-C(68)-C(69) | -37.3(9) |
| C(70)-Fe(52)-C(68)-C(69) | 36.8(4) |
| C(63)-Fe(52)-C(68)-C(69) | -119.0(4) |
| C(71)-Fe(52)-C(68)-C(72) | -38.6(4) |
| C(66)-Fe(52)-C(68)-C(72) | 43.1(8) |
| C(64)-Fe(52)-C(68)-C(72) | 164.7(4) |
| C(67)-Fe(52)-C(68)-C(72) | 79.2(4) |
| C(65)-Fe(52)-C(68)-C(72) | -155.9(7) |
| C(69)-Fe(52)-C(68)-C(72) | -118.6(5) |
| C(70)-Fe(52)-C(68)-C(72) | -81.8(4) |
| C(63)-Fe(52)-C(68)-C(72) | 122.4(4) |
| C(71)-Fe(52)-C(68)-C(73) | -153.9(7) |
| C(66)-Fe(52)-C(68)-C(73) | -72.3(9) |
| C(72)-Fe(52)-C(68)-C(73) | -115.4(8) |
| C(64)-Fe(52)-C(68)-C(73) | 49.3(7) |
| C(67)-Fe(52)-C(68)-C(73) | -36.2(7) |
| C(65)-Fe(52)-C(68)-C(73) | 88.7(10) |
| C(69)-Fe(52)-C(68)-C(73) | 126.1(8) |
| C(70)-Fe(52)-C(68)-C(73) | 162.8(7) |
| C(63)-Fe(52)-C(68)-C(73) | 7.0(7) |
| C(72)-C(68)-C(69)-C(70) | -0.9(6) |
| C(73)-C(68)-C(69)-C(70) | -179.9(5) |
| Fe(52)-C(68)-C(69)-C(70) | -59.4(4) |
| C(72)-C(68)-C(69)-Fe(52) | 58.5(4) |

| | | | |
|---|---|---|---|
| C(73)-C(68)-C(69)-Fe(52) | -120.5(5) | C(69)-C(70)-C(71)-Fe(52) | 59.4(5) |
| C(71)-Fe(52)-C(69)-C(68) | -83.0(4) | C(66)-Fe(52)-C(71)-C(70) | 120.8(5) |
| C(66)-Fe(52)-C(69)-C(68) | -161.2(7) | C(72)-Fe(52)-C(71)-C(70) | -119.7(7) |
| C(72)-Fe(52)-C(69)-C(68) | -38.4(3) | C(64)-Fe(52)-C(71)-C(70) | 47.8(9) |
| C(64)-Fe(52)-C(69)-C(68) | 123.0(4) | C(67)-Fe(52)-C(71)-C(70) | 162.2(5) |
| C(67)-Fe(52)-C(69)-C(68) | 45.0(9) | C(65)-Fe(52)-C(71)-C(70) | 78.9(6) |
| C(65)-Fe(52)-C(69)-C(68) | 166.0(4) | C(69)-Fe(52)-C(71)-C(70) | -37.9(5) |
| C(70)-Fe(52)-C(69)-C(68) | -120.7(7) | C(63)-Fe(52)-C(71)-C(70) | -169.4(6) |
| C(63)-Fe(52)-C(69)-C(68) | 81.0(4) | C(68)-Fe(52)-C(71)-C(70) | -81.3(5) |
| C(71)-Fe(52)-C(69)-C(70) | 37.7(5) | C(66)-Fe(52)-C(71)-C(72) | -119.5(5) |
| C(66)-Fe(52)-C(69)-C(70) | -40.5(10) | C(64)-Fe(52)-C(71)-C(72) | 167.5(6) |
| C(72)-Fe(52)-C(69)-C(70) | 82.3(5) | C(67)-Fe(52)-C(71)-C(72) | -78.1(5) |
| C(64)-Fe(52)-C(69)-C(70) | -116.3(5) | C(65)-Fe(52)-C(71)-C(72) | -161.4(4) |
| C(67)-Fe(52)-C(69)-C(70) | 165.7(7) | C(69)-Fe(52)-C(71)-C(72) | 81.8(4) |
| C(65)-Fe(52)-C(69)-C(70) | -73.3(6) | C(70)-Fe(52)-C(71)-C(72) | 119.7(7) |
| C(63)-Fe(52)-C(69)-C(70) | -158.3(5) | C(63)-Fe(52)-C(71)-C(72) | -49.7(10) |
| C(68)-Fe(52)-C(69)-C(70) | 120.7(7) | C(68)-Fe(52)-C(71)-C(72) | 38.4(4) |
| C(68)-C(69)-C(70)-C(71) | 0.7(8) | C(70)-C(71)-C(72)-C(68) | -0.4(8) |
| Fe(52)-C(69)-C(70)-C(71) | -59.0(5) | Fe(52)-C(71)-C(72)-C(68) | -60.7(4) |
| C(68)-C(69)-C(70)-Fe(52) | 59.7(4) | C(70)-C(71)-C(72)-Fe(52) | 60.4(5) |
| C(66)-Fe(52)-C(70)-C(71) | -77.3(6) | C(69)-C(68)-C(72)-C(71) | 0.7(6) |
| C(72)-Fe(52)-C(70)-C(71) | 37.8(5) | C(73)-C(68)-C(72)-C(71) | 179.8(5) |
| C(64)-Fe(52)-C(70)-C(71) | -158.9(4) | Fe(52)-C(68)-C(72)-C(71) | 59.8(4) |
| C(67)-Fe(52)-C(70)-C(71) | -46.6(11) | C(69)-C(68)-C(72)-Fe(52) | -59.0(4) |
| C(65)-Fe(52)-C(70)-C(71) | -117.4(5) | C(73)-C(68)-C(72)-Fe(52) | 120.1(5) |
| C(69)-Fe(52)-C(70)-C(71) | 118.6(7) | C(66)-Fe(52)-C(72)-C(71) | 79.0(6) |
| C(63)-Fe(52)-C(70)-C(71) | 171.6(5) | C(64)-Fe(52)-C(72)-C(71) | -162.9(8) |
| C(68)-Fe(52)-C(70)-C(71) | 82.0(5) | C(67)-Fe(52)-C(72)-C(71) | 121.7(5) |
| C(71)-Fe(52)-C(70)-C(69) | -118.6(7) | C(65)-Fe(52)-C(72)-C(71) | 42.7(9) |
| C(66)-Fe(52)-C(70)-C(69) | 164.1(5) | C(69)-Fe(52)-C(72)-C(71) | -80.4(5) |
| C(72)-Fe(52)-C(70)-C(69) | -80.8(5) | C(70)-Fe(52)-C(72)-C(71) | -36.9(4) |
| C(64)-Fe(52)-C(70)-C(69) | 82.5(5) | C(63)-Fe(52)-C(72)-C(71) | 163.2(5) |
| C(67)-Fe(52)-C(70)-C(69) | -165.2(8) | C(68)-Fe(52)-C(72)-C(71) | -118.0(6) |
| C(65)-Fe(52)-C(70)-C(69) | 124.0(5) | C(71)-Fe(52)-C(72)-C(68) | 118.0(6) |
| C(63)-Fe(52)-C(70)-C(69) | 53.0(9) | C(66)-Fe(52)-C(72)-C(68) | -163.0(4) |
| C(68)-Fe(52)-C(70)-C(69) | -36.6(4) | C(64)-Fe(52)-C(72)-C(68) | -44.9(10) |
| C(69)-C(70)-C(71)-C(72) | -0.2(8) | C(67)-Fe(52)-C(72)-C(68) | -120.3(4) |
| Fe(52)-C(70)-C(71)-C(72) | -59.6(5) | C(65)-Fe(52)-C(72)-C(68) | 160.7(6) |

| | |
|---|---|
| C(69)-Fe(52)-C(72)-C(68) | 37.6(3) |
| C(70)-Fe(52)-C(72)-C(68) | 81.1(4) |
| C(63)-Fe(52)-C(72)-C(68) | -78.8(4) |
| C(69)-C(68)-C(73)-C(74) | -6.5(9) |
| C(72)-C(68)-C(73)-C(74) | 174.6(5) |
| Fe(52)-C(68)-C(73)-C(74) | -99.5(7) |
| C(68)-C(73)-C(74)-C(75) | 179.6(4) |
| C(73)-C(74)-C(75)-C(76) | -176.5(5) |
| C(73)-C(74)-C(75)-C(77) | 5.8(8) |
| C(77)-C(75)-C(76)-C(78) | -2.7(8) |
| C(74)-C(75)-C(76)-C(78) | 179.3(4) |
| C(76)-C(75)-C(77)-C(79) | 1.8(8) |
| C(74)-C(75)-C(77)-C(79) | 179.6(5) |
| C(79)-N(50)-C(78)-C(76) | 3.3(7) |
| Mo(50)-N(50)-C(78)-C(76) | -174.9(4) |
| C(75)-C(76)-C(78)-N(50) | 0.2(8) |
| C(78)-N(50)-C(79)-C(77) | -4.3(8) |
| Mo(50)-N(50)-C(79)-C(77) | 173.9(4) |
| C(75)-C(77)-C(79)-N(50) | 1.9(9) |
| C(84)-Mo(50)-C(80)-O(80) | -55(30) |
| C(82)-Mo(50)-C(80)-O(80) | 37(30) |
| C(83)-Mo(50)-C(80)-O(80) | -146(30) |
| C(81)-Mo(50)-C(80)-O(80) | 127(30) |
| N(50)-Mo(50)-C(80)-O(80) | -67(32) |
| C(80)-Mo(50)-C(81)-O(81) | 31(6) |
| C(84)-Mo(50)-C(81)-O(81) | 17(7) |
| C(82)-Mo(50)-C(81)-O(81) | 121(6) |
| C(83)-Mo(50)-C(81)-O(81) | -59(6) |
| N(50)-Mo(50)-C(81)-O(81) | -148(6) |
| C(80)-Mo(50)-C(82)-O(82) | 13(13) |
| C(84)-Mo(50)-C(82)-O(82) | 99(13) |
| C(83)-Mo(50)-C(82)-O(82) | -77(14) |
| C(81)-Mo(50)-C(82)-O(82) | -75(13) |
| N(50)-Mo(50)-C(82)-O(82) | -170(13) |
| C(80)-Mo(50)-C(83)-O(83) | -94(9) |
| C(84)-Mo(50)-C(83)-O(83) | 180(100) |
| C(82)-Mo(50)-C(83)-O(83) | -4(12) |
| C(81)-Mo(50)-C(83)-O(83) | -6(9) |
| N(50)-Mo(50)-C(83)-O(83) | 89(9) |
| C(80)-Mo(50)-C(84)-O(84) | -13(6) |
| C(82)-Mo(50)-C(84)-O(84) | -103(6) |
| C(83)-Mo(50)-C(84)-O(84) | 77(6) |
| C(81)-Mo(50)-C(84)-O(84) | 1(8) |
| N(50)-Mo(50)-C(84)-O(84) | 166(6) |

---

Symmetry transformations used to generate equivalent atoms:


C(3)
C(4)
C(2)
C(5)
C(7)
C(11)
C(12A)
C(15)
C(17)
C(18)
C(19)
C(20A)
C(1)
Fe(1)
C(8)
C(6)
C(11A)
C(12)
C(13)
C(19A)
C(20)
C(9)
C(10)
C(14)
C(16)

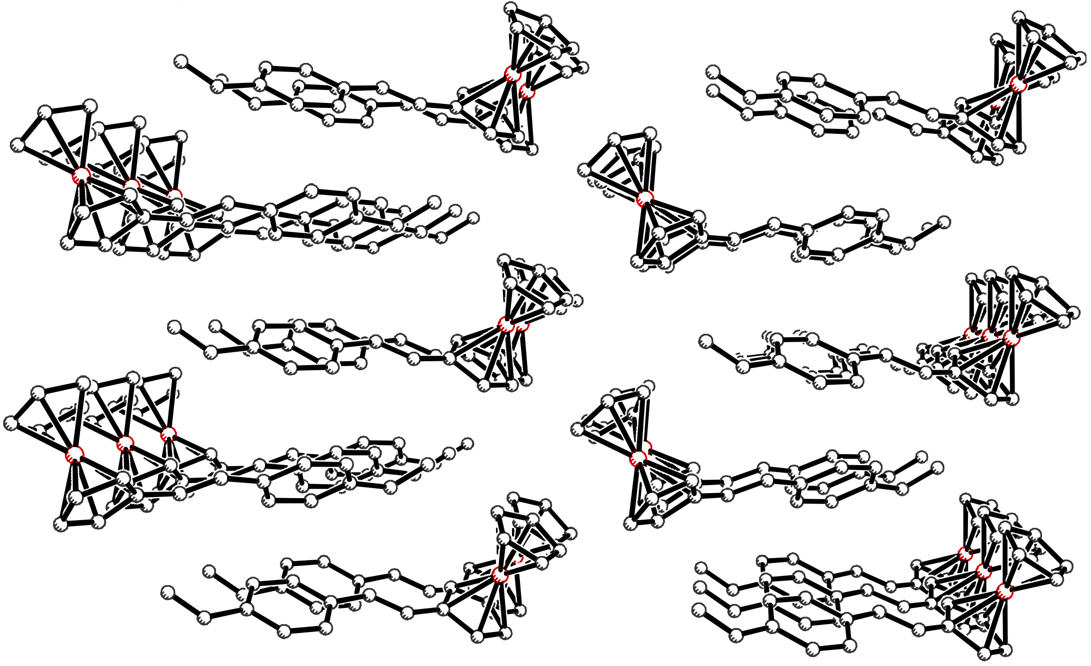


**Table 1**. Crystal data and structure refinement for str129m.

| | | |
|---|---|---|
| Identification code | str129m | |
| Empirical formula | C20 H18 Fe | |
| Formula weight | 314.19 | |
| Temperature | 293(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | P2(1) | |
| Unit cell dimensions | a = 6.2555(5) Å | $\alpha$= 90°. |
| | b = 7.8041(6) Å | $\beta$= 90.590(2)°. |
| | c = 15.5956(12) Å | $\gamma$ = 90°. |
| Volume | 761.31(10) Å$^3$ | |
| Z | 2 | |
| Density (calculated) | 1.371 Mg/m$^3$ | |
| Absorption coefficient | 0.980 mm$^{-1}$ | |
| F(000) | 328 | |
| Crystal size | 0.35 x 0.16 x 0.12 mm$^3$ | |
| Theta range for data collection | 1.31 to 30.52°. | |
| Index ranges | -8<=h<=8, -8<=k<=11, -22<=l<=22 | |
| Reflections collected | 6431 | |
| Independent reflections | 3679 [R(int) = 0.0224] | |
| Completeness to theta = 30.52° | 99.6 % | |
| Absorption correction | Bruker SADABS | |
| Max. and min. transmission | 1.955306 and 1.351363 | |
| Refinement method | Full-matrix least-squares on F$^2$ | |
| Data / restraints / parameters | 3679 / 1 / 188 | |
| Goodness-of-fit on F$^2$ | 0.655 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0394, wR2 = 0.1034 | |
| R indices (all data) | R1 = 0.0712, wR2 = 0.1149 | |
| Absolute structure parameter | -0.03(2) | |
| Largest diff. peak and hole | 0.421 and -0.194 e.Å$^{-3}$ | |

**Table 2**. Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) for str129m. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| Fe(1) | 2121(1) | 6100(1) | 3628(1) | 49(1) |
| C(1) | 2996(8) | 8301(7) | 4225(3) | 82(1) |
| C(2) | 2047(9) | 7163(7) | 4809(3) | 88(1) |
| C(3) | -64(7) | 6811(6) | 4515(3) | 72(1) |
| C(4) | -391(7) | 7736(6) | 3764(3) | 69(1) |
| C(5) | 1451(10) | 8651(6) | 3570(3) | 75(2) |
| C(6) | 1725(7) | 4705(6) | 2519(2) | 68(1) |
| C(7) | 1472(8) | 3682(6) | 3232(3) | 68(1) |
| C(8) | 3311(8) | 3677(6) | 3727(3) | 69(1) |
| C(9) | 4786(6) | 4740(6) | 3320(3) | 74(1) |
| C(10) | 3817(8) | 5393(5) | 2585(3) | 73(1) |
| C(11) | -128(8) | 4684(7) | 1890(4) | 49(2) |
| C(11A) | 1012(18) | 5414(14) | 1640(7) | 56(4) |
| C(12) | 95(8) | 5311(7) | 1118(4) | 50(2) |
| C(12A) | -793(19) | 4706(15) | 1415(7) | 56(3) |
| C(13) | -1620(6) | 5138(5) | 455(2) | 60(1) |
| C(14) | -1038(6) | 5860(6) | -334(3) | 70(1) |
| C(15) | -3598(7) | 4333(6) | 484(2) | 64(1) |
| C(16) | -2372(7) | 5819(6) | -1030(3) | 73(1) |
| C(17) | -4919(6) | 4280(6) | -231(3) | 65(1) |
| C(18) | -4356(7) | 5033(5) | -997(2) | 64(1) |
| C(19) | -6089(11) | 4815(9) | -1677(4) | 68(2) |
| C(19A) | -5130(20) | 5552(16) | -1848(8) | 52(4) |
| C(20) | -6105(11) | 5723(11) | -2381(5) | 88(3) |
| C(20A) | -7180(30) | 4910(20) | -2071(12) | 84(6) |

**Table 3.** Bond lengths [Å] and angles [°] for str129m.

| | |
|---|---|
| Fe(1)-C(2) | 2.021(4) |
| Fe(1)-C(7) | 2.025(5) |
| Fe(1)-C(10) | 2.027(4) |
| Fe(1)-C(1) | 2.027(5) |
| Fe(1)-C(3) | 2.033(4) |
| Fe(1)-C(8) | 2.037(5) |
| Fe(1)-C(5) | 2.037(5) |
| Fe(1)-C(9) | 2.037(4) |
| Fe(1)-C(4) | 2.038(4) |
| Fe(1)-C(6) | 2.055(3) |
| C(1)-C(2) | 1.408(7) |
| C(1)-C(5) | 1.425(8) |
| C(2)-C(3) | 1.420(6) |
| C(3)-C(4) | 1.390(6) |
| C(4)-C(5) | 1.392(7) |
| C(6)-C(7) | 1.379(7) |
| C(6)-C(10) | 1.417(6) |
| C(6)-C(11) | 1.512(7) |
| C(6)-C(11A) | 1.541(11) |
| C(7)-C(8) | 1.379(8) |
| C(8)-C(9) | 1.398(6) |
| C(9)-C(10) | 1.389(6) |
| C(11)-C(12A) | 0.845(10) |
| C(11)-C(11A) | 0.995(11) |
| C(11)-C(12) | 1.308(9) |
| C(11A)-C(12) | 0.994(11) |
| C(11A)-C(12A) | 1.302(19) |
| C(12)-C(12A) | 0.867(11) |
| C(12)-C(13) | 1.488(6) |
| C(12A)-C(13) | 1.616(12) |
| C(13)-C(15) | 1.389(6) |
| C(13)-C(14) | 1.404(6) |
| C(14)-C(16) | 1.363(6) |
| C(15)-C(17) | 1.381(6) |
| C(16)-C(18) | 1.386(6) |
| C(17)-C(18) | 1.381(6) |
| C(18)-C(19A) | 1.465(13) |
| C(18)-C(19) | 1.518(8) |
| C(19)-C(19A) | 0.872(12) |
| C(19)-C(20A) | 0.92(2) |
| C(19)-C(20) | 1.306(11) |
| C(19A)-C(20) | 1.034(12) |
| C(19A)-C(20A) | 1.41(3) |
| C(20)-C(20A) | 1.046(19) |
| C(2)-Fe(1)-C(7) | 130.8(2) |
| C(2)-Fe(1)-C(10) | 149.3(2) |
| C(7)-Fe(1)-C(10) | 66.87(18) |
| C(2)-Fe(1)-C(1) | 40.7(2) |
| C(7)-Fe(1)-C(1) | 169.2(2) |
| C(10)-Fe(1)-C(1) | 117.3(2) |
| C(2)-Fe(1)-C(3) | 41.00(18) |
| C(7)-Fe(1)-C(3) | 109.13(18) |
| C(10)-Fe(1)-C(3) | 169.0(2) |
| C(1)-Fe(1)-C(3) | 68.63(19) |
| C(2)-Fe(1)-C(8) | 108.9(2) |
| C(7)-Fe(1)-C(8) | 39.7(2) |
| C(10)-Fe(1)-C(8) | 67.34(18) |
| C(1)-Fe(1)-C(8) | 130.9(2) |
| C(3)-Fe(1)-C(8) | 116.70(18) |
| C(2)-Fe(1)-C(5) | 68.4(2) |
| C(7)-Fe(1)-C(5) | 149.0(2) |
| C(10)-Fe(1)-C(5) | 109.86(19) |
| C(1)-Fe(1)-C(5) | 41.1(2) |
| C(3)-Fe(1)-C(5) | 67.89(19) |
| C(8)-Fe(1)-C(5) | 170.3(3) |
| C(2)-Fe(1)-C(9) | 117.0(2) |
| C(7)-Fe(1)-C(9) | 66.75(19) |
| C(10)-Fe(1)-C(9) | 39.97(18) |
| C(1)-Fe(1)-C(9) | 109.38(19) |
| C(3)-Fe(1)-C(9) | 149.30(19) |
| C(8)-Fe(1)-C(9) | 40.12(18) |
| C(5)-Fe(1)-C(9) | 131.9(2) |
| C(2)-Fe(1)-C(4) | 67.8(2) |

| | |
|---|---|
| C(7)-Fe(1)-C(4) | 117.59(19) |
| C(10)-Fe(1)-C(4) | 131.65(18) |
| C(1)-Fe(1)-C(4) | 68.0(2) |
| C(3)-Fe(1)-C(4) | 39.93(17) |
| C(8)-Fe(1)-C(4) | 148.78(19) |
| C(5)-Fe(1)-C(4) | 39.9(2) |
| C(9)-Fe(1)-C(4) | 169.96(19) |
| C(2)-Fe(1)-C(6) | 168.5(2) |
| C(7)-Fe(1)-C(6) | 39.49(19) |
| C(10)-Fe(1)-C(6) | 40.61(18) |
| C(1)-Fe(1)-C(6) | 149.9(2) |
| C(3)-Fe(1)-C(6) | 129.89(18) |
| C(8)-Fe(1)-C(6) | 67.24(18) |
| C(5)-Fe(1)-C(6) | 117.2(2) |
| C(9)-Fe(1)-C(6) | 67.57(16) |
| C(4)-Fe(1)-C(6) | 109.46(17) |
| C(2)-C(1)-C(5) | 107.3(5) |
| C(2)-C(1)-Fe(1) | 69.4(3) |
| C(5)-C(1)-Fe(1) | 69.8(3) |
| C(1)-C(2)-C(3) | 108.1(4) |
| C(1)-C(2)-Fe(1) | 69.9(2) |
| C(3)-C(2)-Fe(1) | 69.9(2) |
| C(4)-C(3)-C(2) | 107.4(4) |
| C(4)-C(3)-Fe(1) | 70.2(2) |
| C(2)-C(3)-Fe(1) | 69.1(2) |
| C(3)-C(4)-C(5) | 109.6(4) |
| C(3)-C(4)-Fe(1) | 69.9(2) |
| C(5)-C(4)-Fe(1) | 70.0(3) |
| C(4)-C(5)-C(1) | 107.6(4) |
| C(4)-C(5)-Fe(1) | 70.1(3) |
| C(1)-C(5)-Fe(1) | 69.1(3) |
| C(7)-C(6)-C(10) | 106.0(4) |
| C(7)-C(6)-C(11) | 115.0(4) |
| C(10)-C(6)-C(11) | 138.8(4) |
| C(7)-C(6)-C(11A) | 153.0(6) |
| C(10)-C(6)-C(11A) | 100.8(6) |
| C(11)-C(6)-C(11A) | 38.0(4) |
| C(7)-C(6)-Fe(1) | 69.1(2) |
| C(10)-C(6)-Fe(1) | 68.6(2) |
| C(11)-C(6)-Fe(1) | 129.6(3) |
| C(11A)-C(6)-Fe(1) | 126.1(5) |
| C(8)-C(7)-C(6) | 110.5(4) |
| C(8)-C(7)-Fe(1) | 70.6(3) |
| C(6)-C(7)-Fe(1) | 71.4(3) |
| C(7)-C(8)-C(9) | 107.2(4) |
| C(7)-C(8)-Fe(1) | 69.7(3) |
| C(9)-C(8)-Fe(1) | 69.9(3) |
| C(10)-C(9)-C(8) | 107.9(4) |
| C(10)-C(9)-Fe(1) | 69.6(2) |
| C(8)-C(9)-Fe(1) | 69.9(2) |
| C(9)-C(10)-C(6) | 108.4(4) |
| C(9)-C(10)-Fe(1) | 70.4(2) |
| C(6)-C(10)-Fe(1) | 70.7(2) |
| C(12A)-C(11)-C(11A) | 89.7(13) |
| C(12A)-C(11)-C(12) | 40.8(9) |
| C(11A)-C(11)-C(12) | 48.9(7) |
| C(12A)-C(11)-C(6) | 159.4(11) |
| C(11A)-C(11)-C(6) | 72.6(8) |
| C(12)-C(11)-C(6) | 120.4(5) |
| C(12)-C(11A)-C(11) | 82.2(11) |
| C(12)-C(11A)-C(12A) | 41.7(7) |
| C(11)-C(11A)-C(12A) | 40.5(7) |
| C(12)-C(11A)-C(6) | 149.2(12) |
| C(11)-C(11A)-C(6) | 69.4(7) |
| C(12A)-C(11A)-C(6) | 109.2(9) |
| C(12A)-C(12)-C(11A) | 88.5(13) |
| C(12A)-C(12)-C(11) | 39.6(9) |
| C(11A)-C(12)-C(11) | 48.9(7) |
| C(12A)-C(12)-C(13) | 82.0(9) |
| C(11A)-C(12)-C(13) | 169.0(9) |
| C(11)-C(12)-C(13) | 121.5(5) |
| C(11)-C(12A)-C(12) | 99.6(15) |
| C(11)-C(12A)-C(11A) | 49.8(9) |
| C(12)-C(12A)-C(11A) | 49.8(9) |
| C(11)-C(12A)-C(13) | 165.0(14) |
| C(12)-C(12A)-C(13) | 65.9(8) |

| | |
|---|---|
| C(11A)-C(12A)-C(13) | 115.4(9) |
| C(15)-C(13)-C(14) | 116.7(3) |
| C(15)-C(13)-C(12) | 130.9(4) |
| C(14)-C(13)-C(12) | 112.4(4) |
| C(15)-C(13)-C(12A) | 98.8(5) |
| C(14)-C(13)-C(12A) | 144.4(5) |
| C(12)-C(13)-C(12A) | 32.1(4) |
| C(16)-C(14)-C(13) | 121.8(4) |
| C(17)-C(15)-C(13) | 120.9(3) |
| C(14)-C(16)-C(18) | 121.5(3) |
| C(15)-C(17)-C(18) | 122.0(4) |
| C(17)-C(18)-C(16) | 117.2(4) |
| C(17)-C(18)-C(19A) | 144.7(7) |
| C(16)-C(18)-C(19A) | 97.7(6) |
| C(17)-C(18)-C(19) | 111.7(4) |
| C(16)-C(18)-C(19) | 131.1(4) |
| C(19A)-C(18)-C(19) | 33.9(5) |
| C(19A)-C(19)-C(20A) | 104.4(19) |
| C(19A)-C(19)-C(20) | 52.1(10) |
| C(20A)-C(19)-C(20) | 52.7(13) |
| C(19A)-C(19)-C(18) | 69.7(10) |
| C(20A)-C(19)-C(18) | 168.5(14) |
| C(20)-C(19)-C(18) | 121.7(6) |
| C(19)-C(19A)-C(20) | 86.1(15) |
| C(19)-C(19A)-C(20A) | 38.9(11) |
| C(20)-C(19A)-C(20A) | 47.5(10) |
| C(19)-C(19A)-C(18) | 76.4(10) |
| C(20)-C(19A)-C(18) | 162.1(14) |
| C(20A)-C(19A)-C(18) | 114.6(12) |
| C(19A)-C(20)-C(20A) | 85.7(17) |
| C(19A)-C(20)-C(19) | 41.8(8) |
| C(20A)-C(20)-C(19) | 44.1(12) |
| C(19)-C(20A)-C(20) | 83(2) |
| C(19)-C(20A)-C(19A) | 36.7(11) |
| C(20)-C(20A)-C(19A) | 46.8(11) |

Symmetry transformations used to generate equivalent atoms:

**Table 4.** Anisotropic displacement parameters ($Å^2 x 10^3$) for str129m. The anisotropic displacement factor exponent takes the form: $-2\pi^2[ h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12} ]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| Fe(1) | 51(1) | 49(1) | 48(1) | -6(1) | 1(1) | -2(1) |
| C(1) | 73(3) | 75(3) | 97(3) | -36(3) | -8(3) | -12(2) |
| C(2) | 110(4) | 89(3) | 64(2) | -31(2) | -2(2) | 8(3) |
| C(3) | 79(3) | 62(2) | 75(2) | -16(2) | 27(2) | -3(2) |
| C(4) | 63(2) | 62(3) | 82(3) | -8(2) | 5(2) | 8(2) |
| C(5) | 91(3) | 45(2) | 90(4) | -5(2) | 23(3) | -2(2) |
| C(6) | 78(3) | 70(3) | 56(2) | -23(2) | -13(2) | 19(2) |
| C(7) | 58(2) | 57(3) | 88(3) | -20(2) | 0(2) | -1(2) |
| C(8) | 76(3) | 63(3) | 67(2) | -3(2) | -7(2) | 10(2) |
| C(9) | 50(2) | 79(3) | 91(3) | -27(2) | -3(2) | -1(2) |
| C(10) | 97(3) | 63(2) | 60(2) | -7(2) | 26(2) | 0(2) |
| C(13) | 62(2) | 49(2) | 68(2) | -11(2) | -11(2) | 13(2) |
| C(14) | 61(2) | 51(3) | 100(3) | 1(2) | 15(2) | -7(2) |
| C(15) | 78(3) | 63(2) | 52(2) | 10(2) | 10(2) | 6(2) |
| C(16) | 88(3) | 66(3) | 64(2) | 17(2) | 18(2) | 8(2) |
| C(17) | 55(2) | 62(2) | 78(2) | -6(2) | 4(2) | -7(2) |
| C(18) | 71(2) | 64(2) | 56(2) | -12(2) | -7(2) | 21(2) |

**Table 5**. Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters (Å$^2$x 10 $^3$) for str129m.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1) | 4375 | 8743 | 4260 | 98 |
| H(2) | 2691 | 6719 | 5301 | 105 |
| H(3) | -1047 | 6093 | 4778 | 86 |
| H(4) | -1648 | 7742 | 3440 | 83 |
| H(5) | 1640 | 9363 | 3098 | 90 |
| H(7) | 233 | 3079 | 3361 | 81 |
| H(8) | 3529 | 3078 | 4235 | 82 |
| H(9) | 6172 | 4969 | 3509 | 88 |
| H(10) | 4435 | 6152 | 2200 | 88 |
| H(14) | 292 | 6380 | -383 | 84 |
| H(15) | -4038 | 3823 | 991 | 77 |
| H(16) | -1941 | 6330 | -1539 | 87 |
| H(17) | -6228 | 3720 | -195 | 78 |

**Table 6**.  Torsion angles [°] for str129m.

| | |
|---|---|
| C(7)-Fe(1)-C(1)-C(2) | -42.1(12) |
| C(10)-Fe(1)-C(1)-C(2) | -152.2(3) |
| C(3)-Fe(1)-C(1)-C(2) | 38.0(3) |
| C(8)-Fe(1)-C(1)-C(2) | -69.4(4) |
| C(5)-Fe(1)-C(1)-C(2) | 118.4(5) |
| C(9)-Fe(1)-C(1)-C(2) | -109.3(3) |
| C(4)-Fe(1)-C(1)-C(2) | 81.1(3) |
| C(6)-Fe(1)-C(1)-C(2) | 172.3(3) |
| C(2)-Fe(1)-C(1)-C(5) | -118.4(5) |
| C(7)-Fe(1)-C(1)-C(5) | -160.5(9) |
| C(10)-Fe(1)-C(1)-C(5) | 89.4(4) |
| C(3)-Fe(1)-C(1)-C(5) | -80.4(3) |
| C(8)-Fe(1)-C(1)-C(5) | 172.1(3) |
| C(9)-Fe(1)-C(1)-C(5) | 132.3(3) |
| C(4)-Fe(1)-C(1)-C(5) | -37.3(3) |
| C(6)-Fe(1)-C(1)-C(5) | 53.8(5) |
| C(5)-C(1)-C(2)-C(3) | 0.1(5) |
| Fe(1)-C(1)-C(2)-C(3) | -59.7(3) |
| C(5)-C(1)-C(2)-Fe(1) | 59.8(3) |
| C(7)-Fe(1)-C(2)-C(1) | 170.4(3) |
| C(10)-Fe(1)-C(2)-C(1) | 54.4(6) |
| C(3)-Fe(1)-C(2)-C(1) | -119.1(5) |
| C(8)-Fe(1)-C(2)-C(1) | 131.6(3) |
| C(5)-Fe(1)-C(2)-C(1) | -38.4(3) |
| C(9)-Fe(1)-C(2)-C(1) | 88.7(4) |
| C(4)-Fe(1)-C(2)-C(1) | -81.6(3) |
| C(6)-Fe(1)-C(2)-C(1) | -160.1(9) |
| C(7)-Fe(1)-C(2)-C(3) | -70.5(4) |
| C(10)-Fe(1)-C(2)-C(3) | 173.5(3) |
| C(1)-Fe(1)-C(2)-C(3) | 119.1(5) |
| C(8)-Fe(1)-C(2)-C(3) | -109.3(3) |
| C(5)-Fe(1)-C(2)-C(3) | 80.7(3) |
| C(9)-Fe(1)-C(2)-C(3) | -152.2(3) |
| C(4)-Fe(1)-C(2)-C(3) | 37.5(3) |
| C(6)-Fe(1)-C(2)-C(3) | -41.0(12) |
| C(1)-C(2)-C(3)-C(4) | -0.3(5) |
| Fe(1)-C(2)-C(3)-C(4) | -60.0(3) |
| C(1)-C(2)-C(3)-Fe(1) | 59.7(3) |
| C(2)-Fe(1)-C(3)-C(4) | 118.6(4) |
| C(7)-Fe(1)-C(3)-C(4) | -110.4(3) |
| C(10)-Fe(1)-C(3)-C(4) | -43.7(10) |
| C(1)-Fe(1)-C(3)-C(4) | 80.9(3) |
| C(8)-Fe(1)-C(3)-C(4) | -152.9(3) |
| C(5)-Fe(1)-C(3)-C(4) | 36.5(3) |
| C(9)-Fe(1)-C(3)-C(4) | 173.1(3) |
| C(6)-Fe(1)-C(3)-C(4) | -71.2(3) |
| C(7)-Fe(1)-C(3)-C(2) | 131.0(3) |
| C(10)-Fe(1)-C(3)-C(2) | -162.3(9) |
| C(1)-Fe(1)-C(3)-C(2) | -37.7(3) |
| C(8)-Fe(1)-C(3)-C(2) | 88.5(3) |
| C(5)-Fe(1)-C(3)-C(2) | -82.1(4) |
| C(9)-Fe(1)-C(3)-C(2) | 54.5(5) |
| C(4)-Fe(1)-C(3)-C(2) | -118.6(4) |
| C(6)-Fe(1)-C(3)-C(2) | 170.2(3) |
| C(2)-C(3)-C(4)-C(5) | 0.4(5) |
| Fe(1)-C(3)-C(4)-C(5) | -58.9(3) |
| C(2)-C(3)-C(4)-Fe(1) | 59.3(3) |
| C(2)-Fe(1)-C(4)-C(3) | -38.5(3) |
| C(7)-Fe(1)-C(4)-C(3) | 87.2(3) |
| C(10)-Fe(1)-C(4)-C(3) | 169.9(3) |
| C(1)-Fe(1)-C(4)-C(3) | -82.5(3) |
| C(8)-Fe(1)-C(4)-C(3) | 51.7(4) |
| C(5)-Fe(1)-C(4)-C(3) | -120.9(4) |
| C(9)-Fe(1)-C(4)-C(3) | -159.4(9) |
| C(6)-Fe(1)-C(4)-C(3) | 129.6(3) |
| C(2)-Fe(1)-C(4)-C(5) | 82.4(3) |
| C(7)-Fe(1)-C(4)-C(5) | -151.9(3) |
| C(10)-Fe(1)-C(4)-C(5) | -69.3(4) |
| C(1)-Fe(1)-C(4)-C(5) | 38.3(3) |
| C(3)-Fe(1)-C(4)-C(5) | 120.9(4) |
| C(8)-Fe(1)-C(4)-C(5) | 172.5(4) |
| C(9)-Fe(1)-C(4)-C(5) | -38.5(11) |
| C(6)-Fe(1)-C(4)-C(5) | -109.5(3) |
| C(3)-C(4)-C(5)-C(1) | -0.3(5) |

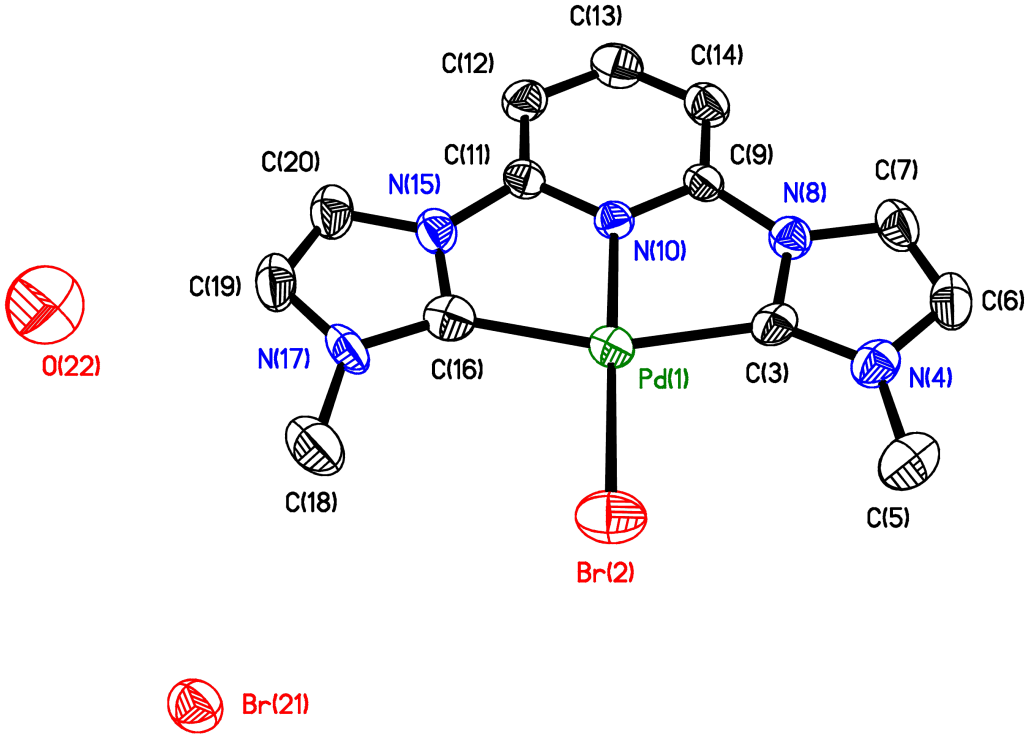
|  |  |  |  |
|---|---|---|---|
| Fe(1)-C(4)-C(5)-C(1) | -59.1(3) | C(7)-Fe(1)-C(6)-C(11) | 105.8(5) |
| C(3)-C(4)-C(5)-Fe(1) | 58.8(3) | C(10)-Fe(1)-C(6)-C(11) | -136.4(6) |
| C(2)-C(1)-C(5)-C(4) | 0.1(6) | C(1)-Fe(1)-C(6)-C(11) | -83.8(6) |
| Fe(1)-C(1)-C(5)-C(4) | 59.7(3) | C(3)-Fe(1)-C(6)-C(11) | 35.8(6) |
| C(2)-C(1)-C(5)-Fe(1) | -59.6(3) | C(8)-Fe(1)-C(6)-C(11) | 142.3(5) |
| C(2)-Fe(1)-C(5)-C(4) | -80.8(3) | C(5)-Fe(1)-C(6)-C(11) | -47.2(5) |
| C(7)-Fe(1)-C(5)-C(4) | 54.1(5) | C(9)-Fe(1)-C(6)-C(11) | -174.0(5) |
| C(10)-Fe(1)-C(5)-C(4) | 132.0(3) | C(4)-Fe(1)-C(6)-C(11) | -4.3(5) |
| C(1)-Fe(1)-C(5)-C(4) | -118.9(4) | C(2)-Fe(1)-C(6)-C(11A) | 118.5(12) |
| C(3)-Fe(1)-C(5)-C(4) | -36.5(3) | C(7)-Fe(1)-C(6)-C(11A) | 154.4(7) |
| C(8)-Fe(1)-C(5)-C(4) | -156.5(10) | C(10)-Fe(1)-C(6)-C(11A) | -87.9(7) |
| C(9)-Fe(1)-C(5)-C(4) | 171.6(2) | C(1)-Fe(1)-C(6)-C(11A) | -35.2(8) |
| C(6)-Fe(1)-C(5)-C(4) | 88.2(3) | C(3)-Fe(1)-C(6)-C(11A) | 84.4(7) |
| C(2)-Fe(1)-C(5)-C(1) | 38.1(3) | C(8)-Fe(1)-C(6)-C(11A) | -169.1(7) |
| C(7)-Fe(1)-C(5)-C(1) | 173.0(3) | C(5)-Fe(1)-C(6)-C(11A) | 1.4(7) |
| C(10)-Fe(1)-C(5)-C(1) | -109.1(3) | C(9)-Fe(1)-C(6)-C(11A) | -125.5(6) |
| C(3)-Fe(1)-C(5)-C(1) | 82.4(3) | C(4)-Fe(1)-C(6)-C(11A) | 44.3(6) |
| C(8)-Fe(1)-C(5)-C(1) | -37.6(12) | C(10)-C(6)-C(7)-C(8) | -1.1(5) |
| C(9)-Fe(1)-C(5)-C(1) | -69.5(4) | C(11)-C(6)-C(7)-C(8) | 174.9(4) |
| C(4)-Fe(1)-C(5)-C(1) | 118.9(4) | C(11A)-C(6)-C(7)-C(8) | 170.2(10) |
| C(6)-Fe(1)-C(5)-C(1) | -152.9(3) | Fe(1)-C(6)-C(7)-C(8) | -60.1(3) |
| C(2)-Fe(1)-C(6)-C(7) | -35.8(11) | C(10)-C(6)-C(7)-Fe(1) | 59.0(3) |
| C(10)-Fe(1)-C(6)-C(7) | 117.8(4) | C(11)-C(6)-C(7)-Fe(1) | -125.0(3) |
| C(1)-Fe(1)-C(6)-C(7) | 170.4(4) | C(11A)-C(6)-C(7)-Fe(1) | -129.8(11) |
| C(3)-Fe(1)-C(6)-C(7) | -70.0(3) | C(2)-Fe(1)-C(7)-C(8) | -68.2(4) |
| C(8)-Fe(1)-C(6)-C(7) | 36.6(3) | C(10)-Fe(1)-C(7)-C(8) | 81.9(3) |
| C(5)-Fe(1)-C(6)-C(7) | -153.0(2) | C(1)-Fe(1)-C(7)-C(8) | -32.9(12) |
| C(9)-Fe(1)-C(6)-C(7) | 80.2(3) | C(3)-Fe(1)-C(7)-C(8) | -109.1(3) |
| C(4)-Fe(1)-C(6)-C(7) | -110.1(3) | C(5)-Fe(1)-C(7)-C(8) | 172.2(3) |
| C(2)-Fe(1)-C(6)-C(10) | -153.6(10) | C(9)-Fe(1)-C(7)-C(8) | 38.2(3) |
| C(7)-Fe(1)-C(6)-C(10) | -117.8(4) | C(4)-Fe(1)-C(7)-C(8) | -151.8(3) |
| C(1)-Fe(1)-C(6)-C(10) | 52.6(5) | C(6)-Fe(1)-C(7)-C(8) | 120.7(4) |
| C(3)-Fe(1)-C(6)-C(10) | 172.2(3) | C(2)-Fe(1)-C(7)-C(6) | 171.2(3) |
| C(8)-Fe(1)-C(6)-C(10) | -81.2(3) | C(10)-Fe(1)-C(7)-C(6) | -38.8(3) |
| C(5)-Fe(1)-C(6)-C(10) | 89.2(3) | C(1)-Fe(1)-C(7)-C(6) | -153.6(10) |
| C(9)-Fe(1)-C(6)-C(10) | -37.6(3) | C(3)-Fe(1)-C(7)-C(6) | 130.3(3) |
| C(4)-Fe(1)-C(6)-C(10) | 132.1(3) | C(8)-Fe(1)-C(7)-C(6) | -120.7(4) |
| C(2)-Fe(1)-C(6)-C(11) | 70.0(12) | C(5)-Fe(1)-C(7)-C(6) | 51.6(4) |

