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Metal compounds with rigid polyaromatic ligands. Catalytic consequences

Doctoral Thesis

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Nomenclature

The nomenclature employed to name the compounds described in this work is:

Ligands: letters of the alphabet (**A-M**).

Ligands precursors: the ligand letter with the acidic protons and its counter-ion. For example, **[L-H₃](I)₃** is the precursor salt of the ligand **L** which contains three acidic C-H bonds and three iodide as counter-ions.

Metal complexes: the number followed by the letter of the coordinated ligand. The complexes have been sorted in order of appearance in the text.

List of abbreviations and symbols

Δ	Refluxing temperature
η	Ligand hapticity
λ	Wavelength
μ	Bridge ligand
Φ	Quantum yield
AcO	Acetate
aNHC	Abnormal N-heterocyclic carbene BIAN bis(imino)acenaphthene
cat	Catalyst
COA	cyclooctane
COD	1,5-cyclooctadiene
COE	cyclooctene
Conv.	Conversion
Cp*	1,2,3,4,5-pentamethylcyclopentadiene
Cp	cyclopentadiene
Cy	Cyclohexyl
C ₆ Me ₆	hexamethylbenzene
CV	Cyclic Voltammetry
DFT	Density Functional Theory
Dipp	Diisopropylphenyl
DME	1,2- Dimethoxyethane

DMSO	Dimethylsulfoxide
DPV	Differential Pulse Voltammetry
EA	Elemental analysis
EtOH	Ethanol
ESI-MS	Electrospray Ionization Mass Spectrometry GC Gas Chromatography
FT-IR	Fourier transform infrared
h	Hour
HMBC	Heteronuclear Multiple Bond Correlation
HSQC	Heteronuclear Single Quantum Coherence iPrOH Iso-propanol
IR	Infrared
K _a	Association Constant
KHMDS	Potassium bis(trimethylsilyl)amide
Me	Methyl
MeOH	Methanol
MIC	Mesoionic carbene
ⁿ Bu	n-Butyl
NBD	2,5-norbornadiene
NBE	Norbornene
NHC	N-heterocyclic carbene
NMP	N-methyl-2-pyrrolidone
NMR	Nuclear magnetic resonance
	δ chemical shift
	br Broad
	d Doublet
	<i>J</i> Coupling constant
	m Multiplet
	ppm Parts per million
	s Singlet
	sp Septuplet
	t Triplet
Ph	Phenyl
R.T.	Room temperature
t	Time
TBAB	<i>tert</i> -butylaluminiumbromide

TBE	<i>tert</i> -butylethene
^t Bu	<i>tert</i> -butyl
TEP	Tolman Electronic Parameter
TM	Transition metal

Chapter 1

General introduction and objectives

1.1 General introduction

Due to their topological and electronic versatility, N-heterocyclic carbene (NHC) ligands have arisen as a useful type of supporting ligands for transition metal compounds.¹ Free NHC ligands are often more sensitive to air and moisture than their corresponding metal complexes, which have proved to be remarkably resistant to oxidation. The first NHC complexes were described by Öfele and Wanzlick in 1968;^{2,3} and Herrmann described the first catalytic application of NHC complexes in 1995.⁴ Ever since, NHCs have been widely studied from any possible point of view, including their preparation,⁵⁻⁸ stability,⁹ stereoelectronic properties,¹⁰⁻¹² coordination strategies,^{8,13,14} and use in homogeneous¹⁵ and asymmetric catalysis,^{16,17} and some books^{1,18-20} have been entirely devoted to the chemistry of this type of ligands.

1.1.1 Metal Carbenes

A free carbene is formally a neutral carbon atom ($:CR_2$) with only six valence electrons; four are involved in bonding, and two are non-bonding. As shown in Figure 1.1, a carbene can have either a singlet or a triplet ground state, depending on the energy splitting between the sp^2 -hybridized σ orbital and the unhybridized p orbital (generally referred to as $p\pi$). Carbenes are rarely stable in the free state; this instability (both thermodynamic and kinetic) contributes to the very strong binding of carbenes to metal atoms by disfavoring dissociation.²¹

Figure 1.1 Singlet and triplet forms of a carbene

Two extreme types of coordinated carbenes can be distinguished, the Fischer and the Schrock type. Carbenes, $L_nM=CR_2$, have Fischer character in complexes containing late transition metals with low oxidation states, having π -acceptor L ligands and π -donor R substituents (-OMe or -NMe₂). Such a carbene behaves as if it carries a δ^+ charge and is electrophilic. In the most common model, the CR_2 ligand in a Fischer carbene is considered to act as a 2e lone-pair donor derived from the singlet carbene. Schrock carbenes are bound to higher oxidation state, early transition metals, having non- π -

acceptor L ligands and non- π -donor R groups. In this case, the carbene behaves as a nucleophile, having a δ^- carbon. The CR_2 ligand in a Schrock carbene is often considered to act like an X_2 -type bis(alkyl), formally derived from the triplet carbene.

Fischer (singlet-derived) carbenes are predominantly σ -donor ligands *via* the hybridized- sp^2 orbital, but the empty p_π orbital on the carbon atom is also π -acceptor *via* back donation from the $\text{M}(\text{d}_\pi)$ orbitals (Figure 1.2, a). Due to the fact that the direct $\text{C} \rightarrow \text{M}$ donation is only partly compensated by $\text{M} \rightarrow \text{C}$ back donation, the carbene carbon has an electrophilic character.

Schrock (triplet derived) carbenes form two covalent bonds *via* interaction of the triplet CR_2 fragment with a metal fragment having two unpaired electrons (Figure 1.2, b). Each M-C bond is polarized toward the carbon because, in this case, the carbon is more electronegative than the metal, leading to a nucleophilic carbene carbon.

Figure 1.2 a) Fischer carbene and b) Schrock carbene

1.1.2 N-heterocyclic carbenes

N-heterocyclic carbenes (NHCs) have a singlet ground state, and the singlet-triplet energy gap is exceptionally large (ca. 84.5 kcal/mol).²² The singlet state is favoured for two reasons.⁹ First, the σ -electron-withdrawing nitrogen atoms inductively stabilize the carbene σ orbital. Additionally, the sp^2 -hybridized nitrogen atoms have filled unhybridized p orbitals whose symmetric combination forms a bonding interaction with the vacant carbene p_π orbital. The antibonding π -type orbital is now higher in energy, so the triplet state is disfavoured (Figure 1.3). Hence, the NHC are considered as Fischer carbenes.

Figure 1.3 The bonding interaction between the vacant carbon $p\pi$ orbital and the filled nitrogen p orbitals results in a large singlet-triplet gap for N-heterocyclic carbenes

NHC ligands form stronger bonds with metal centres than most classical ligands, such as phosphines. This renders NHCs especially resistant to dissociation, and allows the generation of highly electron-rich transition metal centres, which has been beneficial in the development of stable and highly active catalysts.

Along with their chemical stability, the wide coordination versatility of NHC ligands has helped to their great development, affording complexes of almost any transition metal in different oxidation states. Additionally, the easy preparation of NHC-precursors (commonly azolium-based salts) has allowed an almost infinite access to new organometallic topologies. Chart 1.1 depicts some of the known NHC frameworks.

Chart 1.1 Some of the NHC frameworks

1.1.3 Routes to NHC-based complexes

Several methods for the preparation of NHC-based complexes have been described so far and conveniently reviewed.⁵⁻⁸ The most widely employed protocols for the synthesis of NHC-based complexes requires the activation of an azolium-based salt. Other commonly used strategies involve the insertion of a metal into the C=C bond of bis(imidazolidin-2-ylidene) olefins²³⁻²⁵ and the use of carbene adducts.^{14,26,27}

Some of the most widely used routes to NHC-based complexes starting from an azolium-based precursor are:

a) Isolation of the free carbene

The preparation of the first free stable NHC ligand by Arduengo²⁸ broken with the idea that these compounds were too unstable to be used as ligands in the preparation of transition metal complexes. Deprotonation of an azolium salt with a strong base such as NaH or KO^tBu renders the free carbene,^{9,15,29} which can then be reacted with a suitable transition metal complex to yield the NHC metal complex.

b) In situ deprotonation of an azolium salt with a base

The *in situ* deprotonation of an azolium salt to produce the desired NHC has the advantage that the free carbene does not have to be isolated, thus simplifying the reaction workups when the aim is the preparation of the metal complex.

In this context, several strong bases (NaH,^{30,31} LiⁿBu,^{32,33} KO^tBu,^{34,35} NaOEt³⁶ and KN(SiMe₃)₂)³⁷ and weak bases (NEt₃,³⁸⁻⁴⁰ NaOAc⁴¹ and Cs₂CO₃)⁴²) provide very good results. The election of the base is sometimes crucial in order to achieve the desired product. Changes in the basicity and nucleophilicity of the base can produce variations in the reaction products, or undesired activations of the ligand and metal complex. Furthermore, *in situ* deprotonation of imidazolium salts can be achieved by basic ligands on the metal complexes. Commercially available or easy-to-prepare metal complexes with acetate,⁴³ alkoxide,⁴⁴ hydride^{45,46} or acetylacetonate⁴⁷ ligands are frequently used.

c) Transmetallation from a silver-NHC complex

In 1998, Wang and Lin reported that the lability of the Ag(I)-NHC bond could make Ag(I)-NHC complexes useful as carbene transfer agents.⁴⁸ In many cases, the use of Ag(I)-NHC complexes as carbene transfer reagents provides a convenient way to overcome the difficulties arising from using strong bases, inert atmospheres, and complicated workups. This strategy has been successfully employed with a variety of metals such as Au, Cu, Ni, Pd, Pt, Rh, Ir and Ru.^{49,50} The lability of the Ag(I)-NHC bond and the low solubility of the silver halide can be considered the driving forces of the reaction.

d) Activation of the C2-X bond (X = Me, Halogen, H) of an imidazolium cation

Direct oxidative addition of C2-X bonds (X = Me, halogen, H) of imidazolium cations to low-valent transition metal complexes constitutes a facile access to NHC-M complexes under certain circumstances. The oxidative addition of the C-Cl bond in azolium salts to generate carbene complexes has been known since 1974.^{51,52} In 2001, Cavell and co-workers extended the method to 2-iodo-imidazolium salts, and studied the oxidative addition process to group 10 M(0) complexes.⁵³⁻⁵⁵ Years later, our group of research proved that this methodology can be applied to other transition metals, such as iridium⁵⁶ and rhodium.⁵⁷ Recently, Hanh and co-workers developed a one-pot synthesis to obtain Pd and Pt complexes based on protic NH,NH-NHC ligands *via* oxidative addition of the C2-X (X = Cl, Br, I) bond to metal complexes of the type [M(PPh₃)₄] (M = Pd, Pt).⁵⁸

Although the above mentioned strategies are very commonly used for the preparation of NHC-based complexes, new methods involving non-traditional precursors have been reported in the last years. These methods include:

e) Decarboxylation of an imidazolium-2-carboxylate

In 2005, Crabtree and co-workers reported that N,N-disubstituted imidazolium-2-carboxylates, which are air- and moisture-stable species, can transfer NHCs to a variety of metal salts with the concomitant release of CO₂ (Scheme 1.1). This method provides some of the mildest reaction conditions reported in the literature for the preparation of NHC metal complexes of Rh, Ir, Ru, and Pd.^{59,60}

Scheme 1.1 Synthesis of a Rh(I)-NHC complex by decarboxylation of an imidazolium-2-carboxylate

f) Double C(sp³)-H₂ dehydrogenation of neutral N-heterocycles

In a certain number of cases, carbenes may be generated by double C-H bond activation of C(sp³)-H₂ groups.^{61,62} Caulton and co-workers described the first example in which a double C(sp³)-H₂ dehydrogenation of a saturated heterocycle (imidazolidine), afforded a Ru-NHC complex.^{63,64} Recently, our research group reported the coordination of a bis(imidazolinyldene) ligand to rhodium and iridium, using a neutral tetrazabicyclooctane (or bis(imidazolidine)) as the bis(NHC) precursor.⁶⁵ The formation of the bis(NHC) implied a double germinal C-H bond activation of the methylene groups of the bis(imidazolidine), which was facilitated by the presence of an external diolefin (1,5-cyclooctadiene or norbornadiene), acting as hydrogen acceptor (Scheme 1.2). In 2014, Hill prepared a series of PCP-pincer-NHC complexes *via* double C(sp³)-H₂ in the absents of hydrogen acceptors.⁶⁶ In this particular case dihydroperidine-derived PNP pincer complexes as intermediate were proposed. These reactions constituted very rare examples of conversions of neutral N-heterocycles into NHC-complexes.

Scheme 1.2 Synthesis of Ir(I) and Rh(I)-NHC complexes by double C-H bond activation of a C(sp³)H₂

g) Template-controlled cyclization of β-functionalized isocyanides

The nucleophilic attack at the carbon atom of a coordinated isocyanide constitutes an alternative method to generate metal carbene complexes. Protic nucleophiles HX such as alcohols and primary or secondary amines have been particularly useful in this reaction (Scheme 1.3).⁸ In addition, this method allows for the stepwise alkylation of nitrogen atoms of the carbene heterocycle that gives access to complexes with unsymmetrically N,N'-substituted NHC ligands.⁶⁷

Scheme 1.3 Template-controlled cyclization of β -functionalized isocyanides

1.1.4 Quantifying the electronic properties of N-heterocyclic carbene ligands

The nature of the interaction between the NHC ligand and the metal centre has normally been considered as pure σ -donation of a lone pair of electrons from the highest occupied molecular orbital of the NHC ligand, centred on the carbene carbon atom, to empty d orbitals of the metal ($M(d_\pi)$).⁶⁸ Some authors have suggested that the contribution of the π -back donation present in the NHC-metal bonding has not been seen as significant with respect to σ -bonding.^{69,70} However, some experimental and theoretical approaches⁷¹⁻⁷⁶ have demonstrated that the NHC can act as π -acceptor *via* back donation from the $M(d_\pi)$ orbitals, especially in those complexes that contains electron-rich metals.^{77,78}

Several methods have been developed to quantify and compare the electronic properties of NHC ligands. Recently, Nolan has reviewed all these methods,^{68,79} which include experimental and theoretical approaches. Some of the most frequently used methodologies are:

a) Calculation of the Tolman electronic parameter (TEP)

The Tolman electronic parameter (TEP) is by far the most widely used method to evaluate the electronic properties of NHCs. This parameter, originally developed to describe the electronic properties of tertiary phosphine ligands, is based on the measurement of the IR stretching frequencies of the carbonyl ligands of complexes of the type $[Ni(CO)_3(PR_3)]$.⁸⁰ These stretching frequencies are directly related to the electron density at the metal centre (Chart 1.2). High electron density at the metal centre strengthens the metal-carbon bond due to the π -backbonding into the π^*_{CO} anti-bonding orbital, while weakens the carbon-oxygen triple bond. If the electron density at the metal is low, the carbon-oxygen triple bond is stronger.

However, the nickel carbonyl complexes have some disadvantages; they are highly toxic, and require careful handling and disposal. To circumvent these drawbacks, and to extend this parameter to NHC ligands, Crabtree and co-workers established a simple regression formula using complexes of the type of $[\text{IrCl}(\text{CO})_2(\text{NHC})]$ (eq. 1). This correlation was later improved by Nolan, who used a wider set of experimental values (eq. 2). Plenio established a regression formula to correlate the $\nu_{\text{av}}(\text{CO})$ of $[\text{RhCl}(\text{NHC})(\text{CO})_2]$ complexes with the $\nu_{\text{av}}(\text{CO})$ of $[\text{IrCl}(\text{NHC})(\text{CO})_2]$ ones, therefore unifying the Rh and the Ir-scale for the determination of the electron donating properties of NHC ligands (eq. 3).

Chart 1.2

$$\text{TEP} = 0.722 \nu_{\text{av}}(\text{CO})[\text{Ir}] + 593 \text{ cm}^{-1} \quad (1)$$

$$\text{TEP} = 0.847 \nu_{\text{av}}(\text{CO})[\text{Ir}] + 336 \text{ cm}^{-1} \quad (2)$$

$$\text{TEP} = 0.735 \nu_{\text{av}}(\text{CO})[\text{Rh}] + 548.34 \text{ cm}^{-1} \quad (3)$$

b) Electrochemical studies

The electrochemical studies on NHC-based complexes involve the determination of the redox potential of the metal centre, which are influenced by how electron-rich or electron-poor this centre is. Increased electron-donating character of the NHC ligand, results in a decrease of the redox potential. Ir ,⁸¹ Rh ⁸² and Fe ⁸³ complexes bearing different NHC ligands have been studied using electrochemical studies. Using this technique, it is possible to achieve relatively high precision compared to those that rely on the more widespread IR spectroscopy.

c) NMR measurements

As the chemical shift of a given nuclide depends on the electronic environment neighbours of that nuclide, the chemical shift can be used to evaluate the electronic properties of ligands. In this sense, two NMR approaches have been developed for NHC

ligands. The first one was described by Huyn and co-workers.⁸⁴ The authors prepared a series of palladium complexes of the type *trans*-[PdBr₂(ⁱPr₂-bimy)L], where L corresponds to the ligand under study and ⁱPr₂-bimy to the 1,3-diisopropylbenzimidazolin-2-ylidene ligand. The methodology is based on the sensitivity of the constant ⁱPr₂-bimy carbene signal to the donor strengths of the varying co-ligands. The second approach involves the preparation of carbene-phenylphosphinidene adducts.⁷¹ The ³¹P NMR chemical shift of these adducts allows the determination of the π -acceptor properties of the NHC ligands, which in combination with the TEP value, allows the estimation of the σ -donor character of the NHC ligand.

1.1.5 Tuning the electronic properties of N-heterocyclic carbene ligands

Since Herrmann described the first application of NHC-based complexes in catalysis,⁴ the catalytic activity of these compounds has been associated with the electron properties of the NHC ligand.^{12,85} Most of the efforts for tuning the electronic properties of NHC ligands are based on changing the substituents on the N, C4 and C5 atoms, as well as in the nature C4-C5 bridge (I, Chart 1.3).^{76,81,86-89} A very interesting example of the modification of the electron donating properties of a NHC ligand was described by Fürstner and co-workers.⁹⁰ The authors succeeded in controlling the electronic properties of a cyclophane-2-ylidene ligand by changing the substituents of the remote ring of the cyclophane (R groups in II, Chart 1.3), attributing such control to a through-space interaction between the aryl ring and the carbene underneath.

Chart 1.3

Recently, some authors have been interested in the development of NHC ligands that allow the reversible and controlled switching of their electronic properties. Some of the strategies employed involve the incorporation of an electro-active, a proton-sensitive or a photo-sensitive group to the NHC ligand.

a) Incorporation of electro-active groups

This strategy consists in the incorporation of a redox active group, such as ferrocene or a quinone, into the NHC backbone.^{74,91-95} The oxidation/reduction of the ferrocene (or quinone) group allows the modification of the electronic character of the NHC ligand. Bielawski has proposed that the change of ligand donating strength is primary Coulombic in origin, due to the generation of a charged molecule when the redox active group is oxidize/reduce.⁹² Chart 1.4 shows the most relevant examples of this kind of ligands.

Chart 1.4

b) Incorporation of proton-sensitive groups

As shown in Scheme 1.4, the incorporation of an enolate unit in close proximity to the carbene centre allows the modulation of the electronic properties of the NHC ligand by simple addition of a base (or an acid). In this particular case, the addition of base results in a decrease of the TEP value from 2047.5 to 2029.5 cm^{-1} . This strategy has been extensively studied by Glorius,⁹⁶ César and Lavigne.^{97,98}

Scheme 1.4

c) Incorporation of photo-sensitive groups

The presence of a photochromic diarylethene into the backbone of a NHC scaffold facilitated the remote photo-modulation of the donating ability of the carbene ligand, (Scheme 1.5).^{99,100} This behaviour has been widely exploited for the design of molecular switches¹⁰¹⁻¹⁰⁶ and modulating chemical reactivity.¹⁰⁷⁻¹¹⁹ In this sense,

Bielawski and co-workers reported that the catalytic activity of an organocatalyst based on a diarylethene-NHC ligand may be remotely tuned *via* exposure to UV or visible light.¹²⁰

Scheme 1.5

1.1.6 Background in NHC-chemistry in the group of “Organometallic Chemistry and Homogenous Catalysis” of the Universitat Jaume I

The group of “Organometallic Chemistry and Homogenous Catalysis” (QOMCAT) of the Universitat Jaume I was formed in 1999. Since then, QOMCAT has been directed by Prof. Eduardo Peris. The principal aim of the group has been focused in the development of new NHC-based complexes with improved catalytic performances. In the following subsections, some of the more relevant achievements by the group will be described.

1.1.6.1 Complexes based on mono-, di- and tridentate-NHC ligands

The idea of combining the strength of the M-carbene bond with the unique properties of the *pincer*-complexes was accomplished for the first time in 2001 by our group (**III**, Chart 1.5).⁴³ Complex **III** catalysed the Heck C-C coupling reaction in high yields. This complex proved to be thermally very robust. Our group has demonstrated that chelating bis(carbene) ligands can provide highly stable systems that provide high catalytic performances. Keeping in mind this feature, a series of metal complexes based on bis(NHCs) ligands were prepared.¹²¹ In order to modulate the electronic and topological properties of the bis(NHCs), different N-substituents, linkers and backbones were employed (Chart 1.5). Several coordination modes were studied, affording complexes with *chelating*, *bridging* and *tripodal* bis(NHC) (**IV**, **VI**, **VII** respectively, Chart 1.5). The complexes shown in Chart 1.5 were successfully employed in catalytic processes that include hydrosilylation of terminal double and triple bonds, hydroformylation and oxidation of olefins, C-C coupling reactions, hydro- and diboration reactions,

deuteration of organic substrates and borrowing-hydrogen processes. Most of the work development until 2009 was summarized in a micro-review.¹²¹

Chart 1.5

The group has also been interested in the activation of small molecules such as CO₂. In this context, complexes labelled as **VIII**, **IX** and **X** in Chart 1.6, showed high performances in the reduction of CO₂ to formate in the presence of molecular hydrogen or *iso*-propanol *via* a transfer hydrogenation process.^{122,123}

Chart 1.6

The group also succeeded in the preparation of hydrophilic NHC-based complexes soluble in more sustainable solvents such as water or glycerol (Chart 1.7).¹²⁴⁻¹²⁹ The complexes shown in Chart 1.7, which incorporate hydrophilic sulfonate groups, performed very well in the deuteration of arylpyridines, isomerization of allylic alcohols, Suzuki-Miyaura C- C coupling and transfer hydrogenation processes.

Chart 1.7

1.1.7 More than one is better. Complexes with poly(NHC) ligands

Since 2007, the group has been interested in the development of new complexes with poly(NHC) ligands in which the NHC units are disposed geometrically isolated, avoiding the formation of chelating species. In this context, the use of the triazolyldene ligand (*ditz*, Chart 1.8) has allowed the preparation of homo-dimetallc complexes based on Rh(I),¹³⁰ Ir(I),¹³⁰ Ir(III),¹³¹ Ru(II),¹³² Pd(II),^{133,134} Pt(II)¹³⁵ and Au(I)¹³⁶. Probably more interesting are the different approaches developed by our research group for the preparation of hetero-dimetallc species, by combining Ir(I)/Rh(I),¹³⁰ Ir(III)/Rh(I),¹³¹ Ir(III)/Pd(II),^{137,138} Ir(III)/Pt(II),¹³⁵ Ir(III)/Au(I),¹³⁶ Ir(III)/Ru(II)¹³⁹ and Ru(II)/Pd(II)¹⁴⁰ centres. The preparation of such hetero-dimetallc complexes allowed for the study of *tandem* catalytic processes, in which each of the metal centres facilitated mechanistically independent cycles.^{135,136,138,141,142} The hetero-dimetallc complexes were applied in *tandem* catalytic process such as cyclization of 2-aminophenyl ethyl alcohol/alkylation of the resulting indole,¹³¹ dehalogenation/transfer hydrogenation of haloacetophenone,¹³⁸ Suzuki-Miyaura C-C coupling/transfer hydrogenation, and Suzuki-Miyaura C-C coupling/ α -alkylation of haloacetophenones,¹³⁸ combined dehalogenation/transfer hydrogenation, and the Suzuki-Miyaura C-C coupling/transfer hydrogenation,¹⁴³ halo- and nitro-arenes reduction/primary alcohols coupling,¹⁴¹ isomerization/asymmetric hydrophosphination of 1,3-diphenylpropargyl alcohol,¹³⁷ and the hydrodefluorination of organic molecules.¹⁴⁰ All these sophisticated organic transformation are clear examples of the high potential of hetero-dimetallc complexes in the fields of organic synthesis and catalysis.

Chart 1.8

More recently, the group has developed a synthetic procedure for the preparation of bis(NHC) ligands containing π -conjugated systems, as pyrene¹⁴⁴⁻¹⁴⁶ and pyracene^{147,148} (**XV** and **XVI** in Chart 1.9). The pyrene-bis(imidazolylidene) ligand allowed the preparation of homo-dimetallic complexes based on Ir, Rh,¹⁴⁴ Ru¹⁴⁵ and Pt.¹⁴⁶ The diruthenium complex based on the ligand **XV** was tested in the arylation of arylpyridines with aryl halides and in the hydroarylation of alkenes.¹⁴⁵ By comparing the catalytic activity of the diruthenium complex with the monometallic analogue, our group demonstrated that the presence of a second metal is beneficial for the catalytic process.

Chart 1.9

Recently, studies on the photophysical properties of a series of pyrene-bis(azoles) (Chart 1.10),^{144,146} have revealed that these molecules present high quantum yields. In general, the emission and the quantum yields are only slightly sensitive to the nature of the bis(azoles) and their substituents, thus the emissive properties are centred in the pyrene fragment.

Chart 1.10

In our group, some poly(NHC)-based ligands with very sophisticated architectures have been prepared. Some of them are depicted in Chart 1.11.¹⁴⁹⁻¹⁵⁶ The triphenylene-tris(NHC) ligand **XX** allows the preparation of organometallic microporous polymers.¹⁵¹ These materials showed high catalytic activity in the catalytic reduction of nitro-arenes with NaBH_4 and in the three-component Strecker reaction for the synthesis of α -aminonitriles. The coordination of the ligands **XXII** and **XXIII** to Ag give us access to prepare cylinder-like structures.^{153,154} The preparation of these structures represents a remarkable contribution in the field of metallosupramolecular chemistry.

Chart 1.11

1.2 Objectives

During the last years, our group of research has been interest in develop new NHC-based ligands for the preparation of novel homogeneous catalyst. Within this context, this work is focused on the synthesis and characterization of new metallic complexes based on NHC ligands with extended polyaromatic systems, the exploration of their catalytic behaviour and the study of the electronic properties of the new NHC ligands. This general objective can be divided in the more specific objectives:

- Preparation of a series of azolium salts with different number of fused aromatic rings and their coordination to Ir, Rh, Ni and Pd.
- Preparation of new bi- and tris(azolium) salts for the generation of geometrically isolated NHC ligands, and their coordination to different metal fragments.
- Study of the electronic properties of the new NHC ligands in the presence of π -stacking additives, such as pyrene and hexafluorobenzene.
- Study of the interaction between the new NHC ligands and π -stacking additives.
- Evaluation of the catalytic properties of the Ni and Pd complexes in the cross-coupling reactions. The main goal is to evaluate the effect of π -stacing additives in the catalytic behaviour of theses complexes.

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Chapter 2

**Synthesis and characterization of
NHC-based complexes with extended
polyaromatic systems**

2.1 Introduction

Ligands decorated with π -extended polyaromatic rings may offer interesting chemical differences from other non-polyaromatic related ligands, and may also turn into a variety of applications in the field of homogeneous catalysis and material science. One of the main challenges of catalyst design is to tailor the properties of classical catalysts by facilitating reversible non-covalent interactions, such as hydrogen bond, or π -stacking. The resulting catalysts may then possess properties that differ from those shown by analogues lacking the assembling properties. Among N-heterocyclic carbene (NHC) ligands, those featuring fused aromatic rings in their backbones, afford the possibility of facilitating ligand-substrate interactions that may influence the activity of the catalyst. Such interactions, which influence but do not form part of the basic catalytic reaction, constitute the basis of supramolecular catalysis.¹⁻³ Although the preparation of a supramolecular catalyst must incorporate a large degree of design, non-covalent forces are difficult to predict, and therefore the '*a priori*' chances to prepare a catalyst with assembling properties are still very low, thus most of the supramolecular effects in catalysis are recognized '*post-factum*'. Once the 'supramolecular catalyst' has been prepared, the challenge is to determine whether the catalytic activity of the catalyst is influenced by non-covalent assembling properties, for which well-chosen control experiments are required to determine both, the nature of the non-covalent interaction and their direct involvement in the rate and selectivity-determining steps of the catalytic reaction. It is very well recognized that π -stacking interactions play an important role in asymmetric catalysis,³⁻⁹ but its role in non-asymmetric processes has been clearly underestimated.

In the field of NHC chemistry, some interesting NHC ligands decorated with polyaromatic systems have been reported. Chart 2.1 shows some representative examples of polyaromatic NHC ligands based on naphthalene, phenanthrene,¹⁰⁻¹² acetanaphthene,¹³⁻¹⁶ pyracene,^{17,18} and triphenylene.^{19,20} The application of these compounds ranges from the study of the photophysical properties of their related azolium salts, to the study of the catalytic applications of their NHC-based coordination complexes.

Chart 2.1 Polyaromatic ligands

Pyrene is the chromophore of choice in fundamental and applied photochemical research,²¹ due to its fluorescence properties. Since its discovery in 1837 by Laurent,²² this polyaromatic compound has been the subject of tremendous investigation. On the basis of the aforementioned reasons, we thought that the incorporation of pyrene in the framework of a NHC ligand might introduce interesting catalytic properties to its related compounds. Some of these properties, may arise from the ability of pyrene to form π -stacking adducts with aromatic compounds, thus facilitating ligand-substrate interactions. In this chapter we describe the synthesis and characterization of a set of azoliums with extended polyaromatic systems and their related metal complexes. The photophysical properties of these imidazolium salts will also be discussed.

2.2 Results and Discussion

2.2.1 Synthesis and characterization of azolium salts

Aiming to prepare a systematic list of complexes, only differing in the number of fused aromatic rings attached to the NHC-ligand, we prepared a series of NHC ligand precursors based on non-polyaromatic and extended polyaromatic systems. These are shown in Chart 2.2. The imidazoliums **[A-H](X)**²³ and the benzimidazolium **[B-H](X)**,²⁴ were prepared from the known literature methods, while pyrene-imidazolium **[C-H](X)**, phenanthro[4,5-abc]phenazino[11,12-*d*]imidazolium (**[D-H](X)** and **[E-H](X)**) and acetonaphtho[1,2-*b*]quinoxaline[11,12-*d*]imidazolium **[F-H](X)** salts, were synthesized and characterized during the development of this research work.

Chart 2.2 Azolium salts

a) Synthesis and characterization of the pyrene-imidazolium salts

As depicted in Scheme 2.1, the synthesis of the pyrene-based imidazolium salt **[C-H](Br)** was carried out in two steps, starting from pyrene-4,5-dione, which was synthesized according to the method previously reported in the literature.²⁵ The pyrene-imidazole was obtained by condensation of pyrene-4,5-dione, formaldehyde and ammonium acetate, by following the known literature methods for the coupling of similar diketones.¹² Then, pyrene-imidazole reacts with 1 equivalent of *n*-butylbromide in the presence of KOH to afford the corresponding mono-alkylated product, which then reacts in neat *n*-butylbromide at 130°C to yield **[C-H](Br)** as a beige solid (57% yield). In order to avoid possible halide exchange in future coordination reactions, the bromide counter-anion was replaced by hexafluorophosphate, by anion metathesis with NH₄PF₆ in methanol. The reaction afforded **[C-H](PF₆)** almost quantitatively.

 Scheme 2.1 Synthesis of pyrene-based imidazolium salts **[C-H](X)**

The pyrene-based imidazolium salts **[C-H](Br)** and **[C-H](PF₆)** were conveniently characterized by NMR spectroscopy, mass spectrometry and elemental analysis. As an example, the spectroscopic characterization and the molecular structure of **[C-H](Br)** are discussed below in detail.

¹H spectrum of [C-H](Br)

Figure 2.1 shows the ¹H NMR spectrum of [C-H](Br). The number and integration of the signals displayed on the spectrum are in agreement with the *C*_{2v} symmetry of the compound. The signal due to the acidic proton of the NCHN (*a*) appears at 11.69 ppm. The signals assigned to the protons of the pyrene *core* are displayed as two doublets (*b* and *d*) and one multiplet (*c* and *e*). The rest of the signals corresponding to the alkylidene chain are assigned on the ¹H NMR spectrum shown in Figure 2.1.

Figure 2.1 ¹H NMR spectrum of [C-H](Br) in CDCl₃

¹³C{¹H} spectrum of [C-H](Br)

Figure 2.2 shows the ¹³C{¹H} NMR spectrum of [C-H](Br). Again, the number of signals is in agreement with the *C*_{2v} symmetry of the compound. The signal corresponding to the NCHN (*I*) fragment appears at 141.8 ppm. The signals attributed to the pyrene *core* (2 and 3) are displayed in the 119 - 133 ppm region. The rest of the signals due to the carbon atoms of the alkylidene chain are assigned on the ¹³C NMR spectrum shown in the Figure 2.2.

Figure 2.2 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $[\text{C-H}](\text{Br})$ in CDCl_3

Molecular structure of $[\text{C-H}](\text{Br})$

Crystals of $[\text{C-H}](\text{Br})$ suitable for X-ray Diffraction analysis were obtained by slow diffusion of hexane into a concentrated solution of the compound in chloroform. The analysis of the molecular structure of $[\text{C-H}](\text{Br})$, shown in Figure 2.3, confirms the predicted structure for compound $[\text{C-H}](\text{Br})$.

The crystal packing reveals the presence of a π - π interaction between pairs of azolium units, which are disposed in an *anti* orientation. The interaction is through the pyrene *core* with an offset-stacked geometry. The distance between planes is 3.538(3) Å, which is indicative of a π -stacking interaction.²⁶

Figure 2.3 a) Molecular structure of $[\text{C-H}](\text{Br})$. Ellipsoids are given at 50% probability. Hydrogen atoms (except in the NCHN fragment) have been omitted for clarity. b) View of π -stacking present in $[\text{C-H}](\text{Br})$ (hydrogen atoms and bromide omitted)

b) Synthesis and characterization of phenanthro[4,5-abc]phenazino[11,12-d]imidazolium and acetonaphtho[1,2-b]quinoxaline[11,12-d]imidazolium salts.

Following a similar methodology as the one recently developed by Tapu and co-workers,²⁷ we prepared the azoliums **[D-H](X)**, **[E-H](X)** and **[F-H](X)** (Scheme 2.2). The coupling between 1,3-dibutyl-5,6-diaminobenzimidazolium iodide and the corresponding diketone, affords the desired polyaromatic azolium salt, in yields ranging from 70 to 80%. 1,3-Dibutyl-5,6-diaminobenzimidazolium iodide was prepared according to the previously described methodology,²⁷ although we found that the reduction of the nitro group could be more efficiently achieved by using Pd/C and hydrazine in ethanol at 80 °C. This method afforded the diaminobenzimidazolium salt as a white solid in 90% yield. This procedure has the advantage that the catalyst (Pd/C) can be removed from the reaction mixture by simple filtration, and then the desired product can be easily recovered by evaporating the solvent, thus facilitating its purification. In order to circumvent any halide exchanges in the subsequent coordination of the ligands, the iodide salts **[D-H](I)**, **[E-H](I)** and **[F-H](I)** were reacted with NH₄PF₆ to produce the anion metathesis products **[D-H](PF₆)**, **[E-H](PF₆)** and **[F-H](PF₆)**, respectively. The main difference between the pyrene derivatives and the acenaphthenequinone is the number of aromatic rings. The pyrene-dione incorporates four six-membered rings in its structure, while the acenaphthenequinone has two, and one five-membered ring.

Scheme 2.2 Synthesis of the azolium salts **[D-H](X)**, **[E-H](X)** and **[F-H](X)**

All new species were characterized by NMR spectroscopy, mass spectrometry and elemental analysis. Due to the similarity between all the compounds described in this section, only the NMR spectroscopic characterization of **[D-H](I)** is discussed in detail. The experimental details with respect to the synthesis and the characterization of all the products have been included in the Experimental Section (Chapter 6).

^1H spectrum of **[D-H](I)**

Figure 2.4 shows the ^1H NMR spectrum of **[D-H](I)**. The number and integration of the signals displayed on the spectrum are in agreement with the two-fold symmetry of the compound. The signal due to the acidic proton of imidazolium salt (*a*) appears at 10.19 ppm. The aromatic protons are displayed as two doublets (*c* and *e*), one singlet (*b*) and one multiplet (*d, f*) at 9.31, 8.88, 8.43 and 8.15 ppm, respectively. The rest of the signals due to the alkylidene chain are assigned on the NMR spectrum shown in Figure 2.4

Figure 2.4 ^1H NMR spectrum of **[D-H](I)** in $\text{DMSO-}d_6$

$^{13}\text{C}\{^1\text{H}\}$ spectrum of **[D-H](I)**

Figure 2.5 shows the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **[D-H](I)**. The signal corresponding to NCHN fragment (*l*) appears at 147.5 ppm. The signals attributed to the π -extended *core* (2 and 3) are displayed between 111 and 143 ppm. The rest of the signals due to the *n*-butyl chain are assigned on the NMR spectrum shown in Figure 2.5.

Figure 2.5 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of [D-H](I) in $\text{DMSO-}d_6$

2.2.1.1 Luminescence properties of the azolium salts

It is very well known that the optical properties of pyrene derivatives are highly influenced by the functional groups directly attached to the polyaromatic *core*.²⁸⁻³⁰ Also, due to its fluorescence properties, pyrene is the chromophore of choice in fundamental and applied photochemical research,²¹ thus its incorporation into NHC ligands may add interesting photophysical applications to their derived compounds.

Azolium salts have proven to be good fluorophores.^{12,27,30-36} For example, Tapu and co-workers¹² reported the synthesis of the first azolium salt based on phenanthrene. This salt showed a fluorescence quantum yield (Φ) of 0.18. More recently, in our research group, we found very good fluorescence properties for a series of bisazoliums linked by pyrene.^{30,37} In all the series of these azoliums, the N-substituents were alkyl groups, such as methyl, ethyl, *n*-propyl, *n*-butyl. The quantum yields of these compounds range from 0.2 to 0.75.

Based on the above precedents, we decided to evaluate the luminescence properties of the azolium salts [C-H](Br), [C-H](PF₆), [D-H](I), [E-H](I) and [F-H](I). The preliminary studies on the emission properties of these salts were carried out in degassed CH₃CN solutions (Table 2.1). The pyrene-imidazolium salts [C-H](Br) and [C-H](PF₆) exhibited fluorescence emission in the 350-450 nm region, similar to pyrene. The pyrene-imidazoliums display two absorption maxima in CH₃CN, at 245

and 275 nm. With excitation at 317 nm, and using anthracene as standard ($\Phi = 0.27$), the quantum yields of **[C-H](Br)** and **[C-H](PF₆)** were estimated as 0.31 and 0.28, respectively, as determined from the integration of their emission spectra. Both the emissions and the quantum yields are insensitive to the nature of the counter-anions, and the values are very similar to those shown by free pyrene, thus indicating that the emissive properties are centered in the pyrene moiety, with little participation of the heterocycles. Similar studies performed in our group, demonstrated that the luminescence properties of pyrene-containing azoles are not sensitive to the nature of the azoles, and therefore it is concluded that there is a minimum influence of the participation of the heterocycles in the photophysical properties of this type of salts.³⁷

The azolium salts **[D-H](I)** y **[E-H](I)** absorb UV-vis light at $\lambda > 400$ nm and exhibit fluorescence emission in the 450 - 650 nm region in solution. The quantum yields were calculated by integration of their emission spectra, using quinine sulfate as standard, and exciting at 350 nm. Under this conditions, the azolium **[E-H](I)** exhibits the highest quantum yield ($\Phi = 0.32$). For the azolium salts with the fused phenanthro[4,5-abc]phenazine, the presence of the *t*-Bu group in the pyrene fragment of **[E-H](I)** results in a λ_{em} at 560 nm, which is bathochromically shifted by 20 nm relative to **[D-H](I)**. This shift to longer wavelength is consistent with that observed previously by related compounds.³⁸ As a consequence of the more extended π -delocalized system of **[D-H](I)** and **[E-H](I)**, compared with 1,3-dibutyldibenzo[a,c]phenazino[11,12-d]imidazolium tetrafluoroborate (entry 6, Table 2.1) described by Tapu, a hypsochromic shift of up to 13 nm of the absorption maxima was observed. Compound **[F-H](I)** exhibits negligible fluorescence emission (entry 5, Table 2.1).

Table 2.1 Photophysical properties of azoliums with extended polyaromatic systems^a

Entry	Compound	λ_{abs} (nm)	λ_{em} (nm)	Φ_f
1	[C-H](Br)	245, 275	370, 390, 412, 435	0.31 ^[b]
2	[C-H](PF₆)	245, 275	370, 390, 412, 435	0.28 ^[b]
3	[D-H](I)	243, 283, 345	540	0.25 ^[c]
4	[E-H](I)	249, 284, 324	560	0.32 ^[c]
5 ^[d]	[F-H](I)	237, 324	---	---
6	[G-H](BF₄)	256, 414	496	0.02 ²⁷

[a] Measurements were performed in degassed CH₃CN under ambient conditions. The standards for measured the quantum yields were: [b] recrystallized anthracene in degassed EtOH ($\Phi_f = 0.27$) and [c] recrystallized quinine sulfate in degassed 0.5 M H₂SO₄ ($\Phi_f = 0.546$), exciting at 317 and 350 nm, respectively. [d] The emission intensity of **[F-H](I)** was found to be negligible.

2.2.2 Synthesis and characterization of NHC-based complexes

With the imidazolium salts shown in Chart 2.2 in hand, we decided to prepare the related metal complexes of Ir(I), Rh(I), Ni(II) and Pd(II). We thought that these metal complexes should allow us to study the electronic properties of the NHC ligands, and to relate these data with their catalytic activities.

2.2.2.1 Preparation of Rh(I) and Ir(I) complexes

In this section we will describe the preparation of the complexes with all the ligands derived from the imidazolium salts described in the previous sections. Since most of the complexes are new, a special attention will be devoted to the description of their full characterization. The known imidazolylidene and benzoimidazolylidene complexes **1A** and **1B** (Scheme 2.3) were obtained following the literature methods.³⁹

Scheme 2.3 Synthesis of metal complexes **1A-B**

a) Preparation of **1-5C**

The coordination of the pyrene-imidazolylidene ligand (**C**) to rhodium and iridium (Scheme 2.4) can be performed by deprotonating **[C-H](Br)** with potassium bis(trimethylsilylamide) (KHMDs) in THF at -78 °C, followed by the addition of $[MCl(COD)]_2$ (M = Rh, Ir). The reactions carried out with the hexafluorophosphate salt **[C-H](PF₆)**, yielded the chlorinated complexes **1C** and **3C**. For the reactions carried out with the pyrene-azolium bromide **[C-H](Br)**, NaBr was added to the reaction medium in order to facilitate the formation of the brominated complexes **2C** and **4C**. After purification by column chromatography, the complexes were obtained in moderate to high yields (56-86 %). The preparation of the iridium carbonyl complex **5C** was carried out by replacing the COD ligand by carbon monoxide, by bubbling CO into a CH₂Cl₂ solution of the corresponding iridium complex at 0 °C, as depicted Scheme 2.4

Scheme 2.4 Synthesis of metal complexes **1-5C**

All complexes were characterized by NMR spectroscopy, mass spectrometry and elemental analysis. The molecular structures of **1C** and **4C** were unambiguously determined by means of X-ray diffraction. In the following paragraphs, the detailed description of the NMR spectra of complex **4C** and **5C** is provided. All the details regarding the characterization of the rest of the complexes may be found in the Experimental Section (Chapter 6).

^1H NMR spectrum of **4C**

Figure 2.6 shows the ^1H NMR spectrum of **4C**. The number and integration of the signals displayed on the spectrum are in agreement with the two-fold symmetry of the compound. The protons of the pyrene core appear as two doublets and one multiplet at 8.60 (*d*), 8.21 (*b*) and 8.11 ppm (*c*, *e*), respectively. The signals attributed to the $-\text{NCH}_2-$ fragments (*f*) appear as diastereotopic pairs at 5.64 and 5.19 ppm. The rest of the signals attributed to the *n*-butyl groups and COD ligand are conveniently displayed on the spectrum shown in the Figure 2.6.

Figure 2.6 ^1H NMR spectrum of **4C** in CDCl_3

$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **4C**

Figure 2.7 shows the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **4C**. The most characteristic signal is the one attributed to the carbene-carbon (*I*) displayed at 187.6 ppm, falling in the range of previously described NHC-based Ir(I) complexes.^{12,40} The resonances due to the pyrene core (2 and 3) are shown in the 119 - 133 ppm region. The rest of the signals

attributed to the COD ligand and the *n*-butyl chain are conveniently displayed on the spectrum.

Figure 2.7 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **4C** in CDCl_3

Molecular structure of **1C** and **4C**

Crystals of **1C** and **4C** suitable for X-ray diffraction analysis were obtained by slow diffusion of hexane into a concentrated solution of the compound in chloroform. Both complexes are isostructural. Complexes **1C** and **4C** crystallize in the monoclinic space group $\text{P2}_1/\text{c}$. As can be seen in Figure 2.8, the metal centre (Rh or Ir) is coordinated in a square-planar fashion, with the pyrene-NHC (**C**), one 1,5-cyclooctadiene and one halide ligand (Cl or Br) completing the coordination sphere about the iridium atom. Table 2.2 shows the most representative bonds lengths ($\text{\AA}$) and angles ($^\circ$) of both complexes. The pyrene-imidazolylidene ligand is quasi-orthogonally oriented with respect to the coordination plane of the molecule, as seen by the average of the two torsion angles, $\text{N}(1)\text{-C}(1)\text{-Ir}(1)\text{-Br}(1)$ and $\text{N}(2)\text{-C}(1)\text{-Ir}(1)\text{-Br}(1)$, 84.5° (the related angle for **1C** is 84.5°). The average Ir-C distance of the carbons *trans* to the carbene-carbon ($2.168 \text{ \AA}$) are slightly longer than the distances to the *cis*-oriented ones ($2.105 \text{ \AA}$), as a consequence of the *trans* influence of the carbene ligand. The same effect is seen in complex **1C**, for which the related Rh-C average distances are $2.190(5) \text{ \AA}$ and $2.110(7) \text{ \AA}$, respectively. The $\text{M-C}_{\text{carbene}}$ distances are $2.031(4) \text{ \AA}$ and $2.028(5) \text{ \AA}$ for **1C** and **4C**, respectively.

Figure 2.8 a) and c) Molecular structures of **1C** and **4C**, respectively. b) and d) Molecular structures of **1C** and **4C**, respectively, showing the π -stacking between two pyrene fragments. Hydrogen atoms have been omitted for clarity. Ellipsoids are given at 50% of probability.

A more detailed study of the crystal packing of both molecules reveals that there is a two-dimensional π -stacking interaction between pairs of molecules (*b* and *d*, Figure 2.8). The distance between pyrene fragments in **4C** is 3.416(6) Å (the related distance for **1C** is 3.490 (5) Å), falling in the range of previously reported aromatic compounds with π -stacking interactions.²⁶

Table 2.2 Selected bond lengths and angles for **1C** and **4C**

Complex 1C			
Bond	Length (Å)	Bond	Angle (°)
Rh(1)–Cl(1)	2.395(1)	C(1)–Rh(1)–Br(1)	85.9(1)
Rh(1)–C(1)	2.032(4)	N(1)–C(1)–N(2)	106.3(3)
Rh(1)–C(26)	2.108(4)		
Rh(1)–C(27)	2.124(5)		
Rh(1)–C(30)	2.183(4)		
Rh(1)–C(31)	2.191(5)		
Complex 4C			
Bond	Length (Å)	Bond	Angle (°)
Ir(1)–Br(1)	2.481(9)	C(1)–Ir(1)–Br(1)	86.7(1)
Ir(1)–C(1)	2.028(5)	N(1)–C(1)–N(2)	105.9(4)
Ir(1)–C(26)	2.110(5)		
Ir(1)–C(27)	2.100(5)		
Ir(1)–C(30)	2.161(6)		
Ir(1)–C(31)	2.174(6)		

¹H NMR spectrum of **5C**

Figure 2.9 shows the ¹H NMR spectrum of **5C**. The number and integration of the signals displayed on the spectrum are in agreement with the two-fold symmetry of the compound. The signals attributed to the pyrene *core* appear as two doublets and one multiplet at 8.51 (*d*), 8.18 (*b*) and 8.04 (*c*, *e*) ppm, respectively. The protons of the –N-CH₂-CH₂- fragments (*f* and *g*) appear as diastereotopic pairs (5.35 and 5.14 ppm for *f*, 2.25 and 2.07 ppm for *g*). The rest of the signals attributed to the *n*-butyl groups are assigned on the spectrum.

¹³C{¹H} NMR spectrum of **5C**

Figure 2.10 shows the ¹³C{¹H} NMR spectrum of **5C**. The spectrum exhibits one signal due to the metallated carbon (*I*) at 181.3 ppm, and two signals attributed to the CO ligand at 178.5 and 168.1 ppm, falling in the range of the previously described NHC-based Ir(I) complexes.^{12,40} The signals due to the pyrene *core* (2 and 3) are shown in the region between 119 - 133 ppm. The rest of the signals attributed to the *n*-butyl chain are assigned on the spectrum shown in the Figure 2.10.

Figure 2.9 ¹H NMR spectrum of **5C** in CDCl₃

Figure 2.10 ¹³C{¹H} NMR spectrum of **5C** in CDCl₃

c) Preparation of **1-3D**, **1-3E** and **1-3F**

The coordination of **[D-H](X)**, **[E-H](X)** and **[F-H](X)** to iridium, was performed by reacting [IrCl(COD)]₂, KO^tBu and the corresponding azolium salt in THF at room temperature (Scheme 2.5). For the cases in which the azolium salts with iodide were used, an excess of NaI was added to the reaction mixture, in order to avoid mixtures of halides in the final metal complexes. After purification by column chromatography, the complexes were obtained in moderate to high yields (46-78 %). The preparation of the iridium carbonyl complexes **3D**, **3E** and **3F** was carried out by replacing the COD

ligand by carbon monoxide, by bubbling CO into the CH₂Cl₂ solutions of the corresponding iridium complex at 0 °C, as depicted Scheme 2.5.

Scheme 2.5 Synthesis of metal complexes **1-3D**, **1-3E** and **1-3F**

All complexes were characterized by NMR spectroscopy, mass spectrometry and elemental analysis. The molecular structures of **1D** and **1F** were unambiguously determined by means of X-ray diffraction. In the following paragraphs, the detailed description of the NMR spectra of complex **1D** is provided. All the details regarding the characterization of the rest of the complexes may be found in the Experimental Section (Chapter 6).

¹H NMR spectrum of **1D**

Figure 2.11 shows the ¹H NMR spectrum of **1D**. The signals due to the quinoxaline fragment (*b*) and two signals of the pyrene group (*f* and *e*) are shown as a multiplet between 8.13 - 7.96 ppm. The doublets at 8.28 (*c*) and 9.53 (*d*) ppm are attributed to the pyrene fragment. The rest of the signals are in agreement with the two-fold symmetry of the complex, and are displayed on the spectrum shown in Figure 2.11.

Figure 2.11 ^1H NMR spectrum of **1D** in CDCl_3

$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1D**

Figure 2.12 shows the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1D**. The most characteristic signal is the one attributed to the carbene-carbon, displayed at 202.7 ppm (**1**). The signal due to the CH group of the quinoxaline fragment is shown at 106.6 ppm. All the rest of the signals, including those due to the butyl fragment and the COD carbons, are conveniently displayed on the spectrum shown, and are consistent with the structure assigned to the complex.

Figure 2.12 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1D** in CDCl_3

Molecular structure of **1D**

Crystals of **1D** suitable for X-ray diffraction analysis were obtained by slow diffusion of hexane into a concentrated solution of the compound in a dichloromethane/methanol mixture. Figure 2.13 shows the molecular structure of **1D**. As can be seen, the NHC ligand with the extended polyaromatic system is coordinated to the metal centre, and one COD and iodide ligands complete the coordination sphere. The crystal packing of the molecule shows that there is a one-dimensional π -stacking interaction between pairs of molecules, which are disposed in an antiparallel centrosymmetric fashion, at a distance of 3.370 (4) Å. The NHC ligand is quasi-orthogonally oriented with respect to the coordination plane of the molecule, as evidenced by the average of the two torsion angles N(1)-C(1)-Ir(1)-I(1) and N(2)-C(1)-Ir(1)-I(1), 88.12°. The Ir-C(carbene) bond distance is 2.007(4) Å. Interestingly, the plane of the imidazolyliene deviates from the plane formed by the hexacyclic backbone by 14.75°. The distance Ir-C_{olefin} bond *trans* to NHC ligand is longer than the founded at *cis* disposition, due to the *trans* influence of the NHC ligand.

Table 2.3 Selected bond lengths and angles for **1D**

Bond	Length (Å)	Bond	Angle (°)
Ir(1)–I(1)	2.6721(4)	C(1)– Ir(1)–I(1)	88.35(13)
Ir(1)–C(1)	2.007(4)	N(1)–C(1)–N(2)	106.1(4)
Ir(1)– C(32)	2.113(5)		
Ir(1)– C(33)	2.120(5)		
Ir(1)– C(36)	2.197(4)		
Ir(1)–C(37)	2.203(4)

Figure 2.13 a) Molecular structure of **1D**. b) Molecular structure of **1D**, showing the π stacking between polyaromatic systems. Hydrogen atoms have been omitted for clarity. Ellipsoids are given at 50% of probability.

Molecular structure of **1F**

Crystals of **1F** suitable for X-ray diffraction analysis were obtained by slow diffusion of hexane into a concentrated solution of the compound in dichloromethane/methanol mixture. Figure 2.14 shows the molecular structure of **1F**, and corroborates that the polyaromatic NHC ligand is coordinated to iridium. One COD and one iodide complete the coordination sphere about the metal. The polyaromatic ligand contains all six cycles in the same plane. The Ir-C(carbene) bond distance is 2.016(4) Å. The NHC ligand is quasi-orthogonally oriented with respect to the coordination plane of the metal, as indicated by the average of the two torsion angles N(1)-C(1)-Ir(1)-I(1) and N(2)-C(1)-Ir(1)-I(1), 89.37°. As seen for the molecular structure of **1D**, the crystal packing of **1F** shows that there is a one-dimensional π -stacking interaction between pairs of molecules, which are disposed in an antiparallel fashion, at a distance of 3.470(4) Å, which is slightly longer to that shown by **1D**.

Figure 2.14 a) Molecular structure of **1F**. b) Molecular structure of **1F**. Hydrogen atoms have been omitted for clarity. Ellipsoids are given at 50% of probability.

Table 2.4 Selected bond lengths and angles for **1F**

Bond	Length (Å)	Bond	Angle (°)
Ir(1)–I(1)	2.6704(4)	C(1)–Ir(1)–I(1)	89.18(11)
Ir(1)–C(1)	2.016(4)	N(1)–C(1)–N(2)	106.2(3)
Ir(1)–C(32)	2.216(4)		
Ir(1)–C(35)	2.107(4)		
Ir(1)–C(28)	2.134(4)		
Ir(1)–C(31)	2.178(4)		

2.2.2.2 Preparation of Ni(II) and Pd(II) complexes

Aiming to determine the effect of the presence of a polyaromatic fragment at the backbone of the NHC in the catalytic activity of the related metal complexes (this will be described in Chapter 3), and in order to have a good comparative pattern of behaviour, we decided to obtain the nickel (**2A**, **2B** and **6C**) and palladium (**3A**, **3B** and **6C**) complexes by the procedure depicted in Scheme 2.6. By following a known procedure for similar nickel compounds,⁴¹ the reaction of nickelocene, [NiCp₂], with the corresponding azolium bromides ([**A-H**](Br), [**B-H**](Br) or [**C-H**](Br)) in a THF/DMF mixture, afforded complexes **2A**, **2B** and **6C**, in moderate yields (47-56%). For the synthesis of complexes with the general formula [NiCpX(NHC)], it is necessary that the azolium salt has halide counterions, because the strong Ni-X bond formed in the final product thermodynamically triggers the reaction leading to the formation of the product.⁴²

The palladium metal complexes **3A**, **3B** and **7C** were prepared by following a known procedure for similar palladium compounds.⁴³ The reaction of the corresponding hexafluorophosphate azolium salts ([**A-H**](PF₆), [**B-H**](PF₆) or [**C-H**](PF₆)), with PdCl₂ in the presence of K₂CO₃, in neat 3-chloropyridine at 90°C, affords the [PdCl₂(NHC)(3-chloropyridine)] complexes in moderate to high yields (**3A**, 66% yield; **3C**, 50% yield; and **7C**, 31% yield).

Scheme 2.6 Synthesis of complexes **2-3A-B** and **6-7C**

All complexes were characterized by NMR spectroscopy, mass spectrometry and elemental analysis. The molecular structures of **2B**, **6C** and **7C** were unambiguously determined by means of X-ray diffraction. In the following paragraphs, the detailed description of the NMR spectra of complex **6C** and **7C** is provided. All the details regarding the characterization of the rest of the complexes may be found in the Experimental Section (Chapter 6).

^1H NMR spectrum of **6C**

Figure 2.15 shows the ^1H NMR spectrum of **6C**. The signals due to the pyrene fragment are shown as one doublet and two multiplets at 8.63 (*d*), 8.21 (*b*) and 8.11 (*c*, *e*) ppm, respectively. The resonance at 5.45 ppm is assigned to the hydrogen atoms of the Cp ligand. The signals attributed to the *n*-butyl group are displayed on the spectrum.

Figure 2.15 ^1H NMR spectrum of **6C** in CDCl_3

$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **6C**

Figure 2.16 shows the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **6C**. The signal attributed to the metallated carbene-carbon (*I*) appears at 171.9 ppm. The carbons of the pyrene *core* (2 and 3) display their resonances in the 119 - 132 ppm region. The signal due to the Cp ligand appears at 92.7 ppm. The rest of the signals attributed to the *n*-butyl chain are conveniently displayed on the spectrum.

Figure 2.16 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **6C** in CDCl_3

Molecular structure of **2B** and **6C**

Crystals of **2B** and **6C** suitable for X-ray diffraction analysis were obtained by slow diffusion of hexane into concentrated solutions of the compounds in dichloromethane. Complex **2B** crystallizes in the monoclinic space group Pbca , while the space group of complex **6C** is P2_1 . Figure 2.17 shows the molecular structures of **2B** and **6C**. Both complexes are structurally similar, except for the fact that **2B** contains a benzimidazolyliidene ligand, and **6C** has a pyrene-imidazolyliidene. They both present a two-legged piano-stool geometry, in a quasi-pentacoordinated geometry. Table 2.5 shows the most representative bond lengths ($\text{\AA}$) and angles ($^\circ$) for both complexes. The $\text{Ni-C}_{\text{carbene}}$ distances are 1.884(2) and 1.867(6) $\text{\AA}$ for **6C** and **2B**, respectively. The $\text{C(1)-Ni(1)-Cp}(\text{centroid})$ angles are 135.20 (for **6C**) and 134.34 (for **2B**), and correlates well with other known $[\text{NiCpX}(\text{NHC})]$ ($\text{X} = \text{halide}$) complexes.^{42,44,45} It has been proposed that this angle is an indirect indication of the absence of a rotation barrier about the nickel-carbene-carbon bond.⁴⁶ The nickel-carbon bonds *trans* to the NHC ligand are systematically longer than the rest of the Ni-C_{cp} distances, as a consequence of the higher *trans* influence of the NHC ligand.⁴⁷

It is worth mentioning that the crystal packing of complex **6C** exposes a π -stacking interaction between pairs of molecules, which are localized at distances of 3.682(18) $\text{\AA}$ (c, Figure 2.17), while complex **2B** does not show this type of interaction.

Table 2.5 Selected bond lengths and angles for **2B** and **6C**

Complex 2B			
Bond	Length (Å)	Bond	Angle
Ni(1)–Br(1)	2.324(1)	C(1)–Ni(1)–Br(1)	92.5 (2)
Ni(1)–C(1)	1.867(6)		
Ni(1)–Cp _(centroid)	1.760		
Complex 6C			
Bond	Length (Å)	Bond	Angle
Ni(1)–Br(1)	2.323(5)	C(1)–Ni(1)–Br(1)	94.63(7)
Ni(1)–C(1)	1.884(2)		
Ni(1)–Cp _(centroid)	1.766		

a)

b)

c)

Figure 2.17 Molecular structures of **6C** (a) and **2B** (b). Molecular structure of **6C**, showing the π stacking between two pyrene fragments. Hydrogen atoms have been omitted for clarity. Ellipsoids are given at 50% of probability

Figure 2.19 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **7C** in CDCl_3

Molecular structure of **7C**

Crystals of **7C** suitable for X-ray diffraction analysis were obtained by slow diffusion of hexane into a concentrated solution of the compound in dichloromethane. Complex **7C** crystallizes in the monoclinic space group $\text{P2}_1/\text{a}$. Figure 2.20 displays the molecular structure of complex **7C** and shows the palladium atom into a slightly distorted square plane. The molecular structure of **7C** confirms that the NHC-pyrene ligand is bound to palladium, and one 3-chloropyridine and two chloride ligands complete the coordination sphere around the metal. Table 2.6 shows the most representative bond lengths and angles. The $\text{Pd}-\text{C}_{\text{carbene}}$ distance is $1.959(2) \text{ \AA}$. As the molecular structures described before, the molecular packing of **7C** reveals a π - π stacking between two molecules (b, Figure 2.20). The length among pyrene fragments is $3.490(18) \text{ \AA}$, similar to the distance found in the crystal packing of **[C-H](Br)**, **1C**, **4C** and **6C**.

Table 2.6 Selected bond lengths and angles for **7C**

Bond	Length ($\text{\AA}$)	Bond	Angle ($^\circ$)
$\text{Pd}(1)-\text{Cl}(1)$	$2.3030(6)$	$\text{C}(1)-\text{Pd}(1)-\text{Cl}(1)$	$87.22(6)$
$\text{Pd}(1)-\text{Cl}(2)$	$2.2988(7)$	$\text{C}(1)-\text{Pd}(1)-\text{Cl}(2)$	$89.51(7)$
$\text{Pd}(1)-\text{C}(1)$	$1.959(2)$	$\text{C}(1)-\text{Pd}(1)-\text{N}(3)$	$177.33(8)$
$\text{Pd}(1)-\text{N}(3)$	$2.117(2)$

Figure 2.20 a) Molecular structure of **7C**. b) Molecular structure of **7C**, showing the π stacking between two pyrene fragments. Hydrogen atoms have been omitted for clarity. Ellipsoids are given at 50% of probability.

2.2.3 Synthesis and characterization of heterodimetallic complexes

Functionalized NHC-based complexes, especially those in which a metal fragment is attached to the coordinated ligand, have recently attracted much attention.⁴⁸⁻⁵⁰ Ganter and co-workers were recently able to coordinate a $[\text{RuCp}^*]^+$ fragment to a metal-coordinated benzimidazol-2-ylidene ligand.⁴⁹ Additionally, they studied the electronic properties of the related dimetallic complexes and found that the incorporation of the $[\text{RuCp}^*]^+$ fragment into the NHC ligand produces an important decrease of the electron donating strength of the NHC ligand.

With these precedents in mind, we took advantage of the presence of a pyrene fragment into the new NHC ligand and the high affinity of the $[\text{RuCp}^*]^+$ fragment towards η^6 coordination to arenes, in order to prepare heterodimetallic complexes. The reaction of **2C**, **3C** and **4C** with $[\text{RuCp}^*(\text{CH}_3\text{CN})_3](\text{PF}_6)$ in CH_2Cl_2 afforded the heterodimetallic complexes of Rh/Ru (**8C**) and Ir/Ru (**9C** and **10C**) in quasi-quantitative yields (Scheme 2.7).

Scheme 2.7 Synthesis of heterodimetallic complexes

As a consequence of the presence of four aromatic rings in the pyrene *core* of the NHC ligand **C**, we might expect the formation of at least three different isomers (Figure 2.21), depending on where the coordination of the Ru fragment takes place. In isomers **H** and **I**, the Ru fragment is bound to one internal aromatic ring of the pyrene, hence both isomers present a two-fold symmetry. In isomer **G**, the Ru fragment is attached to a lateral aromatic ring, causing the loss of the two-fold symmetry of the molecule. Therefore, distinguishing among the three possible isomers is relatively easy using by NMR spectroscopic techniques (see next subsection). In our case, only isomer **G** was observed.

Figure 2.21 Possible isomers of the dimetallic complexes

The coordination of the Ru fragment at one lateral aromatic ring is in agreement with Clar's aromatic sextet theory, which is often used for describing and comparing the aromatic character.^{51,52} A higher degree of aromaticity is predicted for the structure having the maximum number of disjointed aromatic π sextets (circle representations in Figure 2.21) drawn for the system. In the case of the pyrene-imidazolyliene ligand, the higher degree of electron delocalization is predicted for structure **G**.

Additionally, due to the relative orientation of the halogen ligand in the heterodimetallic complexes, two atropisomers are possible (Figure 2.22). In the *anti*-atropisomer the

$[\text{RuCp}^*]^+$ fragment and the halogen ligand are pointing to different sides of the molecule, while in the *syn*-atropisomer the $[\text{RuCp}^*]^+$ fragment and the halide ligand are pointing to the same side of the molecule. These atropisomers were observed by NMR spectroscopy in a 68:32 (for **8C**) and 55:45 (for **9C** and **10C**) molar ratios. The crystallisation of **10C** afforded exclusively the *syn* isomer, whose molecular structure could be determined by X-ray analysis. Long standing solutions of this isomer in CH_2Cl_2 at room temperature slowly undergo to the formation of mixtures of the two isomers, therefore indicating the interconversion of the two atropisomers. Due to the similarity between all the compounds characterized in this section, only the NMR spectroscopic characterization of **9C** is described below. All details regarding the characterization of all the products can be found in the Experimental Section (Chapter 6).

Figure 2.22 Two possible atropisomers of the dimetallic complexes

Attempts to prepare trimetallic species by binding a second $[\text{RuCp}^*]^+$ fragment modifying both the stoichiometry and the reaction conditions shown in Scheme 2.7 were unsuccessful.

^1H NMR spectrum of **9C**

Figure 2.23 shows the ^1H NMR spectrum of the *syn* isomer of **9C**. The spectrum clearly exhibits the loss of the two-fold symmetry of the pyrene-based NHC ligand. The shift of three signals of the pyrene *core* to lower frequencies provides the first indication that the coordination of the $[\text{RuCp}^*]^+$ fragment has taken place. Another indication is the signal due to the protons of the methyls at the Cp^* ring, which appear at 1.26 ppm. The signals attributed to the $-\text{NCH}_2-$ group are displayed as four multiplets, since the four proton atoms are diastereotopic and non-equivalent. The rest of the signals are in agreement with the proposed structure.

Figure 2.23 ^1H NMR spectrum of **9C** in CD_2Cl_2

$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **9C**

Figure 2.24 shows the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **9C**. Attempts to obtain the ^{13}C NMR spectrum of the *syn* isomer in its pure form were unsuccessful due to the long time required for its acquisition, and for the incipient formation of the *anti* isomer by the slow interconversion between the two atropisomers. The spectrum displays the loss of the two-fold symmetry of the pyrene-imidazolyliene ligand. Probably, the most characteristic signals are those corresponding to the carbene carbons at 191.0 (for *syn*) and 191.4 (for *anti*) ppm. The resonances due to the aromatic carbons of the Cp^* ligand are displayed at 94.5 (*δ-anti*) and 94.1 (*δ-syn*) ppm. The signal corresponding to the methyl groups of the Cp^* ligands (**9**) is shown at 8.7 ppm. The rest of the signals corresponding to both isomers are conveniently displayed on the spectrum shown.

Figure 2.24 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **9C** in CD_2Cl_2

Molecular structure of **10C**

Crystals of **10C** suitable for X-ray Diffraction analysis were obtained by slow diffusion of hexane into a concentrated solution of the compound in CH₂Cl₂. The heterodimetallic complex **10C** crystallized in the triclinic space group P-1. Figure 2.25 shows its molecular structure. As can be seen, the [RuCp*]⁺ group is η^6 -bound to one of the lateral aromatic rings of the pyrene fragment. The structure reveals that the NHC-pyrene ligand is coordinated to iridium, which completes its coordination sphere with a bromide and a COD ligand. The through space Ir-Ru distance is 7.02 Å. Table 2.7 shows the most representative bond lengths (Å) and angles (°). The Ir-C_{carbene} distance (2.016(5) Å) is slightly shorter than that in the monometallic analogue **4C** (2.028(5) Å). It has been suggested that the introduction of a η^6 -bound [RuCp*]⁺ fragment in benzimidazolylides should afford a higher degree of π -backdonation from the metal onto the NHC, thus some shortening in the M-C_{carbene} distance should be expected.⁴⁸ However, the same pronouncement in the π -backdonation should be accompanied by a decrease in the σ -donating character of the ligand, and therefore the two opposite effects may be mutually neutralized.