| | |
|---|---|
| C(9)-Fe(1)-C(7)-C(6) | -82.4(3) |
| C(4)-Fe(1)-C(7)-C(6) | 87.5(3) |
| C(6)-C(7)-C(8)-C(9) | 0.4(5) |
| Fe(1)-C(7)-C(8)-C(9) | -60.2(3) |
| C(6)-C(7)-C(8)-Fe(1) | 60.5(3) |
| C(2)-Fe(1)-C(8)-C(7) | 132.1(3) |
| C(10)-Fe(1)-C(8)-C(7) | -80.6(3) |
| C(1)-Fe(1)-C(8)-C(7) | 172.2(3) |
| C(3)-Fe(1)-C(8)-C(7) | 88.2(3) |
| C(5)-Fe(1)-C(8)-C(7) | -155.7(10) |
| C(9)-Fe(1)-C(8)-C(7) | -118.1(4) |
| C(4)-Fe(1)-C(8)-C(7) | 53.9(5) |
| C(6)-Fe(1)-C(8)-C(7) | -36.4(3) |
| C(2)-Fe(1)-C(8)-C(9) | -109.8(3) |
| C(7)-Fe(1)-C(8)-C(9) | 118.1(4) |
| C(10)-Fe(1)-C(8)-C(9) | 37.5(2) |
| C(1)-Fe(1)-C(8)-C(9) | -69.7(4) |
| C(3)-Fe(1)-C(8)-C(9) | -153.7(3) |
| C(5)-Fe(1)-C(8)-C(9) | -37.6(12) |
| C(4)-Fe(1)-C(8)-C(9) | 172.0(3) |
| C(6)-Fe(1)-C(8)-C(9) | 81.7(3) |
| C(7)-C(8)-C(9)-C(10) | 0.5(5) |
| Fe(1)-C(8)-C(9)-C(10) | -59.5(3) |
| C(7)-C(8)-C(9)-Fe(1) | 60.0(3) |
| C(2)-Fe(1)-C(9)-C(10) | -153.4(3) |
| C(7)-Fe(1)-C(9)-C(10) | 81.2(3) |
| C(1)-Fe(1)-C(9)-C(10) | -109.7(3) |
| C(3)-Fe(1)-C(9)-C(10) | 169.8(3) |
| C(8)-Fe(1)-C(9)-C(10) | 119.0(4) |
| C(5)-Fe(1)-C(9)-C(10) | -69.0(4) |
| C(4)-Fe(1)-C(9)-C(10) | -36.5(11) |
| C(6)-Fe(1)-C(9)-C(10) | 38.2(3) |
| C(2)-Fe(1)-C(9)-C(8) | 87.6(3) |
| C(7)-Fe(1)-C(9)-C(8) | -37.8(3) |
| C(10)-Fe(1)-C(9)-C(8) | -119.0(4) |
| C(1)-Fe(1)-C(9)-C(8) | 131.3(3) |
| C(3)-Fe(1)-C(9)-C(8) | 50.8(4) |
| C(5)-Fe(1)-C(9)-C(8) | 172.0(3) |
| C(4)-Fe(1)-C(9)-C(8) | -155.5(9) |
| C(6)-Fe(1)-C(9)-C(8) | -80.8(3) |
| C(8)-C(9)-C(10)-C(6) | -1.2(5) |
| Fe(1)-C(9)-C(10)-C(6) | -60.9(3) |
| C(8)-C(9)-C(10)-Fe(1) | 59.7(3) |
| C(7)-C(6)-C(10)-C(9) | 1.4(4) |
| C(11)-C(6)-C(10)-C(9) | -173.1(5) |
| C(11A)-C(6)-C(10)-C(9) | -174.6(5) |
| Fe(1)-C(6)-C(10)-C(9) | 60.6(3) |
| C(7)-C(6)-C(10)-Fe(1) | -59.3(3) |
| C(11)-C(6)-C(10)-Fe(1) | 126.3(5) |
| C(11A)-C(6)-C(10)-Fe(1) | 124.8(4) |
| C(2)-Fe(1)-C(10)-C(9) | 51.4(5) |
| C(7)-Fe(1)-C(10)-C(9) | -80.9(3) |
| C(1)-Fe(1)-C(10)-C(9) | 88.1(3) |
| C(3)-Fe(1)-C(10)-C(9) | -151.5(9) |
| C(8)-Fe(1)-C(10)-C(9) | -37.6(3) |
| C(5)-Fe(1)-C(10)-C(9) | 132.4(3) |
| C(4)-Fe(1)-C(10)-C(9) | 172.0(3) |
| C(6)-Fe(1)-C(10)-C(9) | -118.6(4) |
| C(2)-Fe(1)-C(10)-C(6) | 170.0(4) |
| C(7)-Fe(1)-C(10)-C(6) | 37.7(3) |
| C(1)-Fe(1)-C(10)-C(6) | -153.3(3) |
| C(3)-Fe(1)-C(10)-C(6) | -32.9(10) |
| C(8)-Fe(1)-C(10)-C(6) | 81.0(3) |
| C(5)-Fe(1)-C(10)-C(6) | -109.1(3) |
| C(9)-Fe(1)-C(10)-C(6) | 118.6(4) |
| C(4)-Fe(1)-C(10)-C(6) | -69.4(3) |
| C(7)-C(6)-C(11)-C(12A) | -145(3) |
| C(10)-C(6)-C(11)-C(12A) | 29(3) |
| C(11A)-C(6)-C(11)-C(12A) | 32(3) |
| Fe(1)-C(6)-C(11)-C(12A) | 132(3) |
| C(7)-C(6)-C(11)-C(11A) | -176.5(7) |
| C(10)-C(6)-C(11)-C(11A) | -2.4(9) |
| Fe(1)-C(6)-C(11)-C(11A) | 100.7(8) |
| C(7)-C(6)-C(11)-C(12) | -166.0(5) |
| C(10)-C(6)-C(11)-C(12) | 8.2(8) |
| C(11A)-C(6)-C(11)-C(12) | 10.5(7) |

|  |  |  |  |
|---|---|---|---|
| Fe(1)-C(6)-C(11)-C(12) | 111.2(5) | C(6)-C(11)-C(12A)-C(13) | -42(7) |
| C(12A)-C(11)-C(11A)-C(12) | -1.4(10) | C(11A)-C(12)-C(12A)-C(11) | -1.6(12) |
| C(6)-C(11)-C(11A)-C(12) | 167.9(8) | C(13)-C(12)-C(12A)-C(11) | -176.1(11) |
| C(12)-C(11)-C(11A)-C(12A) | 1.4(11) | C(11)-C(12)-C(12A)-C(11A) | 1.6(12) |
| C(6)-C(11)-C(11A)-C(12A) | 169.3(9) | C(13)-C(12)-C(12A)-C(11A) | -174.5(8) |
| C(12A)-C(11)-C(11A)-C(6) | -169.3(9) | C(11A)-C(12)-C(12A)-C(13) | 174.5(8) |
| C(12)-C(11)-C(11A)-C(6) | -167.9(8) | C(11)-C(12)-C(12A)-C(13) | 176.1(11) |
| C(7)-C(6)-C(11A)-C(12) | -17(3) | C(12)-C(11A)-C(12A)-C(11) | 177.9(16) |
| C(10)-C(6)-C(11A)-C(12) | 154.5(19) | C(6)-C(11A)-C(12A)-C(11) | 10.6(9) |
| C(11)-C(6)-C(11A)-C(12) | -23.9(16) | C(11)-C(11A)-C(12A)-C(12) | -177.9(16) |
| Fe(1)-C(6)-C(11A)-C(12) | -134.2(18) | C(6)-C(11A)-C(12A)-C(12) | -167.3(12) |
| C(7)-C(6)-C(11A)-C(11) | 7.0(15) | C(12)-C(11A)-C(12A)-C(13) | -5.6(8) |
| C(10)-C(6)-C(11A)-C(11) | 178.4(6) | C(11)-C(11A)-C(12A)-C(13) | 176.6(14) |
| Fe(1)-C(6)-C(11A)-C(11) | -110.3(7) | C(6)-C(11A)-C(12A)-C(13) | -172.8(6) |
| C(7)-C(6)-C(11A)-C(12A) | -0.4(17) | C(12A)-C(12)-C(13)-C(15) | 1.2(10) |
| C(10)-C(6)-C(11A)-C(12A) | 171.1(8) | C(11A)-C(12)-C(13)-C(15) | -29(5) |
| C(11)-C(6)-C(11A)-C(12A) | -7.3(6) | C(11)-C(12)-C(13)-C(15) | -1.7(8) |
| Fe(1)-C(6)-C(11A)-C(12A) | -117.6(8) | C(12A)-C(12)-C(13)-C(14) | -175.6(8) |
| C(11)-C(11A)-C(12)-C(12A) | 1.4(10) | C(11A)-C(12)-C(13)-C(14) | 154(5) |
| C(6)-C(11A)-C(12)-C(12A) | 24(2) | C(11)-C(12)-C(13)-C(14) | -178.5(5) |
| C(12A)-C(11A)-C(12)-C(11) | -1.4(10) | C(11A)-C(12)-C(13)-C(12A) | -30(4) |
| C(6)-C(11A)-C(12)-C(11) | 22.5(15) | C(11)-C(12)-C(13)-C(12A) | -2.9(8) |
| C(11)-C(11A)-C(12)-C(13) | 31(5) | C(11)-C(12A)-C(13)-C(15) | -164(5) |
| C(12A)-C(11A)-C(12)-C(13) | 30(4) | C(12)-C(12A)-C(13)-C(15) | -179.1(8) |
| C(6)-C(11A)-C(12)-C(13) | 54(6) | C(11A)-C(12A)-C(13)-C(15) | -174.5(9) |
| C(11A)-C(11)-C(12)-C(12A) | -177.8(16) | C(11)-C(12A)-C(13)-C(14) | 22(5) |
| C(6)-C(11)-C(12)-C(12A) | 168.8(14) | C(12)-C(12A)-C(13)-C(14) | 7.0(13) |
| C(12A)-C(11)-C(12)-C(11A) | 177.8(16) | C(11A)-C(12A)-C(13)-C(14) | 11.6(15) |
| C(6)-C(11)-C(12)-C(11A) | -13.4(9) | C(11)-C(12A)-C(13)-C(12) | 15(4) |
| C(12A)-C(11)-C(12)-C(13) | 4.5(12) | C(11A)-C(12A)-C(13)-C(12) | 4.6(7) |
| C(11A)-C(11)-C(12)-C(13) | -173.3(10) | C(15)-C(13)-C(14)-C(16) | 1.9(6) |
| C(6)-C(11)-C(12)-C(13) | 173.3(4) | C(12)-C(13)-C(14)-C(16) | 179.2(4) |
| C(11A)-C(11)-C(12A)-C(12) | 1.6(12) | C(12A)-C(13)-C(14)-C(16) | 175.2(8) |
| C(6)-C(11)-C(12A)-C(12) | -28(3) | C(14)-C(13)-C(15)-C(17) | -0.9(6) |
| C(12)-C(11)-C(12A)-C(11A) | -1.6(12) | C(12)-C(13)-C(15)-C(17) | -177.6(4) |
| C(6)-C(11)-C(12A)-C(11A) | -30(3) | C(12A)-C(13)-C(15)-C(17) | -177.0(5) |
| C(11A)-C(11)-C(12A)-C(13) | -12(5) | C(13)-C(14)-C(16)-C(18) | -1.2(7) |
| C(12)-C(11)-C(12A)-C(13) | -14(4) | C(13)-C(15)-C(17)-C(18) | -0.7(7) |

| | |
|---|---|
| C(15)-C(17)-C(18)-C(16) | 1.5(6) |
| C(15)-C(17)-C(18)-C(19A) | -168.4(9) |
| C(15)-C(17)-C(18)-C(19) | -179.3(4) |
| C(14)-C(16)-C(18)-C(17) | -0.5(6) |
| C(14)-C(16)-C(18)-C(19A) | 173.6(6) |
| C(14)-C(16)-C(18)-C(19) | -179.6(5) |
| C(17)-C(18)-C(19)-C(19A) | 168.7(9) |
| C(16)-C(18)-C(19)-C(19A) | -12.3(11) |
| C(17)-C(18)-C(19)-C(20A) | 108(7) |
| C(16)-C(18)-C(19)-C(20A) | -73(7) |
| C(19A)-C(18)-C(19)-C(20A) | -61(7) |
| C(17)-C(18)-C(19)-C(20) | 165.1(6) |
| C(16)-C(18)-C(19)-C(20) | -15.9(9) |
| C(19A)-C(18)-C(19)-C(20) | -3.6(9) |
| C(20A)-C(19)-C(19A)-C(20) | -6.4(16) |
| C(18)-C(19)-C(19A)-C(20) | -176.1(10) |
| C(20)-C(19)-C(19A)-C(20A) | 6.4(16) |
| C(18)-C(19)-C(19A)-C(20A) | -169.7(13) |
| C(20A)-C(19)-C(19A)-C(18) | 169.7(13) |
| C(20)-C(19)-C(19A)-C(18) | 176.1(10) |
| C(17)-C(18)-C(19A)-C(19) | -18.4(15) |
| C(16)-C(18)-C(19A)-C(19) | 170.7(8) |
| C(17)-C(18)-C(19A)-C(20) | -6(5) |
| C(16)-C(18)-C(19A)-C(20) | -177(4) |
| C(19)-C(18)-C(19A)-C(20) | 13(3) |
| C(17)-C(18)-C(19A)-C(20A) | -11.3(17) |
| C(16)-C(18)-C(19A)-C(20A) | 177.8(11) |
| C(19)-C(18)-C(19A)-C(20A) | 7.1(9) |
| C(19)-C(19A)-C(20)-C(20A) | 5.5(14) |
| C(18)-C(19A)-C(20)-C(20A) | -7(4) |
| C(20A)-C(19A)-C(20)-C(19) | -5.5(14) |
| C(18)-C(19A)-C(20)-C(19) | -12(3) |
| C(20A)-C(19)-C(20)-C(19A) | 172(2) |
| C(18)-C(19)-C(20)-C(19A) | 4.3(11) |
| C(19A)-C(19)-C(20)-C(20A) | -172(2) |
| C(18)-C(19)-C(20)-C(20A) | -167.9(16) |
| C(19A)-C(19)-C(20A)-C(20) | 6.4(16) |
| C(18)-C(19)-C(20A)-C(20) | 64(8) |
| C(20)-C(19)-C(20A)-C(19A) | -6.4(16) |
| C(18)-C(19)-C(20A)-C(19A) | 58(7) |
| C(19A)-C(20)-C(20A)-C(19) | -5.2(13) |
| C(19)-C(20)-C(20A)-C(19A) | 5.2(13) |
| C(20)-C(19A)-C(20A)-C(19) | 171(2) |
| C(18)-C(19A)-C(20A)-C(19) | -11.0(14) |
| C(19)-C(19A)-C(20A)-C(20) | -171(2) |
| C(18)-C(19A)-C(20A)-C(20) | 177.7(14) |

Symmetry transformations used to generate equivalent atoms:


C(13)
C(12)
C(14)
C(11)
C(9)
C(20)
N(15)
C(7)
N(8)
N(10)
C(19)
C(6)
O(22)
N(17)
C(16)
Pd(1)
C(3)
N(4)
C(18)
C(5)
Br(2)
Br(21)

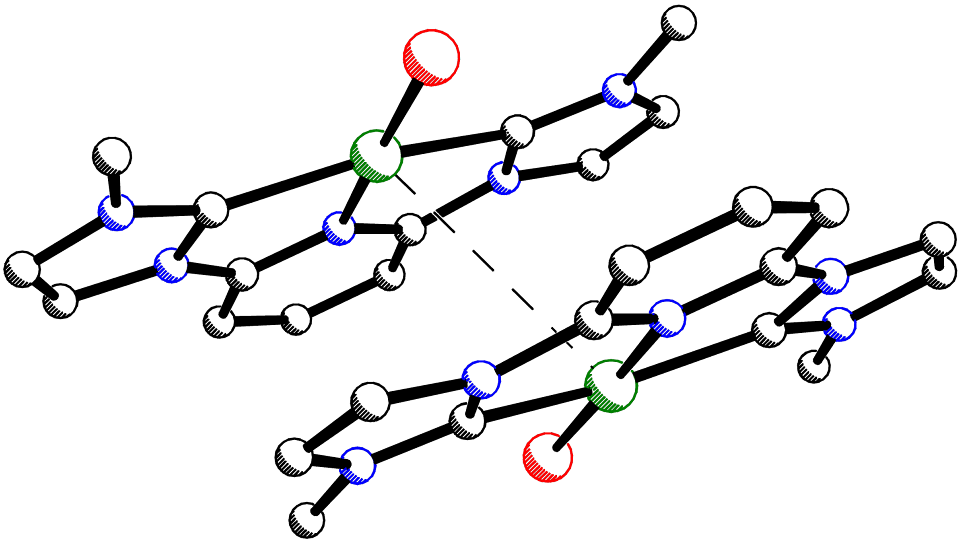


**Table 1**. Crystal data and structure refinement for str132m.

| | | |
|---|---|---|
| Identification code | str132m | |
| Empirical formula | C11 H7 Br2 N5 Pd . H2O | |
| Formula weight | 493.45 | |
| Temperature | 293(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | P2(1)/n | |
| Unit cell dimensions | a = 8.7782(4) Å | $\alpha$= 90°. |
| | b = 14.3181(6) Å | $\beta$= 107.1600(10)°. |
| | c = 13.5684(6) Å | $\gamma$ = 90°. |
| Volume | 1629.46(12) Å$^3$ | |
| Z | 4 | |
| Density (calculated) | 2.011 Mg/m$^3$ | |
| Absorption coefficient | 6.044 mm$^{-1}$ | |
| F(000) | 936 | |
| Crystal size | 0.45 x 0.17 x 0.16 mm$^3$ | |
| Theta range for data collection | 2.12 to 19.78°. | |
| Index ranges | -8<=h<=8, -13<=k<=13, -10<=l<=12 | |
| Reflections collected | 5300 | |
| Independent reflections | 1467 [R(int) = 0.0310] | |
| Completeness to theta = 19.78° | 99.9 % | |
| Absorption correction | Bruker SADABS | |
| Max. and min. transmission | 1.954948 and 0.964859 | |
| Refinement method | Full-matrix least-squares on F$^2$ | |
| Data / restraints / parameters | 1467 / 0 / 194 | |
| Goodness-of-fit on F$^2$ | 0.776 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0225, wR2 = 0.0600 | |
| R indices (all data) | R1 = 0.0259, wR2 = 0.0616 | |
| Largest diff. peak and hole | 0.549 and -0.326 e.Å$^{-3}$ | |

**Table 2**. Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) for str132m. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| Pd(1) | 2114(1) | 4531(1) | 5596(1) | 29(1) |
| Br(2) | 1315(1) | 3607(1) | 6843(1) | 50(1) |
| C(3) | 818(6) | 3906(4) | 4267(4) | 30(1) |
| N(4) | -245(5) | 3244(3) | 3863(4) | 35(1) |
| C(5) | -866(7) | 2553(4) | 4441(5) | 49(2) |
| C(6) | -659(7) | 3253(4) | 2791(5) | 42(2) |
| C(7) | 143(7) | 3935(4) | 2509(4) | 39(2) |
| N(8) | 1067(5) | 4343(3) | 3418(3) | 30(1) |
| C(9) | 2108(6) | 5105(4) | 3566(4) | 27(1) |
| N(10) | 2733(5) | 5288(3) | 4556(3) | 26(1) |
| C(11) | 3769(6) | 5994(4) | 4873(4) | 28(1) |
| C(12) | 4199(7) | 6554(4) | 4178(5) | 37(2) |
| C(13) | 3525(7) | 6349(4) | 3140(5) | 41(2) |
| C(14) | 2466(7) | 5621(4) | 2820(4) | 37(2) |
| N(15) | 4274(5) | 6064(3) | 5957(3) | 32(1) |
| C(16) | 3680(6) | 5441(4) | 6535(5) | 33(1) |
| N(17) | 4420(6) | 5688(3) | 7505(3) | 36(1) |
| C(18) | 4192(8) | 5222(5) | 8410(4) | 55(2) |
| C(19) | 5440(7) | 6436(4) | 7541(5) | 43(2) |
| C(20) | 5342(7) | 6675(4) | 6584(5) | 41(2) |
| Br(21) | 1976(1) | 6435(1) | 10228(1) | 49(1) |
| O(22) | 8106(6) | 5945(4) | 9783(4) | 83(2) |

**Table 3**. Bond lengths [Å] and angles [°] for str132m.

| | |
|---|---|
| Pd(1)-N(10) | 1.979(4) |
| Pd(1)-C(3) | 2.033(6) |
| Pd(1)-C(16) | 2.044(6) |
| Pd(1)-Br(2) | 2.4099(7) |
| C(3)-N(4) | 1.330(7) |
| C(3)-N(8) | 1.384(7) |
| N(4)-C(6) | 1.392(8) |
| N(4)-C(5) | 1.464(7) |
| C(6)-C(7) | 1.324(8) |
| C(7)-N(8) | 1.389(7) |
| N(8)-C(9) | 1.399(7) |
| C(9)-N(10) | 1.319(6) |
| C(9)-C(14) | 1.362(7) |
| N(10)-C(11) | 1.342(7) |
| C(11)-C(12) | 1.374(7) |
| C(11)-N(15) | 1.409(7) |
| C(12)-C(13) | 1.389(8) |
| C(13)-C(14) | 1.379(8) |
| N(15)-C(20) | 1.377(7) |
| N(15)-C(16) | 1.387(6) |
| C(16)-N(17) | 1.333(7) |
| N(17)-C(19) | 1.387(7) |
| N(17)-C(18) | 1.463(7) |
| C(19)-C(20) | 1.321(8) |
| N(10)-Pd(1)-C(3) | 78.9(2) |
| N(10)-Pd(1)-C(16) | 79.6(2) |
| C(3)-Pd(1)-C(16) | 158.5(2) |
| N(10)-Pd(1)-Br(2) | 179.03(13) |
| C(3)-Pd(1)-Br(2) | 100.29(16) |
| C(16)-Pd(1)-Br(2) | 101.18(16) |
| N(4)-C(3)-N(8) | 104.0(4) |
| N(4)-C(3)-Pd(1) | 145.1(4) |
| N(8)-C(3)-Pd(1) | 110.8(4) |
| C(3)-N(4)-C(6) | 111.0(5) |
| C(3)-N(4)-C(5) | 126.1(5) |
| C(6)-N(4)-C(5) | 122.8(5) |
| C(7)-C(6)-N(4) | 108.2(5) |
| C(6)-C(7)-N(8) | 106.0(5) |
| C(3)-N(8)-C(7) | 110.8(4) |
| C(3)-N(8)-C(9) | 119.3(5) |
| C(7)-N(8)-C(9) | 129.9(5) |
| N(10)-C(9)-C(14) | 122.1(5) |
| N(10)-C(9)-N(8) | 111.0(5) |
| C(14)-C(9)-N(8) | 126.9(5) |
| C(9)-N(10)-C(11) | 121.0(4) |
| C(9)-N(10)-Pd(1) | 119.9(4) |
| C(11)-N(10)-Pd(1) | 119.1(4) |
| N(10)-C(11)-C(12) | 121.2(5) |
| N(10)-C(11)-N(15) | 111.3(5) |
| C(12)-C(11)-N(15) | 127.5(5) |
| C(11)-C(12)-C(13) | 116.8(5) |
| C(14)-C(13)-C(12) | 121.7(5) |
| C(9)-C(14)-C(13) | 117.3(5) |
| C(20)-N(15)-C(16) | 111.2(5) |
| C(20)-N(15)-C(11) | 129.6(5) |
| C(16)-N(15)-C(11) | 119.3(5) |
| N(17)-C(16)-N(15) | 103.4(5) |
| N(17)-C(16)-Pd(1) | 145.9(4) |
| N(15)-C(16)-Pd(1) | 110.7(4) |
| C(16)-N(17)-C(19) | 111.2(5) |
| C(16)-N(17)-C(18) | 124.0(5) |
| C(19)-N(17)-C(18) | 124.8(5) |
| C(20)-C(19)-N(17) | 108.1(5) |
| C(19)-C(20)-N(15) | 106.1(5) |

Symmetry transformations used to generate equivalent atoms:

**Table 4**. Anisotropic displacement parameters ($Å^2$x $10^3$) for str132m. The anisotropic displacement factor exponent takes the form: $-2\pi^2$[ $h^2$ $a^{*2}U^{11}$ + ... + 2 h k a* b* $U^{12}$ ]

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| Pd(1) | 29(1) | 31(1) | 27(1) | 2(1) | 9(1) | 5(1) |
| Br(2) | 52(1) | 52(1) | 49(1) | 18(1) | 22(1) | 10(1) |
| C(3) | 19(3) | 29(3) | 43(4) | -2(3) | 10(3) | 6(3) |
| N(4) | 27(3) | 32(3) | 46(4) | -1(3) | 11(3) | 2(2) |
| C(5) | 40(4) | 41(4) | 67(4) | 3(3) | 18(3) | -2(3) |
| C(6) | 31(4) | 42(4) | 47(5) | -17(3) | 2(3) | 3(3) |
| C(7) | 40(4) | 47(4) | 27(4) | -7(3) | 3(3) | 4(3) |
| N(8) | 29(3) | 31(3) | 28(3) | 0(3) | 8(3) | 1(2) |
| C(9) | 24(3) | 34(3) | 22(4) | -1(3) | 7(3) | 4(3) |
| N(10) | 24(3) | 30(3) | 22(3) | 2(2) | 7(2) | 1(2) |
| C(11) | 28(3) | 27(3) | 31(4) | -3(3) | 10(3) | 3(3) |
| C(12) | 38(4) | 33(3) | 46(5) | -6(3) | 19(3) | -6(3) |
| C(13) | 45(4) | 42(4) | 37(5) | 7(3) | 16(3) | 8(3) |
| C(14) | 38(4) | 45(4) | 29(4) | -1(3) | 9(3) | 4(3) |
| N(15) | 32(3) | 33(3) | 30(3) | -6(3) | 7(3) | 2(2) |
| C(16) | 30(3) | 35(3) | 34(4) | 8(3) | 9(3) | 12(3) |
| N(17) | 40(3) | 50(3) | 17(3) | -4(2) | 5(3) | 9(3) |
| C(18) | 57(5) | 73(5) | 34(4) | -4(3) | 13(3) | 10(4) |
| C(19) | 37(4) | 45(4) | 41(5) | -17(3) | 2(3) | 2(3) |
| C(20) | 39(4) | 36(4) | 42(5) | -10(3) | 5(3) | 0(3) |
| Br(21) | 48(1) | 57(1) | 42(1) | 4(1) | 13(1) | 3(1) |

**Table 5**. Hydrogen coordinates ( x 10$^4$) and isotropic displacement parameters (Å$^2$x 10 $^3$) for str132m.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(5A) | -1622 | 2158 | 3967 | 73 |
| H(5B) | -1380 | 2867 | 4881 | 73 |
| H(5C) | -3 | 2180 | 4853 | 73 |
| H(6) | -1374 | 2850 | 2349 | 50 |
| H(7) | 98 | 4105 | 1840 | 47 |
| H(12) | 4909 | 7047 | 4392 | 45 |
| H(13) | 3793 | 6712 | 2647 | 49 |
| H(14) | 2015 | 5487 | 2124 | 45 |
| H(18A) | 4848 | 5516 | 9025 | 82 |
| H(18B) | 4485 | 4576 | 8407 | 82 |
| H(18C) | 3093 | 5267 | 8392 | 82 |
| H(19) | 6080 | 6720 | 8135 | 52 |
| H(20) | 5885 | 7158 | 6375 | 49 |

**Table 6**. Torsion angles [°] for str132m.

| | |
|---|---|
| N(10)-Pd(1)-C(3)-N(4) | -177.4(7) |
| C(16)-Pd(1)-C(3)-N(4) | -179.3(5) |
| Br(2)-Pd(1)-C(3)-N(4) | 2.0(7) |
| N(10)-Pd(1)-C(3)-N(8) | -0.6(3) |
| C(16)-Pd(1)-C(3)-N(8) | -2.5(7) |
| Br(2)-Pd(1)-C(3)-N(8) | 178.8(3) |
| N(8)-C(3)-N(4)-C(6) | 0.3(5) |
| Pd(1)-C(3)-N(4)-C(6) | 177.2(5) |
| N(8)-C(3)-N(4)-C(5) | 177.3(4) |
| Pd(1)-C(3)-N(4)-C(5) | -5.8(9) |
| C(3)-N(4)-C(6)-C(7) | -0.5(6) |
| C(5)-N(4)-C(6)-C(7) | -177.6(5) |
| N(4)-C(6)-C(7)-N(8) | 0.4(6) |
| N(4)-C(3)-N(8)-C(7) | 0.0(5) |
| Pd(1)-C(3)-N(8)-C(7) | -178.1(3) |
| N(4)-C(3)-N(8)-C(9) | 178.3(4) |
| Pd(1)-C(3)-N(8)-C(9) | 0.2(5) |
| C(6)-C(7)-N(8)-C(3) | -0.3(6) |
| C(6)-C(7)-N(8)-C(9) | -178.4(5) |
| C(3)-N(8)-C(9)-N(10) | 0.6(6) |
| C(7)-N(8)-C(9)-N(10) | 178.5(5) |
| C(3)-N(8)-C(9)-C(14) | -178.9(5) |
| C(7)-N(8)-C(9)-C(14) | -0.9(9) |
| C(14)-C(9)-N(10)-C(11) | -0.6(8) |
| N(8)-C(9)-N(10)-C(11) | 179.9(4) |
| C(14)-C(9)-N(10)-Pd(1) | 178.4(4) |
| N(8)-C(9)-N(10)-Pd(1) | -1.1(6) |
| C(3)-Pd(1)-N(10)-C(9) | 1.0(4) |
| C(16)-Pd(1)-N(10)-C(9) | -179.7(4) |
| Br(2)-Pd(1)-N(10)-C(9) | -37(7) |
| C(3)-Pd(1)-N(10)-C(11) | 179.9(4) |
| C(16)-Pd(1)-N(10)-C(11) | -0.8(4) |
| Br(2)-Pd(1)-N(10)-C(11) | 142(7) |
| C(9)-N(10)-C(11)-C(12) | 0.7(7) |
| Pd(1)-N(10)-C(11)-C(12) | -178.2(4) |
| C(9)-N(10)-C(11)-N(15) | 179.7(4) |
| Pd(1)-N(10)-C(11)-N(15) | 0.7(5) |
| N(10)-C(11)-C(12)-C(13) | -0.6(8) |
| N(15)-C(11)-C(12)-C(13) | -179.4(5) |
| C(11)-C(12)-C(13)-C(14) | 0.3(8) |
| N(10)-C(9)-C(14)-C(13) | 0.3(8) |
| N(8)-C(9)-C(14)-C(13) | 179.7(5) |
| C(12)-C(13)-C(14)-C(9) | -0.1(8) |
| N(10)-C(11)-N(15)-C(20) | 178.6(5) |
| C(12)-C(11)-N(15)-C(20) | -2.5(9) |
| N(10)-C(11)-N(15)-C(16) | -0.2(6) |
| C(12)-C(11)-N(15)-C(16) | 178.7(5) |
| C(20)-N(15)-C(16)-N(17) | -0.4(5) |
| C(11)-N(15)-C(16)-N(17) | 178.6(4) |
| C(20)-N(15)-C(16)-Pd(1) | -179.4(3) |
| C(11)-N(15)-C(16)-Pd(1) | -0.4(5) |
| N(10)-Pd(1)-C(16)-N(17) | -177.7(7) |
| C(3)-Pd(1)-C(16)-N(17) | -175.7(5) |
| Br(2)-Pd(1)-C(16)-N(17) | 2.9(7) |
| N(10)-Pd(1)-C(16)-N(15) | 0.6(3) |
| C(3)-Pd(1)-C(16)-N(15) | 2.6(7) |
| Br(2)-Pd(1)-C(16)-N(15) | -178.8(3) |
| N(15)-C(16)-N(17)-C(19) | 0.0(6) |
| Pd(1)-C(16)-N(17)-C(19) | 178.3(5) |
| N(15)-C(16)-N(17)-C(18) | -179.4(5) |
| Pd(1)-C(16)-N(17)-C(18) | -1.1(10) |
| C(16)-N(17)-C(19)-C(20) | 0.5(6) |
| C(18)-N(17)-C(19)-C(20) | 179.9(5) |
| N(17)-C(19)-C(20)-N(15) | -0.7(6) |
| C(16)-N(15)-C(20)-C(19) | 0.7(6) |
| C(11)-N(15)-C(20)-C(19) | -178.1(5) |

Symmetry transformations used to generate equivalent atoms:

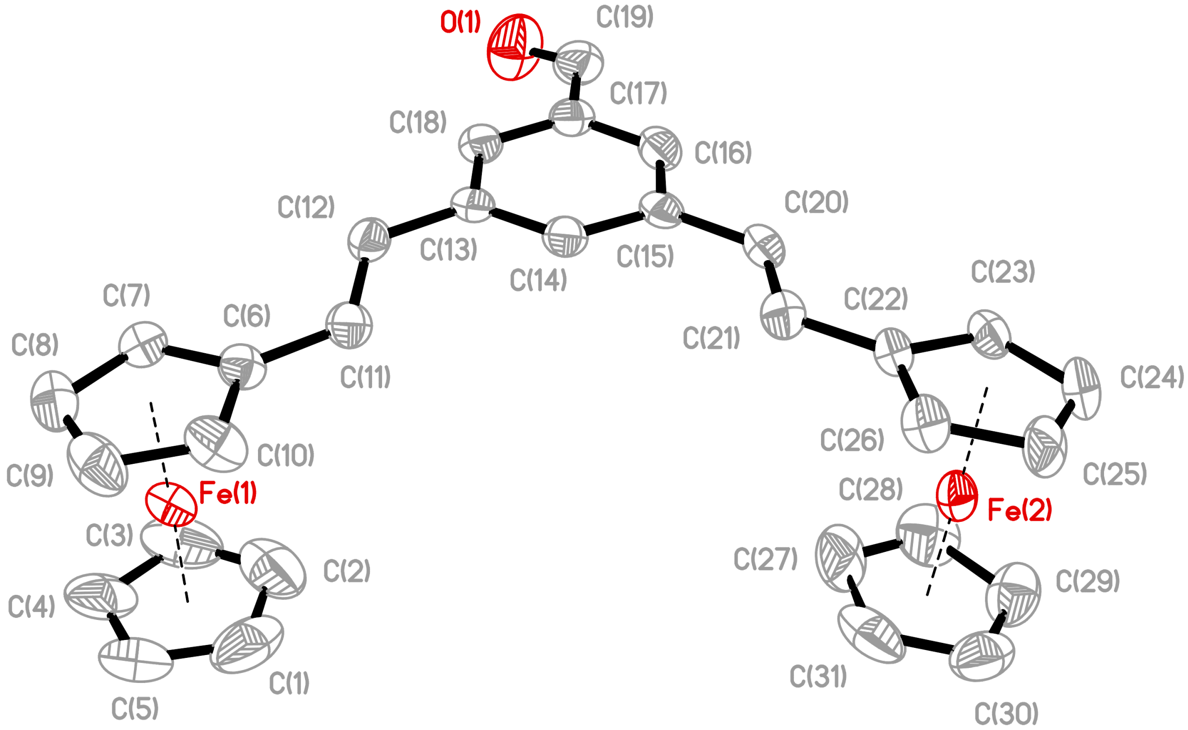

O(1)
C(19)
C(17)
C(18)
C(16)
C(12)
C(20)
C(13)
C(15)
C(14)
C(7)
C(6)
C(23)
C(22)
C(8)
C(11)
C(21)
C(24)
C(10)
C(26)
C(9)
Fe(1)
C(28)
C(25)
C(3)
Fe(2)
C(2)
C(27)
C(29)
C(4)
C(1)
C(31)
C(5)
C(30)

**Table 1**. Crystal data and structure refinement for str157m.

| | | |
|---|---|---|
| Identification code | str157m | |
| Empirical formula | C31 H26 Fe2 O | |
| Formula weight | 526.22 | |
| Temperature | 293(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | P2(1)/c | |
| Unit cell dimensions | a = 18.624(3) Å | α= 90°. |
| | b = 11.2643(17) Å | β= 106.174(3)°. |
| | c = 11.6667(16) Å | γ = 90°. |
| Volume | 2350.6(6) Å$^3$ | |
| Z | 4 | |
| Density (calculated) | 1.487 Mg/m$^3$ | |
| Absorption coefficient | 1.257 mm$^{-1}$ | |
| F(000) | 1088 | |
| Crystal size | 0.75 x 0.61 x 0.59 mm$^3$ | |
| Theta range for data collection | 1.14 to 24.71°. | |
| Index ranges | -16<=h<=21, -13<=k<=13, -13<=l<=12 | |
| Reflections collected | 12559 | |
| Independent reflections | 3994 [R(int) = 0.0512] | |
| Completeness to theta = 24.71° | 99.9 % | |
| Absorption correction | Bruker SADABS | |
| Max. and min. transmission | 1.955004 and 1.310110 | |
| Refinement method | Full-matrix least-squares on F$^2$ | |
| Data / restraints / parameters | 3994 / 0 / 307 | |
| Goodness-of-fit on F$^2$ | 1.064 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0479, wR2 = 0.1135 | |
| R indices (all data) | R1 = 0.0758, wR2 = 0.1226 | |
| Largest diff. peak and hole | 0.506 and -0.376 e.Å$^{-3}$ | |

**Table 2**. Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters (Å$^2$x $10^3$) for str157m. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| Fe(1) | 3915(1) | 3080(1) | -2789(1) | 36(1) |
| C(1) | 4693(4) | 4106(6) | -1658(5) | 78(2) |
| O(1) | -478(2) | 6644(3) | -4493(3) | 73(1) |
| Fe(2) | 2366(1) | 6646(1) | 3831(1) | 33(1) |
| C(2) | 4105(4) | 4833(5) | -2392(8) | 86(2) |
| C(3) | 4095(3) | 4632(5) | -3575(6) | 74(2) |
| C(4) | 4650(3) | 3829(6) | -3585(5) | 68(2) |
| C(5) | 5015(3) | 3497(5) | -2437(5) | 63(2) |
| C(6) | 2905(2) | 2597(4) | -2524(3) | 33(1) |
| C(7) | 2916(2) | 2381(4) | -3721(4) | 38(1) |
| C(8) | 3502(3) | 1581(4) | -3718(4) | 46(1) |
| C(9) | 3867(3) | 1305(4) | -2518(5) | 52(1) |
| C(10) | 3513(3) | 1933(4) | -1782(4) | 46(1) |
| C(11) | 2389(2) | 3340(4) | -2099(4) | 35(1) |
| C(12) | 1716(2) | 3663(4) | -2697(4) | 35(1) |
| C(13) | 1216(2) | 4431(4) | -2242(3) | 31(1) |
| C(14) | 1314(2) | 4596(4) | -1022(3) | 33(1) |
| C(15) | 876(2) | 5393(4) | -580(3) | 33(1) |
| C(16) | 311(2) | 5996(4) | -1408(4) | 37(1) |
| C(17) | 192(2) | 5832(4) | -2622(4) | 36(1) |
| C(18) | 643(2) | 5057(4) | -3036(4) | 35(1) |
| C(19) | -391(3) | 6548(4) | -3449(4) | 50(1) |
| C(20) | 994(2) | 5607(4) | 714(4) | 36(1) |
| C(21) | 1523(2) | 5164(4) | 1610(3) | 37(1) |
| C(22) | 1609(2) | 5445(4) | 2865(3) | 34(1) |
| C(23) | 1241(2) | 6353(4) | 3333(4) | 39(1) |
| C(24) | 1506(3) | 6342(4) | 4587(4) | 46(1) |
| C(25) | 2054(3) | 5445(4) | 4913(4) | 42(1) |
| C(26) | 2117(2) | 4896(4) | 3863(3) | 39(1) |
| C(27) | 2914(3) | 7312(6) | 2692(5) | 68(2) |
| C(28) | 2535(3) | 8214(5) | 3104(5) | 62(2) |
| C(29) | 2821(3) | 8282(4) | 4346(5) | 57(1) |
| C(30) | 3356(3) | 7428(5) | 4709(5) | 58(1) |
| C(31) | 3423(3) | 6795(5) | 3707(6) | 64(2) |