Table 2.7 Selected bond lengths and angles for **10C**

Bond	Lengths (Å)	Bond	Angles (°)
Ir(1)–Br(1)	2.4749(7)	C(1)–Ir(1)–Br(1)	88.63(14)
Ir(1)–C(1)	2.016(5)	N(1)–C(1)–N(2)	105.7(4)
Ir(1)–C(26)	2.105(6)		
Ir(1)–C(27)	2.123(6)		
Ir(1)–C(30)	2.170(6)		
Ir(1)–C(31)	2.186(6)		

The molecular packing of **10C** reveals a π – π interaction between pairs of molecules (Figure 2.25). The average distance between the pyrene fragments is 3.317(8) Å, slightly shorter than the one found for the same type of interaction in **4C** (3.416(6) Å).

Figure 2.25 a) Molecular structure of complex **10C**. b) Molecular structure of **10C**, showing the π -stacking between two pyrene fragments. Hydrogen atoms and counteranion (PF_6^-) have been omitted for clarity. Ellipsoids are given at 50% probability

2.2.3.1 Electronic properties of the heterodimetallic complexes

In order to study the effect of the Ru fragment in the electronic properties of the pyrene-imidazolylidene ligand, we decided to use two approaches. The first one is based on the preparation of the carbonyl derivative of **11C**, and the analysis of its infrared spectrum. The second approach involves electrochemical studies of complex **10C**. In the next sections both approaches are discussed in detail.

2.2.3.1.1 FT-IR spectroscopy studies

Complex **9C** was transformed into its carbonyl derivative by bubbling CO through a solution of the complex in CH_2Cl_2 at 0°C . After workup, the carbonyl derivative **11C** was isolated in 82% yield (Scheme 2.8). Complex **11C** was characterized by NMR and IR spectroscopy, mass spectrometry and elemental analysis. The ^1H NMR spectrum reveals the disappearance of the signals due to the COD protons, thus affording an indication that CO has replaced the COD ligand. As previously mentioned for **11C**, the ^1H NMR spectrum of **11C** reveals the presence of the *syn* and *anti* isomers, in a 63:37 ratio. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum shows the characteristic signal due to the Ir- $\text{C}_{\text{carbene}}$ at 168 ppm, both for the *syn* and *anti* isomers.

 Scheme 2.8 Synthesis of complex **11C**

For comparative purposes, the FT-IR spectra of complexes **5C** and **11C** were recorded in CH_2Cl_2 solutions. Table 2.8 shows the FT-IR CO-stretching frequencies of **5C** and **11C**. Both complexes exhibit two bands due to the CO-stretching frequencies, at 2067.3, 1985.4, and 2073.0, 1990.0 cm^{-1} , respectively. The average ν_{CO} for complex **5C** is 2026.3 cm^{-1} . This value is shifted by 5.2 cm^{-1} to lower wavenumber in comparison with the average ν_{CO} value shown for **11C** (2031.5 cm^{-1}). This result suggests that the Ru fragment reduces the electron-donating strength of the NHC ligand, due to the $[\text{RuCp}^*]^+$ electron-withdrawing character. The same behaviour has been observed in previous reports.⁴⁸⁻⁵⁰

 Table 2.8 IR C-O stretching frequencies of complexes **5C** and **11C**

Complex	$\nu(\text{CO})^{[\text{a}]}(\text{cm}^{-1})$	$\nu(\text{CO})_{\text{av}}(\text{cm}^{-1})$
<p style="text-align: center;">5C</p>	2067.3, 1985.4	2026.3
<p style="text-align: center;">11C</p>	2073.0, 1990.0	2031.5

[a] IR data obtained in CH_2Cl_2 solutions of the complex

2.2.3.1.2 Electrochemical studies

We performed electrochemical measurements of complexes **4C** and **10C** in order to study the influence of the $[\text{RuCp}^*]^+$ fragment on the electronic properties of the pyrene-imidazolyliene ligand. The cyclic voltammetry (CV) and the differential pulse voltammetry (DPV) measurements were performed in CH_3CN , using $[\text{NBu}_4](\text{PF}_6)$ as

electrolyte. By comparing the electrochemical properties of complexes **4C** and **10C** (Figure 2.26 and Table 2.9), we may clearly observe the influence of the introduction of the $[\text{RuCp}^*]^+$ fragment. In the cyclic voltammetry, both complexes **4C** and **10C** show two oxidation waves. The first wave corresponds to the irreversible oxidation of iridium, while the second is assigned to the formation of the radical cation of the pyrene fragment. The $[\text{RuCp}^*]^+$ fragment did not afford any additional redox signal. The typical potential for the oxidation of arene-ruthenium complexes ranges from 1.7 to 2.25 V.⁵³ However, the presence of a second metal (iridium) in the structure of the molecule may shift the potential to higher values, thus exceeding the potential window of the solvent.

The DPV analysis of the redox behaviour allowed us to obtain a more precise value of the potentials. The redox potential of complex **10C** is 0.891 V, while in **4C** is 0.831 V for the oxidation of the iridium centre. This anodic $\Delta E_{1/2}$ shift of 60 mV upon the coordination of the $[\text{RuCp}^*]^+$ fragment to the pyrene-imidazolylidene ligand is lower than the one found for the introduction of the ruthenium fragment in the case of the benzoimidazolylidene ligand (167 mV).⁴⁹ A similar anodic shift is observed for the oxidation of the pyrene fragment, which occurs 1.098 and 1.143V, for **4C** and **10C**, respectively, therefore showing a small shift of 45 mV. The shift to higher redox potential observed in complex **10C** indicates that the presence of the $[\text{RuCp}^*]^+$ fragment decreases the electron-donating strength of the NHC ligand. These results match perfectly with those observed in the FT-IR of the carbonyl complexes **5C** and **11C**.

Figure 2.26 Cyclic voltammetry diagram of complexes **4C** and **10C** (a), and relevant section of the differential pulse voltammetry (DPV) (b). Measurements were performed in dry CH_3CN using 1 mM analyte and 0.1 mM $[\text{NBu}_4]\text{PF}_6$ as the electrolyte at 50 mV/s scan rates and are referenced to the SCE by shifting ferrocene to 450 mV

Table 2.9 Redox potential for complexes **3C** and **9C**^[a]

Complex	$E_{\text{ox}}(\text{Ir}^{\text{I}}/\text{Ir}^{\text{II}})$ (V)	$E_{\text{ox}}(\text{pyrene/pyrene}^{+})$ (V)
4C	0.831	1.098
10C	0.891	1.143

[a] Measurements performed in dry CH_3CN , using 1 mM analyte and 0.1 mM $[\text{NBu}_4]\text{PF}_6$ as the electrolyte. Scan rate: 50 mV/s. Data referenced to the SCE by shifting ferrocene to 450 mV.

2.3 Conclusions

We prepared and characterized a set of azolium salts with a different number of fused aromatic rings in their backbone (**[A-H](X)**, **[B-H](X)**, **[C-H](X)**, **[D-H](X)**, **[E-H](X)** and **[F-H](X)**). We used these NHC-ligand precursors for the preparation of their related complexes (Ir, Rh, Ni and Pd). More precisely:

- A series of $[\text{IrCl}(\text{NHC})(\text{L})]$ ($\text{L} = \text{COD}$ or $(\text{CO})_2$) have been obtained. Six different NHC ligands were selected, which four are new and incorporate an extended polyaromatic system in their backbones (**C**, **D**, **E**, **F**).
- A set of complexes of the form $[\text{PdCl}_2(\text{NHC})(3\text{-chloropyridene})]$ and $[\text{NiBr}(\text{Cp})(\text{NHC})]$ were prepared. We selected the imidazolyliene, benzimidazolyliene and pyrene-imidazolyliene as NHC ligands. In principle, these ligands should provide similar electronic and steric properties to the metal complexes, being good candidates for the study the effect of the polyaromatic system on the catalytic behaviour of these complexes.
- Additionally, we used the pyrene moiety as platform to coordinate a $[\text{RuCp}^*]^+$ fragment. The coordination of the $[\text{RuCp}^*]^+$ fragment to the pyrene fragment allows us the synthesis of heterodimetallic complexes, namely Ru/Ir and Ru/Rh. The presence of the $[\text{RuCp}^*]^+$ on the backbone of the pyrene-imidazolyliene ligand reduces its electron strength as shown by FT-IR and electrochemical studies of the Ru/Ir derivatives.

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Chapter 3

**Tuning the electronic properties of
NHC ligands with polyaromatic
systems. Catalytic consequences.**

3.1 Introduction

Transition metal complexes with N-heterocyclic carbene (NHC) ligands decorated with polyaromatic systems are currently under great attention due to their potential application in homogeneous catalyst and molecular electronics. In the field of molecular electronics, polyaromatic ligands are mainly used for the preparation of materials with properties that are consistent with extensively delocalized systems,^{1,2} such as luminescence.^{3,4}

An interesting application of NHC ligands with extended aromatic systems in the field of catalysis is the possibility of immobilizing the related complexes onto solid surfaces, in which the polyaromatic fragments are used to facilitate non-covalent interactions (generally π -stacking) with the surface of the solid.⁵⁻⁹ Recently, our group demonstrated that the catalytic behaviour of metal complexes featuring polyaromatic-imidazolyliene ligands is influenced by the π -stacking affinities of the substrates with the ligands.⁹⁻¹¹ Furthermore, our group showed that the catalytic activity of a series of mono- and dimetallic NHC complexes of palladium bearing N-methyl-pyrene substituents is highly influenced by the presence of π -stacking additives (pyrene, anthracene and hexafluorobenzene) in the reaction media.⁹ These observations were interpreted as a consequence of the π -stacking interaction between the substrate and the pyrene groups in the NHC-based catalysts. However, although we had demonstrated that the additives effectively formed π -stacking adducts with the ligand, and proved that this interaction yielded important implications in the electron-donating character of the ligand, a comprehensive study in order to quantify the magnitude of this effect was found necessary.

Based on these previous findings, and taking into account the capability of polyaromatic hydrocarbons to produce π -stacking aggregates,¹² we thought that the complexes described in Chapter 2 may help us to undergo a detailed study on the influence of π -stacking interactions on the catalytic behaviour and the donor properties of the related NHC ligands. The aim of this chapter is to shed some light onto the quantification of the π -stacking interaction in this type of systems, and to explain how this non-covalent interaction modifies the electronic properties of the ligands with the extended polyaromatic systems.

3.2 Results and discussion

The results are presented in three subsections. The first one describes the effect of π -stacking additives, such as pyrene or hexafluorobenzene (C_6F_6), on the electronic properties of the iridium (**1A**, **2B**, **5C**, **3D** and **3F**) and nickel (**2A**, **2B** and **6C**) complexes. The studies of the binding between the polyaromatic-functionalized NHC complexes and pyrene (or C_6F_6) are described in the second section. Finally, the third section of this chapter describes the catalytic studies of **2A**, **2B**, **3A**, **3B**, **6C** and **7C** in the Suzuki-Miyaura cross-coupling and α -arylation reactions.

3.2.1 Modification of the electronic properties of NHC ligands by non-covalent interactions

With the series of iridium-carbonyl and nickel complexes described in Chapter 2 (Chart 3.1), we decided to study their electronic properties, and evaluate if they are affected by the presence of π -stacking additives, such as pyrene or hexafluorobenzene. In order to carry out this study, we decided to use three different approaches:

1. FT-IR spectroscopy studies. We studied the effect of different π -stacking additives on the C-O stretching frequencies of the carbonyl complexes **1A-B**, **5C** and **3D-F**
2. DFT calculations. Theoretical calculations were performed in the gas phase, aiming to shed some light on the modification of the electronic properties of the NHC ligands, and to evaluate the energies of the non-covalent interaction between the NHC ligand and the π -stacking additive. These studies were performed by Prof. Dmitri Gusev at the Wilfrid Laurier University (Ontario-Canada).
3. Electrochemical studies. We carried out the cyclic voltammetry studies of the nickel complexes **2A**, **2B** and **6C**, in the presence of different amounts of pyrene, in order to analyse if their redox potentials are affected.

Iridium-carbonyl complexes

Nickel complexes

Chart 3.1 Iridium and nickel complexes

a) FT-IR studies

The FT-IR spectra of complexes **1A**, **1B**, **5C**, **3D** and **3F**, which basically differ in the number of fused aromatic rings at the NHC ligand, were recorded in CH₂Cl₂ solution. Table 3.1 shows the C-O stretching frequencies of the iridium-based carbonyl complexes in the absence of additives, and in the presence of pyrene and hexafluorobenzene (C₆F₆). As can be seen from the data shown, complexes **1B** and **5C** display their average C-O stretching frequencies at $\nu_{\text{av}}(\text{CO})$, 2026.8 and 2026.3 cm⁻¹, respectively. The C-O stretching frequency of complex **1A** is 2023.4 cm⁻¹. These data reflect that the NHC ligands in **1B** and **5C** are electronically similar, while the imidazolylidene ligand in complex **1A** has a slightly higher electron-donating strength.

For complexes **3D** and **3F**, the $\nu_{\text{av}}(\text{CO})$ is exactly the same (2030.2 cm⁻¹), while **3E** exhibits a slightly higher $\nu_{\text{av}}(\text{CO})$ (2030.7 cm⁻¹). This observation indicates that the number of fused aromatic rings at the NHC backbone has little influence in the electron strength of the NHC ligands, as observed by the comparison of the IR spectra of **3D**, **3F** and **3E**.

The addition of pyrene or hexafluorobenzene to the imidazolylidene-based complex (**1A**) has a negligible effect on the C-O stretching frequencies, for which a very small change of -0.4 (for pyrene) and +0.5 cm⁻¹ (for C₆F₆) is observed. In the case of the benzoimidazolylidene ligand in complex **1B**, the addition of pyrene has a negligible effect on the $\nu_{\text{av}}(\text{CO})$ (-0.5 cm⁻¹), while in the presence of C₆F₆ a slightly increase on the

$\nu_{\text{av}}(\text{CO})$ is observed ($+1.0 \text{ cm}^{-1}$). In the case of the polyaromatic-imidazolyidene-based complexes (**5C**, **3D**, **3E** and **3F**), the modification is more pronounced, $\nu_{\text{av}}(\text{CO})$ -1.4 for pyrene and $\nu_{\text{av}}(\text{CO})$ up to $+1.5 \text{ cm}^{-1}$ for C_6F_6 . These results indicate that, when NHC ligands decorated with polyaromatic systems are used, the electron-donating character of the ligand can be modified by simply adding the right π -stacking additive. In this regard, the addition of pyrene produces the increase of the electron-donating character of the ligand, while the addition of hexafluorobenzene produces the opposite effect.

Table 3.1 IR C-O stretching frequencies of $[\text{IrCl}(\text{CO})_2]$ complexes. Effects of the addition of pyrene and hexafluorobenzene^[a]

$[\text{L}(\text{IrCl}(\text{CO})_2)]$	Additive	$\nu(\text{CO})^{[b]} (\text{cm}^{-1})$	$\nu_{\text{av}}(\text{CO}) (\text{cm}^{-1})$	$\Delta\nu_{\text{av}}(\text{CO}) (\text{cm}^{-1})$
1A	-	2065.4, 1981.5	2023.4	0
	Pyrene	2064.4, 1981.5	2023.0	-0.4
	C_6F_6	2065.4, 1982.5	2023.9	0.5
1B	-	2068.3, 1985.4	2026.8	0
	Pyrene	2068.3, 1984.4	2026.3	-0.5
	C_6F_6	2069.3, 1986.3	2027.8	1.0
5C	-	2067.3, 1985.4	2026.3	0
	Pyrene	2066.4, 1983.4	2024.9	-1.4
	C_6F_6	2069.3, 1986.3	2027.8	1.5
3D	-	2071.2, 1989.2	2030.2	0
	Pyrene	2070.2, 1987.3	2028.8	-1.4
	C_6F_6	2073.1, 1990.2	2031.6	1.4
3E	-	2072.1, 1989.2	2030.7	0
	Pyrene	2071.2, 1987.3	2029.2	-1.5
	C_6F_6	2073.1, 1990.2	2031.6	0.9
3F	-	2071.2, 1989.2	2030.2	0
	Pyrene	2070.2, 1987.3	2028.8	-1.4
	C_6F_6	2072.1, 1989.2	2030.7	0.5

[a] IR data obtained in CH_2Cl_2 solutions of the complex with saturated solutions of the additive. [b] The resolution of the IR experiments is 0.5 cm^{-1} .

The maximum change in the frequencies that we observed was 2.9 cm^{-1} (for **5C**), relative to the comparison of the situations in which pyrene or hexafluorobenzene are added. This variation is about six times the precision of the routine IR experiment (0.5 cm^{-1}), which is limited by the bandwidth of the respective absorptions and the spectrometer resolution.

For comparative purposes, it is interesting to note that this maximum change is exactly the same as the one observed when comparing the C-O stretching frequencies of the iridium carbonyl complexes based on N,N'-dimethylimidazolylidene and N,N'-dimethylbenzoimidazolylidene ligands. These two NHC ligands are considered significantly different from their electronic point of view.¹³

b) DFT calculations

In order to shed light on the variation of the C-O stretching frequencies in the presence of π -stacking additives, we derived the $\nu_{\text{av}}(\text{CO})$ value of a model $\text{LNi}(\text{CO})_3$ complex by DFT calculations, in which L is the pyrene-based ligand (Figure 3.1). The relative energies of the π -stacking interaction are -15.2 and -9.6 kcal/mol, for the optimized adducts formed by addition of pyrene and hexafluorobenzene, respectively. These energies may be attributed to the π -stacking energies in the gas phase. An interesting information may be derived from the comparison of the calculated values of $\nu_{\text{av}}(\text{CO})$. The $\nu_{\text{av}}(\text{CO})$ value for the pyrene-imidazolylidene ligand without any additive is 2056.1 cm^{-1} . In the presence of pyrene, the calculated value for $\nu_{\text{av}}(\text{CO})$ is 2052.3 cm^{-1} , which means that the $\nu_{\text{av}}(\text{CO})$ decreases in 3.8 cm^{-1} . When hexafluorobenzene is added, the $\nu_{\text{av}}(\text{CO})$ increases in 2.3 cm^{-1} . This DFT calculated $\nu_{\text{av}}(\text{CO})$ shifts are significantly more pronounced than in the experimental studies, because non-covalent interactions are more favourable in the gas phase. However, it is worth mentioning that the theoretical studies are in agreement with the experimental observation in the sense that the addition of pyrene increases the electron-donor strength of the ligand, while the addition of hexafluorobenzene reduces the electron-donating strength.

Figure 3.1 Variation of the $\nu_{\text{av}}(\text{CO})(\text{cm}^{-1})$ values of a pyrene-fused NHC ligand upon addition of pyrene or hexafluorobenzene. The energies correspond to the optimized structures with pyrene or hexafluorobenzene forming the π -stacking adducts, relative to the situation in which these molecules do not interact with the metal complex. Calculations were carried out in Gaussian09 (revision D.1) using the M06L functional, tight optimizations, and the ultrafine integration grid (a pruned (99,590 grid).

c) Electrochemical studies

Very recently have been proposed in the literature that cyclic voltammetry can be used to study the electronic properties of NHC-complexes.¹⁴⁻¹⁶ In our case, we were interested in studying the effect of a π -stacking additive on the redox potential of the Ni(II) complexes. For this purpose, we chose the Ni(II)-based complexes **2A**, **2B** and **6C** since they show reversible one-electron waves.

We first performed the cyclic voltammetry of the nickel complexes **2A**, **2B** and **6C** in dichloromethane. As shown in Figure 3.2, all the nickel complexes displayed a one-electron reversible wave that corresponds to the metal-centred redox process. The half-wave potentials ($E_{1/2}$) of the metal complexes were determined by the differential pulse voltammetry (DPV) analysis. The $E_{1/2}$ values for complexes **2A** and **6C** were found to be identical (0.659 V), while complex **2B** exhibited a slightly higher value (0.684 V). The slightly higher oxidation potential displayed by **2B**, indicates a slightly lower degree of electron-donating power for the benzimidazolyliidene ligand.

Figure 3.2 Cyclic voltammogram (a) and relevant section of the DPV (b) of complexes **2A**, **2B** and **6C**. Measurements performed in dry CH_2Cl_2 using 0.1 mM analyte, 0.1 M $[\text{NBu}_4]\text{PF}_6$ as the electrolyte at 100 mVs^{-1} scan rates and referenced to SCE by shifting ferrocene to 440 mV

Because we wanted to study whether the electronic properties of the NHC ligands with different number of fused-aromatic rings are modified by the addition of a π -stacking additive, we performed the DPV experiments of the nickel complexes **2A**, **2B** and **6C** in the presence of different amounts of pyrene. For this purpose, we fixed the concentration of the metal complexes, and gradually added successive amounts of pyrene, from 0 to 10 equivalents with respect to the metal complex. The results for complex **6C** are graphically represented in Figure 3.3 (a) (the DPV diagrams for the same experiment carried out with complexes **2A** and **2B** are displayed in the Experimental Section, Chapter 6). As can be seen from the results shown in Figure 3.3, the pyrene–NHC nickel complex **6C** is very sensitive to the addition of pyrene, and a maximum positive shift on the half-wave potential was achieved when one equivalent of pyrene had been added ($\Delta E_{1/2} = 75 \text{ mV}$). For the experiments carried out with complexes **2A** and **2B**, the potential was also modified, and the maximum shift was also achieved for the addition of one equivalent of pyrene, but the shift was much lower than that for **6C** (for **2A**, $\Delta E_{1/2} = 24 \text{ mV}$; for **2B**, $\Delta E_{1/2} = 35 \text{ mV}$). This experiment suggests that the three complexes (**2A**, **2B** and **6C**) are sensitive to the addition of pyrene, but the complex with a pyrene-imidazolyliidene ligand (**6C**) is more sensitive, probably because the pyrene fragment attached to the NHC ligand facilitates the π – π interaction between the NHC ligand and pyrene.

Figure 3.3 a) DPV diagrams of complex **6C**, with addition of different amounts of pyrene (from 0 up to 10 equivalents, from left to right); b) graphical representation of the $E_{1/2}$ values of complexes **2A**, **2B** and **6C**, upon addition of different amounts of pyrene. Measurements performed in dry CH_2Cl_2 using 1 mM analyte, 0.1 M $[\text{NBu}_4]\text{PF}_6$ as the electrolyte, at 100 mVs^{-1} scan rates and referenced to SCE by shifting ferrocene to 440 mV.

3.2.2 Quantification of the non-covalent interactions between NHC ligands and π -stacking additives. Association constants

In the following sections, we will describe our studies aiming to quantify the interaction between polyaromatic-imidazolyliidene-based complexes and π -stacking additives, such as pyrene and hexafluorobenzene. Such studies were performed by ^1H NMR and UV-vis absorption means, and by DFT calculations. We chose **3D** and **7C** as model compounds for our studies.

3.2.2.1 ^1H NMR studies of complex **3D**

One of the most common techniques for the study of intermolecular interactions is NMR spectroscopy, since the formation of host/guest species often produces changes in the chemical shift of various atomic-nuclei present.¹⁷⁻¹⁹ As a result of this variation, it is possible to establish the regioselectivity of the guest binding and the association constant (K_a).^{18,20} If the host-guest equilibrium is fast on the NMR time-scale, the chemical shift observed corresponds to a weighted average of the host-guest complex and the free species, while if the host-guest equilibrium is slow on the NMR time-scale, then the signals due to the free and bound species are observed separately. For the full analysis of the interaction, at least, two sets of ^1H NMR experiments are needed.¹⁷ The first one is known as ‘Job plot’ (also known as the Method of Continuous Variations-

MCV), for the determination of the stoichiometry of the host-guest complex. The second approach is an NMR titration experiment, and provides information about the value of the association constant (K_a).

Among all complexes that we described in Chapter 2 with extended polyaromatic NHC ligands, we selected **3D** to carry out the ^1H NMR experiments, both the Job plots and the NMR titrations. In our case, we will consider that the guest is the organometallic compound, and the host is pyrene or hexafluorobenzene. All the NMR experiments were carried out in a $\text{CD}_3\text{OD}/\text{CDCl}_3$ 1:2 mixture at 25°C (see Experimental Section in Chapter 6 for further details). We chose this methanolic-based mixture because polar solvents favour the π - π interactions, and CDCl_3 facilitates the solubility of the compounds.

One of the first consequences of the analysis of the ^1H NMR spectra after addition of the π -stacking additives is that we can establish in which part of the molecule the interaction occurs. This can be done by simply observing which signal is shifted on the ^1H NMR spectrum.¹⁸ When pyrene is used for the ^1H NMR titration, the proton labelled as H_c is shifted to lower-frequencies (Figure 3.4). When the experiments were performed with C_6F_6 , the signal due to proton H_e is shifted to higher frequencies (Figure 3.5). This observation is in agreement with the deshielding or shielding of the proton, depending on the addition of hexafluorobenzene or pyrene, respectively. The interaction with the above mentioned protons of the complex, allowed us to conclude that the aggregates formed must be similar to the ones showed in Figure 3.6. Pyrene (π -donor ring) prefers to interact with the ring with the lower π -electron density, which in **3D** is the pyrazine fragment (π -acceptor ring). This interaction is in agreement with the shielding at proton H_c . This suggestion is in agreement with the fact that some studies have demonstrated that heterocycles with one or more nitrogen are prone to suffer π - π stacking.²¹ On the other hand, C_6F_6 (π -acceptor ring) prefers to interact with the pyrene fragment (π -donor ring) of **3D**, producing a deshielding at the proton H_e .

Figure 3.4 ^1H NMR spectra of **3D** with the addition of different amounts of pyrene using $\text{CD}_3\text{OD}/\text{CDCl}_3$ 1:2 mixture as solvent at 25°C . The concentration of **3D** was fixed at 3.1 mM. From top to bottom the concentrations of pyrene are: a) 0.00, b) 0.05, c) 0.08, d) 0.11, e) 0.15 and f) 0.22 M

Figure 3.5 ^1H NMR spectra of **3D** with the addition of different amounts of C_6F_6 using $\text{CD}_3\text{OD}/\text{CDCl}_3$ 1:2 mixture as solvent at 25°C . The concentration of **3D** was fixed at 0.31 mM. From top to bottom the concentrations of C_6F_6 are: a) 0.00, b) 0.43, c) 0.72, d) 1.16, e) 1.44 and f) 2.89 M

Figure 3.6 Possible regioselectivity of **3D**-additive.

The Job plot experiment allows to determine the stoichiometry of a host:guest complex, by making up a series of solutions with varying host:guest ratios, so that the total concentration of 'host + guest' is maintained constant ($[H] + [G] = 1.8$ mM using pyrene and **3D**, $[H] + [G] = 1.9$ mM using C_6F_6 and **3D**) and then studying the shifts produced on the 1H NMR signals of the resulting solutions. Figure 3.7a shows the Job plot treatment of complex **3D** with pyrene and hexafluorobenzene. The Job plot reveals a maximum when the same amount of **3D** and pyrene (or hexafluorobenzene) are present (molar fraction, $\chi = 0.5$), and therefore the stoichiometry of the aggregates is 1:1, meaning that the interaction is between one molecule of **3D** and one molecule of additive (pyrene or hexafluorobenzene).

The Benesi-Hildebrand experiment is an NMR titration that consists of maintaining a fixed concentration of the guest ($[3D] = 3.1$ mM using pyrene as additive, $[3D] = 0.31$ mM using C_6F_6 as additive) while gradually increasing the concentration of the host ($[pyrene] = 0.05, 0.08, 0.11, 0.15, 0.22$ M, $[C_6F_6] = 0.43, 0.72, 1.16, 1.44, 2.89$ M). From this experiment, the association constant, K_a , can be obtained using the Equation 3.1,¹⁷ which establishes that the shift in δ ($\Delta\delta$) produced by the host/guest adduct is related to K_a and to the concentration of the host ($[H]$).

$$\frac{1}{\Delta\delta} = \left(\frac{1}{K_a \Delta\delta_{max}} \right) \frac{1}{[H]} + \frac{1}{\Delta\delta_{max}}$$

Equation 3.1 Benesi-Hildebrand treatment

The plots arising from the Benesi-Hildebrand treatment, allowed determining the association constants for the formation of the aggregates between **3D** and the two additives. These are $K_a = 2.21 \text{ M}^{-1}$ and $K_a = 0.13 \text{ M}^{-1}$, for the formation of adducts with pyrene and hexafluorobenzene, respectively (Figure 3.7). These values are in agreement, with our theoretical calculations, which established a higher π -stacking affinity of pyrene compared to the one shown by hexafluorobenzene, with the $Ni(CO)_3$ complex bound to a pyrene-fused NHC.

Figure 3.7 Job plot for determination of stoichiometry of **3D** with a) pyrene and c) C_6F_6 . Determination of the association constant of **3D** with b) pyrene and d) C_6F_6 . For **3D**-pyrene interaction, the Benesi-Hildebrand data treatment gives $\Delta\delta_{\max} = 0.79$ ppm and $K_a = 2.21$ M⁻¹. For **3D**- C_6F_6 interaction, the Benesi-Hildebrand treatment gives $\Delta\delta_{\max} = 0.344$ ppm and $K_a = 0.13$ M⁻¹

3.2.2.2 Quantification of the interaction between pyrene and **7C**

In Section 3.2.1 we demonstrated that π -stacking additives, such as pyrene, can modify the electronic properties of the pyrene-imidazolyliene ligand **C**. In this section we will try to shed some more light onto the nature of the binding between pyrene and complexes with polyaromatic NHC ligands. For the study we have used experimental

and theoretical approaches. The experimental approaches include UV-vis absorption and ^1H NMR titrations, while the theoretical studies are based on DFT methods. The DFT calculations were performed by Dr. Gregori Ujaque at the Universitat Autònoma de Barcelona. In order to carry out these studies we selected pyrene and complex **7C** as model.

UV-vis absorption studies

Compounds that contain conjugated organic groups usually absorb strongly in the ultraviolet or visible regions of the electromagnetic spectrum. If these groups are involved in π -stacking or binding to a guest, then their Uv-vis bands will be shifted in response to the aggregation or host-guest binding.²² We carried out the UV-vis absorption studies of complex **7C** and pyrene in methanol at room temperature. In this study, the concentration of pyrene was kept unchanged while the concentration of **7C** was gradually increased, as described in the literature for related studies.²⁰ As can be seen in Figure 3.8, the intensity of the bands increased upon the addition of increasing amounts of complex **7C**. This effect is typically due to the formation of an π - π -stacking adduct,^{9,20,23-26} which in our case involves the aggregation of pyrene and complex **7C**. At this point, and based on the studies that we carried out with complex **3D**, we believe that the interaction takes place at the pyrene fragment of complex **7C**. In order to corroborate this hypothesis, we carried out ^1H NMR experiments.

Figure 3.8 Enhancement in the intensity of the absorption of pyrene (5×10^{-6} M) with increasing amounts of **7C**, in methanol at room temperature. The concentration of **7C** from bottom to top are 0, 2, 10, 16, 24 and 30 ($\times 10^{-7}$ M)

¹H NMR titration

In order to locate the pyrene-**7C** interaction, we gradually added pyrene (0-10 equivalents) to a CD₃OD/CDCl₃ solution of **7C**, and took the ¹H NMR spectra of the resulting solutions. Figure 3.9 shows the series of ¹H NMR spectra (See Experimental Section in Chapter 6 for further details). By comparing the spectra, it becomes clear that the signals due to the pyrene fragment (*H_b*) of the NHC ligand, are progressively shifted to lower frequencies. This experiment suggests that a π - π interaction is being produced between the pyrene and the polyaromatic fragment of ligand **C**.

Figure 3.9 ¹H NMR titration of complex **7C** with pyrene in CDCl₃/CD₃OD at 25°C. The equivalent of pyrene from the top to bottom are a) 0, b) 1, c) 2, d) 3 and e) 10.

Theoretical studies

The π - π interactions have been largely studied by means of theoretical approaches.²⁷⁻²⁹ We analysed the interaction between pyrene and the palladium-based complexes **3A**, **3B** and **7C**. For DFT-based methods, inclusion of dispersion was shown to be mandatory for their proper description.^{30,31} For complexes **3A**, **3B** and **7C**, we considered that pyrene may interact with any of the aromatic ligands contained in the complexes, thus including 3-chloropyridine. Table 3.2 shows the relative energies for the calculated system palladium complexes interacting with pyrene. In complexes **3A** and **3B**, pyrene prefers to interact to the 3-chloropyridine fragments instead of interacting with the NHC ligands, as observed by the relative energies between 3-chloropyridine and pyrene for complex **3A** (-3.1 kcalmol⁻¹), and **3B** (-1.4 kcal mol⁻¹). However, in the case of complex **7C**, the interaction with the NHC ligand is favoured by 2.3 kcal mol⁻¹. The calculated

energies for the pyrene-complex also demonstrated that the interaction mainly depends of the nature of the NHC-ligand, and the greater the aromatic wall the larger the energy interaction between pyrene and the NHC ligand.

Table 3.2 Relative energies for the calculated system Pd complexes + pyrene.^[a]

Complex	Additive	Pyrene interact with	
		NHC ligand	3-chloropyridine
3A		0	-3.1
3B	pyrene	0	-1.4
7C		0	2.3

[a] Energies in kcal mol⁻¹

Figure 3.10 Optimized geometries for the system complex **7C** + pyrene. a) pyrene on the NHC side, b) pyrene on the 3-chloropyridine side.

3.2.3 Catalytic studies. C-C cross coupling reactions

The preparation of the palladium and nickel complexes with a family of related NHC ligands, offers a good opportunity for the comparison of their catalytic activity, and to determine if the reactions are affected by the addition of π -stacking additives. Among all the C-C cross coupling reactions, we chose the Suzuki-Miyaura coupling and α -arylation of ketones to test the catalytic activity of the Ni and Pd-based complexes. It is well known that both types of metal complexes may display good activities in the Suzuki-Miyaura coupling, although the studies regarding the use of Ni-NHC complexes

in this reaction are still not very common,³²⁻⁴³ and only a few recent examples refer to the use of [NiCp(NHC)X] complexes.^{32-34,36}

In this section we will describe the catalytic studies using the Ni(II) and Pd(II) complexes. We will pay special attention to the results shown by the reactions carried out in the presence of π -stacking additives, such as pyrene.

3.2.3.1 Suzuki-Miyaura coupling

As we mentioned above, many Ni(II) and Pd(II) display good activities in the Suzuki-Miyaura cross-coupling reaction. As shown in Scheme 3.1 the reaction consists of the coupling between an arylboronic acid and an arylhalide. In the following subsection we discuss the results that we obtained using the series of Ni(II) and Pd(II)-based complexes as catalyst.

Scheme 3.1 Suzuki-Miyaura coupling reaction

a) Ni(II) complexes

We decided to test the nickel complexes **2A**, **2B** and **6C** in the Suzuki-Miyaura coupling reaction. The reactions were carried out in toluene at 90°C for 50 minutes, using a 3 mol% of catalyst loading and K₃PO₄ as base. These conditions were similar to those previously reported by several authors.^{32,34,36} The results are summarized in Table 3.3. All the complexes afforded low yields to the final products, compared to other previously reported [NiCp(NHC)X] complexes used in this same reaction.^{32-34,36} Only complex **2B** gave moderate yields for the coupling of 4-bromoacetophenone with phenylboronic acid (entry 6).

b) Pd(II) complexes

In a first screening we tested the complex **7C** in the Suzuki-Miyaura cross-coupling reaction. The reactions were carried out in 1,4-dioxane, in the presence of cesium carbonate, using a 2 mol% of catalyst loading. Table 3.4 displays the results obtained. The catalyst provides good activities for the coupling of a series of arylbromides, when the reactions are allowed to proceed during two hours at 80°C. For the coupling of arylchlorides, longer reaction times or higher temperatures were needed, and even then

only activated arylchlorides (4-chloroacetophenone), could be coupled in moderately high yields (entries 9, 13 and 17, Table 3.4). None of the reactions showed the formation of side-products coming from the homo-coupling of the arylboronic acid, thus despite the moderate yields, all reactions showed excellent selectivities.

This first screening allowed us to establish the reaction conditions to start the comparative studies with complexes **3A** and **3B**. For our study, we decided to study the coupling between phenylboronic acid and bromobenzene, using 2% of catalyst loading, at 80 °C for 2 hours. As shown in Table 3.5, catalyst **7C** exhibits the best catalytic activity under these reaction conditions. We were interested in determining if the addition of a good π -stacking additive may have some influence in the catalytic outcome, and for this reason we added different amounts of pyrene to the reaction medium, and compared the results obtained. The results shown in Table 3.5 (entries 9-12) show that the efficiency of the process is not sensitive to the presence of pyrene, regardless of the amount of pyrene added to the reaction medium. The catalytic activity of complexes **3A** and **3B** was not affected by the addition of 0.35 mmol of pyrene, which represents a 100% mol with respect to the initial amount of substrates. These results clearly contrast with those previously reported by our group, which demonstrated that the presence of pyrene modifies the catalytic activity of complexes containing a polyaromatic fragment in their structure,⁹ so we thought that the results obtained should be affected by other factors. One of the most probably explanation is the possibility that the process is heterogeneously catalysed. In order to evaluate this possibility, we decided to perform the mercury-drop experiment.⁴⁴ In the presence of mercury the yields obtained were clearly lower, indicating that the process is very likely to be heterogeneous, and hence to display little sensitivity to the addition of pyrene (entries 2, 5 and 8, Table 3.5).

Table 3.3 Suzuki-Miyaura cross coupling between phenylboronic acid and aryl halides^[a]

Entry	Catalyst	R	Yield [%] ^[b]
1	 2A	COCH ₃	30
2		CH ₃	8
3		H	11
4		OCH ₃	4
6	 2B	COCH ₃	59
7		CH ₃	22
8		H	17
9		OCH ₃	12
10	 6C	COCH ₃	26
11		CH ₃	11
12		H	28
13		OCH ₃	10

[a] Reaction conditions: a solution of aryl halide (0.18 mmol), phenylboronic acid (0.18 mmol), K₃PO₄ (0.47 mmol), and the catalyst (3 mol %) in toluene (2 mL) was heated at 90 °C for 50 min. [b] Yields obtained by GC analysis using anisole as internal reference.

Table 3.4 Suzuki-Miyaura cross coupling between phenylboronic acid and aryl halides using **7C** as catalyst^[a]

Entry	T(°C)	t (h)	R	X	R'	Yield [%] ^[b]
1	80	2	H	Br	H	79
2	80	2	CH ₃	Br	H	69
3	80	2	COCH ₃	Br	H	84
4	80	2	OCH ₃	Br	H	63
5	80	2	OCH ₃	Br	CH ₃	65
6	80	2	COCH ₃	Cl	H	51
7	80	4	H	Cl	H	9
8	80	4	CH ₃	Cl	H	5
9	80	4	COCH ₃	Cl	H	59
10	80	4	OCH ₃	Cl	H	5
11	100	2	H	Cl	H	10
12	100	2	CH ₃	Cl	H	7
13	100	2	COCH ₃	Cl	H	72
14	100	2	OCH ₃	Cl	H	6

15	120	2	H	Cl	H	19
16	120	2	CH ₃	Cl	H	18
17	120	2	COCH ₃	Cl	H	73
18	120	2	OCH ₃	Cl	H	13

[a] Reaction conditions: aryl halide (0.35 mmol), phenylboronic acid (0.35 mmol), Cs₂CO₃ (0.7 mmol), and the catalyst (2 mol %) in 1,4-dioxane (2 mL). [b] Yields obtained by GC analysis using anisole as internal reference.

Table 3.5 Suzuki-Miyaura coupling between phenylboronic acid and bromobenzene^[a]

Entry	Catalyst	Additive (mmol)	Yield [%] ^[b]
1		-	46
2 ^[c]		Hg	39
3		Pyrene (0.350)	50
4		-	60
5 ^[c]		Hg	38
6		Pyrene (0.350)	60
7		-	71
8 ^[c]		Hg	53
9		Pyrene (0.035)	70
10		Pyrene (0.175)	67
11		Pyrene (0.350)	64
12		Pyrene (0.700)	67

[a] Reaction conditions: a solution of bromobenzene (0.35 mmol), phenylboronic acid (0.35 mmol), Cs₂CO₃ (0.7 mmol), and the catalyst (2 mol %) in 1,4-dioxane (2 mL) was heated at 80°C for 2h. [b] Yields obtained by GC analysis using anisole as internal reference. [c] One drop of mercury was added after 10 min of the reaction start.

3.2.3.2 α -Arylation of ketones

The α -arylation of ketones is a C-C cross coupling reaction, which consists of the coupling between an alkyl-ketone with an aryl halide, affording the corresponding α -arylated product (Scheme 3.2). This reaction was reported in the same year by three different authors, Miura,⁴⁵ Buchwald⁴⁶ and Hartwig.⁴⁷ In general, the reaction is carried out with alkyl-ketone and an aryl halide in the presence of a palladium-based catalyst and a strong base.^{11,46-56} For this reaction, sodium *tert*-butoxide is often the base of choice because it is capable of deprotonating the alkyl-ketone and also form the

catalytic active species of Pd.^{46,48,53} As in other cross-coupling reactions, electron-rich ligands trend to stabilize the palladium(II) intermediate, favouring the oxidative addition of the aryl halide.⁴⁸

Scheme 3.2 α -Arylation of ketones

In this subsection we describe the catalytic activity of the palladium complexes **3A**, **3B** and **7C** in the α -arylation of ketones. We focused our attention in the influence of the addition of pyrene in the efficiency of the process. We also tested the activity of the nickel **2A**, **2B** and **6C**, but they all resulted inactive under the reaction conditions used.

a) Palladium(II) complexes

The reactions were carried out in 1,4-dioxane, using a catalyst loading of 1 mol %. As a model reaction, the coupling between propiophenone and bromotoluene was studied. We decided to run the reactions at a moderate temperature (80 °C), in order to avoid that the decomposition of the catalyst, which may give rise to nanoparticles that may heterogeneously catalyse the process. Interestingly, complex **7C** shows a better activity than **3A** despite both NHC ligands have a similar electron donating strength as we demonstrated above. When the reactions were tested in the presence of 0.05 mmol of pyrene (10% mol with respect to the ketone), the catalytic activity of complexes **3A** and **3B** were not affected, while the activity of complex **7C** clearly decreases. The addition of pyrene reduced the activity of catalyst **7C** by 8–16%, whereas for **3A** and **3B** this variation ranged between 3 and 4%, probably falling within the experimental error. It is worth mentioning that the catalytic activity of **7C** is not affected when aliphatic ketones, such as 3,3-dimethylbutan-2-one and 2,2-dimethylpent-3-one, are used as substrates (entries 27-32, Table 3.6). This result supports the idea of the π -stacking effect influencing the reactivities of those substrates capable of interact *via* π -stacking with the catalyst (aromatic ketones), while not affecting those substrates not capable of π -stacking (aliphatic ketones).

Table 3.6 α -Arylation of ketones using **3A**, **3B** and **7C** as catalysts^[a]

Entry	Complex	X	R ¹	R ²	R ³	Additive	Yield [%] ^[b]
1		Br	H	C ₆ H ₅	CH ₃	--	7
2		Br	H	C ₆ H ₅	CH ₃	Pyrene ^[c]	9
3	 3A	Br	CH ₃	C ₆ H ₅	CH ₃	--	23
4		Br	CH ₃	C ₆ H ₅	CH ₃	Pyrene ^[c]	20
5		Br	OCH ₃	C ₆ H ₅	CH ₃	--	13
6		Br	OCH ₃	C ₆ H ₅	CH ₃	Pyrene ^[c]	10
7		Br	H	C(CH ₃) ₃	H	--	50
8		Br	H	C(CH ₃) ₃	H	Pyrene ^[c]	46
9	 3B	Br	H	C ₆ H ₅	CH ₃	--	36
10		Br	H	C ₆ H ₅	CH ₃	Pyrene ^[c]	31
11		Br	CH ₃	C ₆ H ₅	CH ₃	--	79
12		Br	CH ₃	C ₆ H ₅	CH ₃	Pyrene ^[c]	81
13		Br	OCH ₃	C ₆ H ₅	CH ₃	--	60
14		Br	OCH ₃	C ₆ H ₅	CH ₃	Pyrene ^[c]	59
15	 7C	Br	H	C ₆ H ₅	CH ₃	--	31
16		Br	H	C ₆ H ₅	CH ₃	Pyrene ^[c]	16
17		Br	CH ₃	C ₆ H ₅	CH ₃	--	36
18		Br	CH ₃	C ₆ H ₅	CH ₃	Pyrene ^[c]	27
19		Br	OCH ₃	C ₆ H ₅	CH ₃	--	40
20		Br	OCH ₃	C ₆ H ₅	CH ₃	Pyrene ^[c]	31
21		I	H	C ₆ H ₅	CH ₃	--	38 ^[d]
22		I	H	C ₆ H ₅	CH ₃	Pyrene ^[c]	26 ^[d]
23		I	OCH ₃	C ₆ H ₅	CH ₃	--	78 ^[d]
24		I	OCH ₃	C ₆ H ₅	CH ₃	Pyrene ^[c]	70 ^[d]
25		Br	H	C(CH ₃) ₃	H	--	62
26		Br	H	C(CH ₃) ₃	H	Pyrene ^[c]	66
27		Br	CH ₃	C(CH ₃) ₃	CH ₃	--	36
28		Br	CH ₃	C(CH ₃) ₃	CH ₃	Pyrene ^[c]	35
29		Br	OCH ₃	C(CH ₃) ₃	CH ₃	--	48
30		Br	OCH ₃	C(CH ₃) ₃	CH ₃	Pyrene ^[c]	49
31		I	H	C(CH ₃) ₃	CH ₃	--	63 ^[e]
32		I	H	C(CH ₃) ₃	CH ₃	Pyrene ^[c]	62 ^[e]

[a] Reactions conditions: A solution of aryl halide (0.6 mmol), alky-ketone (0.5 mmol), NaO^tBu (0.7 mmol), and the catalysts (1 mol %) in 1,4-dioxane (2 mL) at 80 °C for 6 h. [b] Yields obtained by GC analysis using anisole as internal reference. [c] 0.05 mmol of pyrene was added. [d] *t* = 1 h. [e] *t* = 2h.

In order to corroborate that these results are consistent all along the process, we carried out the reaction progress analysis. We decided to monitor the α -arylation of propiophenone with 4-bromotoluene, using the three catalysts, namely **3A**, **3B** and **7C** (Figure 3.11). We also studied the reaction progress adding 10% mol of pyrene. The reaction conditions were the same as those shown in Table 3.6. As can be seen in the reaction profiles, upon addition of pyrene, the reaction catalyzed by **7C** shows an important decrease in the activity all along the course of the reaction, and produces a final decrease of the reaction yield of 10%. On the contrary, the reactions catalyzed by **3A** and **3B** were basically unaffected by the addition of pyrene, all along the reaction profile. These results rule out that the difference in activity between the catalyst may be ascribed to the different stabilities of the metal compounds, and indicate that the inhibiting character of pyrene is kinetic in nature.

Figure 3.11 Time-course reaction profiles for the reaction of 4-bromotoluene and propiophenone. Reaction conditions: 4-bromotoluene (0.6 mmol), propiophenone (0.5 mmol), NaOtBu (0.7 mmol), and the catalyst (1 mol%) in 1,4-dioxane (2 mL) at 80 °C. Where stated, 0.05 mmol pyrene was added

3.3 Conclusions

We demonstrated that the electronic properties of the NHC ligands with extended polyaromatic systems, as well as the catalytic activity of the metal complexes, are affected by π -stacking additives. The interaction between the NHC ligand and π -stacking additives is mainly produced on the aromatic fragment of the NHC ligand, and has important catalytic consequences. More precisely:

- The FT-IR studies of the carbonyl complexes described in Chapter 2 demonstrated that the addition of pyrene decreases the CO stretching frequencies, while C₆F₆ causes exactly the opposite effect, and therefore the electronic nature of the NHCs with the polyaromatic backbones can be fine-tuned by the addition of the suitable additive. This observation matches perfectly with the DFT calculations on the formation of π -stacking aggregates between a complex formed by Ni(CO)₃ bound to a pyrene-NHC with a pyrene. The electron-donor strength of the polyaromatic-NHC ligands increases upon addition of pyrene and decreases upon addition of C₆F₆.
- The electrochemical studies of the nickel complexes (**2A**, **2B** and **6C**) have revealed that the presence of a π -stacking additive shifts positively their half-wave potentials. However, the shift is more significant for the case of complex **6C**, having the pyrene-NHC ligand. We thought that this higher positive shift is probably due to the π - π interaction of the pyrene-imidazolyliene ligand with the pyrene.
- The π -stacking affinities and the location of the interaction of complex **3D** with pyrene and hexafluorobenzene, were unambiguously determined by means ¹H NMR. In this particular case, pyrene forms more stable aggregates than hexafluorobenzene, as seen by the higher K_a shown by the first one.
- The addition of pyrene to complex **7C** was studied by UV-vis spectroscopy, ¹H NMR titration and DFT calculations. All these studies have demonstrated unambiguously that the pyrene interacts exclusively over the aromatic-NHC fragment of the complex **7C**, *via* π - π stacking.
- The addition of π -stacking additives has important implications in the catalytic performances of the catalysts. In the catalytic α -arylation of ketones, only the catalytic activity of the pyrene-decorated complex **7C** is partially inhibited by the addition of small amounts of pyrene. Probably the stacking interaction between the pyrene and the NHC ligand is quenching the benefits provided by the presences of the rigid polyaromatic ligand.

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Chapter 4

**Synthesis and characterization of
bis- and tris(NHC) complexes with
highly extended polyaromatic
systems**

4.1 Introduction

Among all the NHC frameworks described in the literature, those featuring rigid isolated carbene moieties, which prevent chelation, have found great utility in several fields.¹⁻⁷ Bis(NHC)s featuring two linearly opposed NHCs are often referred to as *Janus*-type bis(carbenes), due to the analogy with the representation of the roman god *Janus*, who had two faces looking at opposite directions. These ligands can give access to structurally dynamic homopolymers⁸⁻¹¹ and polymetallic catalysts, whose properties are fundamentally different from those provided by their monometallic analogues.² The control over the length and width of the bis(NHC) is very important, because it will influence the catalytic activity and selectivity of the system.^{12,13} Bis(NHC) ligands with rigid polyaromatic linkers constitute excellent building blocks for the preparation of discrete molecular species and supramolecular assemblies, in which the shape of the molecule can be carefully controlled by the right choice of the bis(carbene) ligand.

The first example of a *Janus*-type bis(NHC) ligand reported in the literature, was the benzobis(imidazolylidene) (Chart 4.2, **II**) described by Bielawski and co-workers.¹⁴ The use of this ligand allowed the preparation of homo-dimetallic complexes of Ag(I),¹⁵ Rh(I),^{15,16} Rh(III),¹⁷ Ir(I),¹ Ir(III),¹⁷ Fe(II),¹⁸ Ru(II),^{18,19} Ni(II),^{16,20-22} Pt(II)^{14,16,21-24} and Au(I).²⁵ The through-space distance established by the benzobis(imidazolylidene) ligand between two metals is 10.6 Å. However, this bis(NHC) has never been used for the synthesis of hetero-dimetallic complexes, and therefore has not yet been used in heterometallic catalysis.

Another *Janus*-type bis(NHC) ligand, which has been widely used for the preparation of dimetallic species is the 1,2,4-trimethyltriazol-3,5-diylidene ligand (also called “*ditz*”, **I** in Chart 4.2). By using *ditz*, homo-dimetallic compounds based on Rh(I),²⁶ Ir(I),²⁶ Ir(III),²⁷ Ru(II),²⁸ Pd(II),²⁹⁻³² Pt(II)³³ and Au(I)^{34,35} were described. Probably more interesting are the different approaches developed in our research group for the preparation of hetero-dimetallic species, by combining Ir(I)/Rh(I),²⁶ Ir(III)/Rh(I),²⁷ Ir(III)/Pd(II),^{36,37} Ir(III)/Pt(II),³³ Ir(III)/Au(I),³⁴ Ir(III)/Ru(II)³⁸ and Ru(II)/Pd(II)⁷ centres. The preparation of such hetero-dimetallic complexes allowed for the study several catalytic processes, in which each of the metal centres facilitated mechanistically independent cycles (Chart 4.1).^{2,33,34,37,39} In such studies, it became

evident that the two metals are mutually collaborating in the activation of each individual catalytic reaction comprised in the tandem sequence. These seminal works opened a very innovative conceptual advance in the field of homogeneous catalysis, and many research groups are now on the run for the preparation of heterometallic species for tandem catalysis. From the very simple idea of supporting two orthogonal metal fragments with a single-frame ligand, our research group was able to design highly efficient methods for facilitating sophisticated organic transformations that would otherwise require the use of very complicated experimental procedures.^{2,33,34,37,39}

Chart 4.1 Tandem catalytic process

More recently, our research group developed synthetic procedures for the preparation of *Janus*-type bis(NHC) with extended polyaromatic systems, such as the pyrene-^{40,41} and pyracene-based^{4,42} bis(NHC)s labelled as **III** and **IV** in Chart 4.2, respectively. As can be graphically seen in the chart, these bis(NHC)s allow to establish a metal-to-metal through-space separation in the range of 6-14 Å (**I-IV**) (Chart 4.2).

Chart 4.2 Bis(NHC)-based complexes

Together with these linear bis(NHC)s a set of threefold symmetry rigid tris(NHCs) were also reported (Chart 4.3).^{5,6,43-45} These are restricted to the triptycene-based tris(NHC) reported by Bielawski in 2010 (Chart 4.2, V),⁴⁴ the triphenylene-based-tris(NHC)^{5,6,43} and the tribenzotriquinacene-tris(NHC)⁴⁵ described recently in our laboratories. Compared to V and VII, VI has the advantage of having the three carbenes connected by a π -delocalized polyaromatic system, therefore enabling it with the potential to serve as a building block for constructing electronically active materials.

Chart 4.3 Ligands based on Tris(NHC)

Based on these literature precedents, and in the experience of our research group in the development of new polytopic NHC-based ligands with extended polyaromatic systems, we decided to prepare new *Janus* and star-shaped poly-NHC ligands with higher extended polyaromatic systems (Chart 4.4, K and L). The work described in this chapter constitutes an important leap forward in the design of rigid polytopic carbenes, since it allows the separation between the edges of the ligands at unusual large distances, which enable the separation of the metal fragments at the nano-scale. The preparation of these new systems involves the incorporation of pyrazine fragments in their backbones. The introduction of pyrazine is an extra asset for the application of our ligands, because this fragment is present in a large number of natural⁴⁶⁻⁵⁰ and pharmaceutical⁵¹⁻⁵⁵ compounds. Furthermore, pyrazine is an excellent building block for the design of a manifold molecular-architectures, which have been used in different areas of material science; such as electroluminescent materials,⁵⁶ dyes,⁵⁷ organic semiconductors⁵⁸⁻⁶⁵ and chemical switches.^{66,67}

Chart 4.4 NHC ligands **K** and **L**

4.2 Results and discussion

The results described in this chapter are presented in four subsections. The first one describes the synthesis and characterization of the new bis- and tris(azolium) salts, which are the precursors of bis- and tris(NHC) ligands **K** and **L**, respectively. The coordination of the azolium salts to iridium is described in detail in the second section. The third part of the chapter deals with the study of the electronic properties of the bis(NHC) ligand **K** upon addition of compounds that facilitate the formation of π -stacking aggregates, such as pyrene and hexafluorobenzene. The final section describes the study of the binding between the bis(NHC) **K** and pyrene.

4.2.1 Synthesis and characterization of the bis- and tris(azolium) salts

a) Synthesis and characterization of quinoxalino[2',3':9,10]phenanthro[4,5-abc]phenazine-based bis(azolium) salts

Taking into account the preparation of mono(azolium) salts **[D-H](X)**, **[E-H](X)** and **[F-H](X)** described in Chapter 2, we designed a synthetic procedure based on the direct condensation of pyrene-4,5,9,10-tetraone (or 2,7-di-*tert*-butylpyrene-4,5,9,10-tetraone) with 1,3-dibutyl-5,6-diaminobenzimidazolium iodide.

At this point, it is important to point out that the 1,3-dibutyl-5,6-diaminobenzimidazolium iodide, recently described by Tapu,⁶⁸ constitutes an excellent scaffold for the preparation of NHC ligands with fused polycyclic heteroaromatic moieties. By following the procedure depicted in Scheme 4.1, we were able to prepare

the bis(azolium) salts **[J-H₂](I)₂** and **[K-H₂](I)₂** in 75 and 73% yield, respectively. The presence of the *tert*-butyl group in the framework of **[K-H₂](I)₂** is very important, because increases its solubility in organic solvents, making this bis(azolium) salt more suitable for coordination than **[J-H₂](I)₂**. In order to avoid halide scrambling in future reactions with metals containing halides, the related PF₆⁻ salt was obtained by anion metathesis between **[K-H₂](I)₂** and NH₄PF₆ in a methanol/dichloromethane mixture. These bis(azolium) salts were characterized by NMR spectroscopy, mass spectrometry, and elemental analysis. Attempts to collect the ¹³C NMR spectrum of **[J-H₂](I)₂** were unsuccessful due to its low solubility in organic solvents. As an example, the spectroscopy characterization of **[K-H₂](I)₂** will be discussed in detail.

Scheme 4.1 Synthesis of bis(azolium) salts **[J-H₂](I)₂** and **[K-H₂](X)₂**

¹H NMR of **[K-H₂](I)₂**

Figure 4.1 shows the ¹H NMR spectrum of **[K-H₂](I)₂**. The number and integration of the signals displayed on the spectrum are in agreement with the *D*_{2h} symmetry of the compound. The signal corresponding to the acidic proton of the NCHN (*a*) appears at 10.19 ppm. The signals attributed to the protons of the polyaromatic *core* are displayed

as two singlets (*b* and *c*) at 9.19 and 9.72 ppm. The rest of the signals corresponding to the alkylidene chain are assigned on the ^1H NMR spectrum.

Figure 4.1 ^1H NMR spectrum of $[\text{K-H}_2](\text{I})_2$ in $\text{DMSO-}d_6$

$^{13}\text{C}\{^1\text{H}\}$ spectrum of $[\text{K-H}_2](\text{I})_2$

Figure 4.2 shows the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $[\text{K-H}_2](\text{I})_2$. The signal due to NCHN carbon (*1*) appears at 151.0 ppm. The quaternary carbon atoms (*2*) of the polyaromatic *core* are displayed in the 125-147 ppm region, while the tertiary carbon atoms (*3*) are displayed at 112.4 and 124.7. The rest of the signals due to the *n*-butyl chain are assigned on the NMR spectrum shown in Figure 4.2.

Figure 4.2 $^{13}\text{C}\{^1\text{H}\}$ spectrum of $[\text{K-H}_2](\text{I})_2$ in $\text{DMSO-}d_6$

b) Synthesis and characterization of diquinoxalino[2,3-a:2',3'-c]phenazine-based tris(azolium) salts

The diquinoxalino[2,3-a:2',3'-c]phenazine-based tris(azolium) salt (**[L-H₃](I)₃**) was prepared by the condensation of three equivalents of 1,3-dibutyl-5,6-diaminobenzimidazolium iodide with one equivalent of hexaketocyclohexane, in glacial acetic acid at 140°C (Scheme 4.2). After workup, **[L-H₃](I)₃** was isolated in 84% yield. The compound was characterized by NMR spectroscopy, mass spectrometry and elemental analysis.

Scheme 4.2 Synthesis of the tris(azolium) salt **[L-H₃](I)₃**

¹H NMR spectrum of [L-H₃](I)₃

Figure 4.3 shows the ¹H NMR spectrum of **[L-H₃](I)₃**. All the signals are shown as broad peaks, a feature that is often observed for compounds that have the tendency to form π - π aggregates.^{59,69-71} The number and the integration of the signals are in agreement with the *D*_{3h} symmetry of the molecule. The signal due to the acidic protons of the NCHN fragments (*a*) appears at 10.33 ppm. The resonance assigned to the hydrogen atoms of the quinoxaline fragment (*b*) are displayed as a broad singlet at 9.32 ppm. The rest of the signals due to the *n*-butyl groups are assigned on the NMR spectrum shown in Figure 4.3.

Figure 4.3 ^1H NMR spectrum of $[\text{L-H}_3](\text{I})_3$ in $\text{DMSO-}d_6$

$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $[\text{L-H}_3](\text{I})_3$

Figure 4.4 shows the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $[\text{L-H}_3](\text{I})_3$. The number of the signals is in agreement with the proposed structure and with the D_{3h} symmetry of the tris(azolium) salt. The signal due to the NCHN carbon (1) appears at 149.2 ppm. The signals attributed to the quaternary carbons (2) are displayed at 134.4, 139.3 and 145.2 ppm. The CH carbon of the quinoxaline fragment (3) shows its resonance at 113.4 ppm. The rest of the signals due to the carbons of the alkylidene chain are assigned on the ^{13}C NMR spectrum.

Figure 4.4 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $[\text{L-H}_3](\text{I})_3$ in $\text{DMSO-}d_6$

4.2.2 Synthesis and characterization of the di- and triiridium complexes

a) Coordination of the quinoxalinophenanthrophenazine-based bis(NHC)s

Due to the higher solubility of the di-*tert*-butyl-substituted bis(azolium) salts $[\mathbf{K-H}_2](\mathbf{I})_2$ and $[\mathbf{K-H}_2](\mathbf{PF}_6)_2$, we considered them as more suitable bis(NHC)s precursors than $[\mathbf{J-H}_2](\mathbf{I})_2$, and therefore used them for the coordination to metals. The reaction of $[\mathbf{K-H}_2](\mathbf{PF}_6)_2$ with $[\text{IrCl}(\text{COD})]_2$ in THF in the presence of potassium *tert*-butoxide, allowed the formation of the diiridium complex **2K**, in 39% yield. By following a similar procedure, but with the addition of an excess of KI, the reaction of $[\mathbf{K-H}_2](\mathbf{I})_2$ with $[\text{IrCl}(\text{COD})]_2$ afforded the iodide analogue complex **1K**, in 42% yield. The carbonyl complex **3K** was quasi-quantitatively formed by bubbling CO into a CH_2Cl_2 solution of complex **2K**.

Scheme 4.3 Synthesis of dimetallic complexes **1K**, **2K** and **3K**

Due to the relative orientation of the halogen ligands in complexes **1K**, **2K** and **3K**, the formation of two atropisomers could be expected. As shown in Figure 4.5, in the *anti* atropisomer the two halogens are pointing to different sides of the molecule, while in the *syn* conformer the halogens are orientated to the same side of the molecule. However, the ¹H and ¹³C NMR spectra of **1K**, **2K** and **3K** reveal the formation of only

one atropisomer. X-ray diffraction studies on crystals of **1K** revealed that the compound formed was the *anti* atropisomer (see below for more details).

Figure 4.5 Possible atropisomers of the dimetallic complexes. X = Cl or I. L = CO or 1,5-cyclooctadiene

Complexes **1K**, **2K** and **3K** were characterized by the standard spectroscopic techniques. Due to the similarity between the three complexes, only the ^1H and ^{13}C NMR spectroscopic details of **1K** will be discussed in detail.

^1H NMR spectrum of **1K**

Figure 2.23 shows the ^1H NMR spectrum of complex **1K**. As we mentioned before, the spectrum reveals the presence of only one of the two possible atropisomers. Consistently with the two-fold symmetry of the complex, the aromatic protons corresponding to the pyrene (*c*) and quinoxaline (*b*) fragments are displayed as singlets at 9.81 and 8.12 ppm, respectively. The signal due to the proton of the pyrene central core (*c*) is displayed at higher frequencies than expected, due to its relative proximity to the nitrogen of the pyrazine fragment, which causes the deshielding of the resonance. The rest of the signals attributed to the *n*-butyl group are assigned on the spectrum.

Figure 4.6 ^1H NMR spectrum of **1K** in CDCl_3

$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1K**

The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of complex **1K** is shown in Figure 2.24. The number of signals is in agreement with the proposed structure, and with the two-fold symmetry of the complex. The signal attributed to the metallated carbons appears at 202.8 ppm. The signals due to the tertiary carbon atoms (3) of the polyaromatic linker are displayed at 106.7 and 124.6 ppm, while those due to the quaternary carbons (2) are displayed in the 125–152 ppm region. The rest of the signals corresponding to the COD ligand, *tert*-butyl and *n*-butyl group are conveniently assigned on the spectrum.

Figure 4.7 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1K** in CDCl_3

Molecular structure of **1K**

Crystals of **1K** suitable for X-ray diffraction analysis were obtained by slow evaporation of a solution of the compound in chloroform with a few drops of acetic acid. Compound **1K** crystallizes in the triclinic space group *P*-1. As can be seen in Figure 4.8, the molecule consists of a quinoxalinophenanthrophenazine-bis(imidazol-diylidene), bridging two iridium fragments, which complete their coordination spheres with an iodide and a 1,5-cyclooctadiene ligand. The relative orientation of the two metal fragments is *anti*, with the two iodide ligands pointing at opposite sides of the molecule. The average Ir-C_{carbene} bond distance is 2.01 Å. The molecule displays a remarkably long metal-to-metal through-space distance of 22.37 Å (the longest reported so far for a *Janus*-type bis(NHC) ligand), which is slightly shorter than the through-ligand distance of 22.61 Å, as a consequence of the bow-shaped conformation adopted by the ligand. The crystal packing reveals that the molecules are associated in pairs, in which the

convex parts of the molecules are approaching each other by one of their pyrazine heterocycles.

a)

b)

Figure 4.8 a) Molecular structure of **1K**. b) Molecular structure of **1K**, showing the π -stacking between two pyrene fragments. Hydrogen atoms have been omitted for clarity. Ellipsoids are given at 50% of probability.

Table 4.1 Selected bond lengths and angles for **1K**

Bond	Length (Å)	Bond	Angle (°)
Ir(1)–I(1)	2.6153(9)	C(1)–Ir(1)–I(1)	86.6(3)
Ir(1)–C(1)	2.0130(9)	N(1)–C(1)–N(2)	106.2(9)
Ir(1)–C(3)	2.083(13)	C(2)–Ir(2)–I(2)	87.9(4)
Ir(1)–C(4)	2.082(12)	N(3)–C(2)–N(4)	105.4(10)
Ir(1)–C(5)	2.188(10)		
Ir(1)–C(6)	2.1850(9)		
Ir(2)–I(2)	2.6057(10)		
Ir(2)–C(2)	2.0000(10)		
Ir(2)–C(7)	2.0820(11)		
Ir(2)–C(8)	2.0780(10)		

Ir(2)–C(9)	2.1990(10)
Ir(2)–C(10)	2.1910(10)
Ir(1)–Ir(2)	22.3658(12)

b) Coordination of the diquinoxalino[2,3-a:2',3'-c]phenazine-based tris(NHC)

The coordination of $[\mathbf{L-H}_3](\mathbf{I})_3$ to iridium, was performed by deprotonating the tris(azolium) salt with a NaH/NaO^tBu mixture in THF at -78°C. In order to avoid halide mixtures in the final product, an excess of NaI was added to the reaction mixture (Scheme 4.4). After purification by chromatographic column, the triiridium complex **1L** was obtained in 58% yield. Complex **1L** was characterized by NMR spectroscopy, mass spectrometry and elemental analysis.

According to all possible relative orientations of the iodide ligands in **1L**, two atropisomers should be expected (Figure 4.9). In the *syn* atropisomer the three iodide-ligands are pointing to the same side of the molecule, while the *anti* atropisomer should have two iodide-ligands pointing to the same side of the molecule, and a third one pointing at the other side of the molecule. The ¹H NMR reveals a highly symmetric structure in solution, therefore suggesting that the reaction is selective in the formation of the *syn* isomer.

Scheme 4.4 Synthesis of the triiridium complex **1L**

Figure 4.9 Possible atropisomers of complex **1L**

^1H NMR spectrum of **1L**

Figure 4.10 shows the ^1H NMR spectrum of complex **1L**. The number and integration of the signals displayed on the spectrum are in agreement with the D_{3h} symmetry of the complex, thus suggesting the formation of the *syn* atropisomer. The first evidence of the coordination of the ligand, is the disappearance of the signal that corresponds to the acidic hydrogen of the NCHN fragment from the starting tris(azolium) salt **[L-H₃](I)₃**. The signal due to the quinoxaline fragment (*b*) appears at 8.50 ppm. The rest of the signals attributed to the *n*-butyl chain and COD ligand are conveniently displayed on the spectrum.

Figure 4.10 ^1H NMR spectrum of **1L** in CDCl_3

$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1L**

Figure 4.11 shows the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1L**. The number of signals displayed on the spectrum is in agreement with the D_{3h} symmetry of the complex. The signal due to the metallated carbon atoms (**1**) appears at 205.6 ppm. The signals attributed to the quaternary carbons (**2**) are displayed in the 139-143 ppm region. The signal due to the CH group of the quinoxaline fragment (**3**) is shown at 107.7 ppm. The rest of the signals attributed to the *n*-butyl chain and 1,5-cyclooctadiene ligand are conveniently displayed on the spectrum.

Figure 4.11 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1L** in CDCl_3

4.2.3 Dimetallic complexes with highly extended polyaromatic systems and π -stacking additives

The electronic properties of the bis(NHC) ligand **K** were studied by two approaches. The first one involves the measurement of the CO stretching frequencies of the diiridium carbonyl complex **3K**. We also studied the effect of the presence of π -stacking additives (namely pyrene and hexafluorobenzene), on the CO stretching frequencies of **3K**. The second approach involves DFT studies, which were carried out by Prof. Dimitri Gusev (Wilfrid Laurier University).

a) FT-IR spectroscopy studies

The FT-IR studies of the dimetallic complex **3K** were carried out in CH₂Cl₂ solution (Table 4.2). The CO bands stretched at 1989.2 and 2072.1 cm⁻¹. The average of the frequencies ($\nu_{\text{av}}(\text{CO})$) is exactly the same than that for the monometallic analogue **3E** (2030.7 cm⁻¹), suggesting that both complexes (**3E** and **3K**) are electronically equivalent. The electron donating character of the ligand could be estimated by calculating a TEP value of 2056 cm⁻¹, from the well-known correlations.⁷² This value differs in +2 cm⁻¹ compared to the related pyrene-based bis(imidazolyliene) ligands **VIII** and **IX** (Chart 4.5),⁴⁰ indicating that the presence of the two pyrazine rings results in a slight decrease of the electron donating power of the ligand.