**Table 3.** Bond lengths [Å] and angles [°] for str157m.

| | |
|---|---|
| Fe(1)-C(10) | 2.025(4) |
| Fe(1)-C(1) | 2.027(5) |
| Fe(1)-C(5) | 2.029(5) |
| Fe(1)-C(9) | 2.030(5) |
| Fe(1)-C(7) | 2.034(4) |
| Fe(1)-C(2) | 2.037(5) |
| Fe(1)-C(8) | 2.037(5) |
| Fe(1)-C(4) | 2.039(5) |
| Fe(1)-C(3) | 2.045(5) |
| Fe(1)-C(6) | 2.063(4) |
| C(1)-C(5) | 1.400(8) |
| C(1)-C(2) | 1.442(9) |
| O(1)-C(19) | 1.188(5) |
| Fe(2)-C(31) | 2.020(5) |
| Fe(2)-C(28) | 2.022(5) |
| Fe(2)-C(26) | 2.028(4) |
| Fe(2)-C(27) | 2.031(5) |
| Fe(2)-C(23) | 2.040(4) |
| Fe(2)-C(25) | 2.042(4) |
| Fe(2)-C(30) | 2.042(5) |
| Fe(2)-C(29) | 2.047(5) |
| Fe(2)-C(22) | 2.050(4) |
| Fe(2)-C(24) | 2.061(4) |
| C(2)-C(3) | 1.394(8) |
| C(3)-C(4) | 1.377(8) |
| C(4)-C(5) | 1.375(7) |
| C(6)-C(7) | 1.423(5) |
| C(6)-C(10) | 1.430(6) |
| C(6)-C(11) | 1.461(6) |
| C(7)-C(8) | 1.414(6) |
| C(8)-C(9) | 1.410(7) |
| C(9)-C(10) | 1.411(6) |
| C(11)-C(12) | 1.306(6) |
| C(12)-C(13) | 1.473(6) |
| C(13)-C(18) | 1.394(6) |
| C(13)-C(14) | 1.396(5) |
| C(14)-C(15) | 1.405(6) |
| C(15)-C(16) | 1.391(6) |
| C(15)-C(20) | 1.483(5) |
| C(16)-C(17) | 1.384(5) |
| C(17)-C(18) | 1.387(6) |
| C(17)-C(19) | 1.476(6) |
| C(20)-C(21) | 1.319(6) |
| C(21)-C(22) | 1.462(5) |
| C(22)-C(23) | 1.422(6) |
| C(22)-C(26) | 1.422(6) |
| C(23)-C(24) | 1.407(6) |
| C(24)-C(25) | 1.412(6) |
| C(25)-C(26) | 1.406(6) |
| C(27)-C(28) | 1.396(8) |
| C(27)-C(31) | 1.419(8) |
| C(28)-C(29) | 1.400(7) |
| C(29)-C(30) | 1.366(7) |
| C(30)-C(31) | 1.403(7) |
| C(10)-Fe(1)-C(1) | 107.4(2) |
| C(10)-Fe(1)-C(5) | 123.1(2) |
| C(1)-Fe(1)-C(5) | 40.4(2) |
| C(10)-Fe(1)-C(9) | 40.71(18) |
| C(1)-Fe(1)-C(9) | 121.0(3) |
| C(5)-Fe(1)-C(9) | 106.4(2) |
| C(10)-Fe(1)-C(7) | 68.38(18) |
| C(1)-Fe(1)-C(7) | 161.8(3) |
| C(5)-Fe(1)-C(7) | 156.9(2) |
| C(9)-Fe(1)-C(7) | 68.19(19) |
| C(10)-Fe(1)-C(2) | 123.8(3) |
| C(1)-Fe(1)-C(2) | 41.6(3) |
| C(5)-Fe(1)-C(2) | 68.2(2) |
| C(9)-Fe(1)-C(2) | 158.7(3) |
| C(7)-Fe(1)-C(2) | 124.9(2) |
| C(10)-Fe(1)-C(8) | 68.53(19) |
| C(1)-Fe(1)-C(8) | 156.1(3) |
| C(5)-Fe(1)-C(8) | 120.7(2) |
| C(9)-Fe(1)-C(8) | 40.56(19) |

| | |
|---|---|
| C(7)-Fe(1)-C(8) | 40.65(18) |
| C(2)-Fe(1)-C(8) | 160.1(3) |
| C(10)-Fe(1)-C(4) | 158.8(2) |
| C(1)-Fe(1)-C(4) | 67.2(2) |
| C(5)-Fe(1)-C(4) | 39.5(2) |
| C(9)-Fe(1)-C(4) | 122.9(2) |
| C(7)-Fe(1)-C(4) | 123.2(2) |
| C(2)-Fe(1)-C(4) | 66.8(3) |
| C(8)-Fe(1)-C(4) | 107.6(2) |
| C(10)-Fe(1)-C(3) | 159.9(2) |
| C(1)-Fe(1)-C(3) | 68.2(3) |
| C(5)-Fe(1)-C(3) | 67.1(2) |
| C(9)-Fe(1)-C(3) | 158.7(3) |
| C(7)-Fe(1)-C(3) | 109.3(2) |
| C(2)-Fe(1)-C(3) | 39.9(2) |
| C(8)-Fe(1)-C(3) | 123.7(3) |
| C(4)-Fe(1)-C(3) | 39.4(2) |
| C(10)-Fe(1)-C(6) | 40.93(16) |
| C(1)-Fe(1)-C(6) | 124.7(2) |
| C(5)-Fe(1)-C(6) | 160.4(2) |
| C(9)-Fe(1)-C(6) | 68.63(18) |
| C(7)-Fe(1)-C(6) | 40.65(15) |
| C(2)-Fe(1)-C(6) | 109.2(2) |
| C(8)-Fe(1)-C(6) | 68.67(18) |
| C(4)-Fe(1)-C(6) | 159.0(2) |
| C(3)-Fe(1)-C(6) | 124.2(2) |
| C(5)-C(1)-C(2) | 106.6(5) |
| C(5)-C(1)-Fe(1) | 69.9(3) |
| C(2)-C(1)-Fe(1) | 69.6(3) |
| C(31)-Fe(2)-C(28) | 68.2(2) |
| C(31)-Fe(2)-C(26) | 108.4(2) |
| C(28)-Fe(2)-C(26) | 156.9(2) |
| C(31)-Fe(2)-C(27) | 41.0(2) |
| C(28)-Fe(2)-C(27) | 40.3(2) |
| C(26)-Fe(2)-C(27) | 122.0(2) |
| C(31)-Fe(2)-C(23) | 159.6(2) |
| C(28)-Fe(2)-C(23) | 106.8(2) |
| C(26)-Fe(2)-C(23) | 68.01(18) |
| C(27)-Fe(2)-C(23) | 122.4(2) |
| C(31)-Fe(2)-C(25) | 123.4(2) |
| C(28)-Fe(2)-C(25) | 160.5(2) |
| C(26)-Fe(2)-C(25) | 40.42(16) |
| C(27)-Fe(2)-C(25) | 158.5(2) |
| C(23)-Fe(2)-C(25) | 67.81(18) |
| C(31)-Fe(2)-C(30) | 40.4(2) |
| C(28)-Fe(2)-C(30) | 67.0(2) |
| C(26)-Fe(2)-C(30) | 126.1(2) |
| C(27)-Fe(2)-C(30) | 67.7(2) |
| C(23)-Fe(2)-C(30) | 157.7(2) |
| C(25)-Fe(2)-C(30) | 110.4(2) |
| C(31)-Fe(2)-C(29) | 67.3(2) |
| C(28)-Fe(2)-C(29) | 40.3(2) |
| C(26)-Fe(2)-C(29) | 161.42(19) |
| C(27)-Fe(2)-C(29) | 67.5(2) |
| C(23)-Fe(2)-C(29) | 122.5(2) |
| C(25)-Fe(2)-C(29) | 125.49(19) |
| C(30)-Fe(2)-C(29) | 39.0(2) |
| C(31)-Fe(2)-C(22) | 123.4(2) |
| C(28)-Fe(2)-C(22) | 120.6(2) |
| C(26)-Fe(2)-C(22) | 40.79(16) |
| C(27)-Fe(2)-C(22) | 106.1(2) |
| C(23)-Fe(2)-C(22) | 40.67(16) |
| C(25)-Fe(2)-C(22) | 68.43(17) |
| C(30)-Fe(2)-C(22) | 161.2(2) |
| C(29)-Fe(2)-C(22) | 156.9(2) |
| C(31)-Fe(2)-C(24) | 159.0(2) |
| C(28)-Fe(2)-C(24) | 123.7(2) |
| C(26)-Fe(2)-C(24) | 67.77(18) |
| C(27)-Fe(2)-C(24) | 158.9(2) |
| C(23)-Fe(2)-C(24) | 40.14(16) |
| C(25)-Fe(2)-C(24) | 40.25(18) |
| C(30)-Fe(2)-C(24) | 123.9(2) |
| C(29)-Fe(2)-C(24) | 109.3(2) |
| C(22)-Fe(2)-C(24) | 68.16(17) |
| C(3)-C(2)-C(1) | 107.1(5) |
| C(3)-C(2)-Fe(1) | 70.4(3) |
| C(1)-C(2)-Fe(1) | 68.8(3) |

| | |
|---|---|
| C(4)-C(3)-C(2) | 108.1(6) |
| C(4)-C(3)-Fe(1) | 70.0(3) |
| C(2)-C(3)-Fe(1) | 69.7(3) |
| C(5)-C(4)-C(3) | 109.9(6) |
| C(5)-C(4)-Fe(1) | 69.9(3) |
| C(3)-C(4)-Fe(1) | 70.6(3) |
| C(4)-C(5)-C(1) | 108.3(6) |
| C(4)-C(5)-Fe(1) | 70.6(3) |
| C(1)-C(5)-Fe(1) | 69.7(3) |
| C(7)-C(6)-C(10) | 106.2(4) |
| C(7)-C(6)-C(11) | 128.5(4) |
| C(10)-C(6)-C(11) | 125.3(4) |
| C(7)-C(6)-Fe(1) | 68.6(2) |
| C(10)-C(6)-Fe(1) | 68.1(2) |
| C(11)-C(6)-Fe(1) | 127.9(3) |
| C(8)-C(7)-C(6) | 109.2(4) |
| C(8)-C(7)-Fe(1) | 69.8(3) |
| C(6)-C(7)-Fe(1) | 70.8(2) |
| C(9)-C(8)-C(7) | 107.6(4) |
| C(9)-C(8)-Fe(1) | 69.4(3) |
| C(7)-C(8)-Fe(1) | 69.6(3) |
| C(8)-C(9)-C(10) | 108.4(4) |
| C(8)-C(9)-Fe(1) | 70.0(3) |
| C(10)-C(9)-Fe(1) | 69.5(3) |
| C(9)-C(10)-C(6) | 108.7(4) |
| C(9)-C(10)-Fe(1) | 69.8(3) |
| C(6)-C(10)-Fe(1) | 71.0(2) |
| C(12)-C(11)-C(6) | 127.1(4) |
| C(11)-C(12)-C(13) | 125.5(4) |
| C(18)-C(13)-C(14) | 118.0(4) |
| C(18)-C(13)-C(12) | 120.1(4) |
| C(14)-C(13)-C(12) | 121.9(4) |
| C(13)-C(14)-C(15) | 122.3(4) |
| C(16)-C(15)-C(14) | 117.5(4) |
| C(16)-C(15)-C(20) | 119.8(4) |
| C(14)-C(15)-C(20) | 122.8(4) |
| C(17)-C(16)-C(15) | 121.3(4) |
| C(16)-C(17)-C(18) | 120.1(4) |
| C(16)-C(17)-C(19) | 118.4(4) |
| C(18)-C(17)-C(19) | 121.5(4) |
| C(17)-C(18)-C(13) | 120.8(4) |
| O(1)-C(19)-C(17) | 125.8(5) |
| C(21)-C(20)-C(15) | 127.7(4) |
| C(20)-C(21)-C(22) | 124.1(4) |
| C(23)-C(22)-C(26) | 106.3(3) |
| C(23)-C(22)-C(21) | 127.6(4) |
| C(26)-C(22)-C(21) | 126.0(4) |
| C(23)-C(22)-Fe(2) | 69.3(2) |
| C(26)-C(22)-Fe(2) | 68.8(2) |
| C(21)-C(22)-Fe(2) | 124.1(3) |
| C(24)-C(23)-C(22) | 109.0(4) |
| C(24)-C(23)-Fe(2) | 70.7(3) |
| C(22)-C(23)-Fe(2) | 70.1(2) |
| C(23)-C(24)-C(25) | 107.7(4) |
| C(23)-C(24)-Fe(2) | 69.1(2) |
| C(25)-C(24)-Fe(2) | 69.1(2) |
| C(26)-C(25)-C(24) | 108.0(4) |
| C(26)-C(25)-Fe(2) | 69.3(2) |
| C(24)-C(25)-Fe(2) | 70.6(2) |
| C(25)-C(26)-C(22) | 108.9(4) |
| C(25)-C(26)-Fe(2) | 70.3(3) |
| C(22)-C(26)-Fe(2) | 70.4(2) |
| C(28)-C(27)-C(31) | 107.2(5) |
| C(28)-C(27)-Fe(2) | 69.5(3) |
| C(31)-C(27)-Fe(2) | 69.1(3) |
| C(27)-C(28)-C(29) | 108.3(5) |
| C(27)-C(28)-Fe(2) | 70.2(3) |
| C(29)-C(28)-Fe(2) | 70.8(3) |
| C(30)-C(29)-C(28) | 108.4(5) |
| C(30)-C(29)-Fe(2) | 70.3(3) |
| C(28)-C(29)-Fe(2) | 68.9(3) |
| C(29)-C(30)-C(31) | 109.0(5) |
| C(29)-C(30)-Fe(2) | 70.7(3) |
| C(31)-C(30)-Fe(2) | 68.9(3) |
| C(30)-C(31)-C(27) | 107.1(5) |
| C(30)-C(31)-Fe(2) | 70.7(3) |
| C(27)-C(31)-Fe(2) | 69.9(3) |

---

Symmetry transformations used to generate equivalent atoms:

**Table 4**. Anisotropic displacement parameters ($Å^2$x $10^3$) for str157m. The anisotropic displacement factor exponent takes the form: $-2\pi^2[ h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12} ]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| Fe(1) | 27(1) | 38(1) | 43(1) | 4(1) | 10(1) | 1(1) |
| C(1) | 76(5) | 99(5) | 58(3) | -17(4) | 15(3) | -50(4) |
| O(1) | 79(3) | 84(3) | 44(2) | 3(2) | 0(2) | 24(2) |
| Fe(2) | 39(1) | 37(1) | 27(1) | 2(1) | 13(1) | 3(1) |
| C(2) | 55(4) | 46(4) | 169(7) | -34(4) | 49(5) | -18(3) |
| C(3) | 47(4) | 64(4) | 108(5) | 30(4) | 16(4) | -15(3) |
| C(4) | 38(3) | 99(5) | 66(4) | 8(3) | 16(3) | -24(3) |
| C(5) | 33(3) | 75(4) | 73(4) | 9(3) | 1(3) | -8(3) |
| C(6) | 32(2) | 38(3) | 31(2) | 4(2) | 10(2) | -1(2) |
| C(7) | 35(3) | 41(3) | 37(2) | -5(2) | 8(2) | -3(2) |
| C(8) | 53(3) | 42(3) | 50(3) | -4(2) | 24(2) | 4(2) |
| C(9) | 48(3) | 35(3) | 81(4) | 8(3) | 29(3) | 10(2) |
| C(10) | 39(3) | 52(3) | 47(3) | 18(2) | 13(2) | 8(2) |
| C(11) | 35(3) | 42(3) | 29(2) | 1(2) | 10(2) | -2(2) |
| C(12) | 36(3) | 40(3) | 30(2) | -6(2) | 12(2) | -7(2) |
| C(13) | 23(2) | 36(2) | 34(2) | -3(2) | 8(2) | -6(2) |
| C(14) | 28(2) | 41(3) | 30(2) | 1(2) | 7(2) | -3(2) |
| C(15) | 26(2) | 40(3) | 35(2) | 0(2) | 13(2) | -9(2) |
| C(16) | 34(3) | 38(3) | 43(3) | -1(2) | 17(2) | -1(2) |
| C(17) | 29(2) | 37(3) | 41(3) | -4(2) | 8(2) | -5(2) |
| C(18) | 30(2) | 43(3) | 31(2) | -2(2) | 6(2) | -4(2) |
| C(19) | 36(3) | 56(3) | 53(3) | -8(3) | 4(2) | 4(2) |
| C(20) | 30(2) | 47(3) | 37(2) | -2(2) | 17(2) | -2(2) |
| C(21) | 37(3) | 39(3) | 36(2) | -3(2) | 12(2) | 2(2) |
| C(22) | 33(2) | 41(3) | 31(2) | -3(2) | 16(2) | 0(2) |
| C(23) | 31(3) | 51(3) | 39(2) | -4(2) | 15(2) | 7(2) |
| C(24) | 53(3) | 55(3) | 37(2) | -4(2) | 28(2) | 4(3) |
| C(25) | 52(3) | 54(3) | 24(2) | 9(2) | 18(2) | 1(2) |
| C(26) | 44(3) | 37(3) | 38(2) | 3(2) | 17(2) | 5(2) |
| C(27) | 80(4) | 87(4) | 53(3) | -2(3) | 45(3) | -25(4) |
| C(28) | 70(4) | 56(4) | 66(4) | 19(3) | 27(3) | -9(3) |
| C(29) | 76(4) | 44(3) | 55(3) | -8(3) | 22(3) | -10(3) |
| C(30) | 48(3) | 67(4) | 54(3) | -3(3) | 4(3) | -18(3) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(31) | 43(3) | 55(3) | 107(5) | -4(3) | 41(3) | -6(3) |

**Table 5**. Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters (Å$^2$x 10 $^3$) for str157m.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1) | 4831 | 4051 | -830 | 94 |
| H(2) | 3792 | 5341 | -2125 | 104 |
| H(3) | 3769 | 4981 | -4243 | 89 |
| H(4) | 4762 | 3553 | -4266 | 81 |
| H(5) | 5409 | 2960 | -2215 | 76 |
| H(7) | 2590 | 2712 | -4398 | 46 |
| H(8) | 3625 | 1291 | -4385 | 56 |
| H(9) | 4273 | 795 | -2256 | 63 |
| H(10) | 3651 | 1917 | -952 | 55 |
| H(11) | 2559 | 3612 | -1317 | 42 |
| H(12) | 1536 | 3386 | -3475 | 42 |
| H(14) | 1684 | 4163 | -483 | 40 |
| H(16) | 7 | 6520 | -1140 | 45 |
| H(18) | 562 | 4955 | -3853 | 42 |
| H(19) | -720 | 6962 | -3124 | 60 |
| H(20) | 655 | 6114 | 917 | 44 |
| H(21) | 1863 | 4640 | 1433 | 45 |
| H(23) | 883 | 6870 | 2883 | 47 |
| H(24) | 1348 | 6838 | 5107 | 55 |
| H(25) | 2327 | 5251 | 5687 | 50 |
| H(26) | 2438 | 4274 | 3827 | 47 |
| H(27) | 2845 | 7091 | 1901 | 82 |
| H(28) | 2159 | 8688 | 2633 | 75 |
| H(29) | 2671 | 8818 | 4841 | 69 |
| H(30) | 3632 | 7288 | 5493 | 70 |
| H(31) | 3741 | 6158 | 3708 | 77 |

**Table 6**. Torsion angles [°] for str157m.

| | |
|---|---|
| C(10)-Fe(1)-C(1)-C(5) | 121.0(3) |
| C(9)-Fe(1)-C(1)-C(5) | 78.6(4) |
| C(7)-Fe(1)-C(1)-C(5) | -165.4(6) |
| C(2)-Fe(1)-C(1)-C(5) | -117.4(5) |
| C(8)-Fe(1)-C(1)-C(5) | 44.9(7) |
| C(4)-Fe(1)-C(1)-C(5) | -37.1(4) |
| C(3)-Fe(1)-C(1)-C(5) | -79.9(4) |
| C(6)-Fe(1)-C(1)-C(5) | 162.8(3) |
| C(10)-Fe(1)-C(1)-C(2) | -121.6(4) |
| C(5)-Fe(1)-C(1)-C(2) | 117.4(5) |
| C(9)-Fe(1)-C(1)-C(2) | -164.0(4) |
| C(7)-Fe(1)-C(1)-C(2) | -48.0(8) |
| C(8)-Fe(1)-C(1)-C(2) | 162.2(5) |
| C(4)-Fe(1)-C(1)-C(2) | 80.2(4) |
| C(3)-Fe(1)-C(1)-C(2) | 37.5(3) |
| C(6)-Fe(1)-C(1)-C(2) | -79.8(4) |
| C(5)-C(1)-C(2)-C(3) | 0.2(6) |
| Fe(1)-C(1)-C(2)-C(3) | -60.2(4) |
| C(5)-C(1)-C(2)-Fe(1) | 60.5(4) |
| C(10)-Fe(1)-C(2)-C(3) | -163.9(3) |
| C(1)-Fe(1)-C(2)-C(3) | 118.3(5) |
| C(5)-Fe(1)-C(2)-C(3) | 80.0(4) |
| C(9)-Fe(1)-C(2)-C(3) | 158.9(5) |
| C(7)-Fe(1)-C(2)-C(3) | -78.2(4) |
| C(8)-Fe(1)-C(2)-C(3) | -40.4(8) |
| C(4)-Fe(1)-C(2)-C(3) | 37.1(3) |
| C(6)-Fe(1)-C(2)-C(3) | -120.7(3) |
| C(10)-Fe(1)-C(2)-C(1) | 77.8(4) |
| C(5)-Fe(1)-C(2)-C(1) | -38.3(3) |
| C(9)-Fe(1)-C(2)-C(1) | 40.7(8) |
| C(7)-Fe(1)-C(2)-C(1) | 163.6(3) |
| C(8)-Fe(1)-C(2)-C(1) | -158.7(6) |
| C(4)-Fe(1)-C(2)-C(1) | -81.2(4) |
| C(3)-Fe(1)-C(2)-C(1) | -118.3(5) |
| C(6)-Fe(1)-C(2)-C(1) | 121.0(3) |
| C(1)-C(2)-C(3)-C(4) | -0.5(6) |
| Fe(1)-C(2)-C(3)-C(4) | -59.7(4) |
| C(1)-C(2)-C(3)-Fe(1) | 59.3(4) |
| C(10)-Fe(1)-C(3)-C(4) | 161.1(5) |
| C(1)-Fe(1)-C(3)-C(4) | 80.1(4) |
| C(5)-Fe(1)-C(3)-C(4) | 36.3(4) |
| C(9)-Fe(1)-C(3)-C(4) | -39.8(8) |
| C(7)-Fe(1)-C(3)-C(4) | -119.1(4) |
| C(2)-Fe(1)-C(3)-C(4) | 119.2(5) |
| C(8)-Fe(1)-C(3)-C(4) | -76.2(4) |
| C(6)-Fe(1)-C(3)-C(4) | -161.9(3) |
| C(10)-Fe(1)-C(3)-C(2) | 42.0(8) |
| C(1)-Fe(1)-C(3)-C(2) | -39.0(4) |
| C(5)-Fe(1)-C(3)-C(2) | -82.8(4) |
| C(9)-Fe(1)-C(3)-C(2) | -159.0(6) |
| C(7)-Fe(1)-C(3)-C(2) | 121.7(4) |
| C(8)-Fe(1)-C(3)-C(2) | 164.6(3) |
| C(4)-Fe(1)-C(3)-C(2) | -119.2(5) |
| C(6)-Fe(1)-C(3)-C(2) | 78.9(4) |
| C(2)-C(3)-C(4)-C(5) | 0.6(6) |
| Fe(1)-C(3)-C(4)-C(5) | -59.0(4) |
| C(2)-C(3)-C(4)-Fe(1) | 59.5(4) |
| C(10)-Fe(1)-C(4)-C(5) | -41.2(8) |
| C(1)-Fe(1)-C(4)-C(5) | 37.9(4) |
| C(9)-Fe(1)-C(4)-C(5) | -75.2(4) |
| C(7)-Fe(1)-C(4)-C(5) | -159.1(3) |
| C(2)-Fe(1)-C(4)-C(5) | 83.3(4) |
| C(8)-Fe(1)-C(4)-C(5) | -117.1(4) |
| C(3)-Fe(1)-C(4)-C(5) | 120.9(6) |
| C(6)-Fe(1)-C(4)-C(5) | 166.6(5) |
| C(10)-Fe(1)-C(4)-C(3) | -162.1(6) |
| C(1)-Fe(1)-C(4)-C(3) | -83.0(4) |
| C(5)-Fe(1)-C(4)-C(3) | -120.9(6) |
| C(9)-Fe(1)-C(4)-C(3) | 163.9(4) |
| C(7)-Fe(1)-C(4)-C(3) | 80.0(4) |
| C(2)-Fe(1)-C(4)-C(3) | -37.6(4) |
| C(8)-Fe(1)-C(4)-C(3) | 122.0(4) |
| C(6)-Fe(1)-C(4)-C(3) | 45.7(8) |
| C(3)-C(4)-C(5)-C(1) | -0.4(6) |

|  |  |  |  |
|---|---|---|---|
| Fe(1)-C(4)-C(5)-C(1) | -59.8(4) | C(1)-Fe(1)-C(6)-C(11) | 42.5(5) |
| C(3)-C(4)-C(5)-Fe(1) | 59.4(4) | C(5)-Fe(1)-C(6)-C(11) | 77.5(7) |
| C(2)-C(1)-C(5)-C(4) | 0.1(6) | C(9)-Fe(1)-C(6)-C(11) | 156.2(4) |
| Fe(1)-C(1)-C(5)-C(4) | 60.4(4) | C(7)-Fe(1)-C(6)-C(11) | -122.8(5) |
| C(2)-C(1)-C(5)-Fe(1) | -60.2(4) | C(2)-Fe(1)-C(6)-C(11) | -1.2(5) |
| C(10)-Fe(1)-C(5)-C(4) | 163.5(4) | C(8)-Fe(1)-C(6)-C(11) | -160.1(4) |
| C(1)-Fe(1)-C(5)-C(4) | -119.0(6) | C(4)-Fe(1)-C(6)-C(11) | -76.4(7) |
| C(9)-Fe(1)-C(5)-C(4) | 122.2(4) | C(3)-Fe(1)-C(6)-C(11) | -43.1(5) |
| C(7)-Fe(1)-C(5)-C(4) | 49.5(7) | C(10)-C(6)-C(7)-C(8) | 1.4(5) |
| C(2)-Fe(1)-C(5)-C(4) | -79.6(4) | C(11)-C(6)-C(7)-C(8) | -178.6(4) |
| C(8)-Fe(1)-C(5)-C(4) | 80.5(4) | Fe(1)-C(6)-C(7)-C(8) | 59.4(3) |
| C(3)-Fe(1)-C(5)-C(4) | -36.2(4) | C(10)-C(6)-C(7)-Fe(1) | -58.0(3) |
| C(6)-Fe(1)-C(5)-C(4) | -165.6(5) | C(11)-C(6)-C(7)-Fe(1) | 122.0(5) |
| C(10)-Fe(1)-C(5)-C(1) | -77.5(4) | C(10)-Fe(1)-C(7)-C(8) | -81.8(3) |
| C(9)-Fe(1)-C(5)-C(1) | -118.8(4) | C(1)-Fe(1)-C(7)-C(8) | -161.7(7) |
| C(7)-Fe(1)-C(5)-C(1) | 168.5(5) | C(5)-Fe(1)-C(7)-C(8) | 42.8(6) |
| C(2)-Fe(1)-C(5)-C(1) | 39.4(4) | C(9)-Fe(1)-C(7)-C(8) | -37.8(3) |
| C(8)-Fe(1)-C(5)-C(1) | -160.6(4) | C(2)-Fe(1)-C(7)-C(8) | 161.3(4) |
| C(4)-Fe(1)-C(5)-C(1) | 119.0(6) | C(4)-Fe(1)-C(7)-C(8) | 78.1(4) |
| C(3)-Fe(1)-C(5)-C(1) | 82.7(4) | C(3)-Fe(1)-C(7)-C(8) | 119.6(3) |
| C(6)-Fe(1)-C(5)-C(1) | -46.6(8) | C(6)-Fe(1)-C(7)-C(8) | -120.0(4) |
| C(10)-Fe(1)-C(6)-C(7) | -118.7(4) | C(10)-Fe(1)-C(7)-C(6) | 38.2(3) |
| C(1)-Fe(1)-C(6)-C(7) | 165.4(3) | C(1)-Fe(1)-C(7)-C(6) | -41.7(8) |
| C(5)-Fe(1)-C(6)-C(7) | -159.7(6) | C(5)-Fe(1)-C(7)-C(6) | 162.8(5) |
| C(9)-Fe(1)-C(6)-C(7) | -81.0(3) | C(9)-Fe(1)-C(7)-C(6) | 82.2(3) |
| C(2)-Fe(1)-C(6)-C(7) | 121.6(4) | C(2)-Fe(1)-C(7)-C(6) | -78.7(4) |
| C(8)-Fe(1)-C(6)-C(7) | -37.3(3) | C(8)-Fe(1)-C(7)-C(6) | 120.0(4) |
| C(4)-Fe(1)-C(6)-C(7) | 46.4(7) | C(4)-Fe(1)-C(7)-C(6) | -161.9(3) |
| C(3)-Fe(1)-C(6)-C(7) | 79.7(4) | C(3)-Fe(1)-C(7)-C(6) | -120.4(3) |
| C(1)-Fe(1)-C(6)-C(10) | -76.0(4) | C(6)-C(7)-C(8)-C(9) | -0.7(5) |
| C(5)-Fe(1)-C(6)-C(10) | -41.0(7) | Fe(1)-C(7)-C(8)-C(9) | 59.3(3) |
| C(9)-Fe(1)-C(6)-C(10) | 37.7(3) | C(6)-C(7)-C(8)-Fe(1) | -60.0(3) |
| C(7)-Fe(1)-C(6)-C(10) | 118.7(4) | C(10)-Fe(1)-C(8)-C(9) | -37.5(3) |
| C(2)-Fe(1)-C(6)-C(10) | -119.7(4) | C(1)-Fe(1)-C(8)-C(9) | 47.1(6) |
| C(8)-Fe(1)-C(6)-C(10) | 81.4(3) | C(5)-Fe(1)-C(8)-C(9) | 79.2(3) |
| C(4)-Fe(1)-C(6)-C(10) | 165.1(6) | C(7)-Fe(1)-C(8)-C(9) | -118.9(4) |
| C(3)-Fe(1)-C(6)-C(10) | -161.6(3) | C(2)-Fe(1)-C(8)-C(9) | -169.4(6) |
| C(10)-Fe(1)-C(6)-C(11) | 118.5(5) | C(4)-Fe(1)-C(8)-C(9) | 120.3(3) |

| | | | |
|---|---|---|---|
| C(3)-Fe(1)-C(8)-C(9) | 160.6(3) | C(5)-Fe(1)-C(10)-C(9) | -76.0(4) |
| C(6)-Fe(1)-C(8)-C(9) | -81.6(3) | C(7)-Fe(1)-C(10)-C(9) | 81.2(3) |
| C(10)-Fe(1)-C(8)-C(7) | 81.4(3) | C(2)-Fe(1)-C(10)-C(9) | -160.4(4) |
| C(1)-Fe(1)-C(8)-C(7) | 166.0(5) | C(8)-Fe(1)-C(10)-C(9) | 37.4(3) |
| C(5)-Fe(1)-C(8)-C(7) | -161.9(3) | C(4)-Fe(1)-C(10)-C(9) | -46.0(7) |
| C(9)-Fe(1)-C(8)-C(7) | 118.9(4) | C(3)-Fe(1)-C(10)-C(9) | 168.5(6) |
| C(2)-Fe(1)-C(8)-C(7) | -50.4(7) | C(6)-Fe(1)-C(10)-C(9) | 119.2(4) |
| C(4)-Fe(1)-C(8)-C(7) | -120.7(3) | C(1)-Fe(1)-C(10)-C(6) | 123.3(3) |
| C(3)-Fe(1)-C(8)-C(7) | -80.4(3) | C(5)-Fe(1)-C(10)-C(6) | 164.8(3) |
| C(6)-Fe(1)-C(8)-C(7) | 37.3(2) | C(9)-Fe(1)-C(10)-C(6) | -119.2(4) |
| C(7)-C(8)-C(9)-C(10) | -0.3(6) | C(7)-Fe(1)-C(10)-C(6) | -37.9(2) |
| Fe(1)-C(8)-C(9)-C(10) | 59.0(3) | C(2)-Fe(1)-C(10)-C(6) | 80.4(4) |
| C(7)-C(8)-C(9)-Fe(1) | -59.3(3) | C(8)-Fe(1)-C(10)-C(6) | -81.8(3) |
| C(10)-Fe(1)-C(9)-C(8) | 119.7(4) | C(4)-Fe(1)-C(10)-C(6) | -165.2(5) |
| C(1)-Fe(1)-C(9)-C(8) | -159.7(3) | C(3)-Fe(1)-C(10)-C(6) | 49.3(7) |
| C(5)-Fe(1)-C(9)-C(8) | -118.3(3) | C(7)-C(6)-C(11)-C(12) | 22.5(7) |
| C(7)-Fe(1)-C(9)-C(8) | 37.9(3) | C(10)-C(6)-C(11)-C(12) | -157.5(4) |
| C(2)-Fe(1)-C(9)-C(8) | 170.0(5) | Fe(1)-C(6)-C(11)-C(12) | 114.1(5) |
| C(4)-Fe(1)-C(9)-C(8) | -78.4(3) | C(6)-C(11)-C(12)-C(13) | -178.9(4) |
| C(3)-Fe(1)-C(9)-C(8) | -49.5(7) | C(11)-C(12)-C(13)-C(18) | 157.0(4) |
| C(6)-Fe(1)-C(9)-C(8) | 81.8(3) | C(11)-C(12)-C(13)-C(14) | -20.2(7) |
| C(1)-Fe(1)-C(9)-C(10) | 80.6(4) | C(18)-C(13)-C(14)-C(15) | -2.1(6) |
| C(5)-Fe(1)-C(9)-C(10) | 122.1(3) | C(12)-C(13)-C(14)-C(15) | 175.2(4) |
| C(7)-Fe(1)-C(9)-C(10) | -81.8(3) | C(13)-C(14)-C(15)-C(16) | 2.2(6) |
| C(2)-Fe(1)-C(9)-C(10) | 50.3(7) | C(13)-C(14)-C(15)-C(20) | -177.8(4) |
| C(8)-Fe(1)-C(9)-C(10) | -119.7(4) | C(14)-C(15)-C(16)-C(17) | -0.9(6) |
| C(4)-Fe(1)-C(9)-C(10) | 161.9(3) | C(20)-C(15)-C(16)-C(17) | 179.0(4) |
| C(3)-Fe(1)-C(9)-C(10) | -169.1(5) | C(15)-C(16)-C(17)-C(18) | -0.3(6) |
| C(6)-Fe(1)-C(9)-C(10) | -37.9(3) | C(15)-C(16)-C(17)-C(19) | -176.8(4) |
| C(8)-C(9)-C(10)-C(6) | 1.2(5) | C(16)-C(17)-C(18)-C(13) | 0.4(6) |
| Fe(1)-C(9)-C(10)-C(6) | 60.6(3) | C(19)-C(17)-C(18)-C(13) | 176.8(4) |
| C(8)-C(9)-C(10)-Fe(1) | -59.4(3) | C(14)-C(13)-C(18)-C(17) | 0.8(6) |
| C(7)-C(6)-C(10)-C(9) | -1.6(5) | C(12)-C(13)-C(18)-C(17) | -176.6(4) |
| C(11)-C(6)-C(10)-C(9) | 178.4(4) | C(16)-C(17)-C(19)-O(1) | 167.5(5) |
| Fe(1)-C(6)-C(10)-C(9) | -59.9(3) | C(18)-C(17)-C(19)-O(1) | -9.0(8) |
| C(7)-C(6)-C(10)-Fe(1) | 58.3(3) | C(16)-C(15)-C(20)-C(21) | -176.1(4) |
| C(11)-C(6)-C(10)-Fe(1) | -121.7(4) | C(14)-C(15)-C(20)-C(21) | 3.8(7) |
| C(1)-Fe(1)-C(10)-C(9) | -117.6(4) | C(15)-C(20)-C(21)-C(22) | 178.5(4) |

| | | | |
|---|---|---|---|
| C(20)-C(21)-C(22)-C(23) | -11.1(7) | C(30)-Fe(2)-C(23)-C(24) | -52.5(6) |
| C(20)-C(21)-C(22)-C(26) | 172.7(4) | C(29)-Fe(2)-C(23)-C(24) | -81.6(3) |
| C(20)-C(21)-C(22)-Fe(2) | -100.1(5) | C(22)-Fe(2)-C(23)-C(24) | 119.6(4) |
| C(31)-Fe(2)-C(22)-C(23) | -162.8(3) | C(31)-Fe(2)-C(23)-C(22) | 45.2(7) |
| C(28)-Fe(2)-C(22)-C(23) | -80.1(3) | C(28)-Fe(2)-C(23)-C(22) | 117.6(3) |
| C(26)-Fe(2)-C(22)-C(23) | 118.0(3) | C(26)-Fe(2)-C(23)-C(22) | -38.5(2) |
| C(27)-Fe(2)-C(22)-C(23) | -121.4(3) | C(27)-Fe(2)-C(23)-C(22) | 76.4(3) |
| C(25)-Fe(2)-C(22)-C(23) | 80.6(3) | C(25)-Fe(2)-C(23)-C(22) | -82.3(3) |
| C(30)-Fe(2)-C(22)-C(23) | 170.7(6) | C(30)-Fe(2)-C(23)-C(22) | -172.1(5) |
| C(29)-Fe(2)-C(22)-C(23) | -51.0(5) | C(29)-Fe(2)-C(23)-C(22) | 158.8(3) |
| C(24)-Fe(2)-C(22)-C(23) | 37.1(3) | C(24)-Fe(2)-C(23)-C(22) | -119.6(4) |
| C(31)-Fe(2)-C(22)-C(26) | 79.3(3) | C(22)-C(23)-C(24)-C(25) | 1.3(5) |
| C(28)-Fe(2)-C(22)-C(26) | 161.9(3) | Fe(2)-C(23)-C(24)-C(25) | -58.5(3) |
| C(27)-Fe(2)-C(22)-C(26) | 120.7(3) | C(22)-C(23)-C(24)-Fe(2) | 59.8(3) |
| C(23)-Fe(2)-C(22)-C(26) | -118.0(3) | C(31)-Fe(2)-C(24)-C(23) | -165.2(5) |
| C(25)-Fe(2)-C(22)-C(26) | -37.4(2) | C(28)-Fe(2)-C(24)-C(23) | 75.4(3) |
| C(30)-Fe(2)-C(22)-C(26) | 52.7(7) | C(26)-Fe(2)-C(24)-C(23) | -81.8(3) |
| C(29)-Fe(2)-C(22)-C(26) | -169.0(4) | C(27)-Fe(2)-C(24)-C(23) | 40.4(7) |
| C(24)-Fe(2)-C(22)-C(26) | -80.8(3) | C(25)-Fe(2)-C(24)-C(23) | -119.6(4) |
| C(31)-Fe(2)-C(22)-C(21) | -40.6(5) | C(30)-Fe(2)-C(24)-C(23) | 158.7(3) |
| C(28)-Fe(2)-C(22)-C(21) | 42.1(4) | C(29)-Fe(2)-C(24)-C(23) | 117.8(3) |
| C(26)-Fe(2)-C(22)-C(21) | -119.9(5) | C(22)-Fe(2)-C(24)-C(23) | -37.6(3) |
| C(27)-Fe(2)-C(22)-C(21) | 0.8(4) | C(31)-Fe(2)-C(24)-C(25) | -45.6(7) |
| C(23)-Fe(2)-C(22)-C(21) | 122.1(5) | C(28)-Fe(2)-C(24)-C(25) | -165.0(3) |
| C(25)-Fe(2)-C(22)-C(21) | -157.2(4) | C(26)-Fe(2)-C(24)-C(25) | 37.8(3) |
| C(30)-Fe(2)-C(22)-C(21) | -67.2(7) | C(27)-Fe(2)-C(24)-C(25) | 160.0(6) |
| C(29)-Fe(2)-C(22)-C(21) | 71.1(6) | C(23)-Fe(2)-C(24)-C(25) | 119.6(4) |
| C(24)-Fe(2)-C(22)-C(21) | 159.3(4) | C(30)-Fe(2)-C(24)-C(25) | -81.7(3) |
| C(26)-C(22)-C(23)-C(24) | -1.2(5) | C(29)-Fe(2)-C(24)-C(25) | -122.6(3) |
| C(21)-C(22)-C(23)-C(24) | -177.9(4) | C(22)-Fe(2)-C(24)-C(25) | 82.0(3) |
| Fe(2)-C(22)-C(23)-C(24) | -60.2(3) | C(23)-C(24)-C(25)-C(26) | -0.9(5) |
| C(26)-C(22)-C(23)-Fe(2) | 59.1(3) | Fe(2)-C(24)-C(25)-C(26) | -59.4(3) |
| C(21)-C(22)-C(23)-Fe(2) | -117.7(4) | C(23)-C(24)-C(25)-Fe(2) | 58.5(3) |
| C(31)-Fe(2)-C(23)-C(24) | 164.8(5) | C(31)-Fe(2)-C(25)-C(26) | -78.9(3) |
| C(28)-Fe(2)-C(23)-C(24) | -122.7(3) | C(28)-Fe(2)-C(25)-C(26) | 159.2(6) |
| C(26)-Fe(2)-C(23)-C(24) | 81.1(3) | C(27)-Fe(2)-C(25)-C(26) | -41.4(7) |
| C(27)-Fe(2)-C(23)-C(24) | -164.0(3) | C(23)-Fe(2)-C(25)-C(26) | 81.7(3) |
| C(25)-Fe(2)-C(23)-C(24) | 37.4(3) | C(30)-Fe(2)-C(25)-C(26) | -122.2(3) |

| | | | |
|---|---|---|---|
| C(29)-Fe(2)-C(25)-C(26) | -163.4(3) | C(25)-Fe(2)-C(27)-C(28) | -169.5(5) |
| C(22)-Fe(2)-C(25)-C(26) | 37.7(3) | C(30)-Fe(2)-C(27)-C(28) | -80.2(4) |
| C(24)-Fe(2)-C(25)-C(26) | 118.9(4) | C(29)-Fe(2)-C(27)-C(28) | -37.9(3) |
| C(31)-Fe(2)-C(25)-C(24) | 162.1(3) | C(22)-Fe(2)-C(27)-C(28) | 118.6(3) |
| C(28)-Fe(2)-C(25)-C(24) | 40.3(7) | C(24)-Fe(2)-C(27)-C(28) | 47.6(7) |
| C(26)-Fe(2)-C(25)-C(24) | -118.9(4) | C(28)-Fe(2)-C(27)-C(31) | 118.7(5) |
| C(27)-Fe(2)-C(25)-C(24) | -160.3(6) | C(26)-Fe(2)-C(27)-C(31) | -81.2(4) |
| C(23)-Fe(2)-C(25)-C(24) | -37.3(3) | C(23)-Fe(2)-C(27)-C(31) | -164.0(3) |
| C(30)-Fe(2)-C(25)-C(24) | 118.8(3) | C(25)-Fe(2)-C(27)-C(31) | -50.8(7) |
| C(29)-Fe(2)-C(25)-C(24) | 77.7(3) | C(30)-Fe(2)-C(27)-C(31) | 38.5(3) |
| C(22)-Fe(2)-C(25)-C(24) | -81.2(3) | C(29)-Fe(2)-C(27)-C(31) | 80.8(4) |
| C(24)-C(25)-C(26)-C(22) | 0.1(5) | C(22)-Fe(2)-C(27)-C(31) | -122.7(3) |
| Fe(2)-C(25)-C(26)-C(22) | -60.1(3) | C(24)-Fe(2)-C(27)-C(31) | 166.3(5) |
| C(24)-C(25)-C(26)-Fe(2) | 60.2(3) | C(31)-C(27)-C(28)-C(29) | 1.8(6) |
| C(23)-C(22)-C(26)-C(25) | 0.6(5) | Fe(2)-C(27)-C(28)-C(29) | 60.9(4) |
| C(21)-C(22)-C(26)-C(25) | 177.4(4) | C(31)-C(27)-C(28)-Fe(2) | -59.0(4) |
| Fe(2)-C(22)-C(26)-C(25) | 60.0(3) | C(31)-Fe(2)-C(28)-C(27) | 38.3(3) |
| C(23)-C(22)-C(26)-Fe(2) | -59.4(3) | C(26)-Fe(2)-C(28)-C(27) | -47.4(7) |
| C(21)-C(22)-C(26)-Fe(2) | 117.4(4) | C(23)-Fe(2)-C(28)-C(27) | -120.7(4) |
| C(31)-Fe(2)-C(26)-C(25) | 120.3(3) | C(25)-Fe(2)-C(28)-C(27) | 168.5(5) |
| C(28)-Fe(2)-C(26)-C(25) | -162.4(5) | C(30)-Fe(2)-C(28)-C(27) | 82.2(4) |
| C(27)-Fe(2)-C(26)-C(25) | 163.4(3) | C(29)-Fe(2)-C(28)-C(27) | 118.6(5) |
| C(23)-Fe(2)-C(26)-C(25) | -81.1(3) | C(22)-Fe(2)-C(28)-C(27) | -78.6(4) |
| C(30)-Fe(2)-C(26)-C(25) | 79.0(3) | C(24)-Fe(2)-C(28)-C(27) | -161.4(3) |
| C(29)-Fe(2)-C(26)-C(25) | 46.9(7) | C(31)-Fe(2)-C(28)-C(29) | -80.3(4) |
| C(22)-Fe(2)-C(26)-C(25) | -119.5(4) | C(26)-Fe(2)-C(28)-C(29) | -166.0(5) |
| C(24)-Fe(2)-C(26)-C(25) | -37.6(3) | C(27)-Fe(2)-C(28)-C(29) | -118.6(5) |
| C(31)-Fe(2)-C(26)-C(22) | -120.2(3) | C(23)-Fe(2)-C(28)-C(29) | 120.7(3) |
| C(28)-Fe(2)-C(26)-C(22) | -42.9(6) | C(25)-Fe(2)-C(28)-C(29) | 49.9(8) |
| C(27)-Fe(2)-C(26)-C(22) | -77.1(3) | C(30)-Fe(2)-C(28)-C(29) | -36.4(3) |
| C(23)-Fe(2)-C(26)-C(22) | 38.4(2) | C(22)-Fe(2)-C(28)-C(29) | 162.9(3) |
| C(25)-Fe(2)-C(26)-C(22) | 119.5(4) | C(24)-Fe(2)-C(28)-C(29) | 80.1(4) |
| C(30)-Fe(2)-C(26)-C(22) | -161.5(3) | C(27)-C(28)-C(29)-C(30) | -1.1(6) |
| C(29)-Fe(2)-C(26)-C(22) | 166.4(6) | Fe(2)-C(28)-C(29)-C(30) | 59.4(4) |
| C(24)-Fe(2)-C(26)-C(22) | 81.9(3) | C(27)-C(28)-C(29)-Fe(2) | -60.5(4) |
| C(31)-Fe(2)-C(27)-C(28) | -118.7(5) | C(31)-Fe(2)-C(29)-C(30) | -37.3(3) |
| C(26)-Fe(2)-C(27)-C(28) | 160.1(3) | C(28)-Fe(2)-C(29)-C(30) | -119.8(5) |
| C(23)-Fe(2)-C(27)-C(28) | 77.3(4) | C(26)-Fe(2)-C(29)-C(30) | 42.9(8) |

| | |
|---|---|
| C(27)-Fe(2)-C(29)-C(30) | -81.9(4) |
| C(23)-Fe(2)-C(29)-C(30) | 162.9(3) |
| C(25)-Fe(2)-C(29)-C(30) | 78.5(4) |
| C(22)-Fe(2)-C(29)-C(30) | -160.1(4) |
| C(24)-Fe(2)-C(29)-C(30) | 120.4(3) |
| C(31)-Fe(2)-C(29)-C(28) | 82.5(4) |
| C(26)-Fe(2)-C(29)-C(28) | 162.7(6) |
| C(27)-Fe(2)-C(29)-C(28) | 37.9(3) |
| C(23)-Fe(2)-C(29)-C(28) | -77.2(4) |
| C(25)-Fe(2)-C(29)-C(28) | -161.7(3) |
| C(30)-Fe(2)-C(29)-C(28) | 119.8(5) |
| C(22)-Fe(2)-C(29)-C(28) | -40.3(6) |
| C(24)-Fe(2)-C(29)-C(28) | -119.7(3) |
| C(28)-C(29)-C(30)-C(31) | -0.2(6) |
| Fe(2)-C(29)-C(30)-C(31) | 58.4(4) |
| C(28)-C(29)-C(30)-Fe(2) | -58.5(4) |
| C(31)-Fe(2)-C(30)-C(29) | 120.4(5) |
| C(28)-Fe(2)-C(30)-C(29) | 37.5(3) |
| C(26)-Fe(2)-C(30)-C(29) | -164.4(3) |
| C(27)-Fe(2)-C(30)-C(29) | 81.3(4) |
| C(23)-Fe(2)-C(30)-C(29) | -40.6(7) |
| C(25)-Fe(2)-C(30)-C(29) | -121.7(3) |
| C(22)-Fe(2)-C(30)-C(29) | 155.5(5) |
| C(24)-Fe(2)-C(30)-C(29) | -78.7(4) |
| C(28)-Fe(2)-C(30)-C(31) | -82.9(4) |
| C(26)-Fe(2)-C(30)-C(31) | 75.2(4) |
| C(27)-Fe(2)-C(30)-C(31) | -39.1(3) |
| C(23)-Fe(2)-C(30)-C(31) | -161.0(5) |
| C(25)-Fe(2)-C(30)-C(31) | 118.0(3) |
| C(29)-Fe(2)-C(30)-C(31) | -120.4(5) |
| C(22)-Fe(2)-C(30)-C(31) | 35.1(8) |
| C(24)-Fe(2)-C(30)-C(31) | 161.0(3) |
| C(29)-C(30)-C(31)-C(27) | 1.3(6) |
| Fe(2)-C(30)-C(31)-C(27) | 60.8(4) |
| C(29)-C(30)-C(31)-Fe(2) | -59.5(4) |
| C(28)-C(27)-C(31)-C(30) | -1.9(6) |
| Fe(2)-C(27)-C(31)-C(30) | -61.2(3) |
| C(28)-C(27)-C(31)-Fe(2) | 59.3(4) |
| C(28)-Fe(2)-C(31)-C(30) | 79.7(4) |
| C(26)-Fe(2)-C(31)-C(30) | -124.6(3) |
| C(27)-Fe(2)-C(31)-C(30) | 117.3(5) |
| C(23)-Fe(2)-C(31)-C(30) | 159.2(5) |
| C(25)-Fe(2)-C(31)-C(30) | -82.5(4) |
| C(29)-Fe(2)-C(31)-C(30) | 36.1(3) |
| C(22)-Fe(2)-C(31)-C(30) | -167.2(3) |
| C(24)-Fe(2)-C(31)-C(30) | -48.9(7) |
| C(28)-Fe(2)-C(31)-C(27) | -37.7(3) |
| C(26)-Fe(2)-C(31)-C(27) | 118.0(3) |
| C(23)-Fe(2)-C(31)-C(27) | 41.9(7) |
| C(25)-Fe(2)-C(31)-C(27) | 160.1(3) |
| C(30)-Fe(2)-C(31)-C(27) | -117.3(5) |
| C(29)-Fe(2)-C(31)-C(27) | -81.3(4) |
| C(22)-Fe(2)-C(31)-C(27) | 75.5(4) |
| C(24)-Fe(2)-C(31)-C(27) | -166.3(5) |

Symmetry transformations used to generate equivalent atoms:

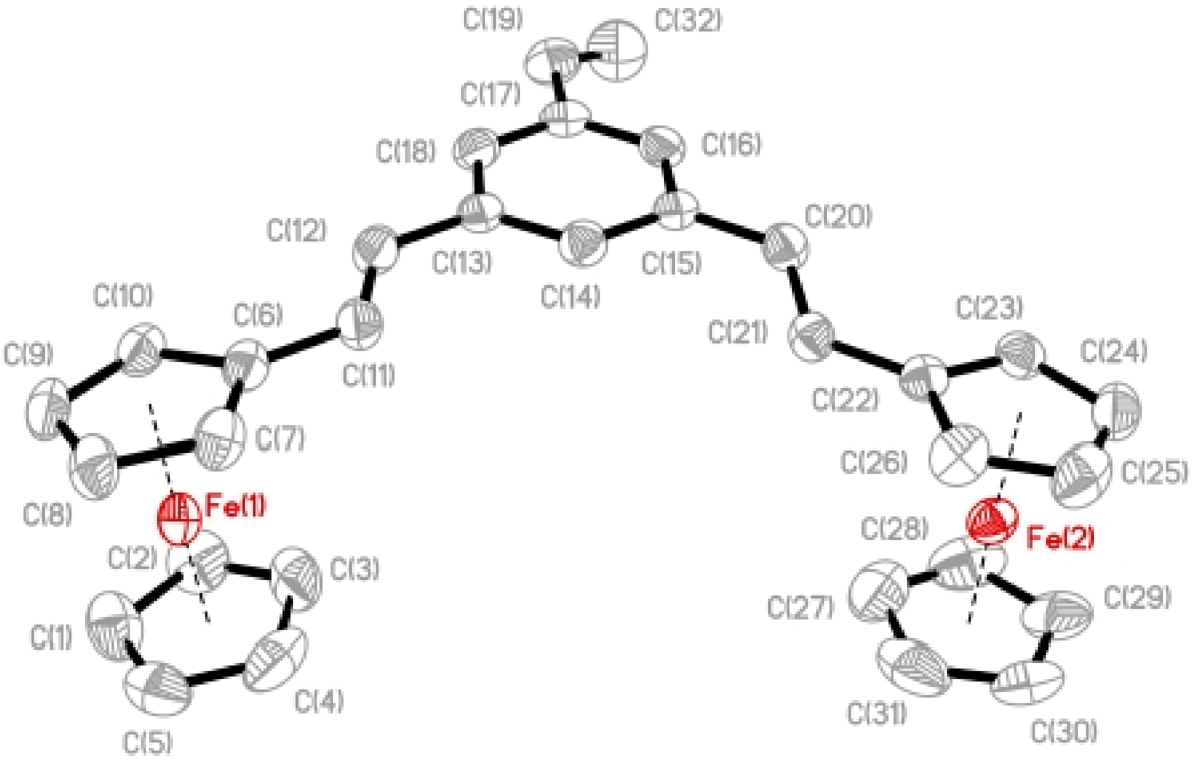

C(19)
C(32)
C(17)
C(18)
C(16)
C(12)
C(13)
C(15)
C(20)
C(14)
C(10)
C(6)
C(9)
C(11)
C(21)
C(23)
C(24)
C(22)
C(7)
C(26)
C(25)
C(8)
Fe(1)
C(28)
Fe(2)
C(2)
C(3)
C(29)
C(27)
C(1)
C(4)
C(31)
C(30)
C(5)

**Table 1**. Crystal data and structure refinement for toto/ str161.

| | | |
|---|---|---|
| Identification code | toto | |
| Empirical formula | $C32\ H28\ Fe2$ | |
| Formula weight | 524.24 | |
| Temperature | 293(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | P2(1)/c | |
| Unit cell dimensions | a = 19.198(2) Å | $\alpha$= 90°. |
| | b = 11.1627(12) Å | $\beta$= 102.890(2)°. |
| | c = 11.5538(12) Å | $\gamma$ = 90°. |
| Volume | 2413.6(4) Å$^3$ | |
| Z | 4 | |
| Density (calculated) | 1.443 Mg/m$^3$ | |
| Absorption coefficient | 1.221 mm$^{-1}$ | |
| F(000) | 1088 | |
| Crystal size | 0.83 x 0.42 x 0.12 mm$^3$ | |
| Theta range for data collection | 1.09 to 26.37°. | |
| Index ranges | -23<=h<=23, -11<=k<=13, -14<=l<=14 | |
| Reflections collected | 14849 | |
| Independent reflections | 4926 [R(int) = 0.0367] | |
| Completeness to theta = 26.37° | 100.0 % | |
| Absorption correction | Bruker SADABS | |
| Max. and min. transmission | 1.955365 and 1.314159 | |
| Refinement method | Full-matrix least-squares on F$^2$ | |
| Data / restraints / parameters | 4926 / 0 / 307 | |
| Goodness-of-fit on F$^2$ | 1.028 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0333, wR2 = 0.0763 | |
| R indices (all data) | R1 = 0.0565, wR2 = 0.0939 | |
| Largest diff. peak and hole | 0.255 and -0.295 e.Å$^{-3}$ | |

**Table 2**. Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters (Å$^2$x $10^3$) for toto. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| Fe(1) | 2432(1) | 3327(1) | 4023(1) | 32(1) |
| C(1) | 2867(2) | 1680(3) | 4481(3) | 55(1) |
| Fe(2) | 3973(1) | 6945(1) | -2710(1) | 35(1) |
| C(2) | 2585(2) | 1735(3) | 3264(3) | 56(1) |
| C(3) | 2930(2) | 2649(3) | 2793(3) | 59(1) |
| C(4) | 3434(2) | 3186(3) | 3747(4) | 60(1) |
| C(5) | 3385(2) | 2566(3) | 4788(3) | 54(1) |
| C(6) | 1704(1) | 4542(2) | 3141(2) | 35(1) |
| C(7) | 2187(2) | 5095(3) | 4111(2) | 38(1) |
| C(8) | 2134(2) | 4507(3) | 5174(2) | 41(1) |
| C(9) | 1618(2) | 3591(3) | 4876(3) | 44(1) |
| C(10) | 1355(2) | 3610(3) | 3629(3) | 41(1) |
| C(11) | 1618(2) | 4870(3) | 1892(2) | 37(1) |
| C(12) | 1103(1) | 4479(3) | 1013(2) | 36(1) |
| C(13) | 1008(1) | 4730(2) | -266(2) | 33(1) |
| C(14) | 1450(1) | 5504(2) | -721(2) | 34(1) |
| C(15) | 1363(1) | 5678(2) | -1946(2) | 33(1) |
| C(16) | 806(1) | 5071(3) | -2704(2) | 37(1) |
| C(17) | 358(1) | 4296(3) | -2282(2) | 36(1) |
| C(18) | 463(1) | 4147(3) | -1061(2) | 37(1) |
| C(19) | -206(2) | 3594(3) | -3076(3) | 49(1) |
| C(20) | 1850(1) | 6426(3) | -2443(2) | 36(1) |
| C(21) | 2508(1) | 6736(2) | -1893(2) | 34(1) |
| C(22) | 3006(1) | 7459(2) | -2375(2) | 33(1) |
| C(23) | 3018(1) | 7651(3) | -3591(2) | 37(1) |
| C(24) | 3587(2) | 8451(3) | -3642(3) | 47(1) |
| C(25) | 3933(2) | 8744(3) | -2467(3) | 51(1) |
| C(26) | 3585(2) | 8132(3) | -1683(3) | 43(1) |
| C(27) | 4150(2) | 5187(3) | -2273(5) | 78(1) |
| C(28) | 4138(2) | 5355(3) | -3480(4) | 66(1) |
| C(29) | 4675(2) | 6165(4) | -3565(3) | 60(1) |
| C(30) | 5027(2) | 6507(3) | -2422(3) | 58(1) |
| C(31) | 4709(2) | 5911(4) | -1609(3) | 73(1) |
| C(32) | -272(2) | 3397(3) | -4196(3) | 65(1) |

**Table 3**. Bond lengths [Å] and angles [°] for toto/str161.

| | |
|---|---|
| Fe(1)-C(4) | 2.023(3) |
| Fe(1)-C(3) | 2.028(3) |
| Fe(1)-C(2) | 2.032(3) |
| Fe(1)-C(5) | 2.032(3) |
| Fe(1)-C(7) | 2.038(3) |
| Fe(1)-C(1) | 2.039(3) |
| Fe(1)-C(10) | 2.041(3) |
| Fe(1)-C(8) | 2.042(3) |
| Fe(1)-C(9) | 2.047(3) |
| Fe(1)-C(6) | 2.048(3) |
| C(1)-C(2) | 1.391(4) |
| C(1)-C(5) | 1.391(5) |
| Fe(2)-C(26) | 2.028(3) |
| Fe(2)-C(25) | 2.031(3) |
| Fe(2)-C(31) | 2.035(3) |
| Fe(2)-C(30) | 2.036(3) |
| Fe(2)-C(27) | 2.036(4) |
| Fe(2)-C(29) | 2.036(3) |
| Fe(2)-C(28) | 2.042(3) |
| Fe(2)-C(24) | 2.044(3) |
| Fe(2)-C(23) | 2.046(3) |
| Fe(2)-C(22) | 2.060(3) |
| C(2)-C(3) | 1.392(5) |
| C(3)-C(4) | 1.427(5) |
| C(4)-C(5) | 1.408(5) |
| C(6)-C(10) | 1.421(4) |
| C(6)-C(7) | 1.425(4) |
| C(6)-C(11) | 1.463(4) |
| C(7)-C(8) | 1.416(4) |
| C(8)-C(9) | 1.412(4) |
| C(9)-C(10) | 1.417(4) |
| C(11)-C(12) | 1.324(4) |
| C(12)-C(13) | 1.475(4) |
| C(13)-C(18) | 1.390(4) |
| C(13)-C(14) | 1.393(4) |
| C(14)-C(15) | 1.401(4) |
| C(15)-C(16) | 1.397(4) |
| C(15)-C(20) | 1.463(4) |
| C(16)-C(17) | 1.383(4) |
| C(17)-C(18) | 1.390(4) |
| C(17)-C(19) | 1.478(4) |
| C(19)-C(32) | 1.291(4) |
| C(20)-C(21) | 1.327(4) |
| C(21)-C(22) | 1.455(4) |
| C(22)-C(23) | 1.427(4) |
| C(22)-C(26) | 1.430(4) |
| C(23)-C(24) | 1.421(4) |
| C(24)-C(25) | 1.410(4) |
| C(25)-C(26) | 1.416(4) |
| C(27)-C(28) | 1.403(6) |
| C(27)-C(31) | 1.423(6) |
| C(28)-C(29) | 1.391(5) |
| C(29)-C(30) | 1.396(5) |
| C(30)-C(31) | 1.397(5) |
| C(4)-Fe(1)-C(3) | 41.24(14) |
| C(4)-Fe(1)-C(2) | 68.32(14) |
| C(3)-Fe(1)-C(2) | 40.11(14) |
| C(4)-Fe(1)-C(5) | 40.63(14) |
| C(3)-Fe(1)-C(5) | 68.24(13) |
| C(2)-Fe(1)-C(5) | 67.61(14) |
| C(4)-Fe(1)-C(7) | 108.75(13) |
| C(3)-Fe(1)-C(7) | 123.15(13) |
| C(2)-Fe(1)-C(7) | 157.86(13) |
| C(5)-Fe(1)-C(7) | 125.42(13) |
| C(4)-Fe(1)-C(1) | 67.85(14) |
| C(3)-Fe(1)-C(1) | 67.44(14) |
| C(2)-Fe(1)-C(1) | 39.96(13) |
| C(5)-Fe(1)-C(1) | 39.97(14) |
| C(7)-Fe(1)-C(1) | 161.15(12) |
| C(4)-Fe(1)-C(10) | 158.11(14) |
| C(3)-Fe(1)-C(10) | 120.91(13) |
| C(2)-Fe(1)-C(10) | 106.00(13) |
| C(5)-Fe(1)-C(10) | 158.64(13) |
| C(7)-Fe(1)-C(10) | 68.08(12) |

| | |
|---|---|
| C(1)-Fe(1)-C(10) | 122.22(13) |
| C(4)-Fe(1)-C(8) | 124.51(14) |
| C(3)-Fe(1)-C(8) | 160.28(14) |
| C(2)-Fe(1)-C(8) | 159.03(13) |
| C(5)-Fe(1)-C(8) | 110.04(13) |
| C(7)-Fe(1)-C(8) | 40.61(11) |
| C(1)-Fe(1)-C(8) | 124.78(13) |
| C(10)-Fe(1)-C(8) | 68.18(12) |
| C(4)-Fe(1)-C(9) | 160.31(14) |
| C(3)-Fe(1)-C(9) | 157.09(15) |
| C(2)-Fe(1)-C(9) | 122.23(14) |
| C(5)-Fe(1)-C(9) | 124.18(13) |
| C(7)-Fe(1)-C(9) | 68.04(12) |
| C(1)-Fe(1)-C(9) | 108.51(13) |
| C(10)-Fe(1)-C(9) | 40.54(11) |
| C(8)-Fe(1)-C(9) | 40.41(11) |
| C(4)-Fe(1)-C(6) | 122.65(13) |
| C(3)-Fe(1)-C(6) | 105.91(12) |
| C(2)-Fe(1)-C(6) | 120.85(12) |
| C(5)-Fe(1)-C(6) | 160.27(13) |
| C(7)-Fe(1)-C(6) | 40.81(10) |
| C(1)-Fe(1)-C(6) | 156.99(13) |
| C(10)-Fe(1)-C(6) | 40.67(11) |
| C(8)-Fe(1)-C(6) | 68.74(11) |
| C(9)-Fe(1)-C(6) | 68.54(11) |
| C(2)-C(1)-C(5) | 108.7(3) |
| C(2)-C(1)-Fe(1) | 69.74(19) |
| C(5)-C(1)-Fe(1) | 69.74(19) |
| C(26)-Fe(2)-C(25) | 40.83(12) |
| C(26)-Fe(2)-C(31) | 107.42(14) |
| C(25)-Fe(2)-C(31) | 121.10(16) |
| C(26)-Fe(2)-C(30) | 122.89(13) |
| C(25)-Fe(2)-C(30) | 106.37(14) |
| C(31)-Fe(2)-C(30) | 40.15(15) |
| C(26)-Fe(2)-C(27) | 123.20(17) |
| C(25)-Fe(2)-C(27) | 158.12(19) |
| C(31)-Fe(2)-C(27) | 40.91(16) |
| C(30)-Fe(2)-C(27) | 67.84(15) |

| | |
|---|---|
| C(26)-Fe(2)-C(29) | 158.88(14) |
| C(25)-Fe(2)-C(29) | 122.64(15) |
| C(31)-Fe(2)-C(29) | 67.56(15) |
| C(30)-Fe(2)-C(29) | 40.09(13) |
| C(27)-Fe(2)-C(29) | 67.41(16) |
| C(26)-Fe(2)-C(28) | 159.38(15) |
| C(25)-Fe(2)-C(28) | 159.04(16) |
| C(31)-Fe(2)-C(28) | 68.04(16) |
| C(30)-Fe(2)-C(28) | 67.49(14) |
| C(27)-Fe(2)-C(28) | 40.24(16) |
| C(29)-Fe(2)-C(28) | 39.89(14) |
| C(26)-Fe(2)-C(24) | 68.50(13) |
| C(25)-Fe(2)-C(24) | 40.50(12) |
| C(31)-Fe(2)-C(24) | 156.22(17) |
| C(30)-Fe(2)-C(24) | 120.96(14) |
| C(27)-Fe(2)-C(24) | 160.74(18) |
| C(29)-Fe(2)-C(24) | 107.33(14) |
| C(28)-Fe(2)-C(24) | 123.94(16) |
| C(26)-Fe(2)-C(23) | 68.54(12) |
| C(25)-Fe(2)-C(23) | 68.34(12) |
| C(31)-Fe(2)-C(23) | 161.66(15) |
| C(30)-Fe(2)-C(23) | 157.15(14) |
| C(27)-Fe(2)-C(23) | 125.18(15) |
| C(29)-Fe(2)-C(23) | 122.67(13) |
| C(28)-Fe(2)-C(23) | 109.06(13) |
| C(24)-Fe(2)-C(23) | 40.67(11) |
| C(26)-Fe(2)-C(22) | 40.93(11) |
| C(25)-Fe(2)-C(22) | 68.65(12) |
| C(31)-Fe(2)-C(22) | 124.70(14) |
| C(30)-Fe(2)-C(22) | 160.16(13) |
| C(27)-Fe(2)-C(22) | 109.21(13) |
| C(29)-Fe(2)-C(22) | 158.71(12) |
| C(28)-Fe(2)-C(22) | 123.87(13) |
| C(24)-Fe(2)-C(22) | 68.52(11) |
| C(23)-Fe(2)-C(22) | 40.66(10) |
| C(1)-C(2)-C(3) | 108.4(3) |
| C(1)-C(2)-Fe(1) | 70.29(18) |
| C(3)-C(2)-Fe(1) | 69.79(19) |
| C(2)-C(3)-C(4) | 107.8(3) |

| | |
|---|---|
| C(2)-C(3)-Fe(1) | 70.10(18) |
| C(4)-C(3)-Fe(1) | 69.22(18) |
| C(5)-C(4)-C(3) | 106.9(3) |
| C(5)-C(4)-Fe(1) | 70.00(18) |
| C(3)-C(4)-Fe(1) | 69.54(18) |
| C(1)-C(5)-C(4) | 108.2(3) |
| C(1)-C(5)-Fe(1) | 70.29(19) |
| C(4)-C(5)-Fe(1) | 69.37(18) |
| C(10)-C(6)-C(7) | 106.7(2) |
| C(10)-C(6)-C(11) | 128.0(3) |
| C(7)-C(6)-C(11) | 125.3(3) |
| C(10)-C(6)-Fe(1) | 69.40(16) |
| C(7)-C(6)-Fe(1) | 69.18(15) |
| C(11)-C(6)-Fe(1) | 124.84(19) |
| C(8)-C(7)-C(6) | 108.8(3) |
| C(8)-C(7)-Fe(1) | 69.87(16) |
| C(6)-C(7)-Fe(1) | 70.01(16) |
| C(9)-C(8)-C(7) | 107.8(2) |
| C(9)-C(8)-Fe(1) | 69.99(17) |
| C(7)-C(8)-Fe(1) | 69.52(15) |
| C(8)-C(9)-C(10) | 108.0(3) |
| C(8)-C(9)-Fe(1) | 69.60(16) |
| C(10)-C(9)-Fe(1) | 69.51(16) |
| C(9)-C(10)-C(6) | 108.7(3) |
| C(9)-C(10)-Fe(1) | 69.95(16) |
| C(6)-C(10)-Fe(1) | 69.93(15) |
| C(12)-C(11)-C(6) | 125.1(3) |
| C(11)-C(12)-C(13) | 127.6(3) |
| C(18)-C(13)-C(14) | 118.2(2) |
| C(18)-C(13)-C(12) | 118.7(3) |
| C(14)-C(13)-C(12) | 123.1(2) |
| C(13)-C(14)-C(15) | 121.4(3) |
| C(16)-C(15)-C(14) | 117.9(2) |
| C(16)-C(15)-C(20) | 119.8(2) |
| C(14)-C(15)-C(20) | 122.2(2) |
| C(17)-C(16)-C(15) | 122.1(3) |
| C(16)-C(17)-C(18) | 118.1(3) |
| C(16)-C(17)-C(19) | 122.7(3) |
| C(18)-C(17)-C(19) | 119.1(3) |
| C(13)-C(18)-C(17) | 122.2(3) |
| C(32)-C(19)-C(17) | 127.4(3) |
| C(21)-C(20)-C(15) | 125.7(2) |
| C(20)-C(21)-C(22) | 126.7(3) |
| C(23)-C(22)-C(26) | 106.9(2) |
| C(23)-C(22)-C(21) | 128.2(2) |
| C(26)-C(22)-C(21) | 125.0(2) |
| C(23)-C(22)-Fe(2) | 69.14(15) |
| C(26)-C(22)-Fe(2) | 68.32(15) |
| C(21)-C(22)-Fe(2) | 128.0(2) |
| C(24)-C(23)-C(22) | 108.5(3) |
| C(24)-C(23)-Fe(2) | 69.59(17) |
| C(22)-C(23)-Fe(2) | 70.21(15) |
| C(25)-C(24)-C(23) | 107.9(3) |
| C(25)-C(24)-Fe(2) | 69.24(18) |
| C(23)-C(24)-Fe(2) | 69.74(17) |
| C(24)-C(25)-C(26) | 108.4(3) |
| C(24)-C(25)-Fe(2) | 70.26(18) |
| C(26)-C(25)-Fe(2) | 69.48(17) |
| C(25)-C(26)-C(22) | 108.4(3) |
| C(25)-C(26)-Fe(2) | 69.69(17) |
| C(22)-C(26)-Fe(2) | 70.75(16) |
| C(28)-C(27)-C(31) | 107.7(3) |
| C(28)-C(27)-Fe(2) | 70.1(2) |
| C(31)-C(27)-Fe(2) | 69.5(2) |
| C(29)-C(28)-C(27) | 108.0(3) |
| C(29)-C(28)-Fe(2) | 69.8(2) |
| C(27)-C(28)-Fe(2) | 69.6(2) |
| C(28)-C(29)-C(30) | 108.7(4) |
| C(28)-C(29)-Fe(2) | 70.3(2) |
| C(30)-C(29)-Fe(2) | 69.93(19) |
| C(29)-C(30)-C(31) | 108.3(3) |
| C(29)-C(30)-Fe(2) | 69.98(18) |
| C(31)-C(30)-Fe(2) | 69.89(19) |
| C(30)-C(31)-C(27) | 107.4(3) |
| C(30)-C(31)-Fe(2) | 70.0(2) |
| C(27)-C(31)-Fe(2) | 69.6(2) |

Symmetry transformations used to generate equivalent atoms:

**Table 4**. Anisotropic displacement parameters ($Å^2$x $10^3$)for toto/ str161. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| Fe(1) | 38(1) | 31(1) | 27(1) | -1(1) | 11(1) | -3(1) |
| C(1) | 77(2) | 36(2) | 56(2) | 7(2) | 20(2) | 8(2) |
| Fe(2) | 31(1) | 32(1) | 42(1) | -3(1) | 9(1) | 0(1) |
| C(2) | 67(2) | 51(2) | 50(2) | -19(2) | 17(2) | 1(2) |
| C(3) | 74(2) | 73(3) | 37(2) | 4(2) | 29(2) | 26(2) |
| C(4) | 46(2) | 47(2) | 98(3) | 4(2) | 39(2) | 1(2) |
| C(5) | 51(2) | 57(2) | 49(2) | -4(2) | 2(2) | 14(2) |
| C(6) | 37(2) | 34(2) | 36(2) | 1(1) | 14(1) | 0(1) |
| C(7) | 45(2) | 32(2) | 40(2) | -4(1) | 16(1) | -7(1) |
| C(8) | 55(2) | 44(2) | 28(2) | -5(1) | 16(1) | 3(1) |
| C(9) | 50(2) | 46(2) | 42(2) | 6(1) | 24(2) | -2(1) |
| C(10) | 35(2) | 48(2) | 42(2) | 3(1) | 13(1) | -6(1) |
| C(11) | 41(2) | 36(2) | 36(2) | 6(1) | 12(1) | 1(1) |
| C(12) | 35(2) | 38(2) | 39(2) | 2(1) | 14(1) | 1(1) |
| C(13) | 30(1) | 35(2) | 35(2) | 2(1) | 10(1) | 7(1) |
| C(14) | 32(1) | 38(2) | 32(1) | -2(1) | 5(1) | 1(1) |
| C(15) | 28(1) | 36(2) | 35(2) | 3(1) | 8(1) | 5(1) |
| C(16) | 34(2) | 45(2) | 29(1) | 4(1) | 4(1) | 7(1) |
| C(17) | 27(1) | 37(2) | 42(2) | -3(1) | 5(1) | 6(1) |
| C(18) | 30(1) | 36(2) | 46(2) | 2(1) | 11(1) | 2(1) |
| C(19) | 36(2) | 55(2) | 52(2) | -5(2) | 4(2) | -2(1) |
| C(20) | 37(2) | 38(2) | 32(1) | 4(1) | 8(1) | 4(1) |
| C(21) | 41(2) | 36(2) | 28(1) | -1(1) | 13(1) | 4(1) |
| C(22) | 34(2) | 29(2) | 36(2) | -3(1) | 9(1) | 3(1) |
| C(23) | 38(2) | 34(2) | 39(2) | 3(1) | 9(1) | 5(1) |
| C(24) | 49(2) | 40(2) | 56(2) | 9(2) | 23(2) | 2(1) |
| C(25) | 49(2) | 33(2) | 75(2) | -9(2) | 20(2) | -10(1) |
| C(26) | 46(2) | 41(2) | 43(2) | -12(1) | 12(1) | -4(1) |
| C(27) | 58(2) | 43(2) | 142(4) | 29(2) | 44(3) | 17(2) |
| C(28) | 50(2) | 51(2) | 95(3) | -27(2) | 11(2) | 10(2) |
| C(29) | 41(2) | 77(3) | 63(2) | -9(2) | 13(2) | 19(2) |
| C(30) | 30(2) | 70(2) | 72(2) | -10(2) | 4(2) | 7(2) |
| C(31) | 72(3) | 88(3) | 57(2) | 15(2) | 12(2) | 43(2) |
| C(32) | 62(2) | 70(3) | 57(2) | -9(2) | 2(2) | -15(2) |

**Table 5**. Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters (Å$^2$x $10^3$) for toto.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1) | 2731 | 1141 | 5004 | 66 |
| H(2) | 2227 | 1244 | 2838 | 67 |
| H(3) | 2847 | 2870 | 1998 | 70 |
| H(4) | 3736 | 3825 | 3693 | 72 |
| H(5) | 3654 | 2721 | 5548 | 65 |
| H(7) | 2486 | 5737 | 4055 | 46 |
| H(8) | 2394 | 4691 | 5933 | 50 |
| H(9) | 1475 | 3068 | 5405 | 53 |
| H(10) | 1010 | 3096 | 3200 | 49 |
| H(11) | 1952 | 5395 | 1700 | 45 |
| H(12) | 761 | 3988 | 1227 | 44 |
| H(14) | 1810 | 5914 | -200 | 41 |
| H(16) | 734 | 5192 | -3519 | 44 |
| H(18) | 159 | 3641 | -766 | 44 |
| H(19) | -552 | 3255 | -2728 | 59 |
| H(20) | 1684 | 6708 | -3212 | 43 |
| H(21) | 2667 | 6463 | -1118 | 41 |
| H(23) | 2707 | 7311 | -4241 | 44 |
| H(24) | 3709 | 8732 | -4328 | 56 |
| H(25) | 4324 | 9252 | -2245 | 61 |
| H(26) | 3711 | 8163 | -858 | 51 |
| H(27) | 3848 | 4692 | -1962 | 93 |
| H(28) | 3826 | 4989 | -4113 | 79 |
| H(29) | 4782 | 6434 | -4267 | 72 |
| H(30) | 5408 | 7039 | -2233 | 70 |
| H(31) | 4838 | 5977 | -787 | 87 |
| H(32A) | 59 | 3714 | -4589 | 77 |
| H(32B) | -651 | 2938 | -4610 | 77 |

**Table 6**. Torsion angles [°] for toto/ str161.

| | |
|---|---|
| C(4)-Fe(1)-C(1)-C(2) | -82.2(2) |
| C(3)-Fe(1)-C(1)-C(2) | -37.5(2) |
| C(5)-Fe(1)-C(1)-C(2) | -120.0(3) |
| C(7)-Fe(1)-C(1)-C(2) | -165.5(3) |
| C(10)-Fe(1)-C(1)-C(2) | 75.8(2) |
| C(8)-Fe(1)-C(1)-C(2) | 160.3(2) |
| C(9)-Fe(1)-C(1)-C(2) | 118.4(2) |
| C(6)-Fe(1)-C(1)-C(2) | 39.9(4) |
| C(4)-Fe(1)-C(1)-C(5) | 37.8(2) |
| C(3)-Fe(1)-C(1)-C(5) | 82.6(2) |
| C(2)-Fe(1)-C(1)-C(5) | 120.0(3) |
| C(7)-Fe(1)-C(1)-C(5) | -45.4(5) |
| C(10)-Fe(1)-C(1)-C(5) | -164.11(19) |
| C(8)-Fe(1)-C(1)-C(5) | -79.7(2) |
| C(9)-Fe(1)-C(1)-C(5) | -121.5(2) |
| C(6)-Fe(1)-C(1)-C(5) | 159.9(3) |
| C(5)-C(1)-C(2)-C(3) | 0.6(4) |
| Fe(1)-C(1)-C(2)-C(3) | 59.6(2) |
| C(5)-C(1)-C(2)-Fe(1) | -59.0(2) |
| C(4)-Fe(1)-C(2)-C(1) | 81.0(2) |
| C(3)-Fe(1)-C(2)-C(1) | 119.3(3) |
| C(5)-Fe(1)-C(2)-C(1) | 37.0(2) |
| C(7)-Fe(1)-C(2)-C(1) | 167.6(3) |
| C(10)-Fe(1)-C(2)-C(1) | -121.4(2) |
| C(8)-Fe(1)-C(2)-C(1) | -50.8(4) |
| C(9)-Fe(1)-C(2)-C(1) | -80.3(2) |
| C(6)-Fe(1)-C(2)-C(1) | -163.02(19) |
| C(4)-Fe(1)-C(2)-C(3) | -38.4(2) |
| C(5)-Fe(1)-C(2)-C(3) | -82.3(2) |
| C(7)-Fe(1)-C(2)-C(3) | 48.3(4) |
| C(1)-Fe(1)-C(2)-C(3) | -119.3(3) |
| C(10)-Fe(1)-C(2)-C(3) | 119.3(2) |
| C(8)-Fe(1)-C(2)-C(3) | -170.1(3) |
| C(9)-Fe(1)-C(2)-C(3) | 160.36(19) |
| C(6)-Fe(1)-C(2)-C(3) | 77.7(2) |
| C(1)-C(2)-C(3)-C(4) | -0.7(4) |
| Fe(1)-C(2)-C(3)-C(4) | 59.2(2) |
| C(1)-C(2)-C(3)-Fe(1) | -59.9(2) |
| C(4)-Fe(1)-C(3)-C(2) | 119.0(3) |
| C(5)-Fe(1)-C(3)-C(2) | 80.6(2) |
| C(7)-Fe(1)-C(3)-C(2) | -160.37(19) |
| C(1)-Fe(1)-C(3)-C(2) | 37.3(2) |
| C(10)-Fe(1)-C(3)-C(2) | -77.8(2) |
| C(8)-Fe(1)-C(3)-C(2) | 169.5(3) |
| C(9)-Fe(1)-C(3)-C(2) | -46.9(4) |
| C(6)-Fe(1)-C(3)-C(2) | -119.3(2) |
| C(2)-Fe(1)-C(3)-C(4) | -119.0(3) |
| C(5)-Fe(1)-C(3)-C(4) | -38.3(2) |
| C(7)-Fe(1)-C(3)-C(4) | 80.6(2) |
| C(1)-Fe(1)-C(3)-C(4) | -81.6(2) |
| C(10)-Fe(1)-C(3)-C(4) | 163.26(19) |
| C(8)-Fe(1)-C(3)-C(4) | 50.5(4) |
| C(9)-Fe(1)-C(3)-C(4) | -165.9(3) |
| C(6)-Fe(1)-C(3)-C(4) | 121.7(2) |
| C(2)-C(3)-C(4)-C(5) | 0.6(4) |
| Fe(1)-C(3)-C(4)-C(5) | 60.3(2) |
| C(2)-C(3)-C(4)-Fe(1) | -59.7(2) |
| C(3)-Fe(1)-C(4)-C(5) | -117.8(3) |
| C(2)-Fe(1)-C(4)-C(5) | -80.4(2) |
| C(7)-Fe(1)-C(4)-C(5) | 123.0(2) |
| C(1)-Fe(1)-C(4)-C(5) | -37.2(2) |
| C(10)-Fe(1)-C(4)-C(5) | -159.3(3) |
| C(8)-Fe(1)-C(4)-C(5) | 80.7(2) |
| C(9)-Fe(1)-C(4)-C(5) | 45.9(5) |
| C(6)-Fe(1)-C(4)-C(5) | 165.94(19) |
| C(2)-Fe(1)-C(4)-C(3) | 37.3(2) |
| C(5)-Fe(1)-C(4)-C(3) | 117.8(3) |
| C(7)-Fe(1)-C(4)-C(3) | -119.3(2) |
| C(1)-Fe(1)-C(4)-C(3) | 80.6(2) |
| C(10)-Fe(1)-C(4)-C(3) | -41.5(4) |
| C(8)-Fe(1)-C(4)-C(3) | -161.6(2) |
| C(9)-Fe(1)-C(4)-C(3) | 163.7(3) |
| C(6)-Fe(1)-C(4)-C(3) | -76.3(2) |
| C(2)-C(1)-C(5)-C(4) | -0.2(4) |

| | |
|---|---|
| Fe(1)-C(1)-C(5)-C(4) | -59.2(2) |
| C(2)-C(1)-C(5)-Fe(1) | 59.0(2) |
| C(3)-C(4)-C(5)-C(1) | -0.2(4) |
| Fe(1)-C(4)-C(5)-C(1) | 59.8(2) |
| C(3)-C(4)-C(5)-Fe(1) | -60.0(2) |
| C(4)-Fe(1)-C(5)-C(1) | -119.3(3) |
| C(3)-Fe(1)-C(5)-C(1) | -80.4(2) |
| C(2)-Fe(1)-C(5)-C(1) | -37.0(2) |
| C(7)-Fe(1)-C(5)-C(1) | 163.59(19) |
| C(10)-Fe(1)-C(5)-C(1) | 39.5(4) |
| C(8)-Fe(1)-C(5)-C(1) | 120.7(2) |
| C(9)-Fe(1)-C(5)-C(1) | 77.7(2) |
| C(6)-Fe(1)-C(5)-C(1) | -156.6(3) |
| C(3)-Fe(1)-C(5)-C(4) | 38.9(2) |
| C(2)-Fe(1)-C(5)-C(4) | 82.3(2) |
| C(7)-Fe(1)-C(5)-C(4) | -77.1(2) |
| C(1)-Fe(1)-C(5)-C(4) | 119.3(3) |
| C(10)-Fe(1)-C(5)-C(4) | 158.8(3) |
| C(8)-Fe(1)-C(5)-C(4) | -120.1(2) |
| C(9)-Fe(1)-C(5)-C(4) | -163.0(2) |
| C(6)-Fe(1)-C(5)-C(4) | -37.3(5) |
| C(4)-Fe(1)-C(6)-C(10) | 160.95(19) |
| C(3)-Fe(1)-C(6)-C(10) | 119.20(19) |
| C(2)-Fe(1)-C(6)-C(10) | 78.3(2) |
| C(5)-Fe(1)-C(6)-C(10) | -171.1(3) |
| C(7)-Fe(1)-C(6)-C(10) | -118.1(2) |
| C(1)-Fe(1)-C(6)-C(10) | 49.7(4) |
| C(8)-Fe(1)-C(6)-C(10) | -80.84(18) |
| C(9)-Fe(1)-C(6)-C(10) | -37.31(17) |
| C(4)-Fe(1)-C(6)-C(7) | -80.9(2) |
| C(3)-Fe(1)-C(6)-C(7) | -122.68(19) |
| C(2)-Fe(1)-C(6)-C(7) | -163.55(18) |
| C(5)-Fe(1)-C(6)-C(7) | -53.0(4) |
| C(1)-Fe(1)-C(6)-C(7) | 167.8(3) |
| C(10)-Fe(1)-C(6)-C(7) | 118.1(2) |
| C(8)-Fe(1)-C(6)-C(7) | 37.28(16) |
| C(9)-Fe(1)-C(6)-C(7) | 80.81(17) |
| C(4)-Fe(1)-C(6)-C(11) | 38.3(3) |
| C(3)-Fe(1)-C(6)-C(11) | -3.4(3) |
| C(2)-Fe(1)-C(6)-C(11) | -44.3(3) |
| C(5)-Fe(1)-C(6)-C(11) | 66.3(5) |
| C(7)-Fe(1)-C(6)-C(11) | 119.3(3) |
| C(1)-Fe(1)-C(6)-C(11) | -73.0(4) |
| C(10)-Fe(1)-C(6)-C(11) | -122.6(3) |
| C(8)-Fe(1)-C(6)-C(11) | 156.5(3) |
| C(9)-Fe(1)-C(6)-C(11) | -159.9(3) |
| C(10)-C(6)-C(7)-C(8) | 0.2(3) |
| C(11)-C(6)-C(7)-C(8) | -178.0(3) |
| Fe(1)-C(6)-C(7)-C(8) | -59.3(2) |
| C(10)-C(6)-C(7)-Fe(1) | 59.53(19) |
| C(11)-C(6)-C(7)-Fe(1) | -118.7(3) |
| C(4)-Fe(1)-C(7)-C(8) | -121.5(2) |
| C(3)-Fe(1)-C(7)-C(8) | -164.92(19) |
| C(2)-Fe(1)-C(7)-C(8) | 160.0(3) |
| C(5)-Fe(1)-C(7)-C(8) | -79.4(2) |
| C(1)-Fe(1)-C(7)-C(8) | -45.3(5) |
| C(10)-Fe(1)-C(7)-C(8) | 81.59(18) |
| C(9)-Fe(1)-C(7)-C(8) | 37.73(17) |
| C(6)-Fe(1)-C(7)-C(8) | 119.9(2) |
| C(4)-Fe(1)-C(7)-C(6) | 118.59(19) |
| C(3)-Fe(1)-C(7)-C(6) | 75.2(2) |
| C(2)-Fe(1)-C(7)-C(6) | 40.2(4) |
| C(5)-Fe(1)-C(7)-C(6) | 160.69(17) |
| C(1)-Fe(1)-C(7)-C(6) | -165.2(4) |
| C(10)-Fe(1)-C(7)-C(6) | -38.28(16) |
| C(8)-Fe(1)-C(7)-C(6) | -119.9(2) |
| C(9)-Fe(1)-C(7)-C(6) | -82.15(17) |
| C(6)-C(7)-C(8)-C(9) | -0.4(3) |
| Fe(1)-C(7)-C(8)-C(9) | -59.8(2) |
| C(6)-C(7)-C(8)-Fe(1) | 59.4(2) |
| C(4)-Fe(1)-C(8)-C(9) | -162.76(19) |
| C(3)-Fe(1)-C(8)-C(9) | 159.1(3) |
| C(2)-Fe(1)-C(8)-C(9) | -40.0(4) |
| C(5)-Fe(1)-C(8)-C(9) | -119.6(2) |
| C(7)-Fe(1)-C(8)-C(9) | 118.9(2) |
| C(1)-Fe(1)-C(8)-C(9) | -77.3(2) |