We also measured the FT-IR spectra of the complex **3K** in the presence of pyrene and hexafluorobenzene, in a similar way that we described in Chapter 3. In this case, the addition of pyrene to a solution of **3K** in CH₂Cl₂, results in a decrease of the $\nu_{\text{av}}(\text{CO})$ value of 1.9 cm⁻¹, while the addition of hexafluorobenzene increases the $\nu_{\text{av}}(\text{CO})$ value in +0.9 cm⁻¹. These results are in the same trend as those that we already described for the same set of IR experiments carried out for the mono-NHC ligand **E** described in Chapter 3. Our new results corroborate that the electronic properties of these types of NHC ligands may be modified in a predictive way, by choosing the right type of additive.

Table 4.2 Carbonyl stretching frequencies for compounds [IrCl(CO)₂]. Effects of the addition of pyrene and hexafluorobenzene^[a]

[IrCl(CO) ₂]	Additive	$\nu(\text{CO})^{[b]}$ (cm ⁻¹)	$\nu_{\text{av}}(\text{CO})$ (cm ⁻¹)	$\Delta\nu_{\text{av}}(\text{CO})$ (cm ⁻¹)
3E	-	2072.1, 1989.2	2030.7	0
	Pyrene	2071.2, 1987.3	2029.2	-1.5
	C ₆ F ₆	2073.1, 1990.2	2031.6	0.9
3K	-	2072.1, 1989.2	2030.7	0
	Pyrene	2070.2, 1987.3	2028.8	-1.9
	C ₆ F ₆	2073.1, 1990.2	2031.6	0.9

[a] IR data obtained in CH₂Cl₂ solutions of the complex with saturated solutions of the additive. [b] The resolution of the IR experiments is 0.5 cm⁻¹.

VIII, R = -CH₃. TEP = 2054 cm⁻¹

IX, R = -CH₂CH₂. TEP = 2054 cm⁻¹

Chart 4.5 Pyrene-based NHC complexes

b) DFT calculations

The synthesis of a bis(NHC)-based complex with an extended polyaromatic system represents a good opportunity to study the electronic communication between both metals, due to the delocalized π -orbitals of the bridging ligand. In this regard, Gusev and Peris suggested that DFT calculations can be used for this propose.⁷³ They postulated that the electronic communication in a dimetallic (CO)₃Ni-NHC-ML_n system should correlate with the variation of the $\nu(\text{CO})$ (or TEP) value for the dinuclear complex relative to the $\nu(\text{CO})$ of (CO)₃Ni-NHC. Then, this tool can be an effective way to determine if there is electronic communication between the metal centres bound to **K**. In order to simplify the calculation, the DFT studies were carried out by modelling the coordinated ligands with N-methyl substituents, and without the *t*Bu fragment at the pyrene *core*. The two species compared are those depicted in Chart 4.6. First, we calculated the TEP value for the bis(NHC) ligand bound to a single Ni(CO)₃ fragment, while keeping the other carbene in its free form (**X**, Chart 4.6). The resulting TEP value is 2059.5 cm⁻¹. The calculated TEP value for the system in which the bis(NHC) ligand is bound to two Ni(CO)₃ fragments (**XI**, Chart 4.6) is 2060 cm⁻¹. This small TEP-shift, indicates that the two metals are basically disconnected, despite being apparently linked by a very effective π -delocalized system.

Chart 4.6

4.2.4 Quantification of the non-covalent interaction between **3K** and pyrene: calculation of the association constants

We wanted to quantify the π -stacking interaction between **3K** and pyrene, and for that reason, we decided to perform an experiment consisting of the ^1H NMR titration of **3K** with pyrene, in a similar way that we described for complex **3D** in Chapter 3. The experiment was carried out in a 1:2 mixture of $\text{CD}_3\text{OD}/\text{CDCl}_3$, at 25°C . The concentration of **3K** was kept constant throughout the experiment ($[\textbf{3K}] = 0.21 \text{ mM}$), while the concentration of pyrene was gradually increased ($[\text{pyrene}] = 0.03, 0.06, 0.08, 0.10, 0.13 \text{ M}$). As shown in Figure 4.12, the signals due to the aromatic protons of complex **3K** are shifted to lower frequencies upon addition of increasing amounts of pyrene. The signal assigned to the hydrogen atoms at the pyrene fragment (H_c) is significantly shifted, from 9.80 to 9.63 ppm. The signal of the hydrogen atoms of the quinoxaline moiety (H_b) is also sensitive to the addition of pyrene, but it shifts to the region where the signals due to the additive appear. Based on this result, we thought that pyrene is interacting over the pyrazine fragment of the complex **3K** (Figure 4.14). By assuming a 1:1 molar stoichiometry of the **3K**/pyrene π -stacking aggregates, and using the Benesi-Hildebrand treatment,⁷⁴ we calculated the association constant (Figure 4.13). The resulting K_a is 11.6 M^{-1} , over one order magnitude higher than the association constant that we found for the interaction of pyrene with the monometallic complex **3D** (2.21 M^{-1}). This is probably due to the fact that complex **3K** has a larger π -delocalized system than **3D**, hence a larger surface to interact with the pyrene molecule. This result is also in agreement with the FT-IR experiments, since the addition of pyrene produces a slightly higher shift in the carbonyl stretching frequencies in the dimetallic complex **3K**.

Our attempts to calculate the association constant of **3K**/hexafluorobenzene were unsuccessful, because we did not observe any change on the ^1H NMR spectrum of **3K** upon addition of hexafluorobenzene.

Figure 4.12 ^1H NMR spectra of **3K** upon addition of different amounts of pyrene using a 1:2 mixture of $\text{CD}_3\text{OD}/\text{CDCl}_3$ as solvent at 25 °C. The concentration of **3K** was fixed at 0.21 mM. From the top to bottom the concentrations of pyrene are: a) 0.00, b) 0.03, c) 0.06, d) 0.08, e) 0.10 and f) 0.13 M

Figure 4.13 Determination of the association constant between **3K** and pyrene using the Benesi-Hildebrand treatment

Figure 4.14 Possible regioselectivity of **3K**/pyrene interaction

4.3 Conclusions

We prepared a series of bis(imidazolium) and one tris(imidazolium) salts with highly extended polyaromatic linkers that incorporate two or three pyrazine units, respectively. The bis(imidazolium) salts were used as precursors of the *Janus*-type bis(NHC) ligand **K** in the preparation of diiridium complexes **1K**, **2K** and **3K**. The molecular structure of **1K** reveals a remarkably long metal-to-metal through-space distance of 22.37 Å, the longest reported so far for a *Janus*-type bis(NHC) ligand. The tris(imidazolium) salt was used as precursor of a star-shaped tris(NHC) ligand in the preparation of a triiridium complex. These results suggest that ligands **K** and **L** may serve as suitable scaffolds for the preparation of sophisticated metallorganic structures, which may include squares, cages and organometallic polymers.

The analysis of the carbonyl stretching frequencies of carbonyl derivative complex **3K**, revealed that the electron-donating power of the bis(NHC) ligand **K** is affected in the presence of π -stacking additives such as pyrene and hexafluorobenzene. The electron-donating power of **K** is increased upon addition of pyrene, while the addition of hexafluorobenzene causes the opposite effect. The DFT calculations demonstrated that the two metal fragments bound to the **K** are basically disconnected.

The identification and quantification of the interaction of complex **3K** with pyrene were studied by means of ^1H NMR spectroscopy, by adding increasing amounts of pyrene to a solution of **3K**. The changes observed in the ^1H NMR spectra allowed us to identify that the π -stacking interaction between pyrene and **3K** occurs mainly at the pyrazine part of the ligand. By assuming a 1:1 molar stoichiometry for the formation of the π -stacking adducts, we estimated the association constant (K_a) between pyrene and complex **3K** using the Benesi-Hildebrand data treatment. The resulting K_a of 11.6 M^{-1} , higher than the calculated for the interaction of pyrene with mono-metallic complex **3D**, clearly shows that pyrene has more affinity for the dimetallic complex.

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Chapter 5

**A novel tetracyclic
bis(imidazolidine) with folded
geometry for the preparation of
NHC-based dimetallic complexes**

5.1 Introduction

In the search for new precursors to multifunctional materials, polytopic N-heterocyclic carbene ligands (NHC) have emerged as very promising tools.^{1,2} Among them, those featuring rigid geometrically isolated carbene moieties that prevent chelation have recently found great utility as building blocks for novel macromolecules with structurally dynamic characteristics and useful electronic properties.³⁻¹⁰ In this regard, there is a growing interest in the development of polytopic carbenes for the design of molecular and supramolecular systems with electronically communicating metal centres.^{7,11,12} Typically, through-ligand metal-metal electronic communication is envisioned as taking place *via* the delocalized π -orbitals of the bridging ligand, as a consequence of the arguable interaction between the metal $d\pi$ orbitals and the π -delocalized system of the NHC ligand through the $M=C$ π -back-bonding. However, our group recently proved that the presence of an extended π -delocalized linker has little effect in the electronic communication between the metals bound to a poly-NHC ligand,¹³ and that the electronic interaction between NHC-bridged dimetallic complexes decays exponentially against the through-ligand metal-to-metal separation.

These observations were especially relevant when comparing fused-bis(imidazolinylienes) (**I** in Chart 5.1) and fused-bis(imidazolylienes) of type **II**. However, the synthetic difficulties found for the preparation of bis(imidazolylienes) of type **II**,¹⁴ and their coordination to metal fragments, make bis(imidazolinylienes) of type **I** especially valuable synthons for the preparation of new dimetallic complexes and metallic-based polymers with interesting applications. Additionally, the shorter intermetallic distance in **I**, due to its folded geometry, may provide benefits in terms of positive catalytic effects. It is well accepted that catalysts containing multiple metal centres in close proximity can lead to better reactivity than the related monometallic systems, in particular for second order kinetic dependence on the catalyst,¹⁵⁻¹⁸ an effect that our group have already proved several times using rigid poly-NHC ligands.¹⁹⁻²⁶

For the coordination of bis(imidazolinylienes) to rhodium and iridium, our group recently used the corresponding neutral tetraazabicyclooctane (or bis(imidazolidine)) as the bis(NHC) precursor.²⁷ The formation of the bis(NHC) implied a double geminal C-H bond activation of the methylene groups of the bis(imidazolidine), which was

facilitated by the presence of an external diolefin (1,5-cyclooctadiene or norbornadiene), acting as a hydrogen acceptor. The reaction constituted one of the very rare examples of conversions of neutral N-heterocycles into NHC complexes.²⁸⁻³⁰ In order to extend the coordination of this type of bis(NHC) ligands to other metals, and therefore widen the scope of its applicability, in this chapter we describe the preparation of a new series of bis(imidazolinylidene)-based complexes, using two synthetic protocols: (i) the double C–H activation methodology, starting from a neutral bis(imidazolidine) and (ii) the traditional use of a bis(azolium) salt in the presence of a base.

Chart 5.1 Fused-bis(imidazolinylidenes) (I) and fused-bis(imidazolylidenes) (II)

5.2 Results and discussion

In the first part of this section we discuss all the aspects regarding the synthesis of the NHC ligand precursors that we have used in this chapter. The second part describes the synthesis of dimetallic iridium and palladium NHC-based complexes. Finally, the catalytic activity of the palladium derivatives in the acylation of aryl halides with hydrocinnamaldehyde is presented.

All the new species were conveniently characterized by NMR spectroscopy, mass spectrometry and elemental analysis. The molecular structures of three of the complexes prepared in this work were unambiguously determined by X-Ray analysis. The experimental details concerning the synthesis and the characterization of all the products have been included in the Experimental Section of this manuscript.

5.2.1 Synthesis and characterization of the bis(NHC) ligand precursors

As we already discussed in the introduction, in a previous work, our group used a tetra-benzyl-substituted bis(imidazolidine) for the preparation of a series of Rh and Ir bis(NHC) complexes by double geminal C-H bond activation of the NCH_2C groups.²⁷ The presence of the benzyl groups resulted convenient, in the sense that facilitated the preparation of the starting ligand precursor in high yield, compared to the yields obtained for other starting materials, as those containing N-Me or other N-alkyl groups. However, its coordination to the metal fragments afforded mixtures of atropisomers due to the restricted rotation of the benzyl rings about the C-N bond, therefore sometimes yielding to mixtures of complexes difficult to identify. In order to circumvent this problem, we decided to synthesize a bis(imidazolidine) analogue in which the N-substituents have been substituted by a butylene linker between the nitrogen atoms of adjacent heterocycles (**[M-H₄]**, in Scheme 5.1). This new situation avoids the potential formation of atropisomers due to rotation of the N-substituents, therefore simplifying the resulting mixture of complexes obtained after coordination. Additionally, the resulting tetracyclic ligand provides the complex with an unusual asymmetric ‘pocket-type’ topology, in which the two faces of the ligand (inner and outer sides) may provide the metal complexes with unusual reactivity patterns.

a) Synthesis and characterization of bis(imidazolidine) [M-H₄]

The tetracyclic bis(imidazolidine) **[M-H₄]** was prepared by condensation of formaldehyde with 1,4-diaminobutane, in a similar manner as that described in the literature for related bis(imidazolidines) containing non-cyclic N-substituents (Scheme 5.1).³¹ Formaldehyde and glyoxal were subsequently added to a methanolic solution of 1,4-diaminobutane and acetic acid. The mixture was stirred at room temperature for seven days. After this time, all the volatile components were removed under vacuum, and the residue was extracted several times with diethyl ether. The combined organic layers were concentrated and washed with cold acetone, giving the desired product as a white crystalline solid in 50% yield.

Scheme 5.1 Synthesis of [M-H₄]*¹H NMR spectrum of [M-H₄]*

Figure 5.1 shows the ¹H NMR spectrum of [M-H₄]. The signal assigned to the protons of the CH groups of the bicyclic compound appears at 4.17 ppm (*b*). The protons of the NCH₂N group are diastereotopic, as observed by the two different doublets appearing at 3.45 and 3.30 ppm (*a*). The resonances due to the diastereotopic protons of the NCH₂ groups of the heterocycle are conveniently assigned on Figure 5.1 (*c*). The signals due to the protons of the other CH₂ groups of the butylene linkers between the nitrogen atoms appear as a broad signal 1.74 ppm (*d*).

¹³C{¹H} NMR spectrum of [M-H₄]

Figure 5.2 shows the ¹³C{¹H} spectrum of [M-H₄]. The signal at 86.6 ppm corresponds to the carbon atoms of the CH groups of the common backbone of the bicyclic compound (2). The signal due to the carbon atom of the NCH₂N moiety is shown at 74.4 ppm (*l*). The signals attributed to the alkylidene chain are conveniently assigned on the NMR spectrum and are consistent with the proposed structure (3 and 4).

Figure 5.1 ¹H NMR spectrum of compound [M-H₄] in CDCl₃

Figure 5.2 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $[\text{M-H}_4]$ in CDCl_3

^{13}C - ^1H HSQC and ^1H - ^1H COSY NMR experiments were carried out in order to confirm the assignment of the signals displayed on the ^1H and ^{13}C NMR spectra (see the Experimental Section for details).

b) Synthesis and characterization of bis(imidazolinium) salt $[\text{M-H}_2](\text{PF}_6)_2$

The bis(imidazolinium) salt $[\text{M-H}_2](\text{PF}_6)_2$ was prepared by oxidation of the bis(imidazolidine) $[\text{M-H}_4]$ using N-bromosuccinimide (NBS), as previously described in the literature for other imidazolidines.^{32,33} A solution of NBS in dimethoxyethane (DME) was added dropwise to a solution of $[\text{M-H}_4]$ in the same solvent (Scheme 5.2). The reaction mixture was stirred at room temperature for 3 h under the exclusion of light. The solid was separated by filtration and solubilized in methanol. NH_4PF_6 was then added in one portion to the methanolic solution and the resulting suspension was stirred for 30 min at room temperature. The desired dicationic salt was isolated by filtration as a white solid in 64% yield.

Scheme 5.2 Synthesis of $[\text{M-H}_2](\text{PF}_6)_2$

¹H NMR spectrum of [M-H₂](PF₆)₂

Figure 5.3 shows the ¹H NMR spectrum of [M-H₂](PF₆)₂. The number and integration of the signals displayed in the spectrum are in agreement with the two-fold symmetry of the compound. The signal due to the acidic proton of the bis(imidazolinium) salt appears at 8.99 ppm (a). The protons of the CH groups of the common backbone of the bicyclic compound appear at 6.66 ppm (b). The resonances due to the protons of the NCH₂ and -CH₂- groups of the heterocycle are conveniently assigned on the NMR spectrum shown in Figure 5.3 (c and d, respectively).

¹³C{¹H} NMR spectrum of [M-H₂](PF₆)₂

Figure 5.4 shows the ¹³C{¹H} NMR spectrum of [M-H₂](PF₆)₂. Again, the number of signals is in agreement with the two-fold symmetry of the compound. The signal due to the two tertiary carbon atoms of the bis(imidazolinium) salt appears at 160.4 ppm (1). The signal assigned to the carbon atom of the CH groups of the common backbone of the bicyclic compound appears at 80.5 ppm (2). The rest of the signals concerning the alkylidene linker are conveniently assigned on the NMR spectrum shown in Figure 5.4 (3 and 4).

Figure 5.3 ¹H NMR spectrum of [M-H₂](PF₆)₂ in DMSO-*d*₆

Figure 5.4 $^{13}\text{C}\{^1\text{H}\}$ spectrum of $[\text{M}-\text{H}_2](\text{PF}_6)_2$ in $\text{DMSO}-d_6$

5.2.2 Synthesis and characterization of the NHC-based complexes

For the preparation of the metal complexes, two strategies have been used:

- 1) Double C-H activation of the $\text{C}(\text{sp}^3)\text{H}_2$ groups of a neutral N-heterocycle. This methodology was used by our research group in 2011,²⁷ allowing the preparation of new NHC-based complexes with sophisticated architectures not accessible from the classical azolium carbene precursors. This methodology has been restrictively used to prepare the diiridium complexes described in this work.
- 2) Activation of a bis(imidazolium) salt with a weak base. This “traditional route” has been used for the preparation of the dipalladium complexes.

a) Preparation of the diiridium complexes by double C-H activation

The reaction of $[\text{M}-\text{H}_4]$ with $[\text{IrCl}(\text{COD})]_2$ in the presence of an excess of 1,5-cyclooctadiene in refluxing toluene, afforded a 1:1 mixture of isomers **1M'** and **1M''** (Scheme 5.3). Isomers **1M'** and **1M''** were easily separated by column chromatography on silica gel (33% and 30% yield, respectively). These isomers are two of the three possible atropisomers resulting from the two different relative orientations of the iridium fragments about the ligand, with the chloride ligands pointing toward the inner cavity or outside the cavity, which in the case of **1M** results in the formation of the *anti* (**1M'**) and *syn* (**1M''**) conformers. The conformer **1M'''**, with the two chloride

ligands pointing towards the inner cavity of the ligand, was not observed. The complete characterization of the complexes and the discussion of their structures will be discussed later. Under the reaction conditions used, the formation of the dimetallic species was always favoured. Attempts to prepare the monometallic species modifying both the stoichiometry and the experimental conditions were unsuccessful. Complexes **1M'** and **1M''** were characterized by NMR spectroscopy, mass spectrometry and elemental analysis. Additionally, the molecular structure of isomer **1M'** was unambiguously confirmed by means of X-Ray analysis.

¹H NMR spectra of complexes **1M'** and **1M''**

Figure 5.5 shows the ¹H NMR spectrum of **1M'**. The disappearance of the signals due to the NCH₂N protons provides the first indication that the metallation may have taken place. The signals due to the CH_{bridge} (*b*) and NCH₂ (*c*) groups are shifted downfield in comparison with the ligand precursor **[M-H₄]** (see Figure 5.5). The signals attributed to protons of the alkylidene linker (*c* and *d*) appear as diastereotopic pairs at 4.91, 3.53, 3.37, 2.04 and 1.92 ppm.

Figure 5.5 ¹H NMR spectrum of **1M'** in CDCl₃

Figure 5.6 shows the ^1H NMR spectrum of complex **1M''**. This spectrum exhibits the signals attributed to the alkylidene linker (*c* and *d*) at 4.73, 3.50 and 1.98 ppm, respectively. The rest of the signals are conveniently assigned on the ^1H NMR shown in Figure 5.6.

$^{13}\text{C}\{^1\text{H}\}$ NMR spectra of complexes **1M'** and **1M''**

Figure 5.7 shows the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of complex **1M'**. The most characteristic signals are those attributed to the metallated carbons at 208.5 and 208.4 ppm (*I*). Also, the spectrum shows four signals due to the olefinic protons of the COD ligands at 86.6, 85.9, 54.3 and 51.9 ppm. These data confirm that the two metal fragments are not symmetry-related. The rest of the signals attributed to the bis(imidazolinylidene) ligand, are conveniently displayed on the spectrum shown in Figure 5.7 and are consistent with the structure assigned to the complex.

Figure 5.6 ^1H NMR spectrum of **1M''** in CDCl_3

Figure 5.7 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1M'** in CDCl_3

Consistent with its two-fold symmetry, the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1M''** (Figure 5.8) shows only one signal for the carbene carbon at 207.9 ppm (*I*), therefore indicating that the two metal fragments are symmetry-related. The carbon atoms of the COD ligand display the typical pattern of a highly symmetric compound (four distinct signals, two due to the CH fragments and two due to CH_2 ones).

Figure 5.8 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1M''** in CDCl_3

Molecular structure of **1M'**

Crystals of **1M'** suitable for X-Ray diffraction analysis were obtained by slow diffusion of hexane into a chloroform solution of the compound. The molecular structure of **1M'** confirms the dimetallic nature of the compound (Figure 5.9). The bicyclic bis(NHC) is

bridging two iridium fragments, which complete their coordination sphere with a chloride and a COD ligand.

Table 5.1 shows the most representative bond lengths (Å) and angles (°). The Ir-C_{carbene} distances are approximately 2.02 Å, similar to those of other dimetallic Ir(I) complexes described by our group.^{27,34} Due to the folded geometry of the NHC ligand, the through-space distance between the two metals is 7.14 Å, similar to that of the dimetallic Ir(I) complex bearing a bis(imidazolinylidene) ligand reported by our group.²⁷ The two planes defined by the backbone-connectedazole rings are at an angle of 64.89°, and the distance between the carbene carbon atoms is 3.691 Å.

Figure 5.9 Molecular diagram of complex **1M'**. Ellipsoids are at 30% probability. Hydrogen atoms have been omitted for clarity

Table 5.1 Selected bond lengths (Å) and angles (°) of complex **1M'**

Bond	Lengths (Å)	Bond	Angles (°)
Ir(1)-C(1)	2.012(8)	C(1)-Ir(1)-Cl(1)	85.1(3)
Ir(1)-Cl(1)	2.36(2)	C(2)-Ir(2)-Cl(2)	89.1(3)
Ir(1)-C(5)	2.11(1)	N(1)-C(2)-N(3)	112.0(7)
Ir(1)-C(6)	2.10(1)	N(2)-C(4)-N(4)	113.1(7)
Ir(1)-C(7)	2.21(1)		
Ir(1)-C(8)	2.17(9)		
Ir(2)-C(4)	2.02(1)		
Ir(2)-Cl(2)	2.365(2)		
Ir(2)-C(9)	2.12(1)		
Ir(2)-C(10)	2.11(1)		
Ir(2)-C(11)	3.12(2)		
Ir(2)-C(12)	2.19(1)		

b) Synthesis and characterization of the carbonyl derivatives

The study of the carbonyl stretching frequencies by IR provides valuable information about the electron-donating ability of the co-ligands coordinated to the metal centre. In order to evaluate the electron-donating ability of the new ligand, the dimetallic complexes **1M'** and **1M''** were transformed into their corresponding carbonyl derivatives. The displacement of the COD ligand by CO was carried out by bubbling carbon monoxide into a solution of the complex **1M'** (or **1M''**) in CH₂Cl₂ at 0 °C (Scheme 5.4).

Each carbonylation led to a mixture of the same two isomers in a 62:38 molar ratio that we could not separate, and that we attributed to the restricted rotation about the M-C carbene bond. The two isomers were isolated in 71% yield starting either from **1M'** or **1M''**. Variable temperature NMR experiments allowed us to confirm that these rotamers do not interconvert. As a consequence of the ligand exchange, we expected the formation of three different isomers (Chart 5.2), depending on the orientation of the chloride ligands. However, when the COD ligand in **1M'** and **1M''** was substituted by the smaller CO, only two isomers were clearly observed by NMR spectroscopy in both reactions. The molecular structure of one of these two isomers (**2M''**) was unambiguously determined by means of X-Ray diffraction.

Scheme 5.4 Synthesis of complex **2M**

Chart 5.2 Possible isomers for the carbonyl derivatives. Only **2M'** and **2M''** were obtained.

¹H NMR spectrum of complexes **2M**

Figure 5.10 shows of the ¹H NMR spectrum of the mixture of isomers **2M'** and **2M''**. Although the ¹H NMR spectrum of the mixture clearly shows the presence of two isomers, the assignment of the signals to each individual isomer was not possible. The signal attributed to the protons of the CH groups of the ligand backbone appears as two singlets, at 5.81 and 5.78 ppm (*b*). The signals corresponding to the protons of the NCH₂ fragments appeared as two multiplets (*c*). Each multiplet overlaps other multiplet of less intensity.

Figure 5.10 ¹H NMR spectrum of complexes **2M**

$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of complexes **2M**

Figure 5.11 shows the $^{13}\text{C}\{^1\text{H}\}$ spectrum of the mixture of the two isomers observed. The spectrum exhibits three signals due to metallated carbons (201.9, 200.7 and 200.3 ppm) and six signals attributed to the CO ligand (181.1, 181.0, 180.9, 167.9, 167.2 and 166.6 ppm).

The number of signals is in agreement with the presence of two isomers. In one of the isomers observed (**2M''**), the two metal fragments are expected to be related by symmetry, therefore, one signal due to the metallated carbons and two signals due to the CO ligands can be assigned to **2M''**. The molecular structure of this complex (*vide infra*) confirmed this assignation, and allowed us to discard that this two-fold symmetry spectrum should be assigned to **2M''** and not to **2M'''** (also presenting symmetry-related metal fragments, but not detected by NMR).

The two metal fragments in **2M'** are not symmetry-related, therefore two signals due to the metallated carbons and four signals due to the CO ligands should be due to this isomer present in the mixture. Consequently, we propose that the other isomer present in the mixture must be **2M'** (Figure 5.11). The rest of the signals are conveniently assigned in Figure 5.11.

Figure 5.11 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of complexes **2M** in CDCl_3

Infrared spectra of 2M

The existence of the different isomers has little effect in the local symmetry about the metals and in the electron-donating power of the ligands, and this justifies why the IR spectra of **2M** displays only two CO stretching bands at 2073 and 1990 cm^{-1} , consistent with the *cis* disposition of the carbonyl ligands.

Table 5.2 shows the IR data corresponding to relevant Ir(I) complexes with saturated-NHCs. Compared to our previously reported tetrabenzylated analogue,²⁷ compound **2M** exhibits a higher $\nu_{\text{av}}(\text{CO})$ in about 3 cm^{-1} , which reveals its lower electron-donating capacity. The same tendency is observed when changing the N-benzyl group by an N-ethyl group in mono(imidazolynylidenes), as can be seen by comparing the data shown in Table 5.2. Compared to the related monocarbenes, the $\nu_{\text{av}}(\text{CO})$ of the biscarbenes reveals their lower electron-donating capacity, most likely due to the relative inductive effect promoted by the presence of the second metal fragment.

Table 5.2 Carbonyl stretching frequencies

Complex	$\nu(\text{CO})(\text{cm}^{-1})^{[a]}$	$\nu_{\text{av}}\text{CO}$	TEP ^[b]
2M	2073, 1990	2032	2057
2071, 1986 ¹	2029	2054
2057, 2001 ³⁵	2029	2055
2051, 2001 ³⁶	2026	2052

[a] IR data obtained in CH_2Cl_2 . [b] Value calculated by linear regression from the experimentally measured $\nu_{\text{av}}(\text{CO})$ of the $[\text{L}(\text{IrCl}(\text{CO})_2)]$ complex using $\text{TEP} = 0.847\nu_{\text{av}}(\text{CO}) + 336$.³⁷

Molecular structure of **2M''**

Crystals of **2M''** suitable for X-Ray diffraction analysis were obtained by slow diffusion of hexane into a chloroform solution of **2M**. The molecular structure of **2M''**, shown in Figure 5.12 confirms the dimetallic nature of the compound. The bis(imidazolinyldene) ligand is bridging the two iridium fragments, which complete their coordination sphere with a chloride and two CO ligands. The two chloride ligands are pointing to the outer side of the ligand.

Table 5.3 shows the most representative bond lengths (Å) and angles (°). The Ir-C_{carbene} distances are approximately 2.08 Å, similar to those of other dimetallic Ir(I) complexes described by our group.^{27,34} Due to the angular nature of the bis(imidazolinyldene) ligand, the through-space distance between the two metals is 7.11 Å, 0.03 Å longer than the distance between the two iridium atoms in **1M'**. The angle stabilised between the planes of the twoazole rings is 64.42°, and the distance between carbene carbon atom is 3.708 Å; therefore, both parameters are very similar to those shows for complex **1M'** and indicate that the differences in the metal-to-metal distances should be ascribed to the longer Ir-C bond distances in **1M'** rather than to topological changes in the bis(NHC) ligand.

Table 5.3 Selected bond lengths (Å) and angles (°) of complex **2M''**

Bond	Lengths (Å)	Bond	Angles (°)
Ir(1)-C(1)	2.08(1)	C(1)-Ir(1)-C(6)	174.3(7)
Ir(1)-Cl(1)	2.34(5)	C(4)-Ir(2)-C(8)	176.5(7)
Ir(1)-C(5)	1.86(2)	N(1)-C(2)-N(3)	112.6(1)
Ir(1)-C(6)	1.91(2)	N(2)-C(3)-N(4)	113.9(1)
Ir(2)-C(2)	2.08(1)		
Ir(2)-Cl(2)	2.34(4)		
Ir(2)-C(7)	1.83(2)		
Ir(2)-C(8)	1.92(2)

Figure 5.12 Molecular diagram of complex **2M''**. Ellipsoids are at 30% probability. Hydrogen atoms have been omitted for clarity.

c) Synthesis and characterization of the palladium NHC-based complexes

As stated earlier, the synthesis of the dimetallic palladium complexes was achieved using a “more classical” route, starting from the bis(imidazolinium) salt **[M-H₂](PF₆)₂** (Scheme 5.5). A mixture of **[M-H₂](PF₆)₂**, [Pd(OAc)₂] and KI was refluxed in acetonitrile for 2 h. The addition of KI to the reaction mixture allows the formation of the corresponding neutral palladium complex. After removal of the volatiles, the crude solid was purified by column chromatography using silica gel, allowing the separation of a yellow band that contained complex **3M**. After the work-up, complex **3M** was isolated in 33% yield.

Scheme 5.5 Synthesis of complex **3M**

The acetonitrile ligand was easily exchanged by 3-chloropyridine by reacting **3M** in neat 3-chloropyridine (Scheme 5.6). This reaction allows us to prepare the dimetallic Pd(II)-based compound **4M** in 82 % yield.

Scheme 5.6 Synthesis of complex **4M**

The two complexes (**3M** and **4M**) were fully characterized by NMR spectroscopy, mass spectroscopy and elemental analysis. The molecular structure of complex **3M** was confirmed by X-ray diffraction means (see the Experimental section in Chapter 6 further for details). In the following paragraphs, only the spectroscopic characterization of **4M** is discussed in detail. All the details concerning the spectroscopic data for compound **3M** can be found in the Experimental Section (Chapter 6).

^1H NMR spectrum of **4M**

Figure 5.13 shows the ^1H NMR spectrum of **4M**. The signal of the CH groups at the central backbone of the ligand (*b*) appears as a singlet at 5.76 ppm. The protons of the NCH_2 groups are displayed as two multiplets at 3.70 and 4.82 ppm (*c*). The remaining CH_2 groups (*d*) of the butylene linker generate two multiplets at 2.03 and 2.25 ppm. The characteristic signals of the 3-chloropyridine ligands are displayed at 7.27, 7.73, 8.90 and 9.01 ppm.

Figure 5.13 ^1H NMR spectrum of **4M** in CDCl_3

$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of complex **4M**

Figure 5.14 shows the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **4M**. The most characteristic signal of the complex is the metallated carbene carbon (*1*) that appears at 184.4 ppm, confirming that the two metals are symmetry-related. The carbons of the CH groups (*2*) of the ligand display their resonance at 79.6 ppm. All the other signals are conveniently assigned on the spectrum.

Figure 5.14 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **4M** in CDCl_3

5.2.3 Catalytic studies. Acylation of aryl halides with hydrocinnamaldehyde

We undertook a preliminary exploration of the catalytic activity of the complexes **3M** and **4M**. As an important benchmark reaction, we chose the acylation of aryl halides. The reaction consists in the cross coupling between one aldehyde (hydrocinnamaldehyde) and one aryl halide, to afford the corresponding aryl alkyl ketone. This reaction was originally development by Xiao,³⁸ and it is a good alternative to the classical Friedel-Craft acylation reaction (which fails for electron-deficient arenes) while also minimizes the requirement of hazardous reagents. Perhaps surprisingly, given this potential importance, only a small number of examples have been reported to date,^{23,39-42} a few of which include intermolecular processes.^{23,38,41,42}

We tested the catalytic activity of complexes **3M** and **4M**, at 120 °C in DMF, in the presence of pyrrolidine, and using almost equimolecular amounts of aryl halide and hydrocinnamaldehyde. As shown in Table 5.4, the activity of the acetonitrile-based complex **3M** is lower than that of the 3-chloropyridine-supported complex **4M**, in agreement with other published results.²³ However, both complexes afford very modest outcomes, especially in comparison to other catalyst previously described.^{23,38,41,42}

Table 5.4 Acylation of Aryl halide with hydrocinnamaldehyde^[a]

Entry	Complex	X	Yield [%] ^[b]
1	3M	I	35
2	4M	I	45
3	3M	Br	12
4	4M	Br	15

[a] Reaction conditions: a solution of aryl halide (0.5 mmol), hydrocinnamaldehyde (0.6 mmol), pyrrolidine (1.0 mmol), 4 Å MS (1g) and the catalyst (2 mol %) in DMF (2 mL) was heated at 120 °C for 16 h. [b] Yields obtained by GC analysis using anisole as internal reference.

5.3 Conclusions

A set of metal complexes bearing a sophisticated back-to-back bis(imidazolinyldene) ligand have been prepared. The complexes were obtained by two methodologies, namely the double C-H activation bond of the C(sp³)-H₂ bond of a neutral bis(imidazolidine) and the activation of a bis(imidazolinium) salt using a weak base. More precisely:

- First, a bis(imidazolidine) with a novel topology has been synthesized by condensation of formaldehyde and 1,4-diaminobutane. This bis(imidazolidine) presents a butylene linker between the nitrogen atoms of the adjacent heterocycles, which leads to a tetracyclic structure.
- Two dimetallic Ir(I) complexes have been prepared by C-H bond activation of the C(sp³)-H₂ groups of the bis(imidazolidine) so obtained, confirming that this methodology provides an alternative to the use of the traditional azolium-based salts.
- A dimetallic Pd(II) complex has been synthesized from a bis(imidazolinium) salt. The bis(imidazolinium) salt was easily prepared by oxidation of the neutral bis(imidazolidine).
- The palladium complexes **3M** and **4M** showed a moderate catalytic activity in the acylation of aryl halides. However, these complexes are ones of the few examples reported in the literature capable to catalyse this reaction. The 3-

chloropyridine-supported complex **4M** performed slightly better than the acetonitrile-based complex **3M**.

5.4 References

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Chapter 6

Experimental Section

6.1 Analytical techniques

Nuclear Magnetic Resonance (NMR)

^1H and ^{13}C NMR spectra were recorded on the following spectrometers at 298 K:

-Varian Innova 300 MHz (^1H 300 MHz, ^{13}C 75 MHz)

-Varian Innova 500 MHz (^1H 500 MHz, ^{13}C 125 MHz)

Chemical shifts are given in ppm (δ), referred to the residual peak of the deuterated solvent (CDCl_3 , CD_2Cl_2 , CD_3CN , acetone- d_6 , CD_3OD and $\text{DMSO}-d_6$) and reported downfield of $\text{Si}(\text{CH}_3)_4$.

Electrospray Mass Spectra (ESI-MS)

Electrospray Mass Spectra (ESI-MS) were recorded on a Micromass Quatro LC instrument; CH_3OH or CH_3CN were used as mobile phase and nitrogen was employed as the drying and nebulizing gas. High Resolution Mass Spectra (HR MS) were recorded on a Q-TOF Premier instrument.

Elemental Analysis

Elemental analyses were carried out on a TrueSpec Miro Series.

Gas Chromatography (GC)

GC analyses were obtained on a Shimadzu GC-2010 apparatus equipped with a FID and Teknokroma (TRB-5MS, 30 m x 0.25 mm x 0.25 μm) column was used.

Infrared Spectroscopy (FT-IR)

Infrared spectra (FT-IR) were performed on a Bruker EQUINOX 55 spectrometer with a spectral window of 4000-600 cm^{-1} . Liquid samples were placed between KBr windows.

Electrochemical measurements

Electrochemical studies were carried out by using an Autolab Potentiostat (Model PGSTAT101) using a three-electrode cell. The cell was equipped with platinum

working and counter electrodes, as well as a silver wire reference electrode. In all experiments CH_2Cl_2 was used as solvent and $[\text{NBu}_4][\text{PF}_6]$ was used as the supporting electrolyte. All redox potentials were referenced to the Fc/Fc^+ couple as internal standard with $E_{1/2}(\text{Fc}/\text{Fc}^+) \text{ vs. SCE} = -0.446 \text{ V}$.

UV-vis spectroscopy

UV-visible absorption spectra were recorded on a Varian Cary Cary 300 BIO spectrophotometer or on a Shimadzu UV-2401PC spectrophotometer, under ambient conditions.

Fluorescence spectroscopy

Emission spectra were recorded on a modular Horiba FluoroLog®-3 spectrofluorometer employing degassed CH_3CN . Quantum yields were determined relative to quinine sulfate in degassed 0.5 M H_2SO_4 as standard ($\Phi_f = 0.546$),¹ exciting at 350 nm or relative to recrystallized anthracene in degassed ethanol as standard ($\Phi_f = 0.27$),¹ exciting at 317 nm.

6.2 Synthesis and Characterization

All the reactions were carried out by using standard Schlenk tube techniques under nitrogen atmosphere unless otherwise stated. Anhydrous solvents were dried using a solvent purification system (SPS M BRAUN) or purchased and degassed prior to use by purging with nitrogen and kept over molecular sieves. All other reagents were used as received from commercial suppliers. Column chromatography was performed on silica gel Merck 60, 62-200 mm unless otherwise stated, using the mixtures of solvents indicated. 1,3-di-*n*-butylimidazolium bromide,² 1,3-di-*n*-butylimidazolium hexafluorophosphate,² 1,3-di-*n*-butyl-benzimidazolium bromide,³ 1,3-di-*n*-butyl-benzimidazolium hexafluorobenzene,³ 1,3-dibutyl-5,6-dinitrobenzimidazolium iodide,⁴ pyrene-4,5,9,10-tetraone,⁵ 2,7-di-*tert*-butylpyrene-4,5,9,10-tetraone,⁵ [1,3-bis(*n*-butyl)imidazole-2-ylidene]dicarbonylchloroiridium,⁶ [1,3-bis(*n*-butyl)benzimidazol-2-ylidene]dicarbonylchlorideiridium,⁶ were prepared according to literature procedures.

6.2.1 Synthesis and characterization of ligand precursors of Chapter 1

Synthesis of [C-H](Br)

[C-H](Br)

[C-H](Br) was prepared in two steps starting from pyrene-4,5-dione:

Step 1: To a solution of pyrene-4,5-dione (500 mg, 2.15 mmol) and ammonium acetate (3.3195 g, 43.07 mmol) in 15 mL of glacial acetic acid was added dropwise formaldehyde (0.200 mL of a 37% aqueous solution, 2.69 mmol). The reaction was refluxed overnight. After cooling, 35 mL of water were added to the reaction mixture and neutralized with concentrated aqueous ammonia (28-30%) to pH 7. The pale brown solid was filtered and washed with water, methanol, and ethyl ether. Yield: 502.1 mg (90%). ^1H NMR (300 MHz, DMSO- d_6): δ 8.71 (d, $^3J_{\text{H-H}} = 7.5$ Hz, 2H, CH_{pyr}), 8.44 (s, 1H, NCHN), 8.23 (d, $^3J_{\text{H-H}} = 7.6$ Hz, 2H, CH_{pyr}), 8.18 (s, 2H, CH_{pyr}), 8.11 (t, $^3J_{\text{H-H}} = 7.6$ Hz, 2H, CH_{pyr}). ^{13}C NMR (75 MHz, DMSO- d_6): δ 139.59 (NCHN), 131.49 (C_{pyr}), 127.63 (CH_{pyr}), 127.30 (C_{pyr}), 126.23 (CH_{pyr}), 125.03 (C_{pyr}), 123.94 (CH_{pyr}), 121.68 (C_{pyr}), 118.70 (CH_{pyr}). Electrospray MS (20 V, m/z): 243.2 $[\text{M} + \text{H}]^+$. Anal. Calcd for $\text{C}_{17}\text{H}_{10}\text{N}_2 \cdot \text{H}_2\text{O}$ (260.30): C, 78.44; H, 4.65; N, 10.77. Found: C, 78.80; H, 5.00; N, 10.40.

Step 2: A solution of the pyrene-imidazole obtained in *step 1* (600 mg, 2.31 mmol) and KOH (194 mg, 3.46 mmol) in DMSO (7 mL) was heated to 50 °C for 2 h. After this time, n-butyl bromide (365 μL , 3.46 mmol) was added and the resulting mixture was stirred at 50 °C for 24 h. The reaction mixture was warmed to room temperature and poured into 10 mL of a 1/1 solution of diethyl ether and water, the organic phase was separated, and the aqueous phase was extracted with diethyl ether (3 X 10 mL). The organic phase and the diethyl ether extracts were combined and concentrated to dryness. Upon removal of the volatiles, the monoalkylated imidazole intermediate was isolated as a yellow solid, and it was used in the next step without further purification. The monoalkylated product was dissolved in 3 mL of n-butyl bromide and heated in a thick-walled Schlenk tube fitted with a Teflon cap at 130 °C for 48 h. The tube was cooled to room temperature, and the desired imidazolium salt was precipitated from the reaction mixture by adding hexane. The solid was collected by filtration and washed with

hexane. Yield: 600 mg (57%). ^1H NMR (300 MHz, CDCl_3): δ 11.69 (s, 1H, NCHN), 8.56 (d, $^3J_{\text{H-H}} = 7.9$ Hz, 2H, CH_{pyr}), 8.38 (d, $^3J_{\text{H-H}} = 7.7$ Hz, 2H, CH_{pyr}), 8.25–8.14 (m, 4H, CH_{pyr}), 5.19 (t, $^3J_{\text{H-H}} = 7.4$ Hz, 4H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 2.37–2.10 (m, 4H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.70–1.65 (m, 4H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.06 (t, $^3J_{\text{H-H}} = 7.3$ Hz, 6H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$). ^{13}C NMR (126 MHz, CDCl_3): δ 141.8 (NCHN), 132.1 (C_{pyr}), 128.4 (C_{pyr}), 127.7 (CH_{pyr}), 127.0 (CH_{pyr}), 126.5 (CH_{pyr}), 123.5 (C_{pyr}), 119.7 (C_{pyr}), 119.2 (CH_{pyr}), 50.7 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 31.5 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 19.7 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 13.7 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$). Electrospray MS (20 V, m/z): 355.4 $[\text{M}]^+$. Anal. Calcd for $\text{C}_{25}\text{H}_{27}\text{BrN}_2 \cdot \text{H}_2\text{O}$ (453.41): C, 66.22; H, 6.45; N, 6.18. Found: C, 66.60; H, 6.10; N, 6.60.

Synthesis of **[C-H](PF₆)**

NH_4PF_6 (190 mg, 1.17 mmol) was added to a solution of salt **[C-H](Br)** (500 mg, 1.10 mmol) in methanol (7 mL). The reaction mixture was stirred at room temperature for 5 h. Then, the beige solid so formed was filtered and washed with methanol and ethyl ether. Yield: 519.9 mg (94%). ^1H NMR (500 MHz, $\text{DMSO}-d_6$): δ 9.87 (s, 1H, NCHN), 8.80 (d, $^3J_{\text{H-H}} = 7.6$ Hz, 2H, CH_{pyr}), 8.50 (d, $^3J_{\text{H-H}} = 7.7$ Hz, 2H, CH_{pyr}), 8.34–8.25 (m, 4H, CH_{pyr}), 5.02 (t, $^3J_{\text{H-H}} = 7.2$ Hz, 4H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 2.14–2.04 (m, 4H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.59–1.48 (m, 4H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.00 (t, $^3J_{\text{H-H}} = 7.3$ Hz, 6H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$). ^{13}C NMR (126 MHz, $\text{DMSO}-d_6$): δ 141.7 (NCHN), 132.0 (C_{pyr}), 128.7 (C_{pyr}), 127.9 (CH_{pyr}), 127.8 (CH_{pyr}), 126.9 (CH_{pyr}), 123.3 (C_{pyr}), 120.6 (C_{pyr}), 120.1 (CH_{pyr}), 50.5 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 31.1 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 19.4 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 14.0 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$). Electrospray MS (20 V, m/z): 355.4 $[\text{M}]^+$. Anal. Calcd for $\text{C}_{25}\text{H}_{27}\text{F}_6\text{N}_2\text{P}$ (500.46): C, 60.00; H, 5.44; N, 5.60. Found: C, 59.70; H, 6.10; N, 5.70.

Synthesis of 1,3-dibutyl-5,6-diaminobenzimidazolium iodide

Hydrazine (8.2 mL of 64% of aqueous solution, 108.19 mmol) was added dropwise to a solution of 1,3-dibutyl-5,6-dinitrobenzimidazolium iodide (1.6 g, 3.57 mmol) and Pd/C (0.4 g of 10% wt. Pd, 0.38 mmol) in 80 mL of deoxygenated ethanol. After 5 minutes, 25 mL of a 1M solution of HCl were added dropwise. The reaction mixture was stirred and heated at 80 °C for 4 h. Then, the solution was cooled

to room temperature and filtered through Celite. The clear solution was concentrated under vacuum and the precipitated white solid was filtered, washed with water and abundant diethyl ether. Yield: 1.24 g (90%). ^1H NMR (300 MHz, $\text{DMSO}-d_6$): δ 9.29 (s, 1H, NCHN), 6.89 (s, 2H, CH_{Ar}), 5.27 (s, 4H, NH_2), 4.25 (t, $^3J_{\text{H-H}} = 6.7$ Hz, 4H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.96-1.73 (m, 4H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.43-1.19 (m, 4H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 0.90 (t, $^3J_{\text{H-H}} = 7.2$ Hz, 6H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$). ^{13}C NMR (75 MHz, $\text{DMSO}-d_6$): δ 137.2 (NCHN), 135.5 (C_{Ar}), 123.8 (C_{Ar}), 94.0 (CH_{Ar}), 45.8 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 30.2 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 19.0 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 13.3 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$). Electrospray MS (20 V, m/z): 261.3 $[\text{M}]^+$. Anal. Calcd. for $\text{C}_{15}\text{H}_{25}\text{IN}_4$ (388.3): C, 46.40; H, 6.49; N, 14.43. Found: C, 46.40; H, 6.47; N, 14.84.

General procedure for the synthesis of [D-H](I), [E-H](I) and [F-H](I)

A solution of 1,3-dibutyl-5,6-diaminobenzimidazolium iodide (0.32 mmol) and the corresponding dione (0.32 mmol) in 50 mL of methanol was refluxed overnight. Then, the reaction mixture was cooled to room temperature and dried under vacuum. The residue was triturated in 5 mL of ethanol. The solid was filtered and subsequently washed with 1 mL of cold ethanol and 10 mL of diethyl ether.

Synthesis of [D-H](I)

Compound [D-H](I) was prepared by reacting 1,3-dibutyl-5,6-diaminobenzimidazolium iodide with pyrene-4,5-dione. Yield: 146.4 mg (78%). ^1H NMR (300 MHz, $\text{DMSO}-d_6$): δ 10.19 (s, 1H, NCHN), 9.30 (d, $^3J_{\text{H-H}} = 7.6$ Hz, 2H, CH_{Ar}), 8.88 (s, 2H, CH_{Ar}), 8.43 (d, $^3J_{\text{H-H}} = 7.7$ Hz, 2H, CH_{Ar}), 8.21-8.09 (m, 4H, CH_{Ar}), 4.65 (t, $^3J_{\text{H-H}} = 7.1$ Hz, 4H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 2.16-1.95 (m, 4H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.62-1.40 (m, 4H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.03 (t, $^3J_{\text{H-H}} = 7.3$ Hz, 6H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$). ^{13}C NMR (75 MHz, $\text{DMSO}-d_6$, 90°C): δ 147.5 (NCHN), 142.8 (C_{Ar}), 138.2 (C_{Ar}), 132.5 (C_{Ar}), 130.6 (CH_{Ar}), 129.6 (C_{Ar}), 127.7 (CH_{Ar}), 126.6 (CH_{Ar}), 124.8 (C_{Ar}), 123.3 (CH_{Ar}), 111.5 (CH_{Ar}), 46.7 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 29.9 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 18.8 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 12.9 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$). Electrospray MS (20 V, m/z): 457.2 $[\text{M}]^+$. Anal. Calcd. for $\text{C}_{31}\text{H}_{29}\text{IN}_4$ (584.5): C, 63.70; H, 5.00; N, 9.59. Found: C, 63.41; H, 5.43; N, 9.61.

Synthesis of [E-H](I)

Compound [E-H](I) was prepared by reacting 1,3-dibutyl-5,6-diaminobenzimidazolium iodide with 2,7-di-*tert*-butylpyrene-4,5-dione. Yield: 180.0 mg (79%). ¹H NMR (300 MHz, DMSO-*d*₆): δ 10.20 (s, 1H, NCHN), 9.54 (s, 2H, CH_{Ar}), 8.93 (br s, 2H, CH_{Ar}), 8.50 (s, 2H, CH_{Ar}), 8.12 (s, 2H, CH_{Ar}), 4.70 (t, ³*J*_{H-H} = 7.2 Hz, 4H, NCH₂CH₂CH₂CH₃), 2.17-2.02 (m, 4H, NCH₂CH₂CH₂CH₃), 1.66 (s, 18H, C(CH₃)₃), 1.61-1.44 (m, 4H, NCH₂CH₂CH₂CH₃), 1.03 (t, ³*J*_{H-H} = 7.3 Hz, 6H, NCH₂CH₂CH₂CH₃). ¹³C NMR (75 MHz, DMSO-*d*₆): δ 149.6 (NCHN), 147.9 (C_{Ar}), 143.5 (C_{Ar}), 138.2 (C_{Ar}), 132.6 (C_{Ar}), 130.8 (C_{Ar}), 127.6 (C_{Ar}), 127.1 (CH_{Ar}), 126.7 (CH_{Ar}), 123.1 (C_{Ar}), 121.0 (CH_{Ar}), 111.7 (CH_{Ar}), 46.9 (NCH₂CH₂CH₂CH₃), 35.2 (NCH₂CH₂CH₂CH₃), 31.6 (C(CH₃)₃), 30.4 (C(CH₃)₃), 19.3 (NCH₂CH₂CH₂CH₃), 13.5 (NCH₂CH₂CH₂CH₃). Electrospray MS (20 V, *m/z*): 569.6 [M]⁺. Anal. Calcd. For C₃₉H₄₅IN₄·H₂O (714.7): C, 65.54; H, 6.63; N, 7.84. Found: C, 65.53; H, 6.76; N, 7.71.

Synthesis of [F-H](I)

Compound [F-H](I) was prepared by reacting 1,3-dibutyl-5,6-diaminobenzimidazolium iodide with acenaphthenequinone. Yield: 122.8 mg (72%). ¹H NMR (500 MHz, DMSO-*d*₆): δ 10.11 (s, 1H, NCHN), 8.99 (s, 2H, CH_{Ar}), 8.45-8.36 (m, 4H, CH_{Ar}), 8.00 (t, ³*J*_{H-H} = 7.5 Hz, 2H, CH_{Ar}), 4.65 (t, ³*J*_{H-H} = 7.2 Hz, 4H, NCH₂CH₂CH₂CH₃), 2.17-1.91 (m, 4H, NCH₂CH₂CH₂CH₃), 1.62-1.30 (m, 4H, NCH₂CH₂CH₂CH₃), 0.99 (t, ³*J*_{H-H} = 6.9 Hz, 6H, NCH₂CH₂CH₂CH₃). ¹³C NMR (75 MHz, DMSO-*d*₆): δ 153.9 (C_{Ar}), 146.7 (NCHN), 138.1 (C_{Ar}), 136.6 (C_{Ar}), 131.9 (C_{Ar}), 130.4 (C_{Ar}), 130.2 (CH_{Ar}), 129.7 (C_{Ar}), 129.1 (CH_{Ar}), 122.0 (CH_{Ar}), 112.8 (CH_{Ar}), 46.9 (NCH₂CH₂CH₂CH₃), 30.4 (NCH₂CH₂CH₂CH₃), 19.2 (NCH₂CH₂CH₂CH₃), 13.4 (NCH₂CH₂CH₂CH₃). Electrospray MS (20 V, *m/z*): 407.2 [M]⁺. Anal. Calcd. for C₂₇H₂₇IN₄ (534.4): C, 60.68; H, 5.09; N, 10.48. Found: C, 59.94; H, 5.10; N, 10.40.

General procedure for the synthesis of [D-H](PF₆), [E-H](PF₆) and [F-H](PF₆)

NH₄PF₆ (1 eq.) was added to a solution of the azolium salt (1 eq.) in a 3:1 mixture methanol/CH₂Cl₂. The reaction mixture was stirred at room temperature overnight. The yellow solid so formed was filtered and washed with methanol and diethyl ether.

Synthesis of [D-H](PF₆)

Compound [D-H](PF₆) was prepared by reacting [D-H](I) (302.1 mg, 0.52 mmol) with NH₄PF₆ (84.2 mg, 0.52 mmol). Yield: 304.5 mg (95%). ¹H NMR (300 MHz, DMSO-*d*₆): δ 10.17 (s, 1H, NCHN), 9.41-9.22 (m, 2H, CH_{Ar}), 9.03-8.77 (m, 2H, CH_{Ar}), 8.60-8.32 (m, 2H, CH_{Ar}), 8.29-8.04 (m, 4H, CH_{Ar}), 4.71-4.55 (m, 4H, NCH₂CH₂CH₂CH₃), 2.18-1.95 (m, 4H, NCH₂CH₂CH₂CH₃), 1.65-1.40 (m, 4H, NCH₂CH₂CH₂CH₃), 1.04 (t, ³J_{H-H} = 7.3 Hz, 6H, NCH₂CH₂CH₂CH₃). ¹³C NMR (75 MHz, DMSO-*d*₆): δ 148.1 (NCHN), 143.2 (C_{Ar}), 138.6 (C_{Ar}), 133.0 (C_{Ar}), 131.0 (C_{Ar}), 130.2 (CH_{Ar}), 128.2 (C_{Ar}), 127.3 (CH_{Ar}), 127.2 (CH_{Ar}), 125.2 (C_{Ar}), 123.7 (CH_{Ar}), 112.0 (CH_{Ar}), 47.0 (NCH₂CH₂CH₂CH₃), 30.4 (NCH₂CH₂CH₂CH₃), 19.2 (NCH₂CH₂CH₂CH₃), 13.5 (NCH₂CH₂CH₂CH₃). Electrospray MS (20 V, *m/z*): 457.2 [M]⁺. Anal. Calcd. For C₃₁H₂₉F₆N₄P·H₂O (620.6): C, 60.00; H, 5.04; N, 9.03. Found: C, 60.05; H, 5.02; N, 9.03.

Synthesis of [E-H](PF₆)

Compound [E-H](PF₆) was prepared by reacting [E-H](I) (159 mg, 0.22 mmol) with NH₄PF₆ (36.3 mg, 0.22 mmol). Yield: (92%). ¹H NMR (300 MHz, DMSO-*d*₆): δ 10.17 (s, 1H, NCHN), 9.53 (s, 2H, CH_{Ar}), 8.95 (s, 2H, CH_{Ar}), 8.49 (s, 2H, CH_{Ar}), 8.11 (s, 2H, CH_{Ar}), 4.68 (t, ³J_{H-H} = 7.6 Hz, 4H, NCH₂CH₂CH₂CH₃), 2.18-1.98 (m, 4H, NCH₂CH₂CH₂CH₃), 1.64 (s, 18H, C(CH₃)₃), 1.58-1.42 (m, 4H, NCH₂CH₂CH₂CH₃), 1.02 (t, ³J_{H-H} = 7.4 Hz, 6H, NCH₂CH₂CH₂CH₃). ¹³C NMR (75 MHz, DMSO-*d*₆): δ 149.6 (NCHN), 148.0 (C_{Ar}), 143.6 (C_{Ar}), 138.3 (C_{Ar}), 132.8 (C_{Ar}), 130.9 (C_{Ar}), 127.7 (C_{Ar}), 127.2 (CH_{Ar}), 126.8 (CH_{Ar}), 123.3 (C_{Ar}), 121.1 (CH_{Ar}), 111.9 (CH_{Ar}), 47.0 (NCH₂CH₂CH₂CH₃), 35.2 (NCH₂CH₂CH₂CH₃), 31.5 (C(CH₃)₃), 30.4 (C(CH₃)₃), 19.3 (NCH₂CH₂CH₂CH₃), 13.5 (NCH₂CH₂CH₂CH₃). Electrospray MS (20 V, *m/z*): 569.6 [M]⁺. Anal. Calcd. For C₃₉H₄₅F₆N₄P (714.8): C, 65.53; H, 6.35; N, 7.84. Found: C, 65.32; H, 6.23; N, 7.83.

Synthesis of [F-H](PF₆)

Compound [F-H](PF₆) was prepared by reacting [F-H](I) (200 mg, 0.37 mmol) with NH₄PF₆ (61.0 mg, 0.37 mmol). Yield: 198.3 (93%). ¹H NMR (500 MHz, DMSO-*d*₆): δ 10.11 (s, 1H, NCHN), 9.04 (s, 2H, CH_{Ar}), 8.48 (d, ³J_{H-H} = 7.0 Hz, 2H, CH_{Ar}), 8.39 (d, ³J_{H-H} = 8.2 Hz, 2H, CH_{Ar}), 8.05-7.98 (m, 2H, CH_{Ar}), 4.67 (t, ³J_{H-H} = 7.3 Hz, 4H, NCH₂CH₂CH₂CH₃), 2.09-1.98 (m, 4H, NCH₂CH₂CH₂CH₃), 1.50-1.40 (m, 4H, NCH₂CH₂CH₂CH₃), 0.99 (t, ³J_{H-H} = 7.4, 6H, NCH₂CH₂CH₂CH₃). ¹³C NMR (75 MHz, DMSO-*d*₆): δ 154.0 (C_{Ar}), 146.7 (NCHN), 138.2 (C_{Ar}), 136.6 (C_{Ar}), 132.0 (C_{Ar}), 130.4 (C_{Ar}), 130.3 (CH_{Ar}), 129.7 (C_{Ar}), 129.2 (CH_{Ar}), 122.1 (CH_{Ar}), 112.8 (CH_{Ar}), 46.9 (NCH₂CH₂CH₂CH₃), 30.4 (NCH₂CH₂CH₂CH₃), 19.2 (NCH₂CH₂CH₂CH₃), 13.4 (NCH₂CH₂CH₂CH₃). Electrospray MS (20 V, *m/z*): 407.2 [M]⁺. Anal. Calcd. For C₂₇H₂₇F₆N₄P·H₂O (570.5): C, 56.84; H, 5.12; N, 9.82. Found: C, 57.14; H, 5.19; N, 9.69.

6.2.2 Synthesis and characterization of metal complexes of Chapter 2

General procedure for the synthesis of 1-4C

KHMDS (1.2 eq) was added dropwise to a solution of the corresponding azolio salt (1 eq.), [MCl(COD)]₂ (M = Rh, Ir, 0.5 eq) in dry THF (10 mL) at -78 °C. The reaction mixture was maintained at -78 °C for 20 min. Then, it was warmed to room temperature and stirred overnight. After removal of the volatiles, the crude solid was dissolved in CH₂Cl₂ and purified by column chromatography using silica gel. Elution with a CH₂Cl₂/acetone mixture (95/5) afforded the separation of a yellow band that contained the desired compound. The final products were precipitated as yellow solids in a CH₂Cl₂/hexane mixture.

Synthesis of 1C

Compound 1C was prepared by reacting [C-H](PF₆) (50 mg, 0.1 mmol) with [RhCl(COD)]₂ (24.7 mg, 0.05 mmol). Yield: 36.1 mg (59%). ¹H NMR (500 MHz, CDCl₃): δ 8.57 (d, ³J_{H-H} = 7.9 Hz, 2H, CH_{pyr}), 8.17 (d, ³J_{H-H} = 7.5 Hz, 2H, CH_{pyr}), 8.09-8.06 (m, 4H, CH_{pyr}), 5.88-5.82 (m, 2H, NCH₂CH₂CH₂CH₃), 5.38-5.32 (m, 2H, NCH₂CH₂CH₂CH₃), 5.22 (br s, 2H, CH_{COD}), 3.50 (br s, 2H, CH_{COD}), 2.54-2.50 (m, 4H, CH₂ COD), 2.44-2.37 (m, 2H,

$\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 2.06–2.05 (m, 6H; 2H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ and 4H, CH_2COD), 1.83–1.78 (m, 4H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.21 (t, $^3J_{\text{H-H}} = 7.4$ Hz, 6H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$). ^{13}C NMR (126 MHz, CDCl_3): δ 191.5 (d, $^1J_{\text{Rh-C}} = 51.7$ Hz, Rh- $\text{C}_{\text{carbene}}$), 132.2 (C_{pyr}), 128.8 (C_{pyr}), 128.2 (CH_{pyr}), 126.2 (CH_{pyr}), 125.2 (CH_{pyr}), 122.7 (C_{pyr}), 121.2 (CH_{pyr}), 119.0 (CH_{pyr}), 99.1 (d, $^1J_{\text{Rh-C}} = 19.9$ Hz, Rh- CH_{COD}), 69.1 (d, $^1J_{\text{Rh-C}} = 14.2$ Hz, Rh- CH_{COD}), 52.1 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 52.0 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 33.2 (CH_2COD), 32.0 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 29.2 (CH_2COD), 20.6 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 14.0 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 13.9 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$). Electrospray MS (20 V, m/z): 606.2 $[\text{M} - \text{Cl} + \text{CH}_3\text{CN}]^+$. HRMS ESI-TOF-MS (positive mode): $[\text{M} - \text{Cl}]^+$ monoisotopic peak 565.2090, calcd 565.2097, $\epsilon_r = 1.2$ ppm. Anal. Calcd for $\text{C}_{33}\text{H}_{38}\text{ClRhN}_2 \cdot 0.5\text{H}_2\text{O}$ (610.04): C, 64.97; H, 6.44; N, 4.59. Found: C, 64.70; H, 6.76; N, 4.70.

Figure 6.1 ^1H - ^1H COSY NMR spectrum of **1C** in CDCl_3

Synthesis of 2C

Compound **2C** was prepared by reacting **[C-H](Br)** (120 mg, 0.26 mmol) with $[\text{RhCl}(\text{COD})]_2$ (69.0 mg, 0.14 mmol) and NaBr (54 mg, 0.53 mmol). Yield: 136.3 mg (80%). ^1H NMR (500 MHz, CDCl_3): δ 8.52 (d, $^3J_{\text{H-H}} = 8$ Hz, 2H, CH_{pyr}), 8.11 (d, $^3J_{\text{H-H}} = 7.5$ Hz, 2H, CH_{pyr}), 8.04–8.00 (m, 4H, CH_{pyr}), 5.82–5.75 (m, 2H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 5.34–5.28 (m, 2H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 5.31 (br s, 2H, CH_{COD}), 3.52 (br s, 2H, CH_{COD}), 2.50–2.41 (m, 6H; 4H, CH_2 COD and 2H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 2.10–2.05 (m, 6H; 4H, CH_2 COD and 2H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.84–1.77 (m, 4H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.21 (t, $^3J_{\text{H-H}} = 7.5$ Hz, 6H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$). ^{13}C NMR (126 MHz, CDCl_3): δ 191.5 (d, $^1J_{\text{Rh-C}} = 52.9$, Rh- $\text{C}_{\text{carbene}}$), 132.2 (C_{pyr}), 128.8 (C_{pyr}), 128.3 (CH_{pyr}), 126.2 (CH_{pyr}), 125.2 (CH_{pyr}), 122.7 (C_{pyr}), 121.2 (C_{pyr}), 118.9 (CH_{pyr}), 99.1 (d, $^1J_{\text{Rh-C}} = 20.2$ Hz, Rh- CH_{COD}), 69.1 (d, $^1J_{\text{Rh-C}} = 15.1$ Hz, Rh- CH_{COD}), 52.1 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 52.0 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 33.2 (CH_2 COD), 32.0 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 29.2 (CH_2 COD), 20.6 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 14.0 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$). Electrospray MS (20 V, m/z): 606.2 $[\text{M} - \text{Br} + \text{CH}_3\text{CN}]^+$. Anal. Calcd for $\text{C}_{33}\text{H}_{38}\text{BrN}_2\text{Rh}$ (645.48): C, 61.40; H, 5.93; N, 4.34. Found: C, 60.50; H, 6.30; N, 4.40.

Synthesis of 3C

Compound **3C** was prepared by reacting **[C-H](PF₆)** (50 mg, 0.1 mmol) with $[\text{IrCl}(\text{COD})]_2$ (33.6 mg, 0.05 mmol). Yield: 38.2 mg (54%). ^1H NMR (500 MHz, CDCl_3): δ 8.60 (d, $^3J_{\text{H-H}} = 8.0$ Hz, 2H, CH_{pyr}), 8.21 (d, $^3J_{\text{H-H}} = 7.6$ Hz, 2H, CH_{pyr}), 8.12–8.09 (m, 4H, CH_{pyr}), 5.64–5.62 (m, 2H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 5.21–5.17 (m, 2H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 4.87 (br s, 2H, CH_{COD}), 3.09 (br s, 2H, CH_{COD}), 2.37–2.31 (m, 6H; 2H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ and 4H, CH_2 COD), 2.08–2.04 (m, 2H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.88–1.86 (m, 2H, CH_2 COD), 1.76–1.72 (m, 4H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.63–1.61 (m, 2H, CH_2 COD), 1.16 (t, $^3J_{\text{H-H}} = 6.8$ Hz, 6H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$). ^{13}C NMR (75 MHz, CDCl_3): δ 187.8 (Ir- $\text{C}_{\text{carbene}}$), 132.2 (C_{pyr}), 128.7 (C_{pyr}), 128.3 (CH_{pyr}), 126.3 (CH_{pyr}), 125.3 (CH_{pyr}), 122.8 (C_{pyr}), 121.3 (C_{pyr}), 119.0 (CH_{pyr}), 85.3 (CH_{COD}), 52.7 (CH_{COD}), 51.6 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 33.8 (CH_2 COD), 31.9 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 29.8 (CH_2 COD), 20.5 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 13.9 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$). Electrospray MS (20 V, m/z): 696.3 $[\text{M} - \text{Cl} + \text{CH}_3\text{CN}]^+$. HRMS ESI-TOF-MS (positive mode): $[\text{M} - \text{Cl} + \text{CH}_3\text{CN}]^+$ monoisotopic peak

696.2929, calcd 696.2932, $\epsilon_r = 0.4$ ppm. Anal. Calcd for $C_{33}H_{38}ClIrN_2 \cdot H_2O$ (708.35): C, 55.95; H, 5.69; N, 3.95. Found: C, 55.90; H, 5.82; N, 3.91.

Figure 6.2 1H - 1H COSY NMR spectrum of **3C** in $CDCl_3$

Figure 6.3 ^{13}C - 1H HSQC NMR spectrum of **3C** in $CDCl_3$

Synthesis of 4C

Compound **4C** was prepared by reacting **[C-H](Br)** (120 mg, 0.26 mmol) with $[\text{IrCl}(\text{COD})]_2$ (94.0 mg, 0.14 mmol) and NaBr (54 mg, 0.53 mmol). Yield: 109.7 mg (56%). ^1H NMR (500 MHz, CDCl_3): δ 8.61 (d, $^3J_{\text{H-H}} = 8$ Hz, 2H, CH_{pyr}), 8.22 (d, $^3J_{\text{H-H}} = 7.5$ Hz, 2H, CH_{pyr}), 8.13–8.10 (m, 4H, CH_{pyr}), 5.68–5.62 (m, 2H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 5.22–5.18 (m, 2H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 4.88 (br s, 2H, CH_{COD}), 3.10 (br s, 2H, CH_{COD}), 2.38–2.32 (m, 6H; 4H, CH_2 COD and 2H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 2.09–2.05 (m, 2H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.89–1.87 (m, 2H, CH_2 COD), 1.77–1.72 (m, 4H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.64–1.62 (m, 2H, CH_2 COD), 1.17 (t, $^3J_{\text{H-H}} = 7.5$ Hz, 6H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$). ^{13}C NMR (75 MHz, CDCl_3): δ 187.8 (Ir- $\text{C}_{\text{carbene}}$), 132.2 (C_{pyr}), 128.7 (C_{pyr}), 128.2 (CH_{pyr}), 126.3 (CH_{pyr}), 125.5 (CH_{pyr}), 122.8 (C_{pyr}), 121.3 (C_{pyr}), 118.9 (CH_{pyr}), 85.3 (CH_{COD}), 52.7 (CH_{COD}), 51.6 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 33.8 (CH_2 COD), 31.9 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 29.8 (CH_2 COD), 20.5 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 13.9 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$). Electrospray MS (20 V, m/z): 696.3 $[\text{M} - \text{Br} + \text{CH}_3\text{CN}]^+$. Anal. Calcd for $\text{C}_{33}\text{H}_{38}\text{BrIrN}_2$ (734.79): C, 53.94; H, 5.21; N, 3.81. Found: C, 54.00; H, 5.50; N, 3.90.