| | | | |
|---|---|---|---|
| C(10)-Fe(1)-C(8)-C(9) | 37.58(17) | C(3)-Fe(1)-C(10)-C(9) | 162.1(2) |
| C(6)-Fe(1)-C(8)-C(9) | 81.45(18) | C(2)-Fe(1)-C(10)-C(9) | 121.21(19) |
| C(4)-Fe(1)-C(8)-C(7) | 78.3(2) | C(5)-Fe(1)-C(10)-C(9) | 52.0(4) |
| C(3)-Fe(1)-C(8)-C(7) | 40.2(4) | C(7)-Fe(1)-C(10)-C(9) | -81.38(19) |
| C(2)-Fe(1)-C(8)-C(7) | -158.9(3) | C(1)-Fe(1)-C(10)-C(9) | 80.8(2) |
| C(5)-Fe(1)-C(8)-C(7) | 121.49(19) | C(8)-Fe(1)-C(10)-C(9) | -37.46(18) |
| C(1)-Fe(1)-C(8)-C(7) | 163.77(18) | C(6)-Fe(1)-C(10)-C(9) | -119.8(3) |
| C(10)-Fe(1)-C(8)-C(7) | -81.33(18) | C(4)-Fe(1)-C(10)-C(6) | -47.5(4) |
| C(9)-Fe(1)-C(8)-C(7) | -118.9(2) | C(3)-Fe(1)-C(10)-C(6) | -78.1(2) |
| C(6)-Fe(1)-C(8)-C(7) | -37.45(16) | C(2)-Fe(1)-C(10)-C(6) | -118.99(18) |
| C(7)-C(8)-C(9)-C(10) | 0.4(3) | C(5)-Fe(1)-C(10)-C(6) | 171.8(3) |
| Fe(1)-C(8)-C(9)-C(10) | -59.1(2) | C(7)-Fe(1)-C(10)-C(6) | 38.41(16) |
| C(7)-C(8)-C(9)-Fe(1) | 59.5(2) | C(1)-Fe(1)-C(10)-C(6) | -159.38(17) |
| C(4)-Fe(1)-C(9)-C(8) | 46.5(5) | C(8)-Fe(1)-C(10)-C(6) | 82.33(18) |
| C(3)-Fe(1)-C(9)-C(8) | -162.0(3) | C(9)-Fe(1)-C(10)-C(6) | 119.8(3) |
| C(2)-Fe(1)-C(9)-C(8) | 164.21(18) | C(10)-C(6)-C(11)-C(12) | 12.5(5) |
| C(5)-Fe(1)-C(9)-C(8) | 80.9(2) | C(7)-C(6)-C(11)-C(12) | -169.7(3) |
| C(7)-Fe(1)-C(9)-C(8) | -37.91(17) | Fe(1)-C(6)-C(11)-C(12) | 102.4(3) |
| C(1)-Fe(1)-C(9)-C(8) | 122.32(19) | C(6)-C(11)-C(12)-C(13) | -176.8(3) |
| C(10)-Fe(1)-C(9)-C(8) | -119.4(3) | C(11)-C(12)-C(13)-C(18) | 174.5(3) |
| C(6)-Fe(1)-C(9)-C(8) | -81.99(18) | C(11)-C(12)-C(13)-C(14) | -3.9(5) |
| C(4)-Fe(1)-C(9)-C(10) | 165.9(4) | C(18)-C(13)-C(14)-C(15) | -1.4(4) |
| C(3)-Fe(1)-C(9)-C(10) | -42.6(4) | C(12)-C(13)-C(14)-C(15) | 177.0(2) |
| C(2)-Fe(1)-C(9)-C(10) | -76.4(2) | C(13)-C(14)-C(15)-C(16) | 1.5(4) |
| C(5)-Fe(1)-C(9)-C(10) | -159.70(19) | C(13)-C(14)-C(15)-C(20) | -175.9(3) |
| C(7)-Fe(1)-C(9)-C(10) | 81.51(19) | C(14)-C(15)-C(16)-C(17) | -1.5(4) |
| C(1)-Fe(1)-C(9)-C(10) | -118.26(19) | C(20)-C(15)-C(16)-C(17) | 176.0(3) |
| C(8)-Fe(1)-C(9)-C(10) | 119.4(3) | C(15)-C(16)-C(17)-C(18) | 1.4(4) |
| C(6)-Fe(1)-C(9)-C(10) | 37.43(17) | C(15)-C(16)-C(17)-C(19) | -176.3(3) |
| C(8)-C(9)-C(10)-C(6) | -0.2(3) | C(14)-C(13)-C(18)-C(17) | 1.3(4) |
| Fe(1)-C(9)-C(10)-C(6) | -59.4(2) | C(12)-C(13)-C(18)-C(17) | -177.2(2) |
| C(8)-C(9)-C(10)-Fe(1) | 59.2(2) | C(16)-C(17)-C(18)-C(13) | -1.3(4) |
| C(7)-C(6)-C(10)-C(9) | 0.0(3) | C(19)-C(17)-C(18)-C(13) | 176.5(3) |
| C(11)-C(6)-C(10)-C(9) | 178.1(3) | C(16)-C(17)-C(19)-C(32) | 15.3(5) |
| Fe(1)-C(6)-C(10)-C(9) | 59.4(2) | C(18)-C(17)-C(19)-C(32) | -162.3(3) |
| C(7)-C(6)-C(10)-Fe(1) | -59.39(19) | C(16)-C(15)-C(20)-C(21) | -157.4(3) |
| C(11)-C(6)-C(10)-Fe(1) | 118.7(3) | C(14)-C(15)-C(20)-C(21) | 20.0(4) |
| C(4)-Fe(1)-C(10)-C(9) | -167.3(3) | C(15)-C(20)-C(21)-C(22) | 178.8(3) |

| | | | |
|---|---|---|---|
| C(20)-C(21)-C(22)-C(23) | -23.2(5) | C(29)-Fe(2)-C(23)-C(24) | -78.3(2) |
| C(20)-C(21)-C(22)-C(26) | 156.1(3) | C(28)-Fe(2)-C(23)-C(24) | -120.3(2) |
| C(20)-C(21)-C(22)-Fe(2) | -115.4(3) | C(22)-Fe(2)-C(23)-C(24) | 119.5(2) |
| C(26)-Fe(2)-C(22)-C(23) | 119.1(2) | C(26)-Fe(2)-C(23)-C(22) | -37.97(17) |
| C(25)-Fe(2)-C(22)-C(23) | 81.19(19) | C(25)-Fe(2)-C(23)-C(22) | -82.02(18) |
| C(31)-Fe(2)-C(22)-C(23) | -165.0(2) | C(31)-Fe(2)-C(23)-C(22) | 42.6(5) |
| C(30)-Fe(2)-C(22)-C(23) | 160.1(4) | C(30)-Fe(2)-C(23)-C(22) | -162.7(3) |
| C(27)-Fe(2)-C(22)-C(23) | -122.0(2) | C(27)-Fe(2)-C(23)-C(22) | 78.3(2) |
| C(29)-Fe(2)-C(22)-C(23) | -45.1(4) | C(29)-Fe(2)-C(23)-C(22) | 162.21(19) |
| C(28)-Fe(2)-C(22)-C(23) | -79.7(2) | C(28)-Fe(2)-C(23)-C(22) | 120.2(2) |
| C(24)-Fe(2)-C(22)-C(23) | 37.54(17) | C(24)-Fe(2)-C(23)-C(22) | -119.5(2) |
| C(25)-Fe(2)-C(22)-C(26) | -37.88(18) | C(22)-C(23)-C(24)-C(25) | 0.8(3) |
| C(31)-Fe(2)-C(22)-C(26) | 76.0(2) | Fe(2)-C(23)-C(24)-C(25) | -58.9(2) |
| C(30)-Fe(2)-C(22)-C(26) | 41.1(5) | C(22)-C(23)-C(24)-Fe(2) | 59.66(19) |
| C(27)-Fe(2)-C(22)-C(26) | 118.9(2) | C(26)-Fe(2)-C(24)-C(25) | 37.71(18) |
| C(29)-Fe(2)-C(22)-C(26) | -164.2(4) | C(31)-Fe(2)-C(24)-C(25) | -46.8(4) |
| C(28)-Fe(2)-C(22)-C(26) | 161.2(2) | C(30)-Fe(2)-C(24)-C(25) | -78.7(2) |
| C(24)-Fe(2)-C(22)-C(26) | -81.52(19) | C(27)-Fe(2)-C(24)-C(25) | 168.8(4) |
| C(23)-Fe(2)-C(22)-C(26) | -119.1(2) | C(29)-Fe(2)-C(24)-C(25) | -120.3(2) |
| C(26)-Fe(2)-C(22)-C(21) | -118.2(3) | C(28)-Fe(2)-C(24)-C(25) | -160.94(19) |
| C(25)-Fe(2)-C(22)-C(21) | -156.0(3) | C(23)-Fe(2)-C(24)-C(25) | 119.4(3) |
| C(31)-Fe(2)-C(22)-C(21) | -42.2(3) | C(22)-Fe(2)-C(24)-C(25) | 81.86(19) |
| C(30)-Fe(2)-C(22)-C(21) | -77.1(5) | C(26)-Fe(2)-C(24)-C(23) | -81.67(18) |
| C(27)-Fe(2)-C(22)-C(21) | 0.7(3) | C(25)-Fe(2)-C(24)-C(23) | -119.4(3) |
| C(29)-Fe(2)-C(22)-C(21) | 77.7(5) | C(31)-Fe(2)-C(24)-C(23) | -166.2(3) |
| C(28)-Fe(2)-C(22)-C(21) | 43.0(3) | C(30)-Fe(2)-C(24)-C(23) | 161.95(18) |
| C(24)-Fe(2)-C(22)-C(21) | 160.3(3) | C(27)-Fe(2)-C(24)-C(23) | 49.4(5) |
| C(23)-Fe(2)-C(22)-C(21) | 122.8(3) | C(29)-Fe(2)-C(24)-C(23) | 120.31(19) |
| C(26)-C(22)-C(23)-C(24) | -1.2(3) | C(28)-Fe(2)-C(24)-C(23) | 79.7(2) |
| C(21)-C(22)-C(23)-C(24) | 178.2(3) | C(22)-Fe(2)-C(24)-C(23) | -37.53(16) |
| Fe(2)-C(22)-C(23)-C(24) | -59.3(2) | C(23)-C(24)-C(25)-C(26) | 0.0(4) |
| C(26)-C(22)-C(23)-Fe(2) | 58.07(19) | Fe(2)-C(24)-C(25)-C(26) | -59.2(2) |
| C(21)-C(22)-C(23)-Fe(2) | -122.5(3) | C(23)-C(24)-C(25)-Fe(2) | 59.2(2) |
| C(26)-Fe(2)-C(23)-C(24) | 81.56(19) | C(26)-Fe(2)-C(25)-C(24) | -119.5(3) |
| C(25)-Fe(2)-C(23)-C(24) | 37.51(18) | C(31)-Fe(2)-C(25)-C(24) | 159.9(2) |
| C(31)-Fe(2)-C(23)-C(24) | 162.2(4) | C(30)-Fe(2)-C(25)-C(24) | 118.8(2) |
| C(30)-Fe(2)-C(23)-C(24) | -43.2(4) | C(27)-Fe(2)-C(25)-C(24) | -170.1(3) |
| C(27)-Fe(2)-C(23)-C(24) | -162.2(2) | C(29)-Fe(2)-C(25)-C(24) | 78.2(2) |

| | | | |
|---|---|---|---|
| C(28)-Fe(2)-C(25)-C(24) | 49.2(4) | C(30)-Fe(2)-C(27)-C(28) | -80.9(2) |
| C(23)-Fe(2)-C(25)-C(24) | -37.66(17) | C(29)-Fe(2)-C(27)-C(28) | -37.4(2) |
| C(22)-Fe(2)-C(25)-C(24) | -81.51(18) | C(24)-Fe(2)-C(27)-C(28) | 40.4(5) |
| C(31)-Fe(2)-C(25)-C(26) | -80.6(2) | C(23)-Fe(2)-C(27)-C(28) | 77.6(2) |
| C(30)-Fe(2)-C(25)-C(26) | -121.7(2) | C(22)-Fe(2)-C(27)-C(28) | 120.1(2) |
| C(27)-Fe(2)-C(25)-C(26) | -50.6(4) | C(26)-Fe(2)-C(27)-C(31) | -77.9(2) |
| C(29)-Fe(2)-C(25)-C(26) | -162.37(18) | C(25)-Fe(2)-C(27)-C(31) | -40.8(5) |
| C(28)-Fe(2)-C(25)-C(26) | 168.7(3) | C(30)-Fe(2)-C(27)-C(31) | 37.8(2) |
| C(24)-Fe(2)-C(25)-C(26) | 119.5(3) | C(29)-Fe(2)-C(27)-C(31) | 81.3(2) |
| C(23)-Fe(2)-C(25)-C(26) | 81.81(19) | C(28)-Fe(2)-C(27)-C(31) | 118.7(3) |
| C(22)-Fe(2)-C(25)-C(26) | 37.97(17) | C(24)-Fe(2)-C(27)-C(31) | 159.0(4) |
| C(24)-C(25)-C(26)-C(22) | -0.7(3) | C(23)-Fe(2)-C(27)-C(31) | -163.7(2) |
| Fe(2)-C(25)-C(26)-C(22) | -60.5(2) | C(22)-Fe(2)-C(27)-C(31) | -121.2(2) |
| C(24)-C(25)-C(26)-Fe(2) | 59.7(2) | C(31)-C(27)-C(28)-C(29) | -0.1(4) |
| C(23)-C(22)-C(26)-C(25) | 1.2(3) | Fe(2)-C(27)-C(28)-C(29) | 59.5(2) |
| C(21)-C(22)-C(26)-C(25) | -178.2(3) | C(31)-C(27)-C(28)-Fe(2) | -59.6(3) |
| Fe(2)-C(22)-C(26)-C(25) | 59.8(2) | C(26)-Fe(2)-C(28)-C(29) | -161.9(3) |
| C(23)-C(22)-C(26)-Fe(2) | -58.59(19) | C(25)-Fe(2)-C(28)-C(29) | 39.4(5) |
| C(21)-C(22)-C(26)-Fe(2) | 122.0(3) | C(31)-Fe(2)-C(28)-C(29) | -80.8(2) |
| C(31)-Fe(2)-C(26)-C(25) | 117.7(2) | C(30)-Fe(2)-C(28)-C(29) | -37.3(2) |
| C(30)-Fe(2)-C(26)-C(25) | 76.4(2) | C(27)-Fe(2)-C(28)-C(29) | -119.1(3) |
| C(27)-Fe(2)-C(26)-C(25) | 159.9(2) | C(24)-Fe(2)-C(28)-C(29) | 75.8(3) |
| C(29)-Fe(2)-C(26)-C(25) | 45.0(5) | C(23)-Fe(2)-C(28)-C(29) | 118.5(2) |
| C(28)-Fe(2)-C(26)-C(25) | -168.5(4) | C(22)-Fe(2)-C(28)-C(29) | 161.2(2) |
| C(24)-Fe(2)-C(26)-C(25) | -37.42(18) | C(26)-Fe(2)-C(28)-C(27) | -42.8(5) |
| C(23)-Fe(2)-C(26)-C(25) | -81.28(19) | C(25)-Fe(2)-C(28)-C(27) | 158.6(4) |
| C(22)-Fe(2)-C(26)-C(25) | -119.0(3) | C(31)-Fe(2)-C(28)-C(27) | 38.3(2) |
| C(25)-Fe(2)-C(26)-C(22) | 119.0(3) | C(30)-Fe(2)-C(28)-C(27) | 81.8(2) |
| C(31)-Fe(2)-C(26)-C(22) | -123.3(2) | C(29)-Fe(2)-C(28)-C(27) | 119.1(3) |
| C(30)-Fe(2)-C(26)-C(22) | -164.61(19) | C(24)-Fe(2)-C(28)-C(27) | -165.1(2) |
| C(27)-Fe(2)-C(26)-C(22) | -81.1(2) | C(23)-Fe(2)-C(28)-C(27) | -122.4(2) |
| C(29)-Fe(2)-C(26)-C(22) | 164.0(3) | C(22)-Fe(2)-C(28)-C(27) | -79.7(2) |
| C(28)-Fe(2)-C(26)-C(22) | -49.5(5) | C(27)-C(28)-C(29)-C(30) | 0.1(4) |
| C(24)-Fe(2)-C(26)-C(22) | 81.58(18) | Fe(2)-C(28)-C(29)-C(30) | 59.6(2) |
| C(23)-Fe(2)-C(26)-C(22) | 37.72(16) | C(27)-C(28)-C(29)-Fe(2) | -59.4(2) |
| C(26)-Fe(2)-C(27)-C(28) | 163.4(2) | C(26)-Fe(2)-C(29)-C(28) | 162.3(4) |
| C(25)-Fe(2)-C(27)-C(28) | -159.5(3) | C(25)-Fe(2)-C(29)-C(28) | -164.3(2) |
| C(31)-Fe(2)-C(27)-C(28) | -118.7(3) | C(31)-Fe(2)-C(29)-C(28) | 82.1(3) |

| | |
|---|---|
| C(30)-Fe(2)-C(29)-C(28) | 119.6(3) |
| C(27)-Fe(2)-C(29)-C(28) | 37.7(2) |
| C(24)-Fe(2)-C(29)-C(28) | -122.6(2) |
| C(23)-Fe(2)-C(29)-C(28) | -80.7(3) |
| C(22)-Fe(2)-C(29)-C(28) | -47.4(5) |
| C(26)-Fe(2)-C(29)-C(30) | 42.7(5) |
| C(25)-Fe(2)-C(29)-C(30) | 76.0(3) |
| C(31)-Fe(2)-C(29)-C(30) | -37.5(2) |
| C(27)-Fe(2)-C(29)-C(30) | -81.9(3) |
| C(28)-Fe(2)-C(29)-C(30) | -119.6(3) |
| C(24)-Fe(2)-C(29)-C(30) | 117.8(2) |
| C(23)-Fe(2)-C(29)-C(30) | 159.7(2) |
| C(22)-Fe(2)-C(29)-C(30) | -167.0(3) |
| C(28)-C(29)-C(30)-C(31) | -0.2(4) |
| Fe(2)-C(29)-C(30)-C(31) | 59.6(2) |
| C(28)-C(29)-C(30)-Fe(2) | -59.8(2) |
| C(26)-Fe(2)-C(30)-C(29) | -163.1(2) |
| C(25)-Fe(2)-C(30)-C(29) | -121.6(2) |
| C(31)-Fe(2)-C(30)-C(29) | 119.3(3) |
| C(27)-Fe(2)-C(30)-C(29) | 80.8(3) |
| C(28)-Fe(2)-C(30)-C(29) | 37.1(2) |
| C(24)-Fe(2)-C(30)-C(29) | -80.0(3) |
| C(23)-Fe(2)-C(30)-C(29) | -48.7(4) |
| C(22)-Fe(2)-C(30)-C(29) | 166.1(3) |
| C(26)-Fe(2)-C(30)-C(31) | 77.7(3) |
| C(25)-Fe(2)-C(30)-C(31) | 119.1(3) |
| C(27)-Fe(2)-C(30)-C(31) | -38.5(3) |
| C(29)-Fe(2)-C(30)-C(31) | -119.3(3) |
| C(28)-Fe(2)-C(30)-C(31) | -82.1(3) |
| C(24)-Fe(2)-C(30)-C(31) | 160.7(2) |
| C(23)-Fe(2)-C(30)-C(31) | -167.9(3) |
| C(22)-Fe(2)-C(30)-C(31) | 46.8(5) |
| C(29)-C(30)-C(31)-C(27) | 0.1(4) |
| Fe(2)-C(30)-C(31)-C(27) | 59.8(2) |
| C(29)-C(30)-C(31)-Fe(2) | -59.7(2) |
| C(28)-C(27)-C(31)-C(30) | 0.0(4) |
| Fe(2)-C(27)-C(31)-C(30) | -60.0(2) |
| C(28)-C(27)-C(31)-Fe(2) | 60.0(2) |
| C(26)-Fe(2)-C(31)-C(30) | -120.7(2) |
| C(25)-Fe(2)-C(31)-C(30) | -78.2(3) |
| C(27)-Fe(2)-C(31)-C(30) | 118.3(3) |
| C(29)-Fe(2)-C(31)-C(30) | 37.4(2) |
| C(28)-Fe(2)-C(31)-C(30) | 80.7(2) |
| C(24)-Fe(2)-C(31)-C(30) | -44.6(5) |
| C(23)-Fe(2)-C(31)-C(30) | 165.1(4) |
| C(22)-Fe(2)-C(31)-C(30) | -162.48(19) |
| C(26)-Fe(2)-C(31)-C(27) | 120.9(2) |
| C(25)-Fe(2)-C(31)-C(27) | 163.5(2) |
| C(30)-Fe(2)-C(31)-C(27) | -118.3(3) |
| C(29)-Fe(2)-C(31)-C(27) | -80.9(3) |
| C(28)-Fe(2)-C(31)-C(27) | -37.7(2) |
| C(24)-Fe(2)-C(31)-C(27) | -163.0(3) |
| C(23)-Fe(2)-C(31)-C(27) | 46.7(5) |
| C(22)-Fe(2)-C(31)-C(27) | 79.2(3) |

---

Symmetry transformations used to generate equivalent atoms:

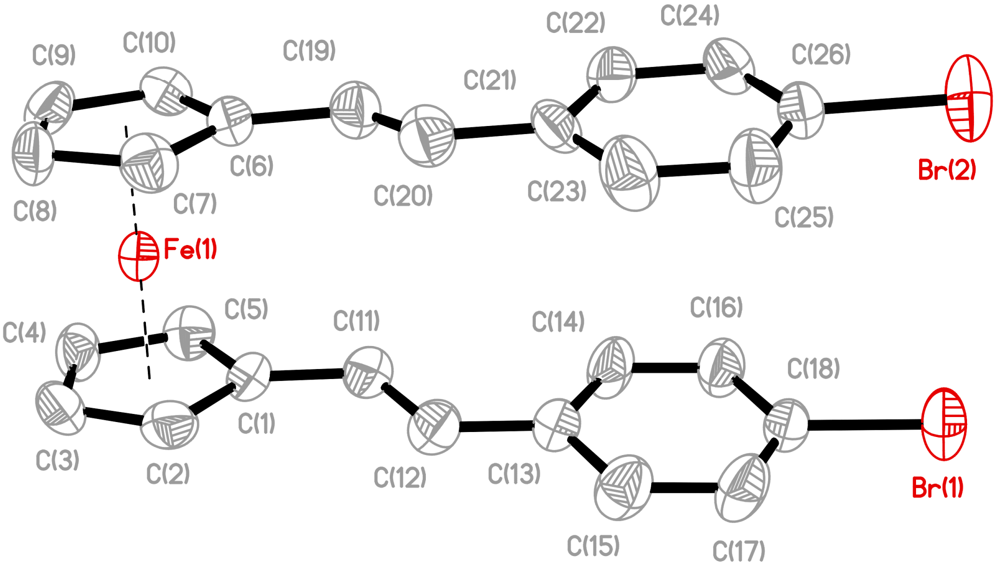

C(9)
C(10)
C(19)
C(21)
C(22)
C(24)
C(26)
C(8)
C(7)
C(6)
C(20)
C(23)
C(25)
Br(2)
Fe(1)
C(4)
C(5)
C(11)
C(14)
C(16)
C(18)
C(3)
C(2)
C(1)
C(12)
C(13)
C(15)
C(17)
Br(1)

**Table 1**. Crystal data and structure refinement for str162m.

| | | |
|---|---|---|
| Identification code | str162m | |
| Empirical formula | C26 H20 Br2 Fe | |
| Formula weight | 548.09 | |
| Temperature | 566(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | P2(1)/c | |
| Unit cell dimensions | a = 6.2534(6) Å | $\alpha$= 90°. |
| | b = 14.1477(13) Å | $\beta$= 94.046(2)°. |
| | c = 24.016(2) Å | $\gamma$ = 90°. |
| Volume | 2119.4(3) Å$^{3}$ | |
| Z | 4 | |
| Density (calculated) | 1.718 Mg/m$^{3}$ | |
| Absorption coefficient | 4.492 mm$^{-1}$ | |
| F(000) | 1088 | |
| Crystal size | 0.5 x 0.2 x 0.1 mm$^{3}$ | |
| Theta range for data collection | 1.67 to 24.71°. | |
| Index ranges | -7<=h<=7, -15<=k<=16, -25<=l<=28 | |
| Reflections collected | 11589 | |
| Independent reflections | 3623 [R(int) = 0.0421] | |
| Completeness to theta = 24.71° | 100.0 % | |
| Absorption correction | Bruker SADABS | |
| Max. and min. transmission | 1.955059 and 1.194273 | |
| Refinement method | Full-matrix least-squares on F$^{2}$ | |
| Data / restraints / parameters | 3623 / 0 / 262 | |
| Goodness-of-fit on F$^{2}$ | 0.983 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0374, wR2 = 0.0822 | |
| R indices (all data) | R1 = 0.0687, wR2 = 0.0907 | |
| Largest diff. peak and hole | 0.786 and -0.738 e.Å$^{-3}$ | |

**Table 2**. Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) for str162m. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| Fe(1) | 4860(1) | 8278(1) | 3772(1) | 33(1) |
| Br(1) | 13124(1) | 9505(1) | 484(1) | 64(1) |
| C(1) | 6693(7) | 9355(3) | 3474(2) | 40(1) |
| Br(2) | 11373(1) | 6681(1) | 258(1) | 70(1) |
| C(2) | 4492(7) | 9634(3) | 3476(2) | 45(1) |
| C(3) | 3896(8) | 9580(3) | 4037(2) | 50(1) |
| C(4) | 5650(8) | 9264(3) | 4371(2) | 47(1) |
| C(5) | 7386(7) | 9116(3) | 4034(2) | 44(1) |
| C(6) | 5190(7) | 7090(3) | 3282(2) | 37(1) |
| C(7) | 3017(7) | 7382(3) | 3270(2) | 44(1) |
| C(8) | 2370(8) | 7361(3) | 3824(2) | 50(1) |
| C(9) | 4122(8) | 7066(3) | 4180(2) | 49(1) |
| C(10) | 5863(7) | 6905(3) | 3846(2) | 44(1) |
| C(11) | 8047(7) | 9295(3) | 3005(2) | 46(1) |
| C(12) | 7604(8) | 9635(3) | 2504(2) | 47(1) |
| C(13) | 8970(7) | 9598(3) | 2032(2) | 42(1) |
| C(14) | 11039(8) | 9229(3) | 2069(2) | 50(1) |
| C(15) | 8226(8) | 9951(3) | 1519(2) | 54(1) |
| C(16) | 12279(8) | 9204(3) | 1614(2) | 51(1) |
| C(17) | 9427(8) | 9927(3) | 1059(2) | 54(1) |
| C(18) | 11428(8) | 9551(3) | 1114(2) | 42(1) |
| C(19) | 6567(7) | 6972(3) | 2819(2) | 45(1) |
| C(20) | 6013(8) | 7114(3) | 2290(2) | 49(1) |
| C(21) | 7363(7) | 7009(3) | 1819(2) | 42(1) |
| C(22) | 9412(7) | 6618(3) | 1863(2) | 44(1) |
| C(23) | 6562(8) | 7296(3) | 1290(2) | 57(1) |
| C(24) | 10600(7) | 6519(3) | 1403(2) | 44(1) |
| C(25) | 7749(8) | 7211(3) | 834(2) | 55(1) |
| C(26) | 9744(7) | 6821(3) | 893(2) | 42(1) |

**Table 3**. Bond lengths [Å] and angles [°] for str162m.

| | |
|---|---|
| Fe(1)-C(4) | 2.037(4) |
| Fe(1)-C(8) | 2.038(4) |
| Fe(1)-C(5) | 2.038(4) |
| Fe(1)-C(9) | 2.043(4) |
| Fe(1)-C(10) | 2.046(4) |
| Fe(1)-C(7) | 2.048(4) |
| Fe(1)-C(3) | 2.052(4) |
| Fe(1)-C(2) | 2.054(4) |
| Fe(1)-C(1) | 2.065(4) |
| Fe(1)-C(6) | 2.072(4) |
| Br(1)-C(18) | 1.909(4) |
| C(1)-C(5) | 1.425(6) |
| C(1)-C(2) | 1.432(6) |
| C(1)-C(11) | 1.459(5) |
| Br(2)-C(26) | 1.904(4) |
| C(2)-C(3) | 1.424(6) |
| C(3)-C(4) | 1.387(7) |
| C(4)-C(5) | 1.415(6) |
| C(6)-C(10) | 1.415(6) |
| C(6)-C(7) | 1.419(6) |
| C(6)-C(19) | 1.463(5) |
| C(7)-C(8) | 1.417(6) |
| C(8)-C(9) | 1.405(6) |
| C(9)-C(10) | 1.415(6) |
| C(11)-C(12) | 1.307(6) |
| C(12)-C(13) | 1.467(6) |
| C(13)-C(15) | 1.379(6) |
| C(13)-C(14) | 1.393(6) |
| C(14)-C(16) | 1.384(6) |
| C(15)-C(17) | 1.379(6) |
| C(16)-C(18) | 1.369(6) |
| C(17)-C(18) | 1.358(6) |
| C(19)-C(20) | 1.309(6) |
| C(20)-C(21) | 1.467(6) |
| C(21)-C(23) | 1.392(6) |
| C(21)-C(22) | 1.392(6) |
| C(22)-C(24) | 1.380(5) |
| C(23)-C(25) | 1.370(6) |
| C(24)-C(26) | 1.370(6) |
| C(25)-C(26) | 1.363(6) |
| C(4)-Fe(1)-C(8) | 122.77(17) |
| C(4)-Fe(1)-C(5) | 40.63(16) |
| C(8)-Fe(1)-C(5) | 158.56(18) |
| C(4)-Fe(1)-C(9) | 106.74(18) |
| C(8)-Fe(1)-C(9) | 40.27(18) |
| C(5)-Fe(1)-C(9) | 122.47(19) |
| C(4)-Fe(1)-C(10) | 122.1(2) |
| C(8)-Fe(1)-C(10) | 67.71(18) |
| C(5)-Fe(1)-C(10) | 107.42(19) |
| C(9)-Fe(1)-C(10) | 40.49(16) |
| C(4)-Fe(1)-C(7) | 159.57(18) |
| C(8)-Fe(1)-C(7) | 40.58(16) |
| C(5)-Fe(1)-C(7) | 158.93(16) |
| C(9)-Fe(1)-C(7) | 68.01(19) |
| C(10)-Fe(1)-C(7) | 67.63(19) |
| C(4)-Fe(1)-C(3) | 39.64(18) |
| C(8)-Fe(1)-C(3) | 108.08(18) |
| C(5)-Fe(1)-C(3) | 67.74(18) |
| C(9)-Fe(1)-C(3) | 121.59(17) |
| C(10)-Fe(1)-C(3) | 157.00(19) |
| C(7)-Fe(1)-C(3) | 124.90(19) |
| C(4)-Fe(1)-C(2) | 67.75(19) |
| C(8)-Fe(1)-C(2) | 123.3(2) |
| C(5)-Fe(1)-C(2) | 68.23(18) |
| C(9)-Fe(1)-C(2) | 157.90(18) |
| C(10)-Fe(1)-C(2) | 160.67(17) |
| C(7)-Fe(1)-C(2) | 109.24(18) |
| C(3)-Fe(1)-C(2) | 40.60(16) |
| C(4)-Fe(1)-C(1) | 68.15(17) |
| C(8)-Fe(1)-C(1) | 159.4(2) |
| C(5)-Fe(1)-C(1) | 40.63(17) |
| C(9)-Fe(1)-C(1) | 159.24(19) |
| C(10)-Fe(1)-C(1) | 123.81(17) |

| | |
|---|---|
| C(7)-Fe(1)-C(1) | 123.72(17) |
| C(3)-Fe(1)-C(1) | 68.16(17) |
| C(2)-Fe(1)-C(1) | 40.71(17) |
| C(4)-Fe(1)-C(6) | 158.02(19) |
| C(8)-Fe(1)-C(6) | 67.95(16) |
| C(5)-Fe(1)-C(6) | 122.75(17) |
| C(9)-Fe(1)-C(6) | 68.03(16) |
| C(10)-Fe(1)-C(6) | 40.19(16) |
| C(7)-Fe(1)-C(6) | 40.29(16) |
| C(3)-Fe(1)-C(6) | 161.33(19) |
| C(2)-Fe(1)-C(6) | 125.05(17) |
| C(1)-Fe(1)-C(6) | 108.73(16) |
| C(5)-C(1)-C(2) | 106.9(4) |
| C(5)-C(1)-C(11) | 124.1(4) |
| C(2)-C(1)-C(11) | 129.0(4) |
| C(5)-C(1)-Fe(1) | 68.7(2) |
| C(2)-C(1)-Fe(1) | 69.2(2) |
| C(11)-C(1)-Fe(1) | 126.3(3) |
| C(3)-C(2)-C(1) | 107.7(4) |
| C(3)-C(2)-Fe(1) | 69.6(2) |
| C(1)-C(2)-Fe(1) | 70.1(2) |
| C(4)-C(3)-C(2) | 108.4(4) |
| C(4)-C(3)-Fe(1) | 69.6(2) |
| C(2)-C(3)-Fe(1) | 69.8(2) |
| C(3)-C(4)-C(5) | 108.9(4) |
| C(3)-C(4)-Fe(1) | 70.8(3) |
| C(5)-C(4)-Fe(1) | 69.7(2) |
| C(4)-C(5)-C(1) | 108.1(4) |
| C(4)-C(5)-Fe(1) | 69.7(2) |
| C(1)-C(5)-Fe(1) | 70.7(2) |
| C(10)-C(6)-C(7) | 107.0(4) |
| C(10)-C(6)-C(19) | 123.8(4) |
| C(7)-C(6)-C(19) | 129.2(4) |
| C(10)-C(6)-Fe(1) | 68.9(2) |
| C(7)-C(6)-Fe(1) | 69.0(2) |
| C(19)-C(6)-Fe(1) | 127.7(3) |
| C(8)-C(7)-C(6) | 108.2(4) |
| C(8)-C(7)-Fe(1) | 69.3(2) |
| C(6)-C(7)-Fe(1) | 70.8(2) |
| C(9)-C(8)-C(7) | 108.4(4) |
| C(9)-C(8)-Fe(1) | 70.1(3) |
| C(7)-C(8)-Fe(1) | 70.1(2) |
| C(8)-C(9)-C(10) | 107.6(4) |
| C(8)-C(9)-Fe(1) | 69.7(2) |
| C(10)-C(9)-Fe(1) | 69.9(2) |
| C(9)-C(10)-C(6) | 108.9(4) |
| C(9)-C(10)-Fe(1) | 69.7(2) |
| C(6)-C(10)-Fe(1) | 70.9(2) |
| C(12)-C(11)-C(1) | 126.4(4) |
| C(11)-C(12)-C(13) | 126.9(4) |
| C(15)-C(13)-C(14) | 116.5(4) |
| C(15)-C(13)-C(12) | 119.9(4) |
| C(14)-C(13)-C(12) | 123.5(4) |
| C(16)-C(14)-C(13) | 121.9(4) |
| C(17)-C(15)-C(13) | 122.5(5) |
| C(18)-C(16)-C(14) | 118.6(4) |
| C(18)-C(17)-C(15) | 118.9(4) |
| C(17)-C(18)-C(16) | 121.6(4) |
| C(17)-C(18)-Br(1) | 119.7(3) |
| C(16)-C(18)-Br(1) | 118.7(3) |
| C(20)-C(19)-C(6) | 126.2(5) |
| C(19)-C(20)-C(21) | 127.3(5) |
| C(23)-C(21)-C(22) | 117.1(4) |
| C(23)-C(21)-C(20) | 119.0(4) |
| C(22)-C(21)-C(20) | 123.9(4) |
| C(24)-C(22)-C(21) | 121.6(4) |
| C(25)-C(23)-C(21) | 121.5(4) |
| C(26)-C(24)-C(22) | 119.0(4) |
| C(26)-C(25)-C(23) | 119.7(4) |
| C(25)-C(26)-C(24) | 121.1(4) |
| C(25)-C(26)-Br(2) | 119.8(3) |
| C(24)-C(26)-Br(2) | 119.1(3) |

---

Symmetry transformations used to generate equivalent atoms:

**Table 4**. Anisotropic displacement parameters ($Å^2$x $10^3$)for str162m. The anisotropic displacement factor exponent takes the form: $-2\pi^2[ h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12} ]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| Fe(1) | 34(1) | 35(1) | 31(1) | 0(1) | 11(1) | 0(1) |
| Br(1) | 78(1) | 78(1) | 39(1) | -3(1) | 23(1) | 0(1) |
| C(1) | 42(3) | 37(2) | 42(3) | 6(2) | 13(2) | -3(2) |
| Br(2) | 70(1) | 100(1) | 42(1) | -9(1) | 25(1) | -1(1) |
| C(2) | 57(3) | 36(2) | 43(3) | 6(2) | 4(2) | 6(2) |
| C(3) | 47(3) | 41(3) | 64(3) | -7(2) | 21(3) | 6(2) |
| C(4) | 58(3) | 49(3) | 36(3) | -13(2) | 17(2) | -10(2) |
| C(5) | 36(3) | 48(3) | 46(3) | -2(2) | 0(2) | -5(2) |
| C(6) | 41(3) | 34(2) | 38(3) | -2(2) | 11(2) | -1(2) |
| C(7) | 46(3) | 45(3) | 41(3) | -8(2) | 1(2) | -3(2) |
| C(8) | 44(3) | 52(3) | 57(3) | -9(2) | 29(3) | -9(2) |
| C(9) | 67(4) | 44(3) | 40(3) | 8(2) | 19(3) | -8(3) |
| C(10) | 46(3) | 37(3) | 51(3) | 2(2) | 11(2) | 8(2) |
| C(11) | 45(3) | 42(3) | 51(3) | 5(2) | 13(2) | 0(2) |
| C(12) | 51(3) | 44(3) | 45(3) | 3(2) | 9(2) | -4(2) |
| C(13) | 47(3) | 41(2) | 37(3) | 3(2) | 10(2) | -1(2) |
| C(14) | 51(3) | 69(3) | 30(2) | 16(2) | 4(2) | 11(3) |
| C(15) | 42(3) | 65(3) | 54(3) | 16(3) | 8(2) | 4(3) |
| C(16) | 53(3) | 62(3) | 38(3) | 11(2) | 10(2) | 15(2) |
| C(17) | 52(3) | 72(3) | 36(3) | 18(2) | 3(2) | 2(3) |
| C(18) | 51(3) | 41(2) | 35(3) | 1(2) | 11(2) | -4(2) |
| C(19) | 43(3) | 46(3) | 47(3) | -4(2) | 12(2) | -3(2) |
| C(20) | 52(3) | 51(3) | 44(3) | -2(2) | 7(2) | 3(2) |
| C(21) | 49(3) | 35(2) | 44(3) | -15(2) | 14(2) | -1(2) |
| C(22) | 57(3) | 45(2) | 30(2) | 0(2) | 4(2) | -1(2) |
| C(23) | 52(3) | 73(3) | 46(3) | -1(3) | 6(3) | 20(3) |
| C(24) | 43(3) | 46(3) | 43(3) | -7(2) | 9(2) | 8(2) |
| C(25) | 59(3) | 71(3) | 34(3) | 2(2) | 9(2) | 16(3) |
| C(26) | 49(3) | 42(3) | 38(3) | -4(2) | 16(2) | -1(2) |

**Table 5**. Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters ($Å^2$x $10^3$) for str162m.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(2) | 3611 | 9818 | 3167 | 54 |
| H(3) | 2558 | 9731 | 4158 | 59 |
| H(4) | 5680 | 9164 | 4754 | 57 |
| H(5) | 8744 | 8901 | 4157 | 52 |
| H(7) | 2165 | 7557 | 2954 | 53 |
| H(8) | 1015 | 7516 | 3933 | 60 |
| H(9) | 4136 | 6991 | 4565 | 59 |
| H(10) | 7227 | 6709 | 3977 | 53 |
| H(11) | 9353 | 8985 | 3068 | 55 |
| H(12) | 6283 | 9931 | 2439 | 56 |
| H(14) | 11605 | 8993 | 2410 | 60 |
| H(15) | 6862 | 10216 | 1482 | 64 |
| H(16) | 13660 | 8957 | 1647 | 61 |
| H(17) | 8876 | 10164 | 718 | 64 |
| H(19) | 7969 | 6777 | 2910 | 54 |
| H(20) | 4604 | 7303 | 2203 | 59 |
| H(22) | 9994 | 6420 | 2210 | 52 |
| H(23) | 5190 | 7551 | 1245 | 68 |
| H(24) | 11960 | 6251 | 1439 | 52 |
| H(25) | 7194 | 7419 | 486 | 66 |

**Table 6**.  Torsion angles [°] for str162m.

| | |
|---|---|
| C(4)-Fe(1)-C(1)-C(5) | 38.0(3) |
| C(8)-Fe(1)-C(1)-C(5) | 164.2(4) |
| C(9)-Fe(1)-C(1)-C(5) | -41.5(6) |
| C(10)-Fe(1)-C(1)-C(5) | -76.9(3) |
| C(7)-Fe(1)-C(1)-C(5) | -160.9(2) |
| C(3)-Fe(1)-C(1)-C(5) | 80.8(3) |
| C(2)-Fe(1)-C(1)-C(5) | 118.8(4) |
| C(6)-Fe(1)-C(1)-C(5) | -118.8(3) |
| C(4)-Fe(1)-C(1)-C(2) | -80.8(3) |
| C(8)-Fe(1)-C(1)-C(2) | 45.4(6) |
| C(5)-Fe(1)-C(1)-C(2) | -118.8(4) |
| C(9)-Fe(1)-C(1)-C(2) | -160.3(4) |
| C(10)-Fe(1)-C(1)-C(2) | 164.3(3) |
| C(7)-Fe(1)-C(1)-C(2) | 80.3(3) |
| C(3)-Fe(1)-C(1)-C(2) | -38.0(3) |
| C(6)-Fe(1)-C(1)-C(2) | 122.4(3) |
| C(4)-Fe(1)-C(1)-C(11) | 155.4(5) |
| C(8)-Fe(1)-C(1)-C(11) | -78.4(6) |
| C(5)-Fe(1)-C(1)-C(11) | 117.4(5) |
| C(9)-Fe(1)-C(1)-C(11) | 75.9(7) |
| C(10)-Fe(1)-C(1)-C(11) | 40.5(5) |
| C(7)-Fe(1)-C(1)-C(11) | -43.5(5) |
| C(3)-Fe(1)-C(1)-C(11) | -161.8(5) |
| C(2)-Fe(1)-C(1)-C(11) | -123.8(5) |
| C(6)-Fe(1)-C(1)-C(11) | -1.4(5) |
| C(5)-C(1)-C(2)-C(3) | 1.1(5) |
| C(11)-C(1)-C(2)-C(3) | -179.7(4) |
| Fe(1)-C(1)-C(2)-C(3) | 59.7(3) |
| C(5)-C(1)-C(2)-Fe(1) | -58.6(3) |
| C(11)-C(1)-C(2)-Fe(1) | 120.5(4) |
| C(4)-Fe(1)-C(2)-C(3) | -36.8(3) |
| C(8)-Fe(1)-C(2)-C(3) | 78.8(3) |
| C(5)-Fe(1)-C(2)-C(3) | -80.7(3) |
| C(9)-Fe(1)-C(2)-C(3) | 42.8(6) |
| C(10)-Fe(1)-C(2)-C(3) | -161.3(5) |
| C(7)-Fe(1)-C(2)-C(3) | 121.6(3) |
| C(1)-Fe(1)-C(2)-C(3) | -118.7(4) |
| C(6)-Fe(1)-C(2)-C(3) | 163.7(3) |
| C(4)-Fe(1)-C(2)-C(1) | 81.9(3) |
| C(8)-Fe(1)-C(2)-C(1) | -162.6(3) |
| C(5)-Fe(1)-C(2)-C(1) | 37.9(2) |
| C(9)-Fe(1)-C(2)-C(1) | 161.5(5) |
| C(10)-Fe(1)-C(2)-C(1) | -42.6(7) |
| C(7)-Fe(1)-C(2)-C(1) | -119.7(3) |
| C(3)-Fe(1)-C(2)-C(1) | 118.7(4) |
| C(6)-Fe(1)-C(2)-C(1) | -77.6(3) |
| C(1)-C(2)-C(3)-C(4) | -0.9(5) |
| Fe(1)-C(2)-C(3)-C(4) | 59.1(3) |
| C(1)-C(2)-C(3)-Fe(1) | -60.0(3) |
| C(8)-Fe(1)-C(3)-C(4) | 119.9(3) |
| C(5)-Fe(1)-C(3)-C(4) | -37.7(3) |
| C(9)-Fe(1)-C(3)-C(4) | 77.7(3) |
| C(10)-Fe(1)-C(3)-C(4) | 44.5(6) |
| C(7)-Fe(1)-C(3)-C(4) | 161.6(2) |
| C(2)-Fe(1)-C(3)-C(4) | -119.7(4) |
| C(1)-Fe(1)-C(3)-C(4) | -81.7(3) |
| C(6)-Fe(1)-C(3)-C(4) | -165.6(5) |
| C(4)-Fe(1)-C(3)-C(2) | 119.7(4) |
| C(8)-Fe(1)-C(3)-C(2) | -120.4(3) |
| C(5)-Fe(1)-C(3)-C(2) | 82.1(3) |
| C(9)-Fe(1)-C(3)-C(2) | -162.5(3) |
| C(10)-Fe(1)-C(3)-C(2) | 164.2(4) |
| C(7)-Fe(1)-C(3)-C(2) | -78.7(3) |
| C(1)-Fe(1)-C(3)-C(2) | 38.1(3) |
| C(6)-Fe(1)-C(3)-C(2) | -45.9(6) |
| C(2)-C(3)-C(4)-C(5) | 0.3(5) |
| Fe(1)-C(3)-C(4)-C(5) | 59.5(3) |
| C(2)-C(3)-C(4)-Fe(1) | -59.2(3) |
| C(8)-Fe(1)-C(4)-C(3) | -78.6(3) |
| C(5)-Fe(1)-C(4)-C(3) | 119.7(4) |
| C(9)-Fe(1)-C(4)-C(3) | -119.6(3) |
| C(10)-Fe(1)-C(4)-C(3) | -161.1(2) |
| C(7)-Fe(1)-C(4)-C(3) | -47.9(6) |
| C(2)-Fe(1)-C(4)-C(3) | 37.6(3) |

| | | | |
|---|---|---|---|
| C(1)-Fe(1)-C(4)-C(3) | 81.7(3) | C(7)-Fe(1)-C(6)-C(10) | -119.0(4) |
| C(6)-Fe(1)-C(4)-C(3) | 167.7(4) | C(3)-Fe(1)-C(6)-C(10) | -162.3(5) |
| C(8)-Fe(1)-C(4)-C(5) | 161.8(3) | C(2)-Fe(1)-C(6)-C(10) | 162.9(3) |
| C(9)-Fe(1)-C(4)-C(5) | 120.7(3) | C(1)-Fe(1)-C(6)-C(10) | 120.6(3) |
| C(10)-Fe(1)-C(4)-C(5) | 79.2(3) | C(4)-Fe(1)-C(6)-C(7) | 161.7(4) |
| C(7)-Fe(1)-C(4)-C(5) | -167.5(5) | C(8)-Fe(1)-C(6)-C(7) | 37.9(3) |
| C(3)-Fe(1)-C(4)-C(5) | -119.7(4) | C(5)-Fe(1)-C(6)-C(7) | -163.1(3) |
| C(2)-Fe(1)-C(4)-C(5) | -82.0(3) | C(9)-Fe(1)-C(6)-C(7) | 81.5(3) |
| C(1)-Fe(1)-C(4)-C(5) | -38.0(3) | C(10)-Fe(1)-C(6)-C(7) | 119.0(3) |
| C(6)-Fe(1)-C(4)-C(5) | 48.1(5) | C(3)-Fe(1)-C(6)-C(7) | -43.3(6) |
| C(3)-C(4)-C(5)-C(1) | 0.4(5) | C(2)-Fe(1)-C(6)-C(7) | -78.2(3) |
| Fe(1)-C(4)-C(5)-C(1) | 60.5(3) | C(1)-Fe(1)-C(6)-C(7) | -120.4(3) |
| C(3)-C(4)-C(5)-Fe(1) | -60.1(3) | C(4)-Fe(1)-C(6)-C(19) | -74.3(6) |
| C(2)-C(1)-C(5)-C(4) | -1.0(5) | C(8)-Fe(1)-C(6)-C(19) | 161.9(5) |
| C(11)-C(1)-C(5)-C(4) | 179.9(4) | C(5)-Fe(1)-C(6)-C(19) | -39.2(5) |
| Fe(1)-C(1)-C(5)-C(4) | -59.9(3) | C(9)-Fe(1)-C(6)-C(19) | -154.5(5) |
| C(2)-C(1)-C(5)-Fe(1) | 58.9(3) | C(10)-Fe(1)-C(6)-C(19) | -117.0(5) |
| C(11)-C(1)-C(5)-Fe(1) | -120.2(4) | C(7)-Fe(1)-C(6)-C(19) | 124.0(5) |
| C(8)-Fe(1)-C(5)-C(4) | -46.0(6) | C(3)-Fe(1)-C(6)-C(19) | 80.6(7) |
| C(9)-Fe(1)-C(5)-C(4) | -77.4(3) | C(2)-Fe(1)-C(6)-C(19) | 45.8(5) |
| C(10)-Fe(1)-C(5)-C(4) | -119.3(3) | C(1)-Fe(1)-C(6)-C(19) | 3.6(5) |
| C(7)-Fe(1)-C(5)-C(4) | 167.9(5) | C(10)-C(6)-C(7)-C(8) | -0.8(5) |
| C(3)-Fe(1)-C(5)-C(4) | 36.8(3) | C(19)-C(6)-C(7)-C(8) | 178.4(4) |
| C(2)-Fe(1)-C(5)-C(4) | 80.7(3) | Fe(1)-C(6)-C(7)-C(8) | -59.5(3) |
| C(1)-Fe(1)-C(5)-C(4) | 118.7(4) | C(10)-C(6)-C(7)-Fe(1) | 58.6(3) |
| C(6)-Fe(1)-C(5)-C(4) | -160.7(3) | C(19)-C(6)-C(7)-Fe(1) | -122.2(4) |
| C(4)-Fe(1)-C(5)-C(1) | -118.7(4) | C(4)-Fe(1)-C(7)-C(8) | -41.3(6) |
| C(8)-Fe(1)-C(5)-C(1) | -164.8(4) | C(5)-Fe(1)-C(7)-C(8) | 161.7(5) |
| C(9)-Fe(1)-C(5)-C(1) | 163.8(2) | C(9)-Fe(1)-C(7)-C(8) | 37.5(3) |
| C(10)-Fe(1)-C(5)-C(1) | 122.0(2) | C(10)-Fe(1)-C(7)-C(8) | 81.4(3) |
| C(7)-Fe(1)-C(5)-C(1) | 49.2(6) | C(3)-Fe(1)-C(7)-C(8) | -76.5(3) |
| C(3)-Fe(1)-C(5)-C(1) | -81.9(3) | C(2)-Fe(1)-C(7)-C(8) | -119.1(3) |
| C(2)-Fe(1)-C(5)-C(1) | -38.0(2) | C(1)-Fe(1)-C(7)-C(8) | -162.0(3) |
| C(6)-Fe(1)-C(5)-C(1) | 80.6(3) | C(6)-Fe(1)-C(7)-C(8) | 119.0(4) |
| C(4)-Fe(1)-C(6)-C(10) | 42.7(5) | C(4)-Fe(1)-C(7)-C(6) | -160.3(5) |
| C(8)-Fe(1)-C(6)-C(10) | -81.1(3) | C(8)-Fe(1)-C(7)-C(6) | -119.0(4) |
| C(5)-Fe(1)-C(6)-C(10) | 77.9(3) | C(5)-Fe(1)-C(7)-C(6) | 42.7(6) |
| C(9)-Fe(1)-C(6)-C(10) | -37.5(3) | C(9)-Fe(1)-C(7)-C(6) | -81.5(3) |

| | | | |
|---|---|---|---|
| C(10)-Fe(1)-C(7)-C(6) | -37.6(2) | C(3)-Fe(1)-C(9)-C(10) | -160.7(3) |
| C(3)-Fe(1)-C(7)-C(6) | 164.5(2) | C(2)-Fe(1)-C(9)-C(10) | 168.0(5) |
| C(2)-Fe(1)-C(7)-C(6) | 121.9(2) | C(1)-Fe(1)-C(9)-C(10) | -47.7(6) |
| C(1)-Fe(1)-C(7)-C(6) | 79.0(3) | C(6)-Fe(1)-C(9)-C(10) | 37.2(3) |
| C(6)-C(7)-C(8)-C(9) | 0.5(5) | C(8)-C(9)-C(10)-C(6) | -0.6(5) |
| Fe(1)-C(7)-C(8)-C(9) | -59.9(3) | Fe(1)-C(9)-C(10)-C(6) | -60.3(3) |
| C(6)-C(7)-C(8)-Fe(1) | 60.4(3) | C(8)-C(9)-C(10)-Fe(1) | 59.7(3) |
| C(4)-Fe(1)-C(8)-C(9) | -76.7(3) | C(7)-C(6)-C(10)-C(9) | 0.9(5) |
| C(5)-Fe(1)-C(8)-C(9) | -42.8(6) | C(19)-C(6)-C(10)-C(9) | -178.4(4) |
| C(10)-Fe(1)-C(8)-C(9) | 38.0(3) | Fe(1)-C(6)-C(10)-C(9) | 59.5(3) |
| C(7)-Fe(1)-C(8)-C(9) | 119.2(4) | C(7)-C(6)-C(10)-Fe(1) | -58.6(3) |
| C(3)-Fe(1)-C(8)-C(9) | -117.9(3) | C(19)-C(6)-C(10)-Fe(1) | 122.1(4) |
| C(2)-Fe(1)-C(8)-C(9) | -160.0(3) | C(4)-Fe(1)-C(10)-C(9) | 77.8(3) |
| C(1)-Fe(1)-C(8)-C(9) | 166.2(4) | C(8)-Fe(1)-C(10)-C(9) | -37.8(3) |
| C(6)-Fe(1)-C(8)-C(9) | 81.6(3) | C(5)-Fe(1)-C(10)-C(9) | 119.9(3) |
| C(4)-Fe(1)-C(8)-C(7) | 164.1(3) | C(7)-Fe(1)-C(10)-C(9) | -81.9(3) |
| C(5)-Fe(1)-C(8)-C(7) | -162.0(4) | C(3)-Fe(1)-C(10)-C(9) | 46.0(6) |
| C(9)-Fe(1)-C(8)-C(7) | -119.2(4) | C(2)-Fe(1)-C(10)-C(9) | -166.3(5) |
| C(10)-Fe(1)-C(8)-C(7) | -81.2(3) | C(1)-Fe(1)-C(10)-C(9) | 161.6(3) |
| C(3)-Fe(1)-C(8)-C(7) | 123.0(3) | C(6)-Fe(1)-C(10)-C(9) | -119.6(4) |
| C(2)-Fe(1)-C(8)-C(7) | 80.8(3) | C(4)-Fe(1)-C(10)-C(6) | -162.6(2) |
| C(1)-Fe(1)-C(8)-C(7) | 47.1(6) | C(8)-Fe(1)-C(10)-C(6) | 81.8(3) |
| C(6)-Fe(1)-C(8)-C(7) | -37.6(3) | C(5)-Fe(1)-C(10)-C(6) | -120.5(3) |
| C(7)-C(8)-C(9)-C(10) | 0.0(5) | C(9)-Fe(1)-C(10)-C(6) | 119.6(4) |
| Fe(1)-C(8)-C(9)-C(10) | -59.8(3) | C(7)-Fe(1)-C(10)-C(6) | 37.7(2) |
| C(7)-C(8)-C(9)-Fe(1) | 59.9(3) | C(3)-Fe(1)-C(10)-C(6) | 165.6(4) |
| C(4)-Fe(1)-C(9)-C(8) | 121.3(3) | C(2)-Fe(1)-C(10)-C(6) | -46.7(7) |
| C(5)-Fe(1)-C(9)-C(8) | 162.9(2) | C(1)-Fe(1)-C(10)-C(6) | -78.8(3) |
| C(10)-Fe(1)-C(9)-C(8) | -118.6(4) | C(5)-C(1)-C(11)-C(12) | -169.0(4) |
| C(7)-Fe(1)-C(9)-C(8) | -37.8(2) | C(2)-C(1)-C(11)-C(12) | 12.0(7) |
| C(3)-Fe(1)-C(9)-C(8) | 80.7(3) | Fe(1)-C(1)-C(11)-C(12) | 103.7(5) |
| C(2)-Fe(1)-C(9)-C(8) | 49.4(6) | C(1)-C(11)-C(12)-C(13) | 178.6(4) |
| C(1)-Fe(1)-C(9)-C(8) | -166.4(4) | C(11)-C(12)-C(13)-C(15) | 176.9(5) |
| C(6)-Fe(1)-C(9)-C(8) | -81.4(3) | C(11)-C(12)-C(13)-C(14) | -3.9(7) |
| C(4)-Fe(1)-C(9)-C(10) | -120.1(3) | C(15)-C(13)-C(14)-C(16) | -1.0(7) |
| C(8)-Fe(1)-C(9)-C(10) | 118.6(4) | C(12)-C(13)-C(14)-C(16) | 179.8(4) |
| C(5)-Fe(1)-C(9)-C(10) | -78.5(3) | C(14)-C(13)-C(15)-C(17) | 1.5(7) |
| C(7)-Fe(1)-C(9)-C(10) | 80.8(3) | C(12)-C(13)-C(15)-C(17) | -179.3(4) |

| | |
|---|---|
| C(13)-C(14)-C(16)-C(18) | -0.2(7) |
| C(13)-C(15)-C(17)-C(18) | -0.8(8) |
| C(15)-C(17)-C(18)-C(16) | -0.5(7) |
| C(15)-C(17)-C(18)-Br(1) | 179.9(4) |
| C(14)-C(16)-C(18)-C(17) | 1.0(7) |
| C(14)-C(16)-C(18)-Br(1) | -179.4(3) |
| C(10)-C(6)-C(19)-C(20) | 178.5(4) |
| C(7)-C(6)-C(19)-C(20) | -0.6(7) |
| Fe(1)-C(6)-C(19)-C(20) | -93.2(5) |
| C(6)-C(19)-C(20)-C(21) | 179.4(4) |
| C(19)-C(20)-C(21)-C(23) | -172.7(5) |
| C(19)-C(20)-C(21)-C(22) | 8.6(7) |
| C(23)-C(21)-C(22)-C(24) | -0.1(6) |
| C(20)-C(21)-C(22)-C(24) | 178.7(4) |
| C(22)-C(21)-C(23)-C(25) | -0.9(7) |
| C(20)-C(21)-C(23)-C(25) | -179.7(4) |
| C(21)-C(22)-C(24)-C(26) | 0.7(6) |
| C(21)-C(23)-C(25)-C(26) | 1.3(7) |
| C(23)-C(25)-C(26)-C(24) | -0.6(7) |
| C(23)-C(25)-C(26)-Br(2) | 178.8(4) |
| C(22)-C(24)-C(26)-C(25) | -0.3(7) |
| C(22)-C(24)-C(26)-Br(2) | -179.8(3) |

Symmetry transformations used to generate equivalent atoms:

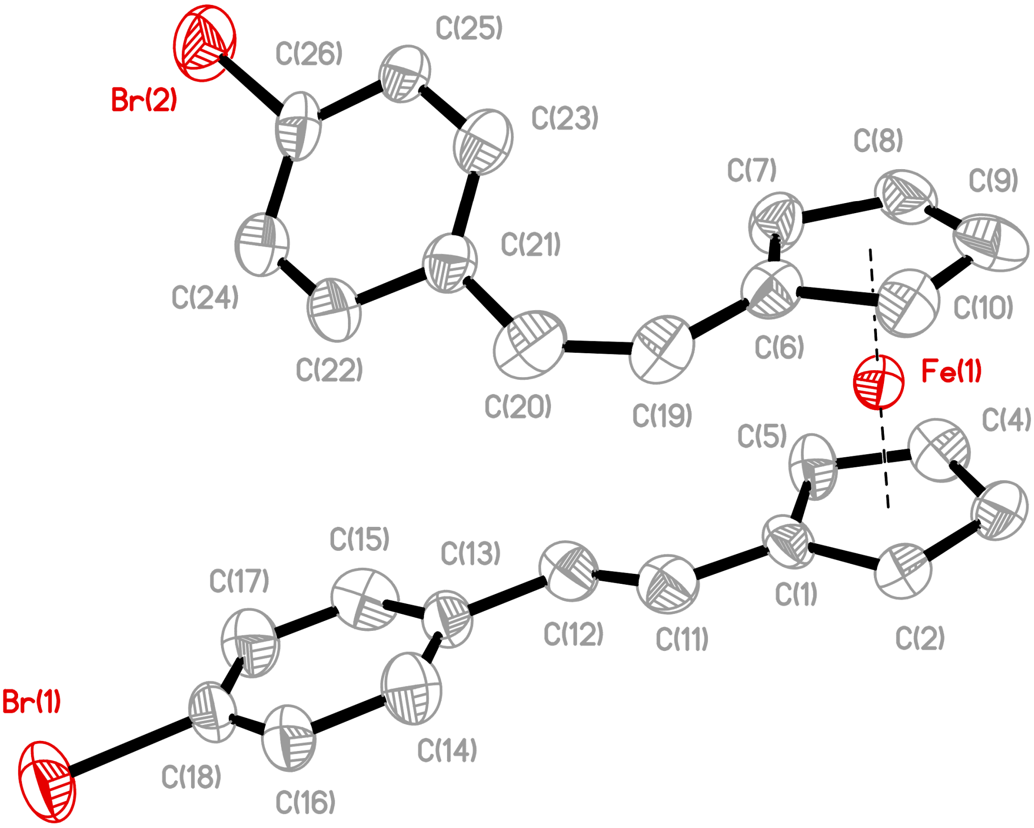

Br(2)
C(26)
C(25)
C(23)
C(7)
C(8)
C(9)
C(21)
C(24)
C(10)
C(22)
C(6)
C(20)
C(19)
Fe(1)
C(5)
C(4)
C(3)
C(15)
C(13)
C(17)
C(12)
C(11)
C(1)
C(2)
Br(1)
C(14)
C(18)
C(16)

**Table 1**. Crystal data and structure refinement for str174m.

| | | |
|---|---|---|
| Identification code | str174m | |
| Empirical formula | C26 H20 Br2 Fe | |
| Formula weight | 548.09 | |
| Temperature | 298(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | P2(1)/c | |
| Unit cell dimensions | a = 6.3542(13) Å | $\alpha$= 90°. |
| | b = 23.123(5) Å | $\beta$= 102.165(4)°. |
| | c = 14.704(3) Å | $\gamma$ = 90°. |
| Volume | 2111.9(7) Å$^3$ | |
| Z | 4 | |
| Density (calculated) | 1.724 Mg/m$^3$ | |
| Absorption coefficient | 4.508 mm$^{-1}$ | |
| F(000) | 1088 | |
| Crystal size | 1.1 x 0.3 x 0.2 mm$^3$ | |
| Theta range for data collection | 1.67 to 24.71°. | |
| Index ranges | -7<=h<=7, -27<=k<=23, -17<=l<=12 | |
| Reflections collected | 11369 | |
| Independent reflections | 3593 [R(int) = 0.0623] | |
| Completeness to theta = 24.71° | 99.8 % | |
| Absorption correction | Bruker | |
| Max. and min. transmission | 1.956673 and 0.937123 | |
| Refinement method | Full-matrix least-squares on F$^2$ | |
| Data / restraints / parameters | 3593 / 0 / 262 | |
| Goodness-of-fit on F$^2$ | 1.092 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0685, wR2 = 0.2051 | |
| R indices (all data) | R1 = 0.0870, wR2 = 0.2105 | |
| Largest diff. peak and hole | 0.630 and -0.779 e.Å$^{-3}$ | |

**Table 2**. Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters (Å$^2$x $10^3$) for str174m. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| Br(1) | 2030(2) | 4585(1) | 770(1) | 64(1) |
| Fe(1) | 11148(2) | 1055(1) | 1952(1) | 32(1) |
| C(1) | 8840(15) | 1422(4) | 901(6) | 37(2) |
| Br(2) | 15193(2) | 4527(1) | 3508(1) | 68(1) |
| C(2) | 8327(16) | 847(4) | 1064(7) | 43(2) |
| C(3) | 10045(17) | 471(4) | 913(7) | 49(3) |
| C(4) | 11587(17) | 829(5) | 643(7) | 48(3) |
| C(5) | 10863(17) | 1420(4) | 655(6) | 42(2) |
| C(6) | 11100(15) | 1478(4) | 3182(6) | 37(2) |
| C(7) | 13062(15) | 1580(4) | 2890(7) | 41(2) |
| C(8) | 14043(16) | 1025(5) | 2830(7) | 48(3) |
| C(9) | 12730(19) | 579(5) | 3082(7) | 58(3) |
| C(10) | 10921(17) | 865(4) | 3282(6) | 43(2) |
| C(11) | 7508(16) | 1923(4) | 1000(6) | 43(2) |
| C(12) | 7807(17) | 2456(4) | 736(7) | 44(2) |
| C(13) | 6412(16) | 2961(4) | 774(7) | 41(2) |
| C(14) | 4568(17) | 2938(4) | 1141(7) | 47(2) |
| C(15) | 6951(18) | 3480(5) | 429(7) | 51(3) |
| C(16) | 3261(17) | 3419(4) | 1155(7) | 43(2) |
| C(17) | 5670(18) | 3968(5) | 448(8) | 54(3) |
| C(18) | 3844(16) | 3921(4) | 796(7) | 45(2) |
| C(19) | 9387(16) | 1860(4) | 3313(7) | 41(2) |
| C(20) | 9163(17) | 2435(5) | 3338(7) | 49(3) |
| C(21) | 10690(15) | 2919(4) | 3369(6) | 37(2) |
| C(22) | 9889(17) | 3459(4) | 3046(7) | 46(3) |
| C(23) | 12849(16) | 2873(4) | 3759(7) | 42(2) |
| C(24) | 11160(16) | 3928(5) | 3068(7) | 48(3) |
| C(25) | 14204(16) | 3353(4) | 3822(6) | 38(2) |
| C(26) | 13361(17) | 3871(4) | 3475(7) | 44(2) |

**Table 3**. Bond lengths [Å] and angles [°] for str174m.

| | |
|---|---|
| Br(1)-C(18) | 1.917(9) |
| Fe(1)-C(8) | 2.014(10) |
| Fe(1)-C(7) | 2.037(9) |
| Fe(1)-C(10) | 2.038(9) |
| Fe(1)-C(2) | 2.040(9) |
| Fe(1)-C(3) | 2.048(9) |
| Fe(1)-C(5) | 2.059(9) |
| Fe(1)-C(6) | 2.062(9) |
| Fe(1)-C(9) | 2.068(10) |
| Fe(1)-C(4) | 2.069(10) |
| Fe(1)-C(1) | 2.075(9) |
| C(1)-C(2) | 1.402(13) |
| C(1)-C(5) | 1.407(13) |
| C(1)-C(11) | 1.460(13) |
| Br(2)-C(26) | 1.906(10) |
| C(2)-C(3) | 1.449(14) |
| C(3)-C(4) | 1.403(15) |
| C(4)-C(5) | 1.444(14) |
| C(6)-C(7) | 1.421(13) |
| C(6)-C(10) | 1.432(13) |
| C(6)-C(19) | 1.446(13) |
| C(7)-C(8) | 1.436(13) |
| C(8)-C(9) | 1.424(16) |
| C(9)-C(10) | 1.409(15) |
| C(11)-C(12) | 1.319(14) |
| C(12)-C(13) | 1.474(13) |
| C(13)-C(15) | 1.374(14) |
| C(13)-C(14) | 1.391(14) |
| C(14)-C(16) | 1.391(13) |
| C(15)-C(17) | 1.394(15) |
| C(16)-C(18) | 1.358(14) |
| C(17)-C(18) | 1.367(15) |
| C(19)-C(20) | 1.338(14) |
| C(20)-C(21) | 1.475(14) |
| C(21)-C(23) | 1.375(13) |
| C(21)-C(22) | 1.394(13) |
| C(22)-C(24) | 1.349(14) |
| C(23)-C(25) | 1.397(13) |
| C(24)-C(26) | 1.406(14) |
| C(25)-C(26) | 1.367(13) |
| C(8)-Fe(1)-C(7) | 41.5(4) |
| C(8)-Fe(1)-C(10) | 67.5(4) |
| C(7)-Fe(1)-C(10) | 68.4(4) |
| C(8)-Fe(1)-C(2) | 164.4(4) |
| C(7)-Fe(1)-C(2) | 153.2(4) |
| C(10)-Fe(1)-C(2) | 109.4(4) |
| C(8)-Fe(1)-C(3) | 125.4(4) |
| C(7)-Fe(1)-C(3) | 163.6(4) |
| C(10)-Fe(1)-C(3) | 119.4(4) |
| C(2)-Fe(1)-C(3) | 41.5(4) |
| C(8)-Fe(1)-C(5) | 119.9(4) |
| C(7)-Fe(1)-C(5) | 107.8(4) |
| C(10)-Fe(1)-C(5) | 165.2(4) |
| C(2)-Fe(1)-C(5) | 67.1(4) |
| C(3)-Fe(1)-C(5) | 68.3(4) |
| C(8)-Fe(1)-C(6) | 68.5(4) |
| C(7)-Fe(1)-C(6) | 40.6(4) |
| C(10)-Fe(1)-C(6) | 40.9(4) |
| C(2)-Fe(1)-C(6) | 120.0(4) |
| C(3)-Fe(1)-C(6) | 154.3(4) |
| C(5)-Fe(1)-C(6) | 127.1(4) |
| C(8)-Fe(1)-C(9) | 40.8(4) |
| C(7)-Fe(1)-C(9) | 69.7(4) |
| C(10)-Fe(1)-C(9) | 40.1(4) |
| C(2)-Fe(1)-C(9) | 127.0(4) |
| C(3)-Fe(1)-C(9) | 106.3(5) |
| C(5)-Fe(1)-C(9) | 153.6(5) |
| C(6)-Fe(1)-C(9) | 69.0(4) |
| C(8)-Fe(1)-C(4) | 107.7(4) |
| C(7)-Fe(1)-C(4) | 127.0(4) |
| C(10)-Fe(1)-C(4) | 152.7(4) |
| C(2)-Fe(1)-C(4) | 67.6(4) |
| C(3)-Fe(1)-C(4) | 39.8(4) |

| | |
|---|---|
| C(5)-Fe(1)-C(4) | 40.9(4) |
| C(6)-Fe(1)-C(4) | 164.9(4) |
| C(9)-Fe(1)-C(4) | 118.4(5) |
| C(8)-Fe(1)-C(1) | 153.9(4) |
| C(7)-Fe(1)-C(1) | 119.2(4) |
| C(10)-Fe(1)-C(1) | 128.4(4) |
| C(2)-Fe(1)-C(1) | 39.8(4) |
| C(3)-Fe(1)-C(1) | 68.7(4) |
| C(5)-Fe(1)-C(1) | 39.8(4) |
| C(6)-Fe(1)-C(1) | 108.7(4) |
| C(9)-Fe(1)-C(1) | 164.5(4) |
| C(4)-Fe(1)-C(1) | 67.8(4) |
| C(2)-C(1)-C(5) | 107.4(8) |
| C(2)-C(1)-C(11) | 125.1(9) |
| C(5)-C(1)-C(11) | 127.5(9) |
| C(2)-C(1)-Fe(1) | 68.7(5) |
| C(5)-C(1)-Fe(1) | 69.5(5) |
| C(11)-C(1)-Fe(1) | 125.7(7) |
| C(1)-C(2)-C(3) | 109.4(9) |
| C(1)-C(2)-Fe(1) | 71.4(5) |
| C(3)-C(2)-Fe(1) | 69.5(5) |
| C(4)-C(3)-C(2) | 106.5(9) |
| C(4)-C(3)-Fe(1) | 70.9(6) |
| C(2)-C(3)-Fe(1) | 68.9(5) |
| C(3)-C(4)-C(5) | 108.2(9) |
| C(3)-C(4)-Fe(1) | 69.3(6) |
| C(5)-C(4)-Fe(1) | 69.2(5) |
| C(1)-C(5)-C(4) | 108.5(9) |
| C(1)-C(5)-Fe(1) | 70.7(5) |
| C(4)-C(5)-Fe(1) | 69.9(5) |
| C(7)-C(6)-C(10) | 106.8(9) |
| C(7)-C(6)-C(19) | 132.1(9) |
| C(10)-C(6)-C(19) | 120.9(9) |
| C(7)-C(6)-Fe(1) | 68.8(5) |
| C(10)-C(6)-Fe(1) | 68.7(5) |
| C(19)-C(6)-Fe(1) | 123.9(7) |
| C(6)-C(7)-C(8) | 106.9(9) |
| C(6)-C(7)-Fe(1) | 70.7(5) |
| C(8)-C(7)-Fe(1) | 68.4(5) |
| C(9)-C(8)-C(7) | 110.2(9) |
| C(9)-C(8)-Fe(1) | 71.7(6) |
| C(7)-C(8)-Fe(1) | 70.1(5) |
| C(10)-C(9)-C(8) | 105.2(10) |
| C(10)-C(9)-Fe(1) | 68.8(6) |
| C(8)-C(9)-Fe(1) | 67.5(6) |
| C(9)-C(10)-C(6) | 110.9(10) |
| C(9)-C(10)-Fe(1) | 71.1(6) |
| C(6)-C(10)-Fe(1) | 70.5(5) |
| C(12)-C(11)-C(1) | 126.2(10) |
| C(11)-C(12)-C(13) | 127.2(10) |
| C(15)-C(13)-C(14) | 118.2(9) |
| C(15)-C(13)-C(12) | 118.6(10) |
| C(14)-C(13)-C(12) | 123.2(9) |
| C(13)-C(14)-C(16) | 122.0(9) |
| C(13)-C(15)-C(17) | 120.4(10) |
| C(18)-C(16)-C(14) | 117.7(10) |
| C(18)-C(17)-C(15) | 119.2(10) |
| C(16)-C(18)-C(17) | 122.4(9) |
| C(16)-C(18)-Br(1) | 118.7(8) |
| C(17)-C(18)-Br(1) | 118.9(8) |
| C(20)-C(19)-C(6) | 134.3(9) |
| C(19)-C(20)-C(21) | 132.9(10) |
| C(23)-C(21)-C(22) | 118.2(9) |
| C(23)-C(21)-C(20) | 123.1(9) |
| C(22)-C(21)-C(20) | 118.6(9) |
| C(24)-C(22)-C(21) | 122.6(10) |
| C(21)-C(23)-C(25) | 120.9(9) |
| C(22)-C(24)-C(26) | 118.2(10) |
| C(26)-C(25)-C(23) | 119.0(9) |
| C(25)-C(26)-C(24) | 121.1(10) |
| C(25)-C(26)-Br(2) | 119.9(8) |
| C(24)-C(26)-Br(2) | 119.0(7) |

---

Symmetry transformations used to generate equivalent atoms:

**Table 4**. Anisotropic displacement parameters (Å$^2$x 10$^3$)for str174m. The anisotropic displacement factor exponent takes the form: $-2\pi^2[ h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12} ]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| Br(1) | 74(1) | 48(1) | 69(1) | 3(1) | 13(1) | 26(1) |
| Fe(1) | 35(1) | 29(1) | 33(1) | -1(1) | 8(1) | 1(1) |
| C(1) | 38(5) | 36(5) | 33(5) | 6(4) | 3(4) | 8(4) |
| Br(2) | 67(1) | 43(1) | 92(1) | -6(1) | 16(1) | -9(1) |
| C(2) | 42(6) | 38(5) | 45(6) | -4(4) | 0(5) | -1(4) |
| C(3) | 51(6) | 41(5) | 50(6) | -17(5) | 2(5) | 3(5) |
| C(4) | 55(7) | 54(6) | 34(5) | -4(5) | 13(5) | 9(5) |
| C(5) | 59(7) | 31(5) | 39(5) | 4(4) | 16(5) | 6(4) |
| C(6) | 43(5) | 39(5) | 28(5) | 0(4) | 9(4) | -4(4) |
| C(7) | 39(5) | 37(5) | 48(6) | -10(4) | 14(5) | -1(4) |
| C(8) | 36(5) | 52(6) | 51(6) | -9(5) | 0(5) | 14(5) |
| C(9) | 59(7) | 65(7) | 41(6) | 7(5) | -13(5) | 9(6) |
| C(10) | 60(7) | 39(5) | 28(5) | 5(4) | 8(5) | -5(5) |
| C(11) | 46(6) | 50(6) | 33(5) | -4(4) | 7(4) | 3(5) |
| C(12) | 46(6) | 52(6) | 34(5) | -3(5) | 10(5) | 9(5) |
| C(13) | 47(6) | 35(5) | 38(5) | -2(4) | 2(5) | 7(4) |
| C(14) | 58(7) | 40(6) | 45(6) | 8(5) | 17(5) | 4(5) |
| C(15) | 49(6) | 63(7) | 42(6) | 6(5) | 13(5) | 1(5) |
| C(16) | 49(6) | 33(5) | 46(6) | 1(4) | 10(5) | 5(4) |
| C(17) | 62(7) | 43(6) | 57(7) | 4(5) | 13(6) | 6(5) |
| C(18) | 48(6) | 37(5) | 46(6) | -8(5) | 2(5) | 14(5) |
| C(19) | 42(6) | 43(6) | 43(6) | -6(4) | 18(4) | -7(4) |
| C(20) | 36(6) | 62(7) | 55(6) | -19(5) | 21(5) | -7(5) |
| C(21) | 40(6) | 37(5) | 34(5) | -7(4) | 10(4) | 2(4) |
| C(22) | 41(6) | 45(6) | 53(6) | -11(5) | 10(5) | 12(5) |
| C(23) | 50(6) | 42(5) | 36(5) | -7(4) | 16(5) | -2(5) |
| C(24) | 49(6) | 45(6) | 49(6) | -12(5) | 9(5) | 8(5) |
| C(25) | 42(5) | 38(5) | 35(5) | -10(4) | 9(4) | 3(4) |
| C(26) | 58(6) | 31(5) | 46(6) | -8(4) | 19(5) | 6(4) |

**Table 5**. Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters ($Å^2$x $10^3$) for str174m.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(2) | 7077 | 726 | 1242 | 52 |
| H(3) | 10112 | 71 | 981 | 58 |
| H(4) | 12857 | 707 | 484 | 57 |
| H(5) | 11608 | 1745 | 522 | 50 |
| H(7) | 13607 | 1937 | 2763 | 49 |
| H(8) | 15347 | 966 | 2652 | 57 |
| H(9) | 13007 | 184 | 3109 | 70 |
| H(10) | 9766 | 680 | 3455 | 51 |
| H(11) | 6337 | 1860 | 1275 | 51 |
| H(12) | 9033 | 2521 | 499 | 52 |
| H(14) | 4196 | 2590 | 1384 | 56 |
| H(15) | 8179 | 3507 | 182 | 61 |
| H(16) | 2031 | 3398 | 1402 | 51 |
| H(17) | 6052 | 4321 | 226 | 65 |
| H(19) | 8170 | 1662 | 3400 | 50 |
| H(20) | 7762 | 2553 | 3335 | 59 |
| H(22) | 8420 | 3498 | 2806 | 56 |
| H(23) | 13414 | 2517 | 3984 | 50 |
| H(24) | 10597 | 4279 | 2822 | 58 |
| H(25) | 15658 | 3321 | 4097 | 46 |

**Table 6**. Torsion angles [°] for str174m.

| | |
|---|---|
| C(8)-Fe(1)-C(1)-C(2) | 166.2(8) |
| C(7)-Fe(1)-C(1)-C(2) | -157.8(6) |
| C(10)-Fe(1)-C(1)-C(2) | -73.3(7) |
| C(3)-Fe(1)-C(1)-C(2) | 38.0(6) |
| C(5)-Fe(1)-C(1)-C(2) | 119.3(8) |
| C(6)-Fe(1)-C(1)-C(2) | -114.7(6) |
| C(9)-Fe(1)-C(1)-C(2) | -35.9(18) |
| C(4)-Fe(1)-C(1)-C(2) | 81.1(6) |
| C(8)-Fe(1)-C(1)-C(5) | 46.9(11) |
| C(7)-Fe(1)-C(1)-C(5) | 82.9(6) |
| C(10)-Fe(1)-C(1)-C(5) | 167.4(6) |
| C(2)-Fe(1)-C(1)-C(5) | -119.3(8) |
| C(3)-Fe(1)-C(1)-C(5) | -81.2(6) |
| C(6)-Fe(1)-C(1)-C(5) | 126.1(6) |
| C(9)-Fe(1)-C(1)-C(5) | -155.2(15) |
| C(4)-Fe(1)-C(1)-C(5) | -38.2(6) |
| C(8)-Fe(1)-C(1)-C(11) | -75.2(13) |
| C(7)-Fe(1)-C(1)-C(11) | -39.2(10) |
| C(10)-Fe(1)-C(1)-C(11) | 45.4(10) |
| C(2)-Fe(1)-C(1)-C(11) | 118.7(11) |
| C(3)-Fe(1)-C(1)-C(11) | 156.7(10) |
| C(5)-Fe(1)-C(1)-C(11) | -122.1(11) |
| C(6)-Fe(1)-C(1)-C(11) | 4.0(9) |
| C(9)-Fe(1)-C(1)-C(11) | 82.8(18) |
| C(4)-Fe(1)-C(1)-C(11) | -160.3(10) |
| C(5)-C(1)-C(2)-C(3) | -0.5(11) |
| C(11)-C(1)-C(2)-C(3) | -178.9(9) |
| Fe(1)-C(1)-C(2)-C(3) | -59.4(7) |
| C(5)-C(1)-C(2)-Fe(1) | 58.9(7) |
| C(11)-C(1)-C(2)-Fe(1) | -119.5(9) |
| C(8)-Fe(1)-C(2)-C(1) | -156.9(14) |
| C(7)-Fe(1)-C(2)-C(1) | 46.9(12) |
| C(10)-Fe(1)-C(2)-C(1) | 127.2(6) |
| C(3)-Fe(1)-C(2)-C(1) | -120.0(9) |
| C(5)-Fe(1)-C(2)-C(1) | -37.3(6) |
| C(6)-Fe(1)-C(2)-C(1) | 83.5(7) |
| C(9)-Fe(1)-C(2)-C(1) | 168.7(6) |
| C(4)-Fe(1)-C(2)-C(1) | -81.9(6) |
| C(8)-Fe(1)-C(2)-C(3) | -37.0(19) |
| C(7)-Fe(1)-C(2)-C(3) | 166.9(9) |
| C(10)-Fe(1)-C(2)-C(3) | -112.8(7) |
| C(5)-Fe(1)-C(2)-C(3) | 82.7(7) |
| C(6)-Fe(1)-C(2)-C(3) | -156.6(6) |
| C(9)-Fe(1)-C(2)-C(3) | -71.3(8) |
| C(4)-Fe(1)-C(2)-C(3) | 38.1(6) |
| C(1)-Fe(1)-C(2)-C(3) | 120.0(9) |
| C(1)-C(2)-C(3)-C(4) | -0.8(11) |
| Fe(1)-C(2)-C(3)-C(4) | -61.3(7) |
| C(1)-C(2)-C(3)-Fe(1) | 60.6(7) |
| C(8)-Fe(1)-C(3)-C(4) | -74.4(8) |
| C(7)-Fe(1)-C(3)-C(4) | -41.6(18) |
| C(10)-Fe(1)-C(3)-C(4) | -156.4(6) |
| C(2)-Fe(1)-C(3)-C(4) | 117.1(9) |
| C(5)-Fe(1)-C(3)-C(4) | 37.6(6) |
| C(6)-Fe(1)-C(3)-C(4) | 169.6(8) |
| C(9)-Fe(1)-C(3)-C(4) | -115.0(7) |
| C(1)-Fe(1)-C(3)-C(4) | 80.5(6) |
| C(8)-Fe(1)-C(3)-C(2) | 168.6(6) |
| C(7)-Fe(1)-C(3)-C(2) | -158.6(14) |
| C(10)-Fe(1)-C(3)-C(2) | 86.5(7) |
| C(5)-Fe(1)-C(3)-C(2) | -79.4(6) |
| C(6)-Fe(1)-C(3)-C(2) | 52.5(12) |
| C(9)-Fe(1)-C(3)-C(2) | 128.0(7) |
| C(4)-Fe(1)-C(3)-C(2) | -117.1(9) |
| C(1)-Fe(1)-C(3)-C(2) | -36.5(6) |
| C(2)-C(3)-C(4)-C(5) | 1.7(11) |
| Fe(1)-C(3)-C(4)-C(5) | -58.4(7) |
| C(2)-C(3)-C(4)-Fe(1) | 60.1(6) |
| C(8)-Fe(1)-C(4)-C(3) | 124.5(6) |
| C(7)-Fe(1)-C(4)-C(3) | 166.5(6) |
| C(10)-Fe(1)-C(4)-C(3) | 49.4(12) |
| C(2)-Fe(1)-C(4)-C(3) | -39.7(6) |
| C(5)-Fe(1)-C(4)-C(3) | -120.0(9) |
| C(6)-Fe(1)-C(4)-C(3) | -162.5(14) |
| C(9)-Fe(1)-C(4)-C(3) | 81.4(7) |
| C(1)-Fe(1)-C(4)-C(3) | -82.9(6) |
| C(8)-Fe(1)-C(4)-C(5) | -115.5(6) |
| C(7)-Fe(1)-C(4)-C(5) | -73.5(7) |
| C(10)-Fe(1)-C(4)-C(5) | 169.5(8) |
| C(2)-Fe(1)-C(4)-C(5) | 80.4(6) |
| C(3)-Fe(1)-C(4)-C(5) | 120.0(9) |
| C(6)-Fe(1)-C(4)-C(5) | -42.5(18) |
| C(9)-Fe(1)-C(4)-C(5) | -158.5(6) |
| C(1)-Fe(1)-C(4)-C(5) | 37.2(6) |
| C(2)-C(1)-C(5)-C(4) | 1.5(11) |
| C(11)-C(1)-C(5)-C(4) | 179.9(9) |
| Fe(1)-C(1)-C(5)-C(4) | 60.0(7) |
| C(2)-C(1)-C(5)-Fe(1) | -58.4(7) |
| C(11)-C(1)-C(5)-Fe(1) | 119.9(10) |
| C(3)-C(4)-C(5)-C(1) | -2.0(11) |
| Fe(1)-C(4)-C(5)-C(1) | -60.5(7) |
| C(3)-C(4)-C(5)-Fe(1) | 58.4(7) |
| C(8)-Fe(1)-C(5)-C(1) | -158.3(5) |
| C(7)-Fe(1)-C(5)-C(1) | -114.5(6) |
| C(10)-Fe(1)-C(5)-C(1) | -41.9(18) |
| C(2)-Fe(1)-C(5)-C(1) | 37.3(6) |
| C(3)-Fe(1)-C(5)-C(1) | 82.4(6) |
| C(6)-Fe(1)-C(5)-C(1) | -73.7(7) |
| C(9)-Fe(1)-C(5)-C(1) | 165.4(9) |