General procedure for the synthesis of 1-2D, 1-2E and 1-2F

A mixture of the corresponding azolium salt (1 eq.), potassium *tert*-butoxide (1.1 eq.) and $[\text{IrCl}(\text{COD})]_2$ (0.5 eq.) in 10 mL of THF was stirred overnight at room temperature. After removal of the volatiles, the crude solid was purified by chromatographic column, using CH_2Cl_2 as eluent.

Synthesis of 1D

Compound **1D** was prepared from **[D-H](I)** (60 mg, 0.10 mmol) in the presence of NaI (46.2 mg, 0.31 mmol). Yield: 54.1 mg (60%). ^1H NMR (300 MHz, CDCl_3): δ 9.53 (d, $^3J_{\text{H-H}} = 7.7$ Hz, 2H, CH_{Ar}), 8.28 (d, $^3J_{\text{H-H}} = 7.7$ Hz, 2H, CH_{Ar}), 8.17–7.96 (m, 6H, CH_{Ar}), 5.09 (br s, 2H, CH_{COD}), 5.00–4.65 (m, 4H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 3.15 (br s, 2H, CH_{COD}), 2.50–2.17 (m, 6H; 4H CH_2 COD and 2H $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 2.17–1.89 (m, 6H; 4H CH_2 COD and 2H $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.75–1.61 (m, 4H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.16 (t, $^3J_{\text{H-H}} = 7.3$ Hz, 6H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$). ^{13}C NMR (75 MHz, CDCl_3): δ 202.7 (Ir- $\text{C}_{\text{carbene}}$), 142.8 (C_{Ar}), 138.6 (C_{Ar}), 137.7 (C_{Ar}), 131.6 (C_{Ar}), 129.6 (C_{Ar}), 129.3 (CH_{Ar}), 127.4 (CH_{Ar}), 126.9 (CH_{Ar}), 126.1 (C_{Ar}), 123.9 (CH_{Ar}), 106.6 (CH_{Ar}), 86.9 (CH_{COD}), 56.6 (CH_{COD}), 48.8

(NCH₂CH₂CH₂CH₃), 33.1 (NCH₂CH₂CH₂CH₃), 30.8 (CH₂ COD), 30.4 (CH₂ COD), 20.8 (NCH₂CH₂CH₂CH₃), 14.0 (NCH₂CH₂CH₂CH₃). Electrospray MS (20 V, *m/z*): 798.4 [M-I+CH₃CN]⁺. Anal. Calcd. for C₃₉H₄₀IIrN₄ (883.9): C, 53.00; H, 4.56; N, 6.34. Found: C, 52.94; H, 4.68; N, 6.59.

Synthesis of 2D

Compound **2D** was prepared from [**D-H**](PF₆) (100 mg, 0.16 mmol). Yield: 100.2 (78%). ¹H NMR (300 MHz, CDCl₃): δ 9.50 (d, ³*J*_{H-H} = 7.8 Hz, 2H, CH_{Ar}), 8.26 (d, ³*J*_{H-H} = 7.8 Hz, 2H, CH_{Ar}), 8.13-7.96 (m, 6H, CH_{Ar}), 5.03-4.72 (m, 6H, 4H NCH₂CH₂CH₂CH₃ and 2H CH_{COD}), 3.14 (br s, 2H, CH_{COD}), 2.46-2.17 (m, 6H, 4H CH₂ COD and 2H NCH₂CH₂CH₂CH₃), 2.17-1.75 (m, 6H, 4H CH₂ COD and 2H NCH₂CH₂CH₂CH₃), 1.75-1.61 (m, 4H, NCH₂CH₂CH₂CH₃), 1.17 (t, ³*J*_{H-H} = 6.7 Hz, 6H, NCH₂CH₂CH₂CH₃). ¹³C NMR (75 MHz, CDCl₃): δ 202.0 (Ir-C_{carbene}), 142.8 (C_{Ar}), 138.6 (C_{Ar}), 137.6 (C_{Ar}), 131.6 (C_{Ar}), 129.6 (C_{Ar}), 129.3 (CH_{Ar}), 127.4 (CH_{Ar}), 126.9 (CH_{Ar}), 126.1 (C_{Ar}), 123.9 (CH_{Ar}), 106.6 (CH_{Ar}), 88.9 (CH_{COD}), 53.3 (CH_{COD}), 49.0 (NCH₂CH₂CH₂CH₃), 33.8 (NCH₂CH₂CH₂CH₃), 31.4 (CH₂ COD), 29.5 (CH₂ COD), 20.8 (NCH₂CH₂CH₂CH₃), 14.0 (NCH₂CH₂CH₂CH₃). Electrospray MS (20 V, *m/z*): 798.4 [M-Cl+CH₃CN]⁺. Anal. Calcd. for C₃₉H₄₀ClIrN₄ (792.4): C, 59.11; H, 5.09; N, 7.07. Found: C, 59.16; H, 5.08; N, 7.08.

Synthesis of 1E

Compound **1E** was prepared from [**E-H**](I) (60 mg, 0.08 mmol) in the presence of NaI (37.8 mg, 0.25 mmol). Yield: 38.3 mg (46%). ¹H NMR (500 MHz, CDCl₃): δ 9.65 (s, 2H, CH_{Ar}), 8.27 (s, 2H, CH_{Ar}), 8.13 (s, 2H, CH_{Ar}), 7.99 (s, 2H, CH_{Ar}), 5.08 (s, 2H, CH_{COD}), 4.90 (td, *J*_{H-H} = 12.8, 5.3 Hz, 2H, NCH₂CH₂CH₂CH₃), 4.79 (td, *J*_{H-H} = 13.0, 5.0 Hz, 2H, NCH₂CH₂CH₂CH₃), 3.15 (s, 2H, CH_{COD}), 2.52-2.19 (m, 8H, 4H CH₂ COD and 4H NCH₂CH₂CH₂CH₃), 2.16-2.01 (m, 2H, CH₂ COD), 2.01-1.90 (m, 2H, CH₂ COD), 1.69 (s, 18H, C(CH₃)₃), 1.54 (s, 4H, NCH₂CH₂CH₂CH₃), 1.17 (t, ³*J*_{H-H} = 7.4 Hz, 6H, NCH₂CH₂CH₂CH₃). ¹³C NMR (75 MHz, CDCl₃): δ 202.1 (Ir-C_{carbene}), 149.8 (C_{Ar}), 143.3 (C_{Ar}), 138.3 (C_{Ar}), 137.4 (C_{Ar}), 131.2 (C_{Ar}), 129.0 (C_{Ar}), 127.4 (CH_{Ar}), 125.8 (CH_{Ar}), 124.1 (C_{Ar}), 121.4 (CH_{Ar}), 106.6 (CH_{Ar}), 86.6 (CH_{COD}), 56.5 (CH_{COD}), 48.8 (NCH₂CH₂CH₂CH₃), 35.7 (C(CH₃)₃), 33.1 (NCH₂CH₂CH₂CH₃), 32.1 (C(CH₃)₃), 30.8

(CH₂ COD), 30.4 (CH₂ COD), 20.8 (NCH₂CH₂CH₂CH₃), 14.0 (NCH₂CH₂CH₂CH₃). Electrospray MS (20 V, *m/z*): 910.4 [M-I+CH₃CN]⁺. Anal. Calcd. for C₄₇H₅₆IrN₄ (996.1): C, 56.67; H, 5.67; N, 5.62. Found: C, 56.29; H, 5.68; N, 5.71.

Synthesis of 2E

Compound **2E** was prepared from **[E-H](PF₆)** (100 mg, 0.14 mmol). Yield: 93.0 (73%). ¹H NMR (300 MHz, CDCl₃): δ 9.63 (s, 2H, CH_{Ar}), 8.26 (s, 2H, CH_{Ar}), 8.03 (s, 2H, CH_{Ar}), 7.95 (s, 2H, CH_{Ar}), 5.14-4.64 (m, 6H, 4H NCH₂CH₂CH₂CH₃ and 2H CH_{COD}), 3.16 (br s, 2H, CH_{COD}), 2.58-2.20 (m, 6H, 4H CH₂ COD and 2H NCH₂CH₂CH₂CH₃), 2.21-1.75 (m, 6H, 4H CH₂ COD and 2H NCH₂CH₂CH₂CH₃), 1.71 (s, 22H, 18H C(CH₃)₃ and 4H NCH₂CH₂CH₂CH₃), 1.19 (t, ³J_{H-H} = 7.3 Hz, 6H, NCH₂CH₂CH₂CH₃). ¹³C NMR (75 MHz, CDCl₃): δ 201.5 (Ir-C_{carbene}), 149.8 (C_{Ar}), 143.3 (C_{Ar}), 138.4 (C_{Ar}), 137.3 (C_{Ar}), 131.3 (C_{Ar}), 129.0 (C_{Ar}), 127.4 (CH_{Ar}), 125.9 (CH_{Ar}), 124.2 (C_{Ar}), 121.5 (CH_{Ar}), 106.7 (CH_{Ar}), 88.7 (CH_{COD}), 53.2 (CH_{COD}), 49.0 (NCH₂CH₂CH₂CH₃), 35.7 (C(CH₃)₃), 33.8 (NCH₂CH₂CH₂CH₃), 32.1 (C(CH₃)₃), 31.4 (CH₂ COD), 29.5 (CH₂ COD), 20.8 (NCH₂CH₂CH₂CH₃), 14.1 (NCH₂CH₂CH₂CH₃). Electrospray MS (20 V, *m/z*): 910.4 [M-Cl+CH₃CN]⁺. Anal. Calcd. for C₄₇H₅₆ClIrN₄ (904.6): C, 62.40; H, 6.24; N, 6.19. Found: C, 62.14; H, 6.31; N, 6.25.

Synthesis of 1F

Compound **1F** was prepared from **[F-H](I)** (50 mg, 0.09 mmol) in the presence of NaI (42.1 mg, 0.28 mmol). Yield: 35.6 mg (46%). ¹H NMR (500 MHz, CDCl₃): δ 8.42 (d, ³J_{H-H} = 6.9 Hz, 2H, CH_{Ar}), 8.13 (d, ³J_{H-H} = 8.2 Hz, 2H, CH_{Ar}), 8.05 (s, 2H, CH_{Ar}), 7.86 (t, ³J_{H-H} = 7.5 Hz, 2H, CH_{Ar}), 5.04 (s, 2H, CH_{COD}), 4.90-4.79 (m, 2H, NCH₂CH₂CH₂CH₃), 4.79-4.68 (m, 2H, NCH₂CH₂CH₂CH₃), 3.10 (s, 2H, CH_{COD}), 2.37-2.16 (m, 6H; 4H CH₂ COD and 2H NCH₂CH₂CH₂CH₃), 2.08-1.85 (m, 6H; 4H CH₂ COD and 2H NCH₂CH₂CH₂CH₃), 1.67-1.57 (m, 4H, NCH₂CH₂CH₂CH₃), 1.11 (t, ³J_{H-H} = 7.3 Hz, 6H, NCH₂CH₂CH₂CH₃). ¹³C NMR (126 MHz, CDCl₃): δ 200.5 (Ir-C_{carbene}), 153.8 (C_{Ar}), 137.6 (C_{Ar}), 136.9 (C_{Ar}), 136.8 (C_{Ar}), 132.0 (C_{Ar}), 130.3 (C_{Ar}), 129.7 (CH_{Ar}), 128.9 (CH_{Ar}), 121.7 (CH_{Ar}), 108.0 (CH_{Ar}), 86.4 (CH_{COD}), 56.4 (CH_{COD}), 48.8 (NCH₂CH₂CH₂CH₃), 33.1 (NCH₂CH₂CH₂CH₃), 30.9 (CH₂ COD), 30.4 (CH₂ COD), 20.8

(NCH₂CH₂CH₂CH₃), 14.0 (NCH₂CH₂CH₂CH₃). Electrospray MS (20 V, *m/z*): 748.4 [M-I+CH₃CN]⁺. Anal. Calcd. for C₃₅H₃₈IrN₄ (833.8): C, 50.42; H, 4.59; N, 6.72. Found: C, 50.10; H, 4.57; N, 6.70.

Synthesis of 2F

Compound **2F** was prepared from [F-H](PF₆) (100 mg, 0.18 mmol). Yield: 68.4 mg (53%). ¹H NMR (300 MHz, CDCl₃): δ 8.41 (d, ³J_{H-H} = 6.9 Hz, 2H, CH_{Ar}), 8.12 (d, ³J_{H-H} = 8.3 Hz, 2H, CH_{Ar}), 8.04 (s, 2H, CH_{Ar}), 7.85 (t, ³J_{H-H} = 7.6 Hz, 2H, CH_{Ar}), 5.05-4.55 (m, 6H, 2H CH_{COD} and 4H NCH₂CH₂CH₂CH₃), 3.08 (br s, 2H, CH_{COD}), 2.50-2.11 (m, 8H, 4H CH₂COD and 4H NCH₂CH₂CH₂CH₃), 2.11-1.73 (m, 4H, 4H CH₂COD), 1.73-1.58 (m, 4H, NCH₂CH₂CH₂CH₃), 1.12 (t, ³J_{H-H} = 7.4 Hz, 6H, NCH₂CH₂CH₂CH₃). ¹³C NMR (75 MHz, CDCl₃): δ 199.9 (Ir-C_{carbene}), 153.7 (C_{Ar}), 137.6 (C_{Ar}), 136.8 (C_{Ar}), 136.7 (C_{Ar}), 132.0 (C_{Ar}), 130.3 (C_{Ar}), 129.7 (CH_{Ar}), 128.9 (CH_{Ar}), 121.7 (CH_{Ar}), 108.0 (CH_{Ar}), 88.4 (CH_{COD}), 53.1 (CH_{COD}), 49.0 (NCH₂CH₂CH₂CH₃), 33.8 (NCH₂CH₂CH₂CH₃), 31.5 (CH₂ COD), 29.5 (CH₂ COD), 20.7 (NCH₂CH₂CH₂CH₃), 14.0 (NCH₂CH₂CH₂CH₃). Electrospray MS (20 V, *m/z*): 748.4 [M-Cl+CH₃CN]⁺. Anal. Calcd. For C₃₅H₃₈ClIrN₄ (742.4): C, 56.63; H, 5.16; N, 7.55. Found: C, 56.46; H, 5.14; N, 7.53.

General procedure for the synthesis of the carbonyl derivatives 5C, 3D, 3E and 3F

CO gas was bubbled through a solution of Ir-COD complex in dichloromethane (5 mL) for 20 minutes at 0°C. The solution was concentrated under reduced pressure, and hexane was added to give carbonyl derivative as a yellow solid.

Synthesis of 5C

Compound **5C** was prepared from **3C** (38.2 mg, 0.05 mmol). Yield: 28.1 mg (77%). ¹H NMR (500 MHz, CDCl₃): δ 8.50 (d, ³J_{H-H} = 8.0 Hz, 2H, CH_{pyr}), 8.18 (d, ³J_{H-H} = 7.6 Hz, 2H, CH_{pyr}), 8.08-8.02 (m, 4H, CH_{pyr}), 5.39-5.30 (m, 2H, NCH₂CH₂CH₂CH₃), 5.20-5.07 (m, 2H, NCH₂CH₂CH₂CH₃), 2.31-2.20 (m, 2H, NCH₂CH₂CH₂CH₃), 2.12-2.02 (m, 2H, NCH₂CH₂CH₂CH₃), 1.80-1.64 (m, 4H, NCH₂CH₂CH₂CH₃), 1.13 (t, ³J_{H-H} = 7.4 Hz, 6H, NCH₂CH₂CH₂CH₃). ¹³C NMR (126 MHz, CDCl₃): δ 181.3 (Ir-C_{carbene}), 178.5 (Ir-CO), 168.1 (Ir-CO), 132.2 (C_{pyr}), 128.7 (C_{pyr}), 128.3 (CH_{pyr}), 126.4 (CH_{pyr}), 126.0

(CH_{pyr}), 123.1 (C_{pyr}), 120.9 (C_{pyr}), 119.0 (CH_{pyr}), 52.1 (NCH₂CH₂CH₂CH₃), 31.4 (NCH₂CH₂CH₂CH₃), 20.3 (NCH₂CH₂CH₂CH₃), 14.0 (NCH₂CH₂CH₂CH₃). Electrospray MS (20 V, *m/z*): 644.2 [M – Cl + CH₃CN]⁺. HRMS ESI-TOF-MS (positive mode): [M – Cl + CH₃CN]⁺ monoisotopic peak 644.1894, calcd 644.1890, ε_r = 0.6 ppm. Anal. Calcd for C₂₇H₂₈ClIrN₂O₂·H₂O (656.19): C, 49.42; H, 4.30; N, 4.27. Found: C, 50.00; H, 4.45; N, 4.24.

Synthesis of 3D

Compound **3D** was prepared from **2D** (50 mg, 0.06 mmol). Yield: 44.9 mg (96%). ¹H NMR (300 MHz, CDCl₃): δ 9.40 (d, ³J_{H-H} = 7.6 Hz, 2H, CH_{Ar}), 8.27 (d, ³J_{H-H} = 7.8 Hz, 2H, CH_{Ar}), 8.18-7.93 (m, 6H, CH_{Ar}), 5.04-4.78 (m, 2H, NCH₂CH₂CH₂CH₃), 4.78-4.54 (m, 2H, NCH₂CH₂CH₂CH₃), 2.31-1.93 (m, 4H NCH₂CH₂CH₂CH₃), 1.75-1.58 (m, 4H, NCH₂CH₂CH₂CH₃), 1.12 (t, ³J_{H-H} = 7.4 Hz, 6H, NCH₂CH₂CH₂CH₃). ¹³C NMR (75 MHz, CDCl₃): δ 191.7 (Ir-C_{carbene}), 181.2 (Ir-CO), 168.3 (Ir-CO), 143.5 (C_{Ar}), 138.6 (C_{Ar}), 136.1 (C_{Ar}), 131.5 (C_{Ar}), 129.7 (CH_{Ar}), 129.2 (C_{Ar}), 127.4 (CH_{Ar}), 127.0 (CH_{Ar}), 126.1 (C_{Ar}), 124.2 (CH_{Ar}), 108.6 (CH_{Ar}), 49.5 (NCH₂CH₂CH₂CH₃), 31.3 (NCH₂CH₂CH₂CH₃), 20.5 (NCH₂CH₂CH₂CH₃), 14.0 (NCH₂CH₂CH₂CH₃). Electrospray MS (20 V, *m/z*): 746.3 [M-Cl+CH₃CN]⁺. Anal. Calcd. for C₃₃H₂₈ClIrN₄O₂ (740.3): C, 53.54; H, 3.81; N, 7.57. Found: C, 53.46; H, 3.92; N, 7.50.

Synthesis of 3E

Compound **3E** was prepared from **2E** (50 mg, 0.06 mmol). Yield: 46.0 (96%). ¹H NMR (300 MHz, CDCl₃): δ 9.61 (s, 2H, CH_{Ar}), 8.27 (s, 2H, CH_{Ar}), 8.13 (s, 2H, CH_{Ar}), 7.96 (s, 2H, CH_{Ar}), 5.10-4.82 (m, 2H, NCH₂CH₂CH₂CH₃), 4.82-4.62 (m, 2H, NCH₂CH₂CH₂CH₃), 2.34-2.04 (m, 4H, NCH₂CH₂CH₂CH₃), 1.76-1.60 (m, 22H, 18H C(CH₃)₃ and 4H NCH₂CH₂CH₂CH₃), 1.13 (t, ³J_{H-H} = 7.3 Hz, 6H, NCH₂CH₂CH₂CH₃). ¹³C NMR (75 MHz, CDCl₃): δ 191.3 (Ir-C_{carbene}), 181.2 (Ir-CO), 168.3 (Ir-CO), 150.0 (C_{Ar}), 144.1 (C_{Ar}), 138.5 (C_{Ar}), 135.9 (C_{Ar}), 131.3 (C_{Ar}), 128.8 (C_{Ar}), 127.5 (CH_{Ar}), 126.3 (CH_{Ar}), 124.3 (C_{Ar}), 121.8 (CH_{Ar}), 108.6 (CH_{Ar}), 49.5 (NCH₂CH₂CH₂CH₃), 35.7 (C(CH₃)₃), 32.1 (C(CH₃)₃), 31.3 (NCH₂CH₂CH₂CH₃), 20.5 (NCH₂CH₂CH₂CH₃), 14.0 (NCH₂CH₂CH₂CH₃). Electrospray MS (20 V, *m/z*): 858.4

$[\text{M-Cl}+\text{CH}_3\text{CN}]^+$. Anal. Calcd. for (870.5): C, 56.57; H, 5.33; N, 6.44. Found: C, 56.88; H, 5.33; N, 6.45.

Synthesis of 3F

Compound **3F** was prepared from **2F** (50 mg, 0.07 mmol). Yield: 44.3 mg (95%). ^1H NMR (500 MHz, CDCl_3): δ 8.42 (d, $^3J_{\text{H-H}} = 6.7$ Hz, 2H, CH_{Ar}), 8.19 (s, 2H, CH_{Ar}), 8.15 (d, $^3J_{\text{H-H}} = 8.0$ Hz, 2H, CH_{Ar}), 7.88 (t, $^3J_{\text{H-H}} = 7.2$ Hz, 2H, CH_{Ar}), 4.97-4.77 (m, 2H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 4.77-4.58 (m, 2H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 2.28-1.94 (m, 4H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.70-1.43 (m, 4H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.08 (t, $^3J_{\text{H-H}} = 7.1$ Hz, 6H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$). ^{13}C NMR (75 MHz, CDCl_3): δ 189.7 (Ir- $\text{C}_{\text{carbene}}$), 181.2 (Ir-CO), 168.3 (Ir-CO), 154.1 (C_{Ar}), 137.7 (C_{Ar}), 137.0 (C_{Ar}), 135.1 (C_{Ar}), 131.4 (C_{Ar}), 130.1 (C_{Ar}), 129.9 (CH_{Ar}), 128.8 (CH_{Ar}), 121.8 (CH_{Ar}), 109.5 (CH_{Ar}), 49.4 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 31.3 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 20.4 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 14.0 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$). Electrospray MS (20 V, m/z): 696.3 $[\text{M-Cl}+\text{CH}_3\text{CN}]^+$. Anal. Calcd. For $\text{C}_{29}\text{H}_{26}\text{ClIrN}_4\text{O}_2$ (690.2) C, 50.46; H, 3.80; N, 8.12. Found: C, 50.40; H, 3.75; N, 8.10.

General procedure for the synthesis of 2A, 2B and 6C

A solution of the corresponding bromide salt (0.64 mmol) and $[\text{NiCp}_2]$ (145.4 mg, 0.77 mmol) in THF (15 mL) was stirred at room temperature for 10 min. Then, DMF (10 mL) was added and the reaction mixture was heated at reflux for 6 h. The reaction mixture was cooled to room temperature and all volatiles were removed under high vacuum. The crude solid residue was dissolved in CH_2Cl_2 (2 mL) and purified by column chromatography using silica gel. Elution with CH_2Cl_2 afforded the separation of a red band that contained the desired complex. The desired complex was purified by precipitation from a mixture of CH_2Cl_2 /hexane.

Synthesis of 2A

Compound **2A** was prepared from 1,3-di-*n*-butylimidazolium bromide (167.2 mg, 0.64 mmol). Yield: 130.2 mg (53%); ^1H NMR (300 MHz, CDCl_3): δ 6.93 (s, 2H, CH_{Im}), 5.26 (s, 5H, CH_{Cp}), 4.99-4.78 (m, 2H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 4.78-4.52 (m, 2H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 2.13-1.72 (m, 4H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.69-1.39 (m, 4H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.05 ppm (t, $^3J_{\text{H-H}} =$

7.0 Hz, 6 H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$). ^{13}C NMR (75 MHz, CDCl_3): δ 159.9 ($\text{Ni-C}_{\text{carbene}}$), 122.0 (CH_{Im}), 91.8 (CH_{Cp}), 52.0 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 33.1 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 20.3 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 14.0 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$). Electrospray MS (20 V, m/z): 303 $[\text{M-Br}]^+$, 344 $[\text{M-Br} + \text{CH}_3\text{CN}]^+$. Anal. Calcd For $\text{C}_{16}\text{H}_{25}\text{BrN}_2\text{Ni}$ (383.98): C 50.05, H 6.56, N 7.30. Found: C 50.10, H 6.66, N 7.25.

Synthesis of 2B

Compound **2B** was prepared from 1,3-di-*n*-butyl-benzimidazolium bromide (199.2 mg, 0.64 mmol). Yield : 130.6 mg (47 %). ^1H NMR (300 MHz, CDCl_3): δ 7.39–7.29 (m, 2 H, CH_{BIm}), 7.25–7.17 (m, 2 H, CH_{BIm}), 5.36 (s, 5 H, CH_{Cp}), 5.33–5.17 (m, 2 H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 5.00–4.79 (m, 2 H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 2.30–2.05 (m, 2 H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 2.01–1.79 (m, 2 H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.73–1.57 (m, 4 H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.12 ppm (t, $^3J_{\text{H-H}} = 7.3$ Hz, 6 H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$). ^{13}C NMR (75 MHz, CDCl_3): δ = 177.1 ($\text{Ni-C}_{\text{carbene}}$), 135.4 (C_{BIm}), 122.5 (CH_{BIm}), 110.1 (CH_{BIm}), 92.4 (CH_{Cp}), 49.8 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 32.0 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 20.7 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 14.1 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$). Electrospray MS (20 V, m/z): 353 $[\text{M-Br}]^+$, 394 $[\text{M-Br} + \text{CH}_3\text{CN}]^+$. Anal. Calcd. For $\text{C}_{20}\text{H}_{27}\text{BrN}_2\text{Ni}$ (434.04): C 55.34, H 6.27, N 6.45. Found: C 55.98, H 6.36, N 6.43.

Synthesis of 6C

Compound **6C** was prepared from **[C-H](Br)** (290.2 mg, 0.64 mmol). Yield: 206.5 mg (56%). ^1H NMR (300 MHz, CDCl_3): δ 8.64 (d, $^3J_{\text{H-H}} = 8.0$ Hz, 2H, CH_{pyr}), 8.23 (d, $^3J_{\text{H-H}} = 5.3$ Hz, 2H, CH_{pyr}), 8.19–8.05 (m, 4H, CH_{pyr}), 6.29–6.04 (m, 2H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 6.01–5.78 (m, 2H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 5.45 (s, 5H, CH_{Cp}), 2.57–2.29 (m, 2H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 2.13–1.98 (m, 2H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.98–1.77 (m, 4H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.25 ppm (t, $^3J_{\text{H-H}} = 5.9$ Hz, 6H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$). ^{13}C NMR (75 MHz, CDCl_3): δ 171.9 ($\text{Ni-C}_{\text{carbene}}$), 132.1 (C_{pyr}), 130.0 (C_{pyr}), 128.2 (CH_{pyr}), 126.3 (CH_{pyr}), 125.5 (CH_{pyr}), 122.7 (C_{pyr}), 120.8 (C_{pyr}), 119.0 (CH_{pyr}), 92.7 (CH_{Cp}), 53.6 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 32.2 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 20.5 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 14.1 ppm ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$). Electrospray MS (20 V, m/z): 477.4 $[\text{M-Br}]^+$. Anal. Calcd. For $\text{C}_{30}\text{H}_{31}\text{BrN}_2\text{Ni} \cdot \text{H}_2\text{O}$ (576.19): C 62.53, H 5.77, N 4.86. Found: C 62.90, H 5.81, N 4.83.

General procedure for the synthesis of 3A, 3B and 7C

A solution of the corresponding hexafluorophosphate salt (0.4 mmol), PdCl₂ (70.8 mg, 0.4 mmol), and K₂CO₃ (165.6 mg, 1.2 mmol) in 3-chloropyridine (4 mL) was heated at 90 °C, overnight. The solution was then cooled to room temperature, diluted with CH₂Cl₂ and passed through a short pad of silica gel covered with a pad of celite, eluting with CH₂Cl₂ until the product was completely recovered. The solution was concentrated and precipitated with hexanes, yielding a yellow solid.

Synthesis of 3A

Compound **3A** was prepared from 1,3-di-*n*-butylimidazolium hexafluorophosphate (130.5 mg, 0.4 mmol). Yield: 58.4 mg (31%); ¹H NMR (500 MHz, CDCl₃): δ 9.06 (s, 1H, CH_{py}), 8.96 (d, ³J_{H-H} = 5.4 Hz, 1H, CH_{py}), 7.77 (d, ³J_{H-H} = 8.2 Hz, 1H, CH_{py}), 7.36–7.29 (m, 1H, CH_{py}), 6.92 (s, 2H, CH_{Im}), 4.54 (t, ³J_{H-H} = 7.5 Hz, 4H, NCH₂CH₂CH₂CH₃), 2.13–1.99 (m, 4H, NCH₂CH₂CH₂CH₃), 1.55–1.44 (m, 4H, NCH₂CH₂CH₂CH₃), 1.02 (t, ³J_{H-H} = 7.3 Hz, 6H, NCH₂CH₂CH₂CH₃). ¹³C NMR (126 MHz, CDCl₃): δ 150.4 (Pd-C_{carbene}), 149.3 (CH_{py}), 146.7 (CH_{py}), 138.2 (C_{py}), 132.8 (CH_{py}), 124.9 (CH_{Im}), 121.7 (CH_{py}), 51.0 (NCH₂CH₂CH₂CH₃), 32.7 (NCH₂CH₂CH₂CH₃), 20.1 (NCH₂CH₂CH₂CH₃), 13.9 (NCH₂CH₂CH₂CH₃). Electrospray MS (20 V, m/z): 436.1 [M-Cl]⁺. Anal. Calcd for C₁₆H₂₄Cl₃N₃Pd (471.16): C 40.79, H 5.13, N 8.92. Found: C 40.30 H, 5.12, N 8.63.

Synthesis of 3B

Compound **3B** was prepared from 1,3-di-*n*-butyl-benzimidazolium hexafluorobenzene (150.5 mg, 0.4 mmol). Yield: 104.2 mg (50%). ¹H NMR (500 MHz, CDCl₃): δ 9.11 (s, 1H, CH_{py}), 9.01 (d, ³J_{H-H} = 5.3 Hz, 1H, CH_{py}), 7.81 (d, ³J_{H-H} = 7.5 Hz, 1H, CH_{py}), 7.41 (d, ³J_{H-H} = 3.0 Hz, 2H, CH_{BIm}), 7.39–7.33 (m, 1H, CH_{py}), 7.29 (m, 2H, CH_{BIm}), 5.04–4.70 (m, 4H, NCH₂CH₂CH₂CH₃), 2.20 (m, 4H, NCH₂CH₂CH₂CH₃), 1.59 (m, 4H, NCH₂CH₂CH₂CH₃), 1.08 ppm (t, ³J_{H-H} = 6.9 Hz, 6H, NCH₂CH₂CH₂CH₃). ¹³C NMR (126 MHz, CDCl₃): δ 161.1 (Pd-C_{carbene}), 150.5 (CH_{py}), 149.3 (CH_{py}), 138.3 (C_{py}), 134.6 (C_{BIm}), 132.9 (CH_{py}), 125.0 (CH_{BIm}), 123.1 (CH_{py}), 110.5 (CH_{BIm}), 48.5 (NCH₂CH₂CH₂CH₃), 31.7 (NCH₂CH₂CH₂CH₃), 20.5 (NCH₂CH₂CH₂CH₃), 14.0 (NCH₂CH₂CH₂CH₃). Electrospray MS (20 V, m/z): 486.0 [M-Cl]⁺. Anal. Calcd for C₂₀H₂₆Cl₃N₃Pd (521.22): C 46.09, H 5.03, N 8.06. Found: C 46.00, H 5.06, N 7.97.

Synthesis of 7C

Compound **7C** was prepared from **[C-H](PF₆)** (200.2 mg, 0.4 mmol). Yield : 170.4 mg (66 %). ¹H NMR (300 MHz, CDCl₃): δ 9.19 (s, 1H, CH_{py}), 9.10 (d, ³J_{H-H} = 5.3 Hz, 1H, CH_{py}), 8.49 (d, ³J_{H-H} = 7.9 Hz, 2H, CH_{pyr}), 8.14 (d, ³J_{H-H} = 7.6 Hz, 2H, CH_{pyr}), 8.10–7.91 (m, 4H, CH_{pyr}), 7.84 (d, ³J_{H-H} = 8.3 Hz, 1H, CH_{py}), 7.41 (m, 1H, CH_{py}), 5.69–5.54 (m, 4 H, NCH₂CH₂CH₂CH₃), 2.54–2.31 (m, 4H, NCH₂CH₂CH₂CH₃), 2.00–1.70 (m, 4H, NCH₂CH₂CH₂CH₃), 1.22 ppm (t, ³J_{H-H} = 7.4Hz, 6H, NCH₂CH₂CH₂CH₃). ¹³CNMR (75MHz, CDCl₃): δ 156.5 (Pd-C_{carbene}), 150.6 (CH_{py}), 149.5 (CH_{py}), 138.3 (C_{py}), 133.0 (C_{pyr}), 132.1 (CH_{py}), 129.0 (C_{pyr}), 128.3 (CH_{pyr}), 126.4 (CH_{pyr}), 125.8 (CH_{pyr}), 125.2 (CH_{py}), 122.8 (C_{pyr}), 120.8 (C_{pyr}), 119.0 (CH_{pyr}), 51.9 (NCH₂CH₂CH₂CH₃), 31.5 (NCH₂CH₂CH₂CH₃), 20.5 (NCH₂CH₂CH₂CH₃), 14.1 (NCH₂CH₂CH₂CH₃). Electrospray MS (20 V, m/z): 651.3 [M-Cl+CH₃CN]⁺. Anal. Calcd for C₃₀H₃₀Cl₃N₃Pd (645.36): C 55.83, H 4.69, N 6.51. Found: C 55.90, H 4.79, N 6.52.

General procedure for the synthesis of 8C, 9C and 10C

A solution of **2C**, **3C** or **4C** (0.13 mmol) and [RuCp*(CH₃CN)₃]PF₆ (65.7 mg, 0.13 mmol) in CH₂Cl₂ (10 mL) was stirred at 0 °C during 30 minutes. The solution was then allowed to reach room temperature and stirred for additional 48 h. After this time, the solution was concentrated under reduced pressure, giving the desired complexes as greenish solids.