| | | | |
|---|---|---|---|
| C(4)-Fe(1)-C(5)-C(1) | 119.0(8) | C(6)-Fe(1)-C(7)-C(8) | 118.0(9) |
| C(8)-Fe(1)-C(5)-C(4) | 82.7(7) | C(9)-Fe(1)-C(7)-C(8) | 36.9(7) |
| C(7)-Fe(1)-C(5)-C(4) | 126.5(6) | C(4)-Fe(1)-C(7)-C(8) | -73.9(8) |
| C(10)-Fe(1)-C(5)-C(4) | -160.9(15) | C(1)-Fe(1)-C(7)-C(8) | -157.0(6) |
| C(2)-Fe(1)-C(5)-C(4) | -81.7(6) | C(6)-C(7)-C(8)-C(9) | -0.2(11) |
| C(3)-Fe(1)-C(5)-C(4) | -36.6(6) | Fe(1)-C(7)-C(8)-C(9) | -60.7(7) |
| C(6)-Fe(1)-C(5)-C(4) | 167.2(6) | C(6)-C(7)-C(8)-Fe(1) | 60.5(7) |
| C(9)-Fe(1)-C(5)-C(4) | 46.4(12) | C(7)-Fe(1)-C(8)-C(9) | 120.4(9) |
| C(1)-Fe(1)-C(5)-C(4) | -119.0(8) | C(10)-Fe(1)-C(8)-C(9) | 38.1(6) |
| C(8)-Fe(1)-C(6)-C(7) | 39.0(6) | C(2)-Fe(1)-C(8)-C(9) | -43.6(19) |
| C(10)-Fe(1)-C(6)-C(7) | 119.0(8) | C(3)-Fe(1)-C(8)-C(9) | -72.9(8) |
| C(2)-Fe(1)-C(6)-C(7) | -155.6(6) | C(5)-Fe(1)-C(8)-C(9) | -156.2(6) |
| C(3)-Fe(1)-C(6)-C(7) | 167.0(9) | C(6)-Fe(1)-C(8)-C(9) | 82.3(7) |
| C(5)-Fe(1)-C(6)-C(7) | -72.9(7) | C(4)-Fe(1)-C(8)-C(9) | -113.2(7) |
| C(9)-Fe(1)-C(6)-C(7) | 82.9(7) | C(1)-Fe(1)-C(8)-C(9) | 171.2(8) |
| C(4)-Fe(1)-C(6)-C(7) | -39.3(17) | C(10)-Fe(1)-C(8)-C(7) | -82.3(6) |
| C(1)-Fe(1)-C(6)-C(7) | -113.4(6) | C(2)-Fe(1)-C(8)-C(7) | -164.0(14) |
| C(8)-Fe(1)-C(6)-C(10) | -80.0(7) | C(3)-Fe(1)-C(8)-C(7) | 166.7(6) |
| C(7)-Fe(1)-C(6)-C(10) | -119.0(8) | C(5)-Fe(1)-C(8)-C(7) | 83.3(7) |
| C(2)-Fe(1)-C(6)-C(10) | 85.5(7) | C(6)-Fe(1)-C(8)-C(7) | -38.1(6) |
| C(3)-Fe(1)-C(6)-C(10) | 48.1(11) | C(9)-Fe(1)-C(8)-C(7) | -120.4(9) |
| C(5)-Fe(1)-C(6)-C(10) | 168.1(6) | C(4)-Fe(1)-C(8)-C(7) | 126.3(6) |
| C(9)-Fe(1)-C(6)-C(10) | -36.1(6) | C(1)-Fe(1)-C(8)-C(7) | 50.8(11) |
| C(4)-Fe(1)-C(6)-C(10) | -158.2(14) | C(7)-C(8)-C(9)-C(10) | 1.0(11) |
| C(1)-Fe(1)-C(6)-C(10) | 127.7(6) | Fe(1)-C(8)-C(9)-C(10) | -58.8(7) |
| C(8)-Fe(1)-C(6)-C(19) | 166.3(9) | C(7)-C(8)-C(9)-Fe(1) | 59.8(7) |
| C(7)-Fe(1)-C(6)-C(19) | 127.3(10) | C(8)-Fe(1)-C(9)-C(10) | 117.7(9) |
| C(10)-Fe(1)-C(6)-C(19) | -113.7(10) | C(7)-Fe(1)-C(9)-C(10) | 80.2(7) |
| C(2)-Fe(1)-C(6)-C(19) | -28.2(9) | C(2)-Fe(1)-C(9)-C(10) | -75.7(8) |
| C(3)-Fe(1)-C(6)-C(19) | -65.6(13) | C(3)-Fe(1)-C(9)-C(10) | -116.5(7) |
| C(5)-Fe(1)-C(6)-C(19) | 54.4(9) | C(5)-Fe(1)-C(9)-C(10) | 169.5(8) |
| C(9)-Fe(1)-C(6)-C(19) | -149.8(9) | C(6)-Fe(1)-C(9)-C(10) | 36.7(6) |
| C(4)-Fe(1)-C(6)-C(19) | 88.1(17) | C(4)-Fe(1)-C(9)-C(10) | -157.8(6) |
| C(1)-Fe(1)-C(6)-C(19) | 13.9(9) | C(1)-Fe(1)-C(9)-C(10) | -47.6(19) |
| C(10)-C(6)-C(7)-C(8) | -0.7(11) | C(7)-Fe(1)-C(9)-C(8) | -37.6(6) |
| C(19)-C(6)-C(7)-C(8) | -176.1(10) | C(10)-Fe(1)-C(9)-C(8) | -117.7(9) |
| Fe(1)-C(6)-C(7)-C(8) | -59.0(6) | C(2)-Fe(1)-C(9)-C(8) | 166.6(6) |
| C(10)-C(6)-C(7)-Fe(1) | 58.4(6) | C(3)-Fe(1)-C(9)-C(8) | 125.7(6) |
| C(19)-C(6)-C(7)-Fe(1) | -117.1(11) | C(5)-Fe(1)-C(9)-C(8) | 51.8(12) |
| C(8)-Fe(1)-C(7)-C(6) | -118.0(9) | C(6)-Fe(1)-C(9)-C(8) | -81.0(7) |
| C(10)-Fe(1)-C(7)-C(6) | -38.0(6) | C(4)-Fe(1)-C(9)-C(8) | 84.4(7) |
| C(2)-Fe(1)-C(7)-C(6) | 52.6(11) | C(1)-Fe(1)-C(9)-C(8) | -165.4(14) |
| C(3)-Fe(1)-C(7)-C(6) | -159.8(14) | C(8)-C(9)-C(10)-C(6) | -1.4(11) |
| C(5)-Fe(1)-C(7)-C(6) | 126.8(6) | Fe(1)-C(9)-C(10)-C(6) | -59.4(7) |
| C(9)-Fe(1)-C(7)-C(6) | -81.1(6) | C(8)-C(9)-C(10)-Fe(1) | 58.0(7) |
| C(4)-Fe(1)-C(7)-C(6) | 168.1(6) | C(7)-C(6)-C(10)-C(9) | 1.3(11) |
| C(1)-Fe(1)-C(7)-C(6) | 84.9(6) | C(19)-C(6)-C(10)-C(9) | 177.4(9) |
| C(10)-Fe(1)-C(7)-C(8) | 80.0(7) | Fe(1)-C(6)-C(10)-C(9) | 59.7(7) |
| C(2)-Fe(1)-C(7)-C(8) | 170.6(9) | C(7)-C(6)-C(10)-Fe(1) | -58.4(7) |
| C(3)-Fe(1)-C(7)-C(8) | -41.8(18) | C(19)-C(6)-C(10)-Fe(1) | 117.6(9) |
| C(5)-Fe(1)-C(7)-C(8) | -115.2(6) | C(8)-Fe(1)-C(10)-C(9) | -38.8(7) |

| | |
|---|---|
| C(7)-Fe(1)-C(10)-C(9) | -83.7(7) |
| C(2)-Fe(1)-C(10)-C(9) | 124.9(7) |
| C(3)-Fe(1)-C(10)-C(9) | 80.3(7) |
| C(5)-Fe(1)-C(10)-C(9) | -161.5(15) |
| C(6)-Fe(1)-C(10)-C(9) | -121.5(9) |
| C(4)-Fe(1)-C(10)-C(9) | 46.3(12) |
| C(1)-Fe(1)-C(10)-C(9) | 165.4(6) |
| C(8)-Fe(1)-C(10)-C(6) | 82.7(6) |
| C(7)-Fe(1)-C(10)-C(6) | 37.7(6) |
| C(2)-Fe(1)-C(10)-C(6) | -113.7(6) |
| C(3)-Fe(1)-C(10)-C(6) | -158.2(6) |
| C(5)-Fe(1)-C(10)-C(6) | -40.1(18) |
| C(9)-Fe(1)-C(10)-C(6) | 121.5(9) |
| C(4)-Fe(1)-C(10)-C(6) | 167.8(8) |
| C(1)-Fe(1)-C(10)-C(6) | -73.1(7) |
| C(2)-C(1)-C(11)-C(12) | -170.5(10) |
| C(5)-C(1)-C(11)-C(12) | 11.4(16) |
| Fe(1)-C(1)-C(11)-C(12) | 101.8(11) |
| C(1)-C(11)-C(12)-C(13) | 175.9(9) |
| C(11)-C(12)-C(13)-C(15) | -177.3(10) |
| C(11)-C(12)-C(13)-C(14) | 2.4(16) |
| C(15)-C(13)-C(14)-C(16) | 0.8(15) |
| C(12)-C(13)-C(14)-C(16) | -178.9(9) |
| C(14)-C(13)-C(15)-C(17) | -0.1(15) |
| C(12)-C(13)-C(15)-C(17) | 179.6(9) |
| C(13)-C(14)-C(16)-C(18) | 0.0(15) |
| C(13)-C(15)-C(17)-C(18) | -1.3(16) |
| C(14)-C(16)-C(18)-C(17) | -1.5(15) |
| C(14)-C(16)-C(18)-Br(1) | 178.1(7) |
| C(15)-C(17)-C(18)-C(16) | 2.2(16) |
| C(15)-C(17)-C(18)-Br(1) | -177.4(8) |
| C(7)-C(6)-C(19)-C(20) | -11.2(19) |
| C(10)-C(6)-C(19)-C(20) | 173.9(11) |
| Fe(1)-C(6)-C(19)-C(20) | -102.3(13) |
| C(6)-C(19)-C(20)-C(21) | -10(2) |
| C(19)-C(20)-C(21)-C(23) | -28.3(17) |
| C(19)-C(20)-C(21)-C(22) | 156.2(12) |
| C(23)-C(21)-C(22)-C(24) | 2.8(15) |
| C(20)-C(21)-C(22)-C(24) | 178.4(9) |
| C(22)-C(21)-C(23)-C(25) | -0.6(14) |
| C(20)-C(21)-C(23)-C(25) | -176.0(9) |
| C(21)-C(22)-C(24)-C(26) | -3.1(15) |
| C(21)-C(23)-C(25)-C(26) | -1.1(14) |
| C(23)-C(25)-C(26)-C(24) | 0.8(14) |
| C(23)-C(25)-C(26)-Br(2) | -177.6(7) |
| C(22)-C(24)-C(26)-C(25) | 1.3(15) |
| C(22)-C(24)-C(26)-Br(2) | 179.7(8) |

---

Symmetry transformations used to generate equivalent atoms:

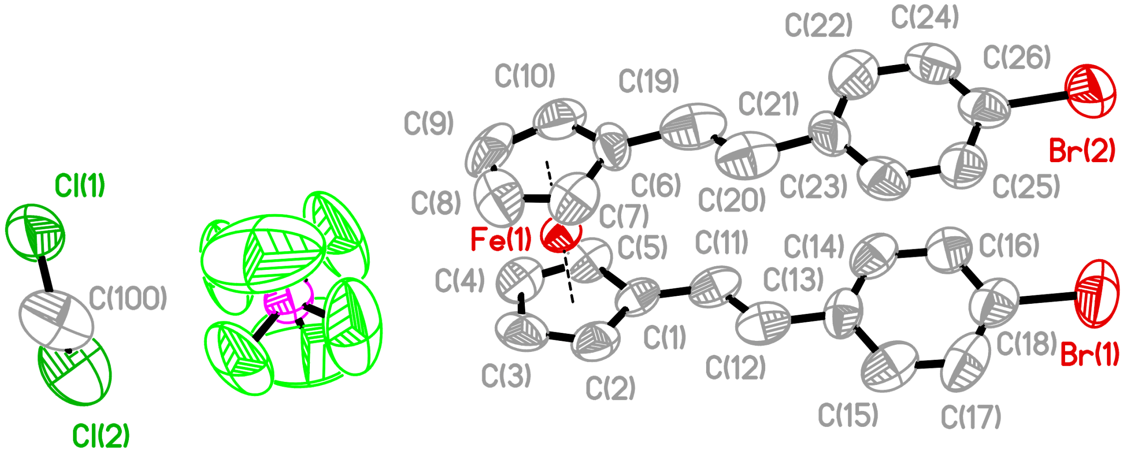

Cl(1)
C(100)
Cl(2)
C(22)
C(24)
C(26)
C(10)
C(19)
C(21)
C(9)
Br(2)
C(6)
C(20)
C(23)
C(25)
C(8)
C(7)
Fe(1)
C(5)
C(11)
C(14)
C(16)
C(4)
C(13)
C(1)
C(18)
Br(1)
C(3)
C(2)
C(12)
C(15)
C(17)

**Table 1**. Crystal data and structure refinement for str193m.

| | | |
|---|---|---|
| Identification code | str193m | |
| Empirical formula | C27 H22 Br2 Cl2 F6 Fe P | |
| Formula weight | 777.99 | |
| Temperature | 293(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Triclinic | |
| Space group | P-1 | |
| Unit cell dimensions | a = 10.2909(9) Å | $\alpha$= 115.345(2)°. |
| | b = 12.2832(11) Å | $\beta$= 106.462(2)°. |
| | c = 13.7003(13) Å | $\gamma$ = 90.559(2)°. |
| Volume | 1483.7(2) Å$^3$ | |
| Z | 2 | |
| Density (calculated) | 1.741 Mg/m$^3$ | |
| Absorption coefficient | 3.490 mm$^{-1}$ | |
| F(000) | 766 | |
| Crystal size | 0.32 x 0.24 x 0.14 mm$^3$ | |
| Theta range for data collection | 1.73 to 19.78°. | |
| Index ranges | -9<=h<=7, -11<=k<=11, -11<=l<=13 | |
| Reflections collected | 4968 | |
| Independent reflections | 2672 [R(int) = 0.0320] | |
| Completeness to theta = 19.78° | 99.9 % | |
| Absorption correction | Bruker SADABS | |
| Refinement method | Full-matrix least-squares on F$^2$ | |
| Data / restraints / parameters | 2672 / 0 / 352 | |
| Goodness-of-fit on F$^2$ | 1.049 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0641, wR2 = 0.1673 | |
| R indices (all data) | R1 = 0.0936, wR2 = 0.1845 | |
| Largest diff. peak and hole | 0.638 and -0.496 e.Å$^{-3}$ | |

**Table 2**. Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) for str193m. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| Fe(1) | 3149(1) | 8926(1) | 978(1) | 48(1) |
| Br(1) | 8888(2) | 6530(1) | 6625(1) | 125(1) |
| P(1) | 1595(3) | 11351(4) | -1260(4) | 83(1) |
| F(1) | 2928(10) | 11001(16) | -805(15) | 238(8) |
| C(1) | 4170(12) | 9786(10) | 2786(9) | 57(3) |
| Cl(1) | -1775(5) | 12128(5) | -4052(5) | 178(2) |
| Br(2) | 6989(2) | 3292(1) | 3943(1) | 111(1) |
| C(2) | 4769(13) | 10279(10) | 2238(10) | 71(3) |
| F(2) | 2326(10) | 12076(11) | -1652(12) | 190(5) |
| Cl(2) | -501(7) | 14439(5) | -2045(6) | 184(2) |
| C(3) | 3770(17) | 10759(9) | 1653(10) | 80(4) |
| F(3) | 868(11) | 10517(15) | -958(16) | 243(8) |
| C(4) | 2516(13) | 10543(10) | 1825(11) | 76(4) |
| F(4) | 219(10) | 11628(17) | -1758(17) | 254(9) |
| C(5) | 2763(12) | 9953(10) | 2503(9) | 66(3) |
| F(5) | 1750(20) | 12348(18) | -200(16) | 361(14) |
| C(6) | 3114(14) | 7003(9) | 209(9) | 65(3) |
| F(6) | 1440(20) | 10368(18) | -2369(15) | 339(13) |
| C(7) | 3869(13) | 7574(12) | -208(10) | 73(3) |
| C(8) | 3000(20) | 8155(11) | -706(10) | 85(4) |
| C(9) | 1717(17) | 8011(12) | -599(12) | 96(5) |
| C(10) | 1798(13) | 7291(11) | -23(11) | 80(4) |
| C(11) | 4772(13) | 9162(10) | 3465(9) | 71(3) |
| C(12) | 6068(14) | 9044(10) | 3763(9) | 72(3) |
| C(13) | 6701(14) | 8408(11) | 4438(9) | 64(3) |
| C(14) | 5968(12) | 7673(12) | 4673(10) | 72(3) |
| C(15) | 8115(14) | 8563(12) | 4866(12) | 86(4) |
| C(16) | 6637(15) | 7097(10) | 5304(10) | 73(3) |
| C(17) | 8787(15) | 8019(14) | 5501(12) | 92(4) |
| C(18) | 8036(17) | 7290(12) | 5729(10) | 79(4) |
| C(19) | 3574(16) | 6276(11) | 847(11) | 91(4) |
| C(20) | 4766(15) | 6096(11) | 1200(11) | 84(4) |
| C(21) | 5181(17) | 5365(10) | 1848(9) | 66(3) |

|  |  |  |  |  |
|---|---|---|---|---|
| C(22) | 4336(14) | 4668(12) | 2020(11) | 79(4) |
| C(23) | 6553(15) | 5384(9) | 2257(10) | 70(3) |
| C(24) | 4886(16) | 4072(10) | 2698(11) | 78(4) |
| C(25) | 7098(13) | 4757(11) | 2864(10) | 71(3) |
| C(26) | 6242(17) | 4134(10) | 3096(9) | 66(3) |
| C(100) | -381(16) | 13129(13) | -3242(15) | 137(6) |

**Table 3**. Bond lengths [Å] and angles [°] for str193m.

| | |
|---|---|
| Fe(1)-C(8) | 2.040(11) |
| Fe(1)-C(9) | 2.046(11) |
| Fe(1)-C(3) | 2.046(10) |
| Fe(1)-C(4) | 2.050(10) |
| Fe(1)-C(5) | 2.083(10) |
| Fe(1)-C(7) | 2.083(11) |
| Fe(1)-C(10) | 2.086(11) |
| Fe(1)-C(2) | 2.094(10) |
| Fe(1)-C(6) | 2.130(10) |
| Fe(1)-C(1) | 2.150(11) |
| Br(1)-C(18) | 1.881(14) |
| P(1)-F(5) | 1.406(14) |
| P(1)-F(6) | 1.443(15) |
| P(1)-F(1) | 1.486(10) |
| P(1)-F(4) | 1.499(10) |
| P(1)-F(2) | 1.507(9) |
| P(1)-F(3) | 1.517(10) |
| C(1)-C(2) | 1.398(16) |
| C(1)-C(5) | 1.430(14) |
| C(1)-C(11) | 1.460(16) |
| Cl(1)-C(100) | 1.642(16) |
| Br(2)-C(26) | 1.883(12) |
| C(2)-C(3) | 1.412(16) |
| Cl(2)-C(100) | 1.775(16) |
| C(3)-C(4) | 1.418(16) |
| C(4)-C(5) | 1.378(16) |
| C(6)-C(10) | 1.387(16) |
| C(6)-C(7) | 1.416(16) |
| C(6)-C(19) | 1.492(18) |
| C(7)-C(8) | 1.365(17) |
| C(8)-C(9) | 1.382(18) |
| C(9)-C(10) | 1.406(18) |
| C(11)-C(12) | 1.309(15) |
| C(12)-C(13) | 1.475(17) |
| C(13)-C(14) | 1.364(16) |
| C(13)-C(15) | 1.384(16) |
| C(14)-C(16) | 1.385(16) |
| C(15)-C(17) | 1.359(18) |
| C(16)-C(18) | 1.367(16) |
| C(17)-C(18) | 1.363(18) |
| C(19)-C(20) | 1.245(16) |
| C(20)-C(21) | 1.500(18) |
| C(21)-C(22) | 1.350(16) |
| C(21)-C(23) | 1.359(16) |
| C(22)-C(24) | 1.418(17) |
| C(23)-C(25) | 1.375(16) |
| C(24)-C(26) | 1.334(16) |
| C(25)-C(26) | 1.348(15) |
| C(8)-Fe(1)-C(9) | 39.5(5) |
| C(8)-Fe(1)-C(3) | 108.2(5) |
| C(9)-Fe(1)-C(3) | 120.5(7) |
| C(8)-Fe(1)-C(4) | 125.0(6) |
| C(9)-Fe(1)-C(4) | 107.7(5) |
| C(3)-Fe(1)-C(4) | 40.5(5) |
| C(8)-Fe(1)-C(5) | 161.3(7) |
| C(9)-Fe(1)-C(5) | 126.4(6) |
| C(3)-Fe(1)-C(5) | 66.0(5) |
| C(4)-Fe(1)-C(5) | 38.9(4) |
| C(8)-Fe(1)-C(7) | 38.6(5) |
| C(9)-Fe(1)-C(7) | 66.1(5) |
| C(3)-Fe(1)-C(7) | 125.1(6) |
| C(4)-Fe(1)-C(7) | 160.7(6) |
| C(5)-Fe(1)-C(7) | 159.3(6) |
| C(8)-Fe(1)-C(10) | 65.6(6) |
| C(9)-Fe(1)-C(10) | 39.8(5) |
| C(3)-Fe(1)-C(10) | 156.2(6) |
| C(4)-Fe(1)-C(10) | 122.4(5) |
| C(5)-Fe(1)-C(10) | 112.1(5) |
| C(7)-Fe(1)-C(10) | 65.6(5) |
| C(8)-Fe(1)-C(2) | 122.5(6) |
| C(9)-Fe(1)-C(2) | 155.7(7) |
| C(3)-Fe(1)-C(2) | 39.9(5) |
| C(4)-Fe(1)-C(2) | 67.0(5) |

|  |  |  |  |
|---|---|---|---|
| C(5)-Fe(1)-C(2) | 65.3(5) | C(2)-C(1)-Fe(1) | 68.6(6) |
| C(7)-Fe(1)-C(2) | 110.5(5) | C(5)-C(1)-Fe(1) | 67.7(6) |
| C(10)-Fe(1)-C(2) | 163.2(6) | C(11)-C(1)-Fe(1) | 125.6(7) |
| C(8)-Fe(1)-C(6) | 65.0(5) | C(1)-C(2)-C(3) | 109.1(11) |
| C(9)-Fe(1)-C(6) | 65.7(5) | C(1)-C(2)-Fe(1) | 73.0(6) |
| C(3)-Fe(1)-C(6) | 162.2(6) | C(3)-C(2)-Fe(1) | 68.3(6) |
| C(4)-Fe(1)-C(6) | 157.1(6) | C(2)-C(3)-C(4) | 107.8(12) |
| C(5)-Fe(1)-C(6) | 125.8(5) | C(2)-C(3)-Fe(1) | 71.9(7) |
| C(7)-Fe(1)-C(6) | 39.3(4) | C(4)-C(3)-Fe(1) | 69.9(6) |
| C(10)-Fe(1)-C(6) | 38.4(4) | C(5)-C(4)-C(3) | 107.1(11) |
| C(2)-Fe(1)-C(6) | 128.2(5) | C(5)-C(4)-Fe(1) | 71.8(6) |
| C(8)-Fe(1)-C(1) | 156.6(6) | C(3)-C(4)-Fe(1) | 69.6(6) |
| C(9)-Fe(1)-C(1) | 163.4(7) | C(4)-C(5)-C(1) | 110.3(11) |
| C(3)-Fe(1)-C(1) | 66.1(5) | C(4)-C(5)-Fe(1) | 69.2(6) |
| C(4)-Fe(1)-C(1) | 66.5(5) | C(1)-C(5)-Fe(1) | 72.8(6) |
| C(5)-Fe(1)-C(1) | 39.4(4) | C(10)-C(6)-C(7) | 107.3(11) |
| C(7)-Fe(1)-C(1) | 124.4(5) | C(10)-C(6)-C(19) | 122.8(15) |
| C(10)-Fe(1)-C(1) | 128.8(6) | C(7)-C(6)-C(19) | 129.8(13) |
| C(2)-Fe(1)-C(1) | 38.4(4) | C(10)-C(6)-Fe(1) | 69.1(6) |
| C(6)-Fe(1)-C(1) | 113.1(5) | C(7)-C(6)-Fe(1) | 68.6(6) |
| F(5)-P(1)-F(6) | 177.2(14) | C(19)-C(6)-Fe(1) | 124.8(8) |
| F(5)-P(1)-F(1) | 91.8(12) | C(8)-C(7)-C(6) | 107.4(12) |
| F(6)-P(1)-F(1) | 89.1(12) | C(8)-C(7)-Fe(1) | 69.0(7) |
| F(5)-P(1)-F(4) | 90.8(12) | C(6)-C(7)-Fe(1) | 72.1(6) |
| F(6)-P(1)-F(4) | 88.4(12) | C(7)-C(8)-C(9) | 110.2(13) |
| F(1)-P(1)-F(4) | 176.8(11) | C(7)-C(8)-Fe(1) | 72.4(7) |
| F(5)-P(1)-F(2) | 93.5(11) | C(9)-C(8)-Fe(1) | 70.5(7) |
| F(6)-P(1)-F(2) | 83.8(10) | C(8)-C(9)-C(10) | 106.7(12) |
| F(1)-P(1)-F(2) | 88.8(6) | C(8)-C(9)-Fe(1) | 70.0(7) |
| F(4)-P(1)-F(2) | 93.0(6) | C(10)-C(9)-Fe(1) | 71.7(7) |
| F(5)-P(1)-F(3) | 91.6(12) | C(6)-C(10)-C(9) | 108.5(13) |
| F(6)-P(1)-F(3) | 91.1(11) | C(6)-C(10)-Fe(1) | 72.5(6) |
| F(1)-P(1)-F(3) | 90.0(6) | C(9)-C(10)-Fe(1) | 68.6(7) |
| F(4)-P(1)-F(3) | 88.0(6) | C(12)-C(11)-C(1) | 125.0(12) |
| F(2)-P(1)-F(3) | 174.8(10) | C(11)-C(12)-C(13) | 126.1(13) |
| C(2)-C(1)-C(5) | 105.7(11) | C(14)-C(13)-C(15) | 117.5(12) |
| C(2)-C(1)-C(11) | 129.5(11) | C(14)-C(13)-C(12) | 123.7(13) |
| C(5)-C(1)-C(11) | 124.7(12) | C(15)-C(13)-C(12) | 118.8(14) |

| | |
|---|---|
| C(13)-C(14)-C(16) | 120.3(12) |
| C(17)-C(15)-C(13) | 122.9(14) |
| C(18)-C(16)-C(14) | 120.4(13) |
| C(15)-C(17)-C(18) | 118.7(13) |
| C(17)-C(18)-C(16) | 120.2(13) |
| C(17)-C(18)-Br(1) | 121.2(12) |
| C(16)-C(18)-Br(1) | 118.6(13) |
| C(20)-C(19)-C(6) | 126.7(14) |
| C(19)-C(20)-C(21) | 124.8(15) |
| C(22)-C(21)-C(23) | 117.8(12) |
| C(22)-C(21)-C(20) | 126.7(14) |
| C(23)-C(21)-C(20) | 115.5(14) |
| C(21)-C(22)-C(24) | 120.0(12) |
| C(21)-C(23)-C(25) | 122.6(12) |
| C(26)-C(24)-C(22) | 119.6(12) |
| C(26)-C(25)-C(23) | 118.7(12) |
| C(24)-C(26)-C(25) | 120.9(12) |
| C(24)-C(26)-Br(2) | 120.3(12) |
| C(25)-C(26)-Br(2) | 118.8(12) |
| Cl(1)-C(100)-Cl(2) | 117.5(9) |

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2$x $10^3$)for str193m. The anisotropic displacement factor exponent takes the form: $-2\pi^2[ h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12} ]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| Fe(1) | 49(1) | 44(1) | 41(1) | 9(1) | 14(1) | 8(1) |
| Br(1) | 148(2) | 102(1) | 85(1) | 33(1) | -4(1) | 51(1) |
| P(1) | 46(2) | 111(3) | 108(3) | 64(3) | 23(2) | 12(2) |
| F(1) | 104(7) | 420(20) | 370(20) | 331(19) | 94(10) | 97(10) |
| C(1) | 54(8) | 59(7) | 39(7) | 8(6) | 10(6) | 1(6) |
| Cl(1) | 103(3) | 216(5) | 238(6) | 169(5) | -17(3) | -38(3) |
| Br(2) | 137(1) | 84(1) | 93(1) | 50(1) | -4(1) | -3(1) |
| C(2) | 68(8) | 59(8) | 60(8) | 13(7) | 7(7) | -5(7) |
| F(2) | 118(7) | 256(12) | 330(16) | 233(13) | 100(9) | 32(8) |
| Cl(2) | 220(6) | 160(5) | 223(6) | 101(5) | 117(5) | 75(4) |
| C(3) | 111(12) | 45(7) | 60(9) | 6(6) | 21(8) | -15(8) |
| F(3) | 140(9) | 356(18) | 460(20) | 354(19) | 141(12) | 81(10) |
| C(4) | 69(9) | 56(8) | 78(10) | 12(7) | 15(7) | 24(7) |
| F(4) | 85(7) | 450(20) | 440(20) | 390(20) | 80(10) | 85(10) |
| C(5) | 68(9) | 68(8) | 50(8) | 10(7) | 25(6) | 15(7) |
| F(5) | 410(30) | 270(20) | 221(18) | -69(16) | 137(19) | -22(19) |
| C(6) | 95(10) | 45(7) | 51(8) | 23(6) | 16(7) | 21(7) |
| F(6) | 380(30) | 286(19) | 190(15) | -36(15) | 94(17) | -108(19) |
| C(7) | 81(9) | 77(8) | 48(8) | 15(7) | 26(7) | 17(8) |
| C(8) | 139(14) | 70(9) | 47(8) | 20(7) | 41(9) | 26(10) |
| C(9) | 99(13) | 66(9) | 55(9) | -7(8) | -19(8) | 29(9) |
| C(10) | 65(10) | 60(8) | 81(10) | 13(8) | 6(7) | 1(7) |
| C(11) | 62(9) | 71(8) | 52(8) | 4(7) | 15(7) | -2(7) |
| C(12) | 74(10) | 68(8) | 52(8) | 4(7) | 24(7) | -1(7) |
| C(13) | 78(10) | 67(8) | 38(7) | 18(6) | 13(7) | 24(7) |
| C(14) | 62(8) | 76(8) | 53(8) | 12(7) | 12(7) | 10(8) |
| C(15) | 61(10) | 97(10) | 78(10) | 18(8) | 26(8) | 14(8) |
| C(16) | 90(11) | 63(8) | 47(8) | 12(7) | 13(7) | 8(7) |
| C(17) | 73(10) | 105(11) | 67(10) | 19(9) | 10(8) | 35(10) |
| C(18) | 83(11) | 70(9) | 53(8) | 7(7) | 12(8) | 14(8) |
| C(19) | 87(11) | 72(9) | 76(10) | -5(8) | 35(9) | 0(9) |
| C(20) | 78(10) | 62(8) | 80(10) | -5(8) | 38(8) | 13(8) |
| C(21) | 96(12) | 37(7) | 49(8) | 12(6) | 10(8) | 13(8) |

|  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|
| C(22) | 74(9) | 69(9) | 74(10) | 17(8) | 19(7) | 21(8) |
| C(23) | 89(11) | 43(7) | 60(8) | 9(6) | 24(7) | 4(7) |
| C(24) | 95(12) | 60(8) | 73(9) | 25(7) | 27(8) | -12(8) |
| C(25) | 76(9) | 55(7) | 60(8) | 13(7) | 10(7) | 10(7) |
| C(26) | 85(10) | 48(7) | 52(8) | 11(6) | 21(8) | -5(7) |
| C(100) | 118(13) | 112(12) | 204(19) | 71(13) | 85(13) | 35(10) |

**Table 5**. Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters (Å$^2$x $10^3$) for str193m.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(2) | 5679 | 10290 | 2256 | 85 |
| H(3) | 3910 | 11146 | 1231 | 96 |
| H(4) | 1683 | 10760 | 1535 | 91 |
| H(5) | 2109 | 9700 | 2741 | 80 |
| H(7) | 4789 | 7557 | -153 | 87 |
| H(8) | 3227 | 8585 | -1065 | 102 |
| H(9) | 952 | 8329 | -859 | 115 |
| H(10) | 1088 | 7048 | 170 | 96 |
| H(11) | 4190 | 8822 | 3705 | 85 |
| H(12) | 6645 | 9395 | 3528 | 87 |
| H(14) | 5016 | 7558 | 4408 | 86 |
| H(15) | 8629 | 9061 | 4713 | 103 |
| H(16) | 6131 | 6576 | 5439 | 88 |
| H(17) | 9739 | 8141 | 5775 | 110 |
| H(19) | 2899 | 5922 | 997 | 109 |
| H(20) | 5451 | 6440 | 1052 | 101 |
| H(22) | 3392 | 4578 | 1694 | 95 |
| H(23) | 7146 | 5839 | 2122 | 84 |
| H(24) | 4305 | 3639 | 2864 | 94 |
| H(25) | 8039 | 4762 | 3109 | 85 |
| H(10A) | -67 | 13402 | -3715 | 164 |
| H(10B) | 321 | 12714 | -2968 | 164 |

**Table 6**. Torsion angles [°] for str193m.

| | |
|---|---|
| C(8)-Fe(1)-C(1)-C(2) | 42.7(16) |
| C(9)-Fe(1)-C(1)-C(2) | -154.8(17) |
| C(3)-Fe(1)-C(1)-C(2) | -37.7(7) |
| C(4)-Fe(1)-C(1)-C(2) | -82.1(8) |
| C(5)-Fe(1)-C(1)-C(2) | -118.4(10) |
| C(7)-Fe(1)-C(1)-C(2) | 79.6(9) |
| C(10)-Fe(1)-C(1)-C(2) | 164.3(8) |
| C(6)-Fe(1)-C(1)-C(2) | 122.9(8) |
| C(8)-Fe(1)-C(1)-C(5) | 161.1(12) |
| C(9)-Fe(1)-C(1)-C(5) | -36(2) |
| C(3)-Fe(1)-C(1)-C(5) | 80.7(8) |
| C(4)-Fe(1)-C(1)-C(5) | 36.3(7) |
| C(7)-Fe(1)-C(1)-C(5) | -162.0(8) |
| C(10)-Fe(1)-C(1)-C(5) | -77.4(9) |
| C(2)-Fe(1)-C(1)-C(5) | 118.4(10) |
| C(6)-Fe(1)-C(1)-C(5) | -118.7(8) |
| C(8)-Fe(1)-C(1)-C(11) | -81.4(18) |
| C(9)-Fe(1)-C(1)-C(11) | 81(2) |
| C(3)-Fe(1)-C(1)-C(11) | -161.8(13) |
| C(4)-Fe(1)-C(1)-C(11) | 153.8(13) |
| C(5)-Fe(1)-C(1)-C(11) | 117.6(14) |
| C(7)-Fe(1)-C(1)-C(11) | -44.5(13) |
| C(10)-Fe(1)-C(1)-C(11) | 40.2(13) |
| C(2)-Fe(1)-C(1)-C(11) | -124.1(14) |
| C(6)-Fe(1)-C(1)-C(11) | -1.2(12) |
| C(5)-C(1)-C(2)-C(3) | 1.1(11) |
| C(11)-C(1)-C(2)-C(3) | 178.1(10) |
| Fe(1)-C(1)-C(2)-C(3) | 58.9(7) |
| C(5)-C(1)-C(2)-Fe(1) | -57.8(7) |
| C(11)-C(1)-C(2)-Fe(1) | 119.2(11) |
| C(8)-Fe(1)-C(2)-C(1) | -161.4(8) |
| C(9)-Fe(1)-C(2)-C(1) | 162.8(12) |
| C(3)-Fe(1)-C(2)-C(1) | 119.4(11) |
| C(4)-Fe(1)-C(2)-C(1) | 80.7(8) |
| C(5)-Fe(1)-C(2)-C(1) | 38.0(7) |
| C(7)-Fe(1)-C(2)-C(1) | -120.0(8) |
| C(10)-Fe(1)-C(2)-C(1) | -47(2) |
| C(6)-Fe(1)-C(2)-C(1) | -79.2(9) |
| C(8)-Fe(1)-C(2)-C(3) | 79.3(10) |
| C(9)-Fe(1)-C(2)-C(3) | 43.4(16) |
| C(4)-Fe(1)-C(2)-C(3) | -38.7(8) |
| C(5)-Fe(1)-C(2)-C(3) | -81.4(8) |
| C(7)-Fe(1)-C(2)-C(3) | 120.6(9) |
| C(10)-Fe(1)-C(2)-C(3) | -166.2(16) |
| C(6)-Fe(1)-C(2)-C(3) | 161.4(8) |
| C(1)-Fe(1)-C(2)-C(3) | -119.4(11) |
| C(1)-C(2)-C(3)-C(4) | -0.9(12) |
| Fe(1)-C(2)-C(3)-C(4) | 61.0(7) |
| C(1)-C(2)-C(3)-Fe(1) | -61.8(7) |
| C(8)-Fe(1)-C(3)-C(2) | -119.3(10) |
| C(9)-Fe(1)-C(3)-C(2) | -160.8(9) |
| C(4)-Fe(1)-C(3)-C(2) | 117.6(11) |
| C(5)-Fe(1)-C(3)-C(2) | 79.7(8) |
| C(7)-Fe(1)-C(3)-C(2) | -80.0(9) |
| C(10)-Fe(1)-C(3)-C(2) | 170.1(12) |
| C(6)-Fe(1)-C(3)-C(2) | -55.0(19) |
| C(1)-Fe(1)-C(3)-C(2) | 36.3(7) |
| C(8)-Fe(1)-C(3)-C(4) | 123.1(10) |
| C(9)-Fe(1)-C(3)-C(4) | 81.6(10) |
| C(5)-Fe(1)-C(3)-C(4) | -37.9(7) |
| C(7)-Fe(1)-C(3)-C(4) | 162.4(8) |
| C(10)-Fe(1)-C(3)-C(4) | 52.6(16) |
| C(2)-Fe(1)-C(3)-C(4) | -117.6(11) |
| C(6)-Fe(1)-C(3)-C(4) | -172.6(14) |
| C(1)-Fe(1)-C(3)-C(4) | -81.2(8) |
| C(2)-C(3)-C(4)-C(5) | 0.3(12) |
| Fe(1)-C(3)-C(4)-C(5) | 62.5(7) |
| C(2)-C(3)-C(4)-Fe(1) | -62.2(8) |
| C(8)-Fe(1)-C(4)-C(5) | 166.8(8) |
| C(9)-Fe(1)-C(4)-C(5) | 126.6(9) |
| C(3)-Fe(1)-C(4)-C(5) | -116.8(11) |
| C(7)-Fe(1)-C(4)-C(5) | -165.2(13) |
| C(10)-Fe(1)-C(4)-C(5) | 85.5(9) |
| C(2)-Fe(1)-C(4)-C(5) | -78.7(8) |

| | |
|---|---|
| C(6)-Fe(1)-C(4)-C(5) | 57.3(15) |
| C(1)-Fe(1)-C(4)-C(5) | -36.7(7) |
| C(8)-Fe(1)-C(4)-C(3) | -76.4(10) |
| C(9)-Fe(1)-C(4)-C(3) | -116.5(10) |
| C(5)-Fe(1)-C(4)-C(3) | 116.8(11) |
| C(7)-Fe(1)-C(4)-C(3) | -48.4(17) |
| C(10)-Fe(1)-C(4)-C(3) | -157.7(9) |
| C(2)-Fe(1)-C(4)-C(3) | 38.1(7) |
| C(6)-Fe(1)-C(4)-C(3) | 174.2(11) |
| C(1)-Fe(1)-C(4)-C(3) | 80.1(8) |
| C(3)-C(4)-C(5)-C(1) | 0.5(12) |
| Fe(1)-C(4)-C(5)-C(1) | 61.5(7) |
| C(3)-C(4)-C(5)-Fe(1) | -61.0(7) |
| C(2)-C(1)-C(5)-C(4) | -1.0(11) |
| C(11)-C(1)-C(5)-C(4) | -178.2(9) |
| Fe(1)-C(1)-C(5)-C(4) | -59.3(7) |
| C(2)-C(1)-C(5)-Fe(1) | 58.3(7) |
| C(11)-C(1)-C(5)-Fe(1) | -118.8(10) |
| C(8)-Fe(1)-C(5)-C(4) | -36(2) |
| C(9)-Fe(1)-C(5)-C(4) | -71.8(10) |
| C(3)-Fe(1)-C(5)-C(4) | 39.4(7) |
| C(7)-Fe(1)-C(5)-C(4) | 166.2(12) |
| C(10)-Fe(1)-C(5)-C(4) | -114.8(9) |
| C(2)-Fe(1)-C(5)-C(4) | 83.3(8) |
| C(6)-Fe(1)-C(5)-C(4) | -156.2(8) |
| C(1)-Fe(1)-C(5)-C(4) | 120.3(10) |
| C(8)-Fe(1)-C(5)-C(1) | -156.2(16) |
| C(9)-Fe(1)-C(5)-C(1) | 167.8(9) |
| C(3)-Fe(1)-C(5)-C(1) | -81.0(8) |
| C(4)-Fe(1)-C(5)-C(1) | -120.3(10) |
| C(7)-Fe(1)-C(5)-C(1) | 45.9(16) |
| C(10)-Fe(1)-C(5)-C(1) | 124.9(8) |
| C(2)-Fe(1)-C(5)-C(1) | -37.0(7) |
| C(6)-Fe(1)-C(5)-C(1) | 83.5(8) |
| C(8)-Fe(1)-C(6)-C(10) | -81.7(9) |
| C(9)-Fe(1)-C(6)-C(10) | -38.0(8) |
| C(3)-Fe(1)-C(6)-C(10) | -152.6(16) |
| C(4)-Fe(1)-C(6)-C(10) | 39.9(16) |
| C(5)-Fe(1)-C(6)-C(10) | 80.6(9) |
| C(7)-Fe(1)-C(6)-C(10) | -119.4(11) |
| C(2)-Fe(1)-C(6)-C(10) | 165.5(9) |
| C(1)-Fe(1)-C(6)-C(10) | 123.9(9) |
| C(8)-Fe(1)-C(6)-C(7) | 37.7(7) |
| C(9)-Fe(1)-C(6)-C(7) | 81.4(9) |
| C(3)-Fe(1)-C(6)-C(7) | -33.2(19) |
| C(4)-Fe(1)-C(6)-C(7) | 159.3(13) |
| C(5)-Fe(1)-C(6)-C(7) | -160.0(7) |
| C(10)-Fe(1)-C(6)-C(7) | 119.4(11) |
| C(2)-Fe(1)-C(6)-C(7) | -75.1(9) |
| C(1)-Fe(1)-C(6)-C(7) | -116.7(8) |
| C(8)-Fe(1)-C(6)-C(19) | 162.1(16) |
| C(9)-Fe(1)-C(6)-C(19) | -154.2(16) |
| C(3)-Fe(1)-C(6)-C(19) | 91(2) |
| C(4)-Fe(1)-C(6)-C(19) | -76.3(18) |
| C(5)-Fe(1)-C(6)-C(19) | -35.6(15) |
| C(7)-Fe(1)-C(6)-C(19) | 124.4(16) |
| C(10)-Fe(1)-C(6)-C(19) | -116.2(17) |
| C(2)-Fe(1)-C(6)-C(19) | 49.3(15) |
| C(1)-Fe(1)-C(6)-C(19) | 7.7(14) |
| C(10)-C(6)-C(7)-C(8) | -1.8(12) |
| C(19)-C(6)-C(7)-C(8) | -178.3(11) |
| Fe(1)-C(6)-C(7)-C(8) | -60.3(8) |
| C(10)-C(6)-C(7)-Fe(1) | 58.5(8) |
| C(19)-C(6)-C(7)-Fe(1) | -118.1(11) |
| C(9)-Fe(1)-C(7)-C(8) | 37.2(9) |
| C(3)-Fe(1)-C(7)-C(8) | -74.4(11) |
| C(4)-Fe(1)-C(7)-C(8) | -38.0(18) |
| C(5)-Fe(1)-C(7)-C(8) | 168.9(12) |
| C(10)-Fe(1)-C(7)-C(8) | 80.9(9) |
| C(2)-Fe(1)-C(7)-C(8) | -116.8(10) |
| C(6)-Fe(1)-C(7)-C(8) | 117.4(11) |
| C(1)-Fe(1)-C(7)-C(8) | -157.5(9) |
| C(8)-Fe(1)-C(7)-C(6) | -117.4(11) |
| C(9)-Fe(1)-C(7)-C(6) | -80.2(9) |
| C(3)-Fe(1)-C(7)-C(6) | 168.2(8) |
| C(4)-Fe(1)-C(7)-C(6) | -155.4(13) |

| | | | |
|---|---|---|---|
| C(5)-Fe(1)-C(7)-C(6) | 51.5(16) | C(7)-Fe(1)-C(9)-C(10) | 79.9(8) |
| C(10)-Fe(1)-C(7)-C(6) | -36.5(7) | C(2)-Fe(1)-C(9)-C(10) | 167.1(11) |
| C(2)-Fe(1)-C(7)-C(6) | 125.8(8) | C(6)-Fe(1)-C(9)-C(10) | 36.7(8) |
| C(1)-Fe(1)-C(7)-C(6) | 85.1(8) | C(1)-Fe(1)-C(9)-C(10) | -53(2) |
| C(6)-C(7)-C(8)-C(9) | 1.7(13) | C(7)-C(6)-C(10)-C(9) | 1.2(13) |
| Fe(1)-C(7)-C(8)-C(9) | -60.6(8) | C(19)-C(6)-C(10)-C(9) | 178.1(10) |
| C(6)-C(7)-C(8)-Fe(1) | 62.3(8) | Fe(1)-C(6)-C(10)-C(9) | 59.4(8) |
| C(9)-Fe(1)-C(8)-C(7) | -119.8(12) | C(7)-C(6)-C(10)-Fe(1) | -58.2(7) |
| C(3)-Fe(1)-C(8)-C(7) | 124.0(9) | C(19)-C(6)-C(10)-Fe(1) | 118.7(10) |
| C(4)-Fe(1)-C(8)-C(7) | 165.6(8) | C(8)-C(9)-C(10)-C(6) | -0.2(13) |
| C(5)-Fe(1)-C(8)-C(7) | -167.7(14) | Fe(1)-C(9)-C(10)-C(6) | -61.8(8) |
| C(10)-Fe(1)-C(8)-C(7) | -80.7(8) | C(8)-C(9)-C(10)-Fe(1) | 61.6(8) |
| C(2)-Fe(1)-C(8)-C(7) | 82.4(10) | C(8)-Fe(1)-C(10)-C(6) | 79.9(9) |
| C(6)-Fe(1)-C(8)-C(7) | -38.3(8) | C(9)-Fe(1)-C(10)-C(6) | 118.7(12) |
| C(1)-Fe(1)-C(8)-C(7) | 52.5(16) | C(3)-Fe(1)-C(10)-C(6) | 159.6(12) |
| C(3)-Fe(1)-C(8)-C(9) | -116.3(10) | C(4)-Fe(1)-C(10)-C(6) | -162.8(8) |
| C(4)-Fe(1)-C(8)-C(9) | -74.6(11) | C(5)-Fe(1)-C(10)-C(6) | -120.3(8) |
| C(5)-Fe(1)-C(8)-C(9) | -48(2) | C(7)-Fe(1)-C(10)-C(6) | 37.3(7) |
| C(7)-Fe(1)-C(8)-C(9) | 119.8(12) | C(2)-Fe(1)-C(10)-C(6) | -43(2) |
| C(10)-Fe(1)-C(8)-C(9) | 39.0(8) | C(1)-Fe(1)-C(10)-C(6) | -78.3(9) |
| C(2)-Fe(1)-C(8)-C(9) | -157.8(9) | C(8)-Fe(1)-C(10)-C(9) | -38.8(8) |
| C(6)-Fe(1)-C(8)-C(9) | 81.5(9) | C(3)-Fe(1)-C(10)-C(9) | 40.8(17) |
| C(1)-Fe(1)-C(8)-C(9) | 172.2(11) | C(4)-Fe(1)-C(10)-C(9) | 78.5(11) |
| C(7)-C(8)-C(9)-C(10) | -0.9(14) | C(5)-Fe(1)-C(10)-C(9) | 121.0(10) |
| Fe(1)-C(8)-C(9)-C(10) | -62.7(8) | C(7)-Fe(1)-C(10)-C(9) | -81.4(9) |
| C(7)-C(8)-C(9)-Fe(1) | 61.8(9) | C(2)-Fe(1)-C(10)-C(9) | -161.4(16) |
| C(3)-Fe(1)-C(9)-C(8) | 81.6(10) | C(6)-Fe(1)-C(10)-C(9) | -118.7(12) |
| C(4)-Fe(1)-C(9)-C(8) | 124.0(10) | C(1)-Fe(1)-C(10)-C(9) | 163.0(9) |
| C(5)-Fe(1)-C(9)-C(8) | 162.8(8) | C(2)-C(1)-C(11)-C(12) | 6.2(18) |
| C(7)-Fe(1)-C(9)-C(8) | -36.4(8) | C(5)-C(1)-C(11)-C(12) | -177.4(10) |
| C(10)-Fe(1)-C(9)-C(8) | -116.2(12) | Fe(1)-C(1)-C(11)-C(12) | 96.7(13) |
| C(2)-Fe(1)-C(9)-C(8) | 50.8(16) | C(1)-C(11)-C(12)-C(13) | -179.3(9) |
| C(6)-Fe(1)-C(9)-C(8) | -79.5(9) | C(11)-C(12)-C(13)-C(14) | 12.0(18) |
| C(1)-Fe(1)-C(9)-C(8) | -169.2(15) | C(11)-C(12)-C(13)-C(15) | -167.7(11) |
| C(8)-Fe(1)-C(9)-C(10) | 116.2(12) | C(15)-C(13)-C(14)-C(16) | -0.9(16) |
| C(3)-Fe(1)-C(9)-C(10) | -162.2(8) | C(12)-C(13)-C(14)-C(16) | 179.4(10) |
| C(4)-Fe(1)-C(9)-C(10) | -119.7(9) | C(14)-C(13)-C(15)-C(17) | -0.1(17) |
| C(5)-Fe(1)-C(9)-C(10) | -80.9(10) | C(12)-C(13)-C(15)-C(17) | 179.6(11) |

|  |  |
|---|---|
| C(13)-C(14)-C(16)-C(18) | 2.1(17) |
| C(13)-C(15)-C(17)-C(18) | -0.1(19) |
| C(15)-C(17)-C(18)-C(16) | 1.3(19) |
| C(15)-C(17)-C(18)-Br(1) | -178.8(9) |
| C(14)-C(16)-C(18)-C(17) | -2.3(17) |
| C(14)-C(16)-C(18)-Br(1) | 177.8(8) |
| C(10)-C(6)-C(19)-C(20) | -171.3(12) |
| C(7)-C(6)-C(19)-C(20) | 5(2) |
| Fe(1)-C(6)-C(19)-C(20) | -85.2(16) |
| C(6)-C(19)-C(20)-C(21) | 179.5(10) |
| C(19)-C(20)-C(21)-C(22) | 9.3(19) |
| C(19)-C(20)-C(21)-C(23) | -173.5(12) |
| C(23)-C(21)-C(22)-C(24) | 5.6(16) |
| C(20)-C(21)-C(22)-C(24) | -177.1(10) |
| C(22)-C(21)-C(23)-C(25) | -2.2(16) |
| C(20)-C(21)-C(23)-C(25) | -179.7(10) |
| C(21)-C(22)-C(24)-C(26) | -4.7(17) |
| C(21)-C(23)-C(25)-C(26) | -2.4(16) |
| C(22)-C(24)-C(26)-C(25) | 0.0(17) |
| C(22)-C(24)-C(26)-Br(2) | -177.3(8) |
| C(23)-C(25)-C(26)-C(24) | 3.5(16) |
| C(23)-C(25)-C(26)-Br(2) | -179.2(8) |

Symmetry transformations used to generate equivalent atoms:

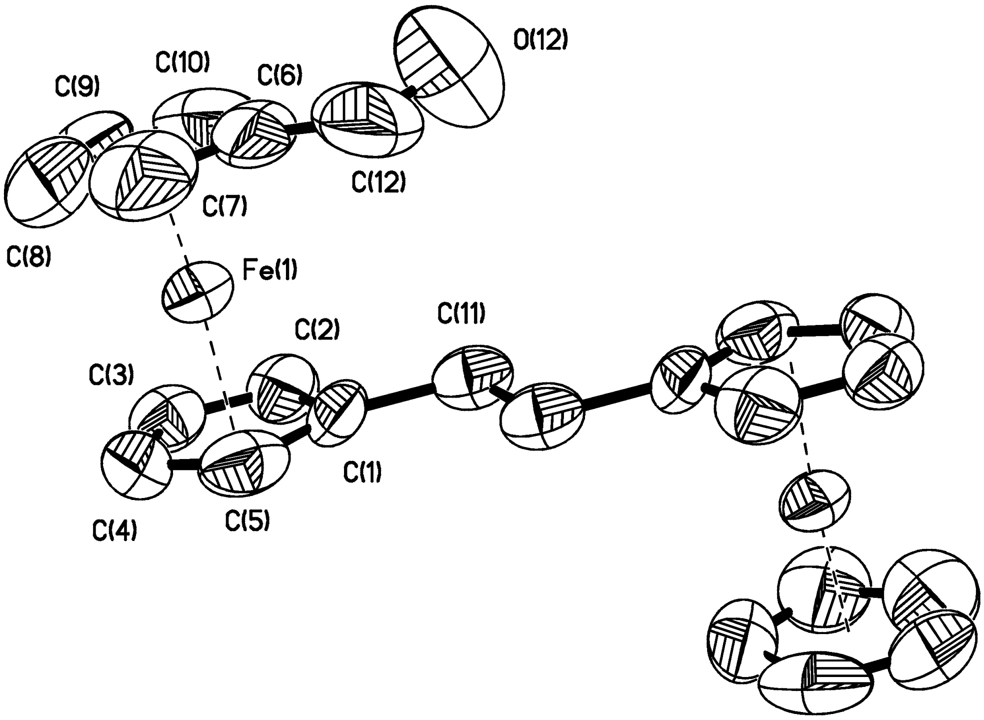

O(12)
C(9)
C(10)
C(6)
C(12)
C(7)
C(8)
Fe(1)
C(11)
C(2)
C(3)
C(1)
C(4)
C(5)

**Table 1**. Crystal data and structure refinement for str196m.

| | | |
|---|---|---|
| Identification code | str196m | |
| Empirical formula | C23 H20 Fe2 O | |
| Formula weight | 424.09 | |
| Temperature | 293(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | C2/c | |
| Unit cell dimensions | a = 22.861(3) Å | $\alpha$= 90°. |
| | b = 7.5781(8) Å | $\beta$= 108.025(2)°. |
| | c = 10.9377(12) Å | $\gamma$ = 90°. |
| Volume | 1801.9(3) Å$^3$ | |
| Z | 4 | |
| Density (calculated) | 1.563 Mg/m$^3$ | |
| Absorption coefficient | 1.618 mm$^{-1}$ | |
| F(000) | 872 | |
| Crystal size | 0.40 x 0.25 x 0.12 mm$^3$ | |
| Theta range for data collection | 1.87 to 24.71°. | |
| Index ranges | -25<=h<=26, -8<=k<=8, -12<=l<=12 | |
| Reflections collected | 4813 | |
| Independent reflections | 1538 [R(int) = 0.0254] | |
| Completeness to theta = 24.71° | 100.0 % | |
| Absorption correction | Bruker SADABS | |
| Max. and min. transmission | 1.954887 and 1.254912 | |
| Refinement method | Full-matrix least-squares on F$^2$ | |
| Data / restraints / parameters | 1538 / 0 / 136 | |
| Goodness-of-fit on F$^2$ | 1.078 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0570, wR2 = 0.1575 | |
| R indices (all data) | R1 = 0.0728, wR2 = 0.1663 | |
| Largest diff. peak and hole | 1.048 and -0.489 e.Å$^{-3}$ | |

**Table 2**. Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters (Å$^2$x $10^3$) for str196m. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| Fe(1) | 3648(1) | 2327(1) | 9314(1) | 57(1) |
| C(1) | 4234(3) | 4280(8) | 10222(7) | 78(2) |
| C(2) | 4138(3) | 3076(9) | 11110(6) | 76(2) |
| C(3) | 3526(3) | 3021(8) | 11007(5) | 69(2) |
| C(4) | 3220(3) | 4190(7) | 10039(6) | 72(2) |
| C(5) | 3653(3) | 4970(8) | 9559(6) | 78(2) |
| C(6) | 3945(5) | 1183(15) | 7993(12) | 140(5) |
| C(7) | 3334(6) | 1758(14) | 7409(8) | 115(3) |
| C(8) | 2981(5) | 918(18) | 7995(11) | 134(4) |
| C(9) | 3295(5) | -158(13) | 8873(12) | 123(3) |
| C(10) | 3892(5) | -100(10) | 8957(9) | 110(3) |
| C(11A) | 4696(7) | 5110(30) | 9643(19) | 70(4) |
| C(11) | 4933(13) | 4348(17) | 10334(15) | 65(4) |
| O(12) | 4942(8) | 940(30) | 8178(17) | 189(7) |
| C(12) | 4416(11) | 1740(30) | 7710(20) | 166(11) |

**Table 3.** Bond lengths [Å] and angles [°] for str196m.

| | |
|---|---|
| Fe(1)-C(6) | 1.977(6) |
| Fe(1)-C(10) | 1.995(6) |
| Fe(1)-C(4) | 2.015(5) |
| Fe(1)-C(2) | 2.018(5) |
| Fe(1)-C(5) | 2.020(6) |
| Fe(1)-C(3) | 2.026(5) |
| Fe(1)-C(7) | 2.030(7) |
| Fe(1)-C(1) | 2.036(5) |
| Fe(1)-C(8) | 2.046(8) |
| Fe(1)-C(9) | 2.047(8) |
| C(1)-C(2) | 1.399(9) |
| C(1)-C(5) | 1.403(9) |
| C(1)-C(11A) | 1.52(2) |
| C(1)-C(11) | 1.57(3) |
| C(2)-C(3) | 1.370(8) |
| C(3)-C(4) | 1.392(8) |
| C(4)-C(5) | 1.388(8) |
| C(6)-C(12) | 1.28(3) |
| C(6)-C(7) | 1.414(14) |
| C(6)-C(10) | 1.467(13) |
| C(7)-C(8) | 1.336(14) |
| C(8)-C(9) | 1.294(13) |
| C(9)-C(10) | 1.339(13) |
| C(11A)-C(11)#1 | 0.935(15) |
| C(11A)-C(11) | 0.970(14) |
| C(11A)-C(11A)#1 | 1.38(3) |
| C(11)-C(11A)#1 | 0.935(15) |
| C(11)-C(11)#1 | 1.32(3) |
| O(12)-C(12) | 1.30(3) |
| O(12)-O(12)#2 | 1.59(3) |
| C(6)-Fe(1)-C(10) | 43.4(4) |
| C(6)-Fe(1)-C(4) | 156.0(5) |
| C(10)-Fe(1)-C(4) | 157.2(4) |
| C(6)-Fe(1)-C(2) | 128.5(4) |
| C(10)-Fe(1)-C(2) | 110.2(3) |
| C(4)-Fe(1)-C(2) | 67.1(3) |
| C(6)-Fe(1)-C(5) | 122.9(4) |
| C(10)-Fe(1)-C(5) | 161.8(4) |
| C(4)-Fe(1)-C(5) | 40.2(2) |
| C(2)-Fe(1)-C(5) | 67.3(3) |
| C(6)-Fe(1)-C(3) | 163.3(5) |
| C(10)-Fe(1)-C(3) | 123.0(4) |
| C(4)-Fe(1)-C(3) | 40.3(2) |
| C(2)-Fe(1)-C(3) | 39.6(2) |
| C(5)-Fe(1)-C(3) | 67.5(2) |
| C(6)-Fe(1)-C(7) | 41.3(4) |
| C(10)-Fe(1)-C(7) | 68.6(4) |
| C(4)-Fe(1)-C(7) | 119.5(4) |
| C(2)-Fe(1)-C(7) | 166.6(4) |
| C(5)-Fe(1)-C(7) | 109.4(4) |
| C(3)-Fe(1)-C(7) | 152.7(4) |
| C(6)-Fe(1)-C(1) | 110.7(3) |
| C(10)-Fe(1)-C(1) | 125.8(4) |
| C(4)-Fe(1)-C(1) | 68.0(2) |
| C(2)-Fe(1)-C(1) | 40.4(3) |
| C(5)-Fe(1)-C(1) | 40.5(3) |
| C(3)-Fe(1)-C(1) | 67.8(2) |
| C(7)-Fe(1)-C(1) | 128.8(4) |
| C(6)-Fe(1)-C(8) | 66.7(4) |
| C(10)-Fe(1)-C(8) | 64.7(4) |
| C(4)-Fe(1)-C(8) | 107.2(4) |
| C(2)-Fe(1)-C(8) | 154.3(5) |
| C(5)-Fe(1)-C(8) | 125.7(5) |
| C(3)-Fe(1)-C(8) | 119.8(4) |
| C(7)-Fe(1)-C(8) | 38.3(4) |
| C(1)-Fe(1)-C(8) | 163.2(5) |
| C(6)-Fe(1)-C(9) | 67.9(4) |
| C(10)-Fe(1)-C(9) | 38.7(4) |
| C(4)-Fe(1)-C(9) | 122.2(3) |
| C(2)-Fe(1)-C(9) | 123.2(4) |
| C(5)-Fe(1)-C(9) | 158.2(4) |
| C(3)-Fe(1)-C(9) | 107.4(4) |
| C(7)-Fe(1)-C(9) | 64.8(4) |

| | |
|---|---|
| C(1)-Fe(1)-C(9) | 159.3(5) |
| C(8)-Fe(1)-C(9) | 36.8(4) |
| C(2)-C(1)-C(5) | 106.0(5) |
| C(2)-C(1)-C(11A) | 146.5(10) |
| C(5)-C(1)-C(11A) | 107.5(10) |
| C(2)-C(1)-C(11) | 110.0(8) |
| C(5)-C(1)-C(11) | 144.0(8) |
| C(11A)-C(1)-C(11) | 36.6(6) |
| C(2)-C(1)-Fe(1) | 69.1(3) |
| C(5)-C(1)-Fe(1) | 69.1(3) |
| C(11A)-C(1)-Fe(1) | 122.1(6) |
| C(11)-C(1)-Fe(1) | 124.3(5) |
| C(3)-C(2)-C(1) | 109.8(6) |
| C(3)-C(2)-Fe(1) | 70.5(3) |
| C(1)-C(2)-Fe(1) | 70.5(3) |
| C(2)-C(3)-C(4) | 107.7(6) |
| C(2)-C(3)-Fe(1) | 69.9(3) |
| C(4)-C(3)-Fe(1) | 69.4(3) |
| C(5)-C(4)-C(3) | 108.0(6) |
| C(5)-C(4)-Fe(1) | 70.1(3) |
| C(3)-C(4)-Fe(1) | 70.3(3) |
| C(4)-C(5)-C(1) | 108.5(6) |
| C(4)-C(5)-Fe(1) | 69.7(3) |
| C(1)-C(5)-Fe(1) | 70.4(3) |
| C(12)-C(6)-C(7) | 125.2(19) |
| C(12)-C(6)-C(10) | 131(2) |
| C(7)-C(6)-C(10) | 103.8(8) |
| C(12)-C(6)-Fe(1) | 122.3(9) |
| C(7)-C(6)-Fe(1) | 71.4(4) |
| C(10)-C(6)-Fe(1) | 69.0(4) |
| C(8)-C(7)-C(6) | 107.1(10) |
| C(8)-C(7)-Fe(1) | 71.5(5) |
| C(6)-C(7)-Fe(1) | 67.3(4) |
| C(9)-C(8)-C(7) | 112.2(11) |
| C(9)-C(8)-Fe(1) | 71.6(5) |
| C(7)-C(8)-Fe(1) | 70.2(5) |
| C(8)-C(9)-C(10) | 110.5(11) |
| C(8)-C(9)-Fe(1) | 71.5(6) |
| C(10)-C(9)-Fe(1) | 68.6(4) |
| C(9)-C(10)-C(6) | 106.4(9) |
| C(9)-C(10)-Fe(1) | 72.8(5) |
| C(6)-C(10)-Fe(1) | 67.7(4) |
| C(11)#1-C(11A)-C(11) | 88(2) |
| C(11)#1-C(11A)-C(11A)#1 | 44.8(11) |
| C(11)-C(11A)-C(11A)#1 | 42.8(14) |
| C(11)#1-C(11A)-C(1) | 155(2) |
| C(11)-C(11A)-C(1) | 74(3) |
| C(11A)#1-C(11A)-C(1) | 115(3) |
| C(11A)#1-C(11)-C(11A) | 92(2) |
| C(11A)#1-C(11)-C(11)#1 | 47.3(15) |
| C(11A)-C(11)-C(11)#1 | 45.1(11) |
| C(11A)#1-C(11)-C(1) | 155(2) |
| C(11A)-C(11)-C(1) | 69(3) |
| C(11)#1-C(11)-C(1) | 113(3) |
| C(12)-O(12)-O(12)#2 | 92(2) |
| C(6)-C(12)-O(12) | 120(3) |

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+1,-z+2 #2 -x+1,y,-z+3/2

**Table 4**. Anisotropic displacement parameters ($Å^2$x $10^3$) for str196m. The anisotropic displacement factor exponent takes the form: $-2\pi^2[ h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12} ]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| Fe(1) | 66(1) | 48(1) | 54(1) | -9(1) | 16(1) | -7(1) |
| C(1) | 69(4) | 75(4) | 100(4) | -45(3) | 43(4) | -36(3) |
| C(2) | 63(4) | 86(4) | 64(3) | -23(3) | -3(3) | 0(3) |
| C(3) | 88(4) | 67(3) | 57(3) | -6(3) | 28(3) | -10(3) |
| C(4) | 62(4) | 73(4) | 85(4) | -17(3) | 26(3) | 2(3) |
| C(5) | 114(6) | 48(3) | 82(4) | -5(3) | 47(4) | -9(3) |
| C(6) | 143(9) | 151(9) | 180(10) | -123(8) | 128(8) | -80(7) |
| C(7) | 141(9) | 131(7) | 78(5) | -41(5) | 43(6) | -24(7) |
| C(8) | 98(7) | 163(10) | 126(8) | -82(7) | 15(6) | -28(7) |
| C(9) | 121(8) | 88(6) | 167(10) | -65(6) | 56(7) | -44(5) |
| C(10) | 140(8) | 70(4) | 113(6) | -31(4) | 30(6) | 23(5) |
| C(11A) | 52(9) | 75(10) | 84(12) | -19(10) | 23(9) | -24(10) |
| C(11) | 80(13) | 54(7) | 54(8) | -3(6) | 10(8) | 4(9) |
| O(12) | 141(13) | 222(19) | 225(19) | -18(13) | 91(13) | 20(13) |
| C(12) | 118(17) | 190(20) | 180(20) | -125(19) | 38(17) | 7(17) |

**Table 5**. Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters ($Å^2$x $10^3$) for str196m.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(2) | 4444 | 2412 | 11684 | 91 |
| H(3) | 3347 | 2328 | 11497 | 83 |
| H(4) | 2799 | 4410 | 9762 | 87 |
| H(5) | 3571 | 5809 | 8907 | 93 |
| H(7) | 3201 | 2569 | 6741 | 138 |
| H(8) | 2559 | 1086 | 7796 | 160 |
| H(9) | 3129 | -871 | 9374 | 148 |
| H(10) | 4209 | -745 | 9516 | 132 |
| H(12) | 4382 | 2716 | 7175 | 199 |

**Table 6**. Torsion angles [°] for str196m.

| | |
|---|---|
| C(6)-Fe(1)-C(1)-C(2) | -125.7(6) |
| C(10)-Fe(1)-C(1)-C(2) | -79.0(5) |
| C(4)-Fe(1)-C(1)-C(2) | 80.1(4) |
| C(5)-Fe(1)-C(1)-C(2) | 117.4(5) |
| C(3)-Fe(1)-C(1)-C(2) | 36.4(4) |
| C(7)-Fe(1)-C(1)-C(2) | -169.1(5) |
| C(8)-Fe(1)-C(1)-C(2) | 156.5(11) |
| C(9)-Fe(1)-C(1)-C(2) | -43.7(10) |
| C(6)-Fe(1)-C(1)-C(5) | 116.9(6) |
| C(10)-Fe(1)-C(1)-C(5) | 163.6(4) |
| C(4)-Fe(1)-C(1)-C(5) | -37.3(4) |
| C(2)-Fe(1)-C(1)-C(5) | -117.4(5) |
| C(3)-Fe(1)-C(1)-C(5) | -81.0(4) |
| C(7)-Fe(1)-C(1)-C(5) | 73.5(6) |
| C(8)-Fe(1)-C(1)-C(5) | 39.1(12) |
| C(9)-Fe(1)-C(1)-C(5) | -161.1(9) |
| C(6)-Fe(1)-C(1)-C(11A) | 18.8(12) |
| C(10)-Fe(1)-C(1)-C(11A) | 65.5(12) |
| C(4)-Fe(1)-C(1)-C(11A) | -135.4(11) |
| C(2)-Fe(1)-C(1)-C(11A) | 144.5(12) |
| C(5)-Fe(1)-C(1)-C(11A) | -98.1(12) |
| C(3)-Fe(1)-C(1)-C(11A) | -179.0(12) |
| C(7)-Fe(1)-C(1)-C(11A) | -24.6(12) |
| C(8)-Fe(1)-C(1)-C(11A) | -59.0(17) |
| C(9)-Fe(1)-C(1)-C(11A) | 100.8(14) |
| C(6)-Fe(1)-C(1)-C(11) | -25.1(10) |
| C(10)-Fe(1)-C(1)-C(11) | 21.6(10) |
| C(4)-Fe(1)-C(1)-C(11) | -179.3(9) |
| C(2)-Fe(1)-C(1)-C(11) | 100.6(10) |
| C(5)-Fe(1)-C(1)-C(11) | -142.0(10) |
| C(3)-Fe(1)-C(1)-C(11) | 137.0(9) |
| C(7)-Fe(1)-C(1)-C(11) | -68.5(10) |
| C(8)-Fe(1)-C(1)-C(11) | -102.9(15) |
| C(9)-Fe(1)-C(1)-C(11) | 56.9(13) |
| C(5)-C(1)-C(2)-C(3) | -0.2(6) |
| C(11A)-C(1)-C(2)-C(3) | -176.8(11) |
| C(11)-C(1)-C(2)-C(3) | -180.0(6) |
| Fe(1)-C(1)-C(2)-C(3) | -59.8(4) |
| C(5)-C(1)-C(2)-Fe(1) | 59.6(4) |
| C(11A)-C(1)-C(2)-Fe(1) | -117.0(12) |
| C(11)-C(1)-C(2)-Fe(1) | -120.2(6) |
| C(6)-Fe(1)-C(2)-C(3) | -163.5(5) |
| C(10)-Fe(1)-C(2)-C(3) | -117.7(5) |
| C(4)-Fe(1)-C(2)-C(3) | 37.9(4) |
| C(5)-Fe(1)-C(2)-C(3) | 81.7(4) |
| C(7)-Fe(1)-C(2)-C(3) | 160.1(14) |
| C(1)-Fe(1)-C(2)-C(3) | 120.4(6) |
| C(8)-Fe(1)-C(2)-C(3) | -44.3(10) |
| C(9)-Fe(1)-C(2)-C(3) | -76.6(5) |
| C(6)-Fe(1)-C(2)-C(1) | 76.2(6) |
| C(10)-Fe(1)-C(2)-C(1) | 121.9(5) |
| C(4)-Fe(1)-C(2)-C(1) | -82.4(4) |
| C(5)-Fe(1)-C(2)-C(1) | -38.6(4) |
| C(3)-Fe(1)-C(2)-C(1) | -120.4(6) |
| C(7)-Fe(1)-C(2)-C(1) | 39.7(16) |
| C(8)-Fe(1)-C(2)-C(1) | -164.6(9) |
| C(9)-Fe(1)-C(2)-C(1) | 163.1(5) |
| C(1)-C(2)-C(3)-C(4) | 0.4(6) |
| Fe(1)-C(2)-C(3)-C(4) | -59.4(4) |
| C(1)-C(2)-C(3)-Fe(1) | 59.8(4) |
| C(6)-Fe(1)-C(3)-C(2) | 50.8(11) |
| C(10)-Fe(1)-C(3)-C(2) | 82.1(6) |
| C(4)-Fe(1)-C(3)-C(2) | -118.9(5) |
| C(5)-Fe(1)-C(3)-C(2) | -81.1(4) |
| C(7)-Fe(1)-C(3)-C(2) | -170.1(7) |
| C(1)-Fe(1)-C(3)-C(2) | -37.1(4) |
| C(8)-Fe(1)-C(3)-C(2) | 159.6(6) |
| C(9)-Fe(1)-C(3)-C(2) | 121.5(5) |
| C(6)-Fe(1)-C(3)-C(4) | 169.7(9) |
| C(10)-Fe(1)-C(3)-C(4) | -159.1(5) |
| C(2)-Fe(1)-C(3)-C(4) | 118.9(5) |
| C(5)-Fe(1)-C(3)-C(4) | 37.8(4) |
| C(7)-Fe(1)-C(3)-C(4) | -51.2(9) |
| C(1)-Fe(1)-C(3)-C(4) | 81.7(4) |

| | | | |
|---|---|---|---|
| C(8)-Fe(1)-C(3)-C(4) | -81.5(6) | C(9)-Fe(1)-C(5)-C(4) | 42.6(11) |
| C(9)-Fe(1)-C(3)-C(4) | -119.6(5) | C(6)-Fe(1)-C(5)-C(1) | -83.7(6) |
| C(2)-C(3)-C(4)-C(5) | -0.5(6) | C(10)-Fe(1)-C(5)-C(1) | -47.2(11) |
| Fe(1)-C(3)-C(4)-C(5) | -60.2(4) | C(4)-Fe(1)-C(5)-C(1) | 119.5(5) |
| C(2)-C(3)-C(4)-Fe(1) | 59.7(4) | C(2)-Fe(1)-C(5)-C(1) | 38.5(4) |
| C(6)-Fe(1)-C(4)-C(5) | -54.1(9) | C(3)-Fe(1)-C(5)-C(1) | 81.6(4) |
| C(10)-Fe(1)-C(4)-C(5) | 169.3(8) | C(7)-Fe(1)-C(5)-C(1) | -127.6(5) |
| C(2)-Fe(1)-C(4)-C(5) | 81.4(4) | C(8)-Fe(1)-C(5)-C(1) | -167.1(5) |
| C(3)-Fe(1)-C(4)-C(5) | 118.7(5) | C(9)-Fe(1)-C(5)-C(1) | 162.1(10) |
| C(7)-Fe(1)-C(4)-C(5) | -85.6(5) | C(10)-Fe(1)-C(6)-C(12) | -126(2) |
| C(1)-Fe(1)-C(4)-C(5) | 37.6(4) | C(4)-Fe(1)-C(6)-C(12) | 77(2) |
| C(8)-Fe(1)-C(4)-C(5) | -125.4(6) | C(2)-Fe(1)-C(6)-C(12) | -48(2) |
| C(9)-Fe(1)-C(4)-C(5) | -162.7(5) | C(5)-Fe(1)-C(6)-C(12) | 38(2) |
| C(6)-Fe(1)-C(4)-C(3) | -172.7(7) | C(3)-Fe(1)-C(6)-C(12) | -87(2) |
| C(10)-Fe(1)-C(4)-C(3) | 50.6(9) | C(7)-Fe(1)-C(6)-C(12) | 120(2) |
| C(2)-Fe(1)-C(4)-C(3) | -37.3(4) | C(1)-Fe(1)-C(6)-C(12) | -5(2) |
| C(5)-Fe(1)-C(4)-C(3) | -118.7(5) | C(8)-Fe(1)-C(6)-C(12) | 157(2) |
| C(7)-Fe(1)-C(4)-C(3) | 155.7(5) | C(9)-Fe(1)-C(6)-C(12) | -163(2) |
| C(1)-Fe(1)-C(4)-C(3) | -81.1(4) | C(10)-Fe(1)-C(6)-C(7) | 113.5(7) |
| C(8)-Fe(1)-C(4)-C(3) | 116.0(6) | C(4)-Fe(1)-C(6)-C(7) | -43.7(10) |
| C(9)-Fe(1)-C(4)-C(3) | 78.6(6) | C(2)-Fe(1)-C(6)-C(7) | -168.0(5) |
| C(3)-C(4)-C(5)-C(1) | 0.4(6) | C(5)-Fe(1)-C(6)-C(7) | -82.2(6) |
| Fe(1)-C(4)-C(5)-C(1) | -59.9(4) | C(3)-Fe(1)-C(6)-C(7) | 152.9(10) |
| C(3)-C(4)-C(5)-Fe(1) | 60.3(4) | C(1)-Fe(1)-C(6)-C(7) | -125.8(6) |
| C(2)-C(1)-C(5)-C(4) | -0.1(6) | C(8)-Fe(1)-C(6)-C(7) | 36.4(6) |
| C(11A)-C(1)-C(5)-C(4) | 177.9(6) | C(9)-Fe(1)-C(6)-C(7) | 76.4(6) |
| C(11)-C(1)-C(5)-C(4) | 179.5(10) | C(4)-Fe(1)-C(6)-C(10) | -157.2(7) |
| Fe(1)-C(1)-C(5)-C(4) | 59.5(4) | C(2)-Fe(1)-C(6)-C(10) | 78.5(6) |
| C(2)-C(1)-C(5)-Fe(1) | -59.6(4) | C(5)-Fe(1)-C(6)-C(10) | 164.3(5) |
| C(11A)-C(1)-C(5)-Fe(1) | 118.4(6) | C(3)-Fe(1)-C(6)-C(10) | 39.4(12) |
| C(11)-C(1)-C(5)-Fe(1) | 120.1(10) | C(7)-Fe(1)-C(6)-C(10) | -113.5(7) |
| C(6)-Fe(1)-C(5)-C(4) | 156.9(6) | C(1)-Fe(1)-C(6)-C(10) | 120.7(6) |
| C(10)-Fe(1)-C(5)-C(4) | -166.7(9) | C(8)-Fe(1)-C(6)-C(10) | -77.2(6) |
| C(2)-Fe(1)-C(5)-C(4) | -80.9(4) | C(9)-Fe(1)-C(6)-C(10) | -37.1(6) |
| C(3)-Fe(1)-C(5)-C(4) | -37.9(4) | C(12)-C(6)-C(7)-C(8) | -177.7(11) |
| C(7)-Fe(1)-C(5)-C(4) | 113.0(5) | C(10)-C(6)-C(7)-C(8) | 1.0(8) |
| C(1)-Fe(1)-C(5)-C(4) | -119.5(5) | Fe(1)-C(6)-C(7)-C(8) | -60.8(6) |
| C(8)-Fe(1)-C(5)-C(4) | 73.5(6) | C(12)-C(6)-C(7)-Fe(1) | -116.9(11) |

|  |  |  |  |
|---|---|---|---|
| C(10)-C(6)-C(7)-Fe(1) | 61.8(5) | C(7)-C(8)-C(9)-Fe(1) | 58.6(7) |
| C(6)-Fe(1)-C(7)-C(8) | 118.4(10) | C(6)-Fe(1)-C(9)-C(8) | -80.3(8) |
| C(10)-Fe(1)-C(7)-C(8) | 75.9(8) | C(10)-Fe(1)-C(9)-C(8) | -121.8(10) |
| C(4)-Fe(1)-C(7)-C(8) | -80.4(8) | C(4)-Fe(1)-C(9)-C(8) | 75.1(8) |
| C(2)-Fe(1)-C(7)-C(8) | 163.2(13) | C(2)-Fe(1)-C(9)-C(8) | 157.2(7) |
| C(5)-Fe(1)-C(7)-C(8) | -123.4(7) | C(5)-Fe(1)-C(9)-C(8) | 44.0(14) |
| C(3)-Fe(1)-C(7)-C(8) | -45.0(12) | C(3)-Fe(1)-C(9)-C(8) | 116.7(7) |
| C(1)-Fe(1)-C(7)-C(8) | -164.7(7) | C(7)-Fe(1)-C(9)-C(8) | -35.1(7) |
| C(9)-Fe(1)-C(7)-C(8) | 33.8(7) | C(1)-Fe(1)-C(9)-C(8) | -170.4(7) |
| C(10)-Fe(1)-C(7)-C(6) | -42.5(6) | C(6)-Fe(1)-C(9)-C(10) | 41.5(7) |
| C(4)-Fe(1)-C(7)-C(6) | 161.2(5) | C(4)-Fe(1)-C(9)-C(10) | -163.1(5) |
| C(2)-Fe(1)-C(7)-C(6) | 44.8(17) | C(2)-Fe(1)-C(9)-C(10) | -80.9(7) |
| C(5)-Fe(1)-C(7)-C(6) | 118.1(6) | C(5)-Fe(1)-C(9)-C(10) | 165.8(7) |
| C(3)-Fe(1)-C(7)-C(6) | -163.4(7) | C(3)-Fe(1)-C(9)-C(10) | -121.4(6) |
| C(1)-Fe(1)-C(7)-C(6) | 76.8(7) | C(7)-Fe(1)-C(9)-C(10) | 86.7(6) |
| C(8)-Fe(1)-C(7)-C(6) | -118.4(10) | C(1)-Fe(1)-C(9)-C(10) | -48.6(13) |
| C(9)-Fe(1)-C(7)-C(6) | -84.6(6) | C(8)-Fe(1)-C(9)-C(10) | 121.8(10) |
| C(6)-C(7)-C(8)-C(9) | -1.3(10) | C(8)-C(9)-C(10)-C(6) | -0.3(9) |
| Fe(1)-C(7)-C(8)-C(9) | -59.4(7) | Fe(1)-C(9)-C(10)-C(6) | -59.6(5) |
| C(6)-C(7)-C(8)-Fe(1) | 58.1(5) | C(8)-C(9)-C(10)-Fe(1) | 59.3(7) |
| C(6)-Fe(1)-C(8)-C(9) | 83.7(8) | C(12)-C(6)-C(10)-C(9) | 178.2(11) |
| C(10)-Fe(1)-C(8)-C(9) | 36.0(7) | C(7)-C(6)-C(10)-C(9) | -0.5(8) |
| C(4)-Fe(1)-C(8)-C(9) | -121.1(7) | Fe(1)-C(6)-C(10)-C(9) | 63.0(5) |
| C(2)-Fe(1)-C(8)-C(9) | -48.2(13) | C(12)-C(6)-C(10)-Fe(1) | 115.2(12) |
| C(5)-Fe(1)-C(8)-C(9) | -161.5(6) | C(7)-C(6)-C(10)-Fe(1) | -63.4(5) |
| C(3)-Fe(1)-C(8)-C(9) | -79.1(8) | C(6)-Fe(1)-C(10)-C(9) | -116.5(9) |
| C(7)-Fe(1)-C(8)-C(9) | 122.9(11) | C(4)-Fe(1)-C(10)-C(9) | 39.5(11) |
| C(1)-Fe(1)-C(8)-C(9) | 168.3(9) | C(2)-Fe(1)-C(10)-C(9) | 118.3(7) |
| C(6)-Fe(1)-C(8)-C(7) | -39.2(7) | C(5)-Fe(1)-C(10)-C(9) | -163.1(10) |
| C(10)-Fe(1)-C(8)-C(7) | -86.9(8) | C(3)-Fe(1)-C(10)-C(9) | 76.1(7) |
| C(4)-Fe(1)-C(8)-C(7) | 116.0(7) | C(7)-Fe(1)-C(10)-C(9) | -75.9(7) |
| C(2)-Fe(1)-C(8)-C(7) | -171.1(7) | C(1)-Fe(1)-C(10)-C(9) | 160.9(6) |
| C(5)-Fe(1)-C(8)-C(7) | 75.6(8) | C(8)-Fe(1)-C(10)-C(9) | -34.3(7) |
| C(3)-Fe(1)-C(8)-C(7) | 158.0(6) | C(4)-Fe(1)-C(10)-C(6) | 156.0(8) |
| C(1)-Fe(1)-C(8)-C(7) | 45.4(15) | C(2)-Fe(1)-C(10)-C(6) | -125.2(6) |
| C(9)-Fe(1)-C(8)-C(7) | -122.9(11) | C(5)-Fe(1)-C(10)-C(6) | -46.6(12) |
| C(7)-C(8)-C(9)-C(10) | 1.0(11) | C(3)-Fe(1)-C(10)-C(6) | -167.4(6) |
| Fe(1)-C(8)-C(9)-C(10) | -57.6(6) | C(7)-Fe(1)-C(10)-C(6) | 40.6(5) |

z+3/2

#1 -x+1,-y+1,-z+2    #2 -x+1,y,-z+3

| | |
|---|---|
| C(1)-Fe(1)-C(10)-C(6) | -82.6(7) |
| C(8)-Fe(1)-C(10)-C(6) | 82.2(7) |
| C(9)-Fe(1)-C(10)-C(6) | 116.5(9) |
| C(2)-C(1)-C(11A)-C(11)#1 | -49(7) |
| C(5)-C(1)-C(11A)-C(11)#1 | 135(6) |
| C(11)-C(1)-C(11A)-C(11)#1 | -44(6) |
| Fe(1)-C(1)-C(11A)-C(11)#1 | -149(6) |
| C(2)-C(1)-C(11A)-C(11) | -5.0(19) |
| C(5)-C(1)-C(11A)-C(11) | 178.4(11) |
| Fe(1)-C(1)-C(11A)-C(11) | -105.7(11) |
| C(2)-C(1)-C(11A)-C(11A)#1 | -17(2) |
| C(5)-C(1)-C(11A)-C(11A)#1 | 165.9(15) |
| C(11)-C(1)-C(11A)-C(11A)#1 | -12.5(11) |
| Fe(1)-C(1)-C(11A)-C(11A)#1 | -118.2(14) |
| C(11)#1-C(11A)-C(11)-C(11A)#1 | 0.000(3) |
| C(1)-C(11A)-C(11)-C(11A)#1 | -163.2(13) |
| C(11A)#1-C(11A)-C(11)-C(11)#1 | 0.000(7) |
| C(1)-C(11A)-C(11)-C(11)#1 | -163.2(13) |
| C(11)#1-C(11A)-C(11)-C(1) | 163.2(13) |
| C(11A)#1-C(11A)-C(11)-C(1) | 163.2(13) |
| C(2)-C(1)-C(11)-C(11A)#1 | -139(5) |
| C(5)-C(1)-C(11)-C(11A)#1 | 42(6) |
| C(11A)-C(1)-C(11)-C(11A)#1 | 44(5) |
| Fe(1)-C(1)-C(11)-C(11A)#1 | 143(5) |
| C(2)-C(1)-C(11)-C(11A) | 177.1(11) |
| C(5)-C(1)-C(11)-C(11A) | -2.6(18) |
| Fe(1)-C(1)-C(11)-C(11A) | 99.2(12) |
| C(2)-C(1)-C(11)-C(11)#1 | -170.1(13) |
| C(5)-C(1)-C(11)-C(11)#1 | 10(2) |
| C(11A)-C(1)-C(11)-C(11)#1 | 12.8(10) |
| Fe(1)-C(1)-C(11)-C(11)#1 | 112.1(13) |
| C(7)-C(6)-C(12)-O(12) | -170.2(13) |
| C(10)-C(6)-C(12)-O(12) | 11(2) |
| Fe(1)-C(6)-C(12)-O(12) | 100.7(19) |
| O(12)#2-O(12)-C(12)-C(6) | 134.2(14) |

---

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+1,-z+2    #2 -x+1,y,-