Synthesis of 8C

Compound **8C** was prepared from **2C** (83.9 mg, 0.13 mmol). Yield: 125.8 mg (94 %). ¹H NMR (500 MHz, CD₂Cl₂): δ (*anti isomer*) 8.55-8.48 (m, 1H, CH_{pyr}), 8.20-8.08 (m, 3H, CH_{pyr}), 7.56-7.50 (m, 1H, CH_{pyr}), 6.78 (d, ³J_{H-H} = 6.1 Hz, 1H, CH_{pyr}), 6.48 (d, ³J_{H-H} = 4.5 Hz, 1H, CH_{pyr}), 6.39-6.34 (m, 1H, CH_{pyr}), 6.14-6.04 (m, 1H, NCH₂CH₂CH₂CH₃), 5.67-5.56 (m, 1H, NCH₂CH₂CH₂CH₃), 5.43-5.31 (m, 1H, NCH₂CH₂CH₂CH₃), 5.22 (br s, 2H, CH_{COD}), 5.11-5.01 (m, 1H, NCH₂CH₂CH₂CH₃), 3.59 (br s, 2H, CH_{COD}), 2.56-2.10 (m, 8H; 4H, NCH₂CH₂CH₂CH₃ and 4H, CH₂ COD), 2.09-1.88 (m, 4H, CH₂ COD), 1.87-1.61 (m, 4H, NCH₂CH₂CH₂CH₃), 1.18 (s, 15H, C₅(CH₃)₅), 1.15-1.09 (m, 6H, NCH₂CH₂CH₂CH₃). δ (*syn isomer*) 8.55-8.48 (m, 1H,

CH_{pyr}), 8.20-8.08 (m, 3H, CH_{pyr}), 7.56-7.50 (m, 1H, CH_{pyr}), 6.70 (d, $^3J_{\text{H-H}} = 7.0$ Hz, 1H, CH_{pyr}), 6.51 (d, $^3J_{\text{H-H}} = 6.0$ Hz, 1H, CH_{pyr}), 6.31 (t, $^3J_{\text{H-H}} = 6.2$ Hz, 1H, CH_{pyr}), 6.05-5.92 (m, 2H, $NCH_2CH_2CH_2CH_3$), 4.69-4.59 (m, 2H, $NCH_2CH_2CH_2CH_3$), 3.64 (br s, 2H, CH_{COD}), 2.56-2.10 (m, 8H; 4H, $NCH_2CH_2CH_2CH_3$ and 4H, CH_2_{COD}), 2.09-1.88 (m, 4H, CH_2_{COD}), 1.87-1.61 (m, 4H, $NCH_2CH_2CH_2CH_3$), 1.18 (s, 15H, $C_5(CH_3)_5$), 1.15-1.09 (m, 6H, $NCH_2CH_2CH_2CH_3$). ^{13}C NMR (126 MHz, CD_2Cl_2): δ (**anti isomer**) 133.3 (CH_{pyr}), 132.8 (C_{pyr}), 129.8 (CH_{pyr}), 128.5 (C_{pyr}), 128.3 (CH_{pyr}), 125.0 (C_{pyr}), 124.4 (C_{pyr}), 122.5 (CH_{pyr}), 122.3 (CH_{pyr}), 121.6 (C_{pyr}), 99.72 (d, $^1J_{\text{Rh-C}} = 18.9$ Hz, Rh- CH_{COD}), 94.5 (CH_{pyr}), 93.8 ($C_5(CH_3)_5$), 87.7 (CH_{pyr}), 87.5 (C_{pyr}), 86.9 (C_{pyr}), 85.9 (C_{pyr}), 79.1 (CH_{pyr}), 70.99 (d, $^1J_{\text{Rh-C}} = 10.3$ Hz, Rh- CH_{COD}), 52.1 ($NCH_2CH_2CH_2CH_3$), 51.8 ($NCH_2CH_2CH_2CH_3$), 33.1 (CH_2_{COD}), 32.6 ($NCH_2CH_2CH_2CH_3$), 30.7 ($NCH_2CH_2CH_2CH_3$), 29.0 (CH_2_{COD}), 20.2 ($NCH_2CH_2CH_2CH_3$), 19.9 ($NCH_2CH_2CH_2CH_3$), 13.5 ($NCH_2CH_2CH_2CH_3$), 13.5 ($NCH_2CH_2CH_2CH_3$), 8.6 ($C_5(CH_3)_5$). δ (**syn isomer**) 195.5 (d, $^1J_{\text{Rh-C}} = 50.9$ Hz, Rh- C_{carbene}), 133.3 (CH_{pyr}), 132.8 (C_{pyr}), 129.8 (CH_{pyr}), 128.5 (C_{pyr}), 128.3 (CH_{pyr}), 124.9 (C_{pyr}), 124.4 (C_{pyr}), 122.5 (CH_{pyr}), 122.3 (CH_{pyr}), 121.5 (C_{pyr}), 99.00 (d, $^1J_{\text{Rh-C}} = 15.7$ Hz, Rh- CH_{COD}), 94.4 (CH_{pyr}), 94.1 ($C_5(CH_3)_5$), 87.7 (CH_{pyr}), 87.5 (C_{pyr}), 87.1 (C_{pyr}), 86.0 (C_{pyr}), 78.8 (CH_{pyr}), 69.67 (d, $^1J_{\text{Rh-C}} = 14.5$ Hz, Rh- CH_{COD}), 52.1 ($NCH_2CH_2CH_2CH_3$), 51.8 ($NCH_2CH_2CH_2CH_3$), 33.1 (CH_2_{COD}), 32.7 ($NCH_2CH_2CH_2CH_3$), 29.6 ($NCH_2CH_2CH_2CH_3$), 29.0 (CH_2_{COD}), 20.3 ($NCH_2CH_2CH_2CH_3$), 20.1 ($NCH_2CH_2CH_2CH_3$), 13.7 ($NCH_2CH_2CH_2CH_3$), 13.4 ($NCH_2CH_2CH_2CH_3$), 8.8 ($C_5(CH_3)_5$). HRMS ESI-TOF-MS (positive mode): $[M]^+$ monoisotopic peak 883.1504, calcd 883.1493, $\epsilon_r=1.2$ ppm.

Synthesis of 9C

Compound **9C** was prepared from **3C** (92.0 mg, 0.13 mmol). Overall yield: 135.3 mg (97 %). The crude product was recrystallized from a CH_2Cl_2 /hexane (1:20) mixture, affording exclusively the *syn* isomer (85 mg, 61 % yield). ^1H NMR (500

MHz, CD_2Cl_2): δ 8.60 (d, $^3J_{\text{H-H}} = 7.5$ Hz, 1H, CH_{pyr}), 8.30-8.12 (m, 3H, CH_{pyr}), 7.64 (d, $^3J_{\text{H-H}} = 9.1$ Hz, 1H, CH_{pyr}), 6.82 (d, $^3J_{\text{H-H}} = 6.2$ Hz, 1H, CH_{pyr}), 6.61 (d, $^3J_{\text{H-H}} = 5.9$ Hz, 1H, CH_{pyr}), 6.43 (t, $^3J_{\text{H-H}} = 6.1$ Hz, 1H, CH_{pyr}), 5.95-5.89 (m, 1H, $NCH_2CH_2CH_2CH_3$), 5.84-5.69 (m, 1H, $NCH_2CH_2CH_2CH_3$), 5.10-4.99 (m, 1H, $NCH_2CH_2CH_2CH_3$), 4.77 (br s, 2H, CH_{COD}), 4.73-4.64 (m, 1H, $NCH_2CH_2CH_2CH_3$), 3.36-3.16 (br s, 2H, CH_{COD}),

2.50-2.36 (m, 2H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 2.36-2.24 (m, 4H, CH_2COD), 2.15-2.09 (m, 2H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 2.03-1.64 (m, 6H; 4H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ and 2H, CH_2COD), 1.35-1.23 (m, 15H, $\text{C}_5(\text{CH}_3)_5$), 1.23-1.12 (m, 6H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$). ^{13}C NMR (126 MHz, CD_2Cl_2): δ (**anti isomer**) 191.4 (Ir- $\text{C}_{\text{carbene}}$), 133.4 (CH_{pyr}), 132.8 (C_{pyr}), 130.8 (C_{pyr}), 129.8 (CH_{pyr}), 128.5 (C_{pyr}), 124.9 (CH_{pyr}), 124.0 (C_{pyr}), 122.5 (CH_{pyr}), 122.3 (C_{pyr}), 121.7 (C_{pyr}), 94.5 (CH_{pyr}), 93.9 ($\text{C}_5(\text{CH}_3)_5$), 87.6 (C_{pyr}), 94.5 (CH_{pyr}), 93.9 (Cp^*), 87.6 (C_{pyr}), 87.2 (CH_{pyr}), 87.0 (CH_{COD}), 86.4 (C_{pyr}), 86.0 (C_{pyr}), 79.2 (CH_{pyr}), 52.3 (CH_{COD}), 51.5 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 33.6 (CH_2COD), 31.0 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 29.3 (CH_2COD), 19.7 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 13.5 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 13.4 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 8.6 ($\text{C}_5(\text{CH}_3)_5$). δ (**syn isomer**) 191.0 (Ir- $\text{C}_{\text{carbene}}$), 133.3 (CH_{pyr}), 132.8 (C_{pyr}), 130.4 (C_{pyr}), 129.8 (CH_{pyr}), 128.4 (C_{pyr}), 125.0 (CH_{pyr}), 124.3 (C_{pyr}), 122.5 (CH_{pyr}), 122.3 (C_{pyr}), 121.6 (C_{pyr}), 94.5 (CH_{pyr}), 94.0 ($\text{C}_5(\text{CH}_3)_5$), 87.5 (C_{pyr}), 87.3 (CH_{pyr}), 86.9 (CH_{COD}), 86.3 (C_{pyr}), 86.1 (C_{pyr}), 79.0 (CH_{pyr}), 52.3 (CH_{COD}), 51.7 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 33.4 (CH_2COD), 31.0 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 29.5 (CH_2COD), 20.1 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 20.0 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 13.6 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 13.3 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 8.7 ($\text{C}_5(\text{CH}_3)_5$). Electrospray MS (20 V, m/z): 927.3 $[\text{M}]^+$. HRMS ESI-TOF-MS (positive mode): $[\text{M}]^+$ monoisotopic peak 927.2581, calcd. 927.2571, $\epsilon_r = 1.1$ ppm.

Figure 6.4 ^1H - ^1H COSY spectrum of **9C** (*syn* isomer) in CD_2Cl_2

Synthesis of **10C**

Compound **10C** was prepared from **4C** (95.5 mg, 0.13 mmol).

Yield: 125.8 mg (94 %). ^1H NMR (500 MHz, CDCl_3): δ (**anti**

isomer) 8.55-8.51 (m, 1H, CH_{pyr}), 8.17-8.14 (m, 3H, CH_{pyr}),

7.71 (d, $^3J_{\text{H-H}} = 9$ Hz, 1H, CH_{pyr}), 7.04 (d, $^3J_{\text{H-H}} = 6$ Hz, 1H,

CH_{pyr}), 6.78 (d, $^3J_{\text{H-H}} = 6$ Hz, 1H, CH_{pyr}), 6.70 (t, $^3J_{\text{H-H}} = 6$ Hz, 1H, CH_{pyr}), 5.97-5.92 (m,

2H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 5.06-5.02 (m, 2H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 4.87 (br s, 2H,

CH_{COD}), 2.91 (br s, 2H, CH_{COD}), 2.45-2.17 (m, 8H; 4H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ and 4H,

CH_2COD), 2.06-1.55 (m, 8H; 4H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ and 4H, CH_2COD), 1.35-1.27 (m,

15H, $\text{C}_5(\text{CH}_3)_5$), 1.20-1.16 (m, 6H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$). δ (**syn isomer**) 8.55-8.51 (m,

1H, CH_{pyr}), 8.17-8.14 (m, 3H, CH_{pyr}), 7.74 (d, $^3J_{\text{H-H}} = 9$ Hz, 1H, CH_{pyr}), 6.89 (d, $^3J_{\text{H-H}} =$

6 Hz, 1H, CH_{pyr}), 6.85 (d, $^3J_{\text{H-H}} = 6$ Hz, 1H, CH_{pyr}), 6.65 (t, $^3J_{\text{H-H}} = 5$ Hz, 1H, CH_{pyr}),

5.88-5.77 (m, 2H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 4.94 (br s, CH_{COD}), 4.71-4.64 (m, 2H,

$\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 3.25 (br s, 2H, CH_{COD}), 2.45-2.17 (m, 8H; 4H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$

and 4H, CH_2COD), 2.06-1.55 (m, 8H; 4H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ and 4H, CH_2COD), 1.35-

1.27 (m, 15H, $\text{C}_5(\text{CH}_3)_5$), 1.20-1.16 (m, 6H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$). ^{13}C NMR (126 MHz,

CD_2Cl_2): δ (**anti isomer**) 191.4 (Ir- $\text{C}_{\text{carbene}}$), 133.4 (CH_{pyr}), 132.8 (C_{pyr}), 130.8 (C_{pyr}),

129.8 (CH_{pyr}), 128.5 (C_{pyr}), 124.9 (CH_{pyr}), 124.0 (C_{pyr}), 122.5 (CH_{pyr}), 122.3 (C_{pyr}),

121.7 (C_{pyr}), 94.5 (CH_{pyr}), 93.9 ($\text{C}_5(\text{CH}_3)_5$), 87.6 (C_{pyr}), 94.5 (CH_{pyr}), 93.9 (Cp^*), 87.6

(C_{pyr}), 87.2 (CH_{pyr}), 87.0 (CH_{COD}), 86.4 (C_{pyr}), 86.0 (C_{pyr}), 79.2 (CH_{pyr}), 52.3 (CH_{COD}),

51.5 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 33.6 (CH_2COD), 31.0 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 29.3 (CH_2COD),

19.7 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 13.5 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 13.4 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 8.6

($\text{C}_5(\text{CH}_3)_5$). δ (**syn isomer**) 191.0 (Ir- $\text{C}_{\text{carbene}}$), 133.3 (CH_{pyr}), 132.8 (C_{pyr}), 130.4 (C_{pyr}),

129.8 (CH_{pyr}), 128.4 (C_{pyr}), 125.0 (CH_{pyr}), 124.3 (C_{pyr}), 122.5 (CH_{pyr}), 122.3 (C_{pyr}),

121.6 (C_{pyr}), 94.5 (CH_{pyr}), 94.0 ($\text{C}_5(\text{CH}_3)_5$), 87.5 (C_{pyr}), 87.3 (CH_{pyr}), 86.9 (CH_{COD}),

86.3 (C_{pyr}), 86.1 (C_{pyr}), 79.0 (CH_{pyr}), 52.3 (CH_{COD}), 51.7 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 33.4

(CH_2COD), 31.0 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 29.5 (CH_2COD), 20.1 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 20.0

($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 13.6 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 13.3 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 8.7

($\text{C}_5(\text{CH}_3)_5$). Electrospray MS (20 V, m/z): 971.2 $[\text{M}]^+$. HRMS ESI-TOF-MS (positive

mode): $[\text{M}]^+$ monoisotopic peak 971.2063, calcd. 971.2061, $\epsilon_r = 0.2$ ppm.

Synthesis of 11C

CO gas was bubbled through a solution of **9C** (30 mg, 0.03 mmol) in dichloromethane (5 mL) at 0°C during 20 min. The solution was concentrated under reduced pressure, and hexane was added to get complex **11C** as a light yellow solid. The solid so obtained contained a mixture of isomers *syn* and *anti* in a 63:37 ratio. Yield: 23.4 mg (82 %). ¹H NMR (500 MHz, CD₂Cl₂): δ (*anti* isomer) 8.53-8.48 (m, 1H, CH_{pyr}), 8.21-8.11 (m, 3H, CH_{pyr}), 7.56 (d, ³J_{H-H} = 9.2 Hz, 1H, CH_{pyr}), 6.86-6.81 (m, 1H, CH_{pyr}), 6.62-6.55 (m, 1H, CH_{pyr}), 6.47-6.39 (m, 1H, CH_{pyr}), 5.44-5.32 (m, 2H, NCH₂CH₂CH₂CH₃), 5.10-5.00 (m, 1H, NCH₂CH₂CH₂CH₃), 4.83-4.73 (m, 1H, NCH₂CH₂CH₂CH₃), 2.17-2.01 (m, 2H, NCH₂CH₂CH₂CH₃), 1.96-1.85 (m, 2H, NCH₂CH₂CH₂CH₃), 1.71-1.57 (m, 2H, NCH₂CH₂CH₂CH₃); 1.56-1.44 (m, 2H, NCH₂CH₂CH₂CH₃), 1.16 (C₅(CH₃)₅), 1.09-0.97 (m, 6H, NCH₂CH₂CH₂CH₃). δ (*syn* isomer) 8.53-8.48 (m, 1H, CH_{pyr}), 8.21-8.11 (m, 3H, CH_{pyr}), 7.58 (d, ³J_{H-H} = 9.2 Hz, CH_{pyr}), 6.86-6.81 (m, 1H, CH_{pyr}), 6.62-6.55 (m, 1H, CH_{pyr}), 6.47-6.39 (m, 1H, CH_{pyr}), 5.64-5.54 (m, 1H, NCH₂CH₂CH₂CH₃), 5.30-5.13 (m, 2H, NCH₂CH₂CH₂CH₃), 4.61-4.51 (m, 1H, NCH₂CH₂CH₂CH₃), 2.17-2.01 (m, 2H, NCH₂CH₂CH₂CH₃), 1.96-1.85 (m, 2H, NCH₂CH₂CH₂CH₃), 1.71-1.57 (m, 2H, NCH₂CH₂CH₂CH₃), 1.56-1.44 (m, 2H, NCH₂CH₂CH₂CH₃), 1.19 (C₅(CH₃)₅), 1.09-0.97 (m, 6H, NCH₂CH₂CH₂CH₃). ¹³C NMR (126 MHz, CD₂Cl₂): δ (*anti* isomer) 183.2 (Ir-CO), 180.7 (Ir-CO), 168.0 (Ir-C_{carbene}), 133.4 (CH_{pyr}), 132.9 (C_{pyr}), 130.4 (C_{pyr}), 130.1 (C_{pyr}), 129.3 (CH_{pyr}), 125.1 (CH_{pyr}), 124.6 (C_{pyr}), 122.5 (C_{pyr}), 122.3 (CH_{pyr}), 122.2 (C_{pyr}), 94.6 (C₅(CH₃)₅), 94.2 (C_{pyr}), 88.0 (C_{pyr}), 87.7 (CH_{pyr}), 86.4 (CH_{pyr}), 86.0 (C_{pyr}), 79.5 (CH_{pyr}), 52.4 (NCH₂CH₂CH₂CH₃), 31.5 (NCH₂CH₂CH₂CH₃), 31.3 (NCH₂CH₂CH₂CH₃), 19.8 (NCH₂CH₂CH₂CH₃), 13.8 (NCH₂CH₂CH₂CH₃), 13.5 (NCH₂CH₂CH₂CH₃), 8.6 (C₅(CH₃)₅). δ (*syn* isomer) 183.2 (Ir-CO), 180.9 (Ir-CO), 168.1 (Ir-C_{carbene}), 133.4 (CH_{pyr}), 133.1 (C_{pyr}), 130.4 (C_{pyr}), 130.1 (C_{pyr}), 129.2 (CH_{pyr}), 125.2 (CH_{pyr}), 124.6 (C_{pyr}), 122.5 (C_{pyr}), 122.3 (CH_{pyr}), 122.2 (C_{pyr}), 94.5 (C₅(CH₃)₅), 94.2 (C_{pyr}), 88.0 (C_{pyr}), 87.7 (CH_{pyr}), 86.4 (CH_{pyr}), 86.0 (C_{pyr}), 79.5 (CH_{pyr}), 52.4 (NCH₂CH₂CH₂CH₃), 32.1 (NCH₂CH₂CH₂CH₃), 31.1 (NCH₂CH₂CH₂CH₃), 19.9 (NCH₂CH₂CH₂CH₃), 19.9 (NCH₂CH₂CH₂CH₃), 13.6 (NCH₂CH₂CH₂CH₃), 13.4 (NCH₂CH₂CH₂CH₃), 8.7 (C₅(CH₃)₅). IR (KBr): 2073 (ν_{C=O}), 1990 (ν_{C=O}) cm⁻¹. Electrospray MS (20 V, *m/z*): 875.2 [M]⁺. HRMS ESI-TOF-MS (positive mode): [M]⁺ monoisotopic peak 875.1529, calcd 875.1525, ε_r = 0.5 ppm.

Figure 6.5 ^1H - ^1H COSY spectrum of **11C** (mixture of isomers *syn* and *anti*) in CD_2Cl_2

Figure 6.6 ^{13}C - ^1H HSQC spectrum of **11C** (mixture of *syn* and *anti* isomers) in CD_2Cl_2

6.2.3 Synthesis and characterization of ligand precursors of Chapter 4

General procedure for the synthesis of $[\text{J-H}_2](\text{I})_2$ and $[\text{K-H}_2](\text{X})_2$

A mixture of 1,3-dibutyl-5,6-diaminobenzimidazolium iodide (2.2 equiv) and the corresponding tetraone (1 equiv) in methanol (50 mL) was refluxed overnight. The reaction mixture was then cooled to room temperature and concentrated under vacuum. The solid so formed was separated by filtration and washed subsequently with a small amount of ethanol and diethyl ether.

Synthesis of $[\text{J-H}_2](\text{I})_2$

Compound $[\text{J-H}_2](\text{I})_2$ was prepared by reacting 1,3-dibutyl-5,6-diaminobenzimidazolium iodide (163 mg, 0.42 mmol) with pyrene-4,5,9,10-tetraone (50 mg, 0.19 mmol). Yield: 143.2 mg (75%). ^1H NMR (300 MHz, $\text{DMSO-}d_6$): δ 10.18 (br s, 2H, NCHN), 9.48–9.24 (m, 4H, CH_{Ar}), 8.91 (s, 4H, CH_{Ar}), 8.40–8.12 (m, 2H, CH_{Ar}), 4.63 (br s, 8H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 2.06 (br s, 8H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.69–1.31 (br m, 8H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.05 (br s, 12H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$). Attempts to record the ^{13}C NMR spectrum of $[\text{J-H}_2](\text{I})_2$ were unsuccessful due to the low solubility of the compound. ESI-MS (20 V, m/z): 356.4 $[\text{M}]^{2+}$. Anal. Calcd for $\text{C}_{46}\text{H}_{48}\text{I}_2\text{N}_8 \cdot 2\text{H}_2\text{O}$ (1002.8): C, 55.10; H, 5.23; N, 11.17. Found: C, 55.63; H, 5.30; N, 11.09.

Synthesis of $[\text{K-H}_2](\text{I})_2$

Compound $[\text{K-H}_2](\text{I})_2$ was prepared by reacting 1,3-dibutyl-5,6-diaminobenzimidazolium iodide (300 mg, 0.77 mmol) with 2,7-di-tert-butylpyrene-4,5,9,10-tetraone (131 mg, 0.35 mmol). Yield: 276.7 mg (73%). ^1H NMR (500 MHz, $\text{DMSO-}d_6$): δ 10.19 (s, 2H, NCHN), 9.72 (s, 4H, CH_{Ar}), 9.19 (s, 4H, CH_{Ar}), 4.72 (t, $^3J_{\text{H-H}} = 7.1$ Hz, 8H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 2.18–1.99 (m, 8H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.76 (s, 18H, $\text{C}(\text{CH}_3)_3$), 1.65–1.43 (m, 8H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.05 (t, $^3J_{\text{H-H}} = 7.4$ Hz, 12H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$). ^{13}C NMR (126 MHz, $\text{DMSO-}d_6$): δ 151.0 (C_{Ar}), 146.4 (NCHN), 142.6 (C_{Ar}), 138.5 (C_{Ar}), 133.3 (C_{Ar}), 128.6 (C_{Ar}), 125.3 (C_{Ar}), 124.8 (CH_{Ar}), 112.5 (CH_{Ar}), 47.0 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 35.5 ($\text{C}(\text{CH}_3)_3$), 31.4 ($\text{C}(\text{CH}_3)_3$), 30.5 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 19.2 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 13.5

(NCH₂CH₂CH₂CH₃). ESI-MS (20 V, m/z): 412.4 [M]²⁺. Anal. Calcd for C₅₄H₆₄I₂N₈ (1078.9): C, 60.11; H, 5.98; N, 10.39. Found: C, 60.00; H, 6.02; N, 10.31.

Synthesis of [K-H₂](PF₆)₂

NH₄PF₆ (77.3 mg, 0.48 mmol) was added to a solution of [K-H₂](I)₂ (255.9 mg, 0.24 mmol) in a 3:1 mixture of methanol/CH₂Cl₂. The reaction mixture was stirred at room temperature overnight. The yellow solid so formed was then separated by filtration and washed with methanol and diethyl

ether. Yield: 252.7 mg (93%). ¹H NMR (300 MHz, DMSO-*d*₆): δ 10.17 (s, 2H, NCHN), 9.69 (s, 4H, CH_{Ar}), 9.12 (s, 4H, CH_{Ar}), 4.83–4.56 (m, 8H, NCH₂CH₂CH₂CH₃), 2.21–1.97 (m, 8H, NCH₂CH₂CH₂CH₃), 1.77 (s, 18H, C(CH₃)₃), 1.64–1.45 (m, 8H, NCH₂CH₂CH₂CH₃), 1.05 (t, ³J_{H-H} = 7.3 Hz, 12H, NCH₂CH₂CH₂CH₃). ¹³C NMR (75 MHz, DMSO-*d*₆): δ 150.9 (C_{Ar}), 148.0 (C_{Ar}), 142.3 (C_{Ar}), 138.3 (C_{Ar}), 133.1 (C_{Ar}), 128.2 (C_{Ar}), 124.9 (C_{Ar}), 124.6 (CH_{Ar}), 112.2 (CH_{Ar}), 47.0 (NCH₂CH₂CH₂CH₃), 35.5 (C(CH₃)₃), 31.5 (C(CH₃)₃), 30.4 (NCH₂CH₂CH₂CH₃), 19.3 (NCH₂CH₂CH₂CH₃), 13.5 (NCH₂CH₂CH₂CH₃). ESI-MS (20 V, m/z): 412.3 [M]²⁺. Anal. Calcd. for C₅₄H₆₄F₁₂N₈P₂·2H₂O (1151.1): C, 56.34; H, 5.95; N, 9.73. Found: C, 56.57; H, 5.92; N, 9.73.

Synthesis of [L-H₃](I)₃

A solution of 1,3-dibutyl-5,6-diaminobenzimidazolium iodide (300 mg, 0.80 mmol) and hexaketocyclohexane (84.3 mg, 0.27 mmol) in 15 mL of glacial acetic acid was heated at 140°C overnight. All the volatiles are removed under vacuum, the residue is suspended in ethanol, filtered and washed with

ethanol. Yield : 303.0 (83%). ¹H NMR (300 MHz, DMSO-*d*₆): δ 10.33 (s, 3H, NCHN), 9.32 (s, 6H, CH_{Ar}), 4.79 (s, 12H, NCH₂CH₂CH₂CH₃), 2.11 (s, 12H, NCH₂CH₂CH₂CH₃), 1.55 (s, 12H, NCH₂CH₂CH₂CH₃), 1.04 (s, 18H, NCH₂CH₂CH₂CH₃). ¹³C NMR (126 MHz, DMSO-*d*₆): δ 149.2 (NCHN), 145.2 (C_{Ar}), 139.3 (C_{Ar}), 134.4 (C_{Ar}), 113.4 (CH_{Ar}), 47.2 (NCH₂CH₂CH₂CH₃), 30.4 (NCH₂CH₂CH₂CH₃), 19.3 (NCH₂CH₂CH₂CH₃), 13.5 (NCH₂CH₂CH₂CH₃). ESI-MS (20 V, m/z): 281.2 [M-(I)₃]³⁺. Anal. Calcd. for

$C_{51}H_{63}I_3N_{12} \cdot 8H_2O$ (1368.96): C, 44.75; H, 5.82; N, 12.28. Found: C, 44.88; H, 5.85; N, 12.24.

6.2.4 Synthesis and characterization of metal complexes of Chapter 4

General procedure for the synthesis of 1K and 2K

A mixture of the corresponding bis(azolium) salt (1 equiv), potassium *tert*-butoxide (2.2 equiv), and $[IrCl(COD)]_2$ (1 equiv) in THF (10 mL) was stirred overnight at room temperature. After removal of the volatiles, the crude solid was purified by column chromatography using CH_2Cl_2 as eluent.

Synthesis of 1K

Compound **1K** was prepared by reacting the bis(azolium) salt $[K-H_2](I)_2$ (70 mg, 0.06 mmol), potassium *tert*-butoxide (16.0 mg, 0.14 mmol), KI (59.76 mg, 0.36 mmol), and $[IrCl(COD)]_2$ (43.6 mg, 0.06 mmol). Yield: 45.2 mg (42%). 1H NMR (300 MHz, $CDCl_3$): δ 9.81 (s, 4H, CH_{Ar}), 8.12 (s, 4H, CH_{Ar}), 5.08 (br s, 4H, CH_{COD}), 4.99–4.65 (m, 8H, $NCH_2CH_2CH_2CH_3$), 3.04 (br s, 4H, CH_{COD}), 2.50–2.16 (m, 16H, 8H CH_2_{COD} and 8H $NCH_2CH_2CH_2CH_3$), 2.16–1.88 (m, 8H, CH_2_{COD}), 1.84 (s, 18H, $C(CH_3)_3$), 1.77–1.63 (m, 8H, $NCH_2CH_2CH_2CH_3$), 1.19 (t, $^3J_{H-H} = 7.4$ Hz, 12H, $NCH_2CH_2CH_2CH_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 202.8 (Ir- $C_{carbene}$), 151.1 (C_{Ar}), 142.5 (C_{Ar}), 138.6 (C_{Ar}), 137.8 (C_{Ar}), 129.5 (C_{Ar}), 125.6 (C_{Ar}), 124.6 (CH_{Ar}), 106.7 (CH_{Ar}), 86.9 (CH_{COD}), 56.5 (CH_{COD}), 48.8 ($NCH_2CH_2CH_2CH_3$), 36.2 ($C(CH_3)_3$), 33.1 ($NCH_2CH_2CH_2CH_3$), 32.1 ($C(CH_3)_3$), 30.8 (CH_2_{COD}), 30.3 (CH_2_{COD}), 20.8 ($NCH_2CH_2CH_2CH_3$), 14.1 ($NCH_2CH_2CH_2CH_3$). HRMS ESI-TOF-MS (positive mode): m/z calcd, 1592.5544 $[M-I + CH_3CN]^+$ (monoisotopic peak); found, 1592.5741. Anal. Calcd. for $C_{70}H_{86}I_2N_8$ (1677.7): C, 50.11; H, 5.17; N, 6.68. Found: C, 49.83; H, 5.04; N, 6.68.

Synthesis of 2K

Compound **2K** was prepared by reacting the bis(azolium) salt $[K-H_2](PF_6)_2$ (100.0 mg, 0.09 mmol), potassium *tert*-butoxide (21.4 mg, 0.19 mmol), and $[IrCl(COD)]_2$ (58.4 mg, 0.09 mmol). Yield: 52.8 (39%).

^1H NMR (300 MHz, CDCl_3): δ 9.81 (s, 4H, CH_{Ar}), 8.20 (s, 4H, CH_{Ar}), 5.14–4.73 (m, 12H, 4H CH_{COD} and 8H $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 3.10 (br s, 4H, C_{HCOD}), 2.36 (br s, 16H, 8H CH_2_{COD} and 8H $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 2.24–1.65 (m, 34H, 8H CH_2_{COD} , 8H $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ and 18H $\text{C}(\text{CH}_3)_3$), 1.19 (t, $^3J_{\text{H-H}} = 7.3$ Hz, 12H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$). ^{13}C NMR (75 MHz, CDCl_3): δ 202.2 (Ir- $\text{C}_{\text{carbene}}$), 151.2 (C_{Ar}), 142.7 (C_{Ar}), 138.7 (C_{Ar}), 137.7 (C_{Ar}), 129.6 (C_{Ar}), 125.8 (C_{Ar}), 124.7 (CH_{Ar}), 106.8 (CH_{Ar}), 88.9 (CH_{COD}), 53.3 (CH_{COD}), 49.1 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 36.1 ($\text{C}(\text{CH}_3)_3$), 33.8 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 32.1 ($\text{C}(\text{CH}_3)_3$), 31.4 (CH_2_{COD}), 29.5 (CH_2_{COD}), 20.8 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 14.1 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$). HRMS ESI-TOF-MS (positive mode): m/z calcd, 1500.6188 [$\text{M}-\text{Cl}+\text{CH}_3\text{CN}$] $^+$ (monoisotopic peak); found, 1500.6385. Anal. Calcd. for $\text{C}_{70}\text{H}_{86}\text{Cl}_2\text{Ir}_2\text{N}_8\cdot 3\text{H}_2\text{O}$ (1548.9): C, 54.28; H, 5.99; N, 7.23. Found: C, 54.37; H, 5.95; N, 7.35.

Synthesis of **3K**

CO gas was bubbled through a solution of complex **2K** (50 mg, 0.03 mmol) in dichloromethane (5 mL) at 0 °C during 20 min. The solution was concentrated under reduced pressure, and hexane was added to give carbonyl derivative **3K** as a yellow solid. Yield: 45.0 mg (96%). ^1H NMR (300 MHz, CDCl_3): δ 9.85 (s, 4H, CH_{Ar}), 8.45 (s, 4H, CH_{Ar}), 5.10–4.87 (m, 4H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 4.87–4.65 (m, 4H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 2.42–2.07 (m, 8H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.80 (s, 18H, $\text{C}(\text{CH}_3)_3$), 1.73–1.48 (m, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.23–0.99 (m, 12H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$). ^{13}C NMR (75 MHz, CDCl_3): δ 192.2 (Ir- $\text{C}_{\text{carbene}}$), 181.2 (Ir-CO), 168.2 (Ir-CO), 151.5 (C_{Ar}), 143.5 (C_{Ar}), 138.8 (C_{Ar}), 136.5 (C_{Ar}), 129.4 (C_{Ar}), 126.2 (C_{Ar}), 125.4 (CH_{Ar}), 109.1 (CH_{Ar}), 49.6 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 36.2 ($\text{C}(\text{CH}_3)_3$), 32.0 ($\text{C}(\text{CH}_3)_3$), 31.4 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 20.5 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 14.1 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$). HRMS ESI-TOF-MS (positive mode): m/z calcd, 1391.3608 [$\text{M}+\text{H}$] $^+$ (monoisotopic peak); found, 1391.3599. Anal. Calcd. for $\text{C}_{58}\text{H}_{62}\text{Cl}_2\text{Ir}_2\text{N}_8\text{O}_4\cdot 3\text{H}_2\text{O}$ (1444.6): C, 48.22; H, 4.74; N, 7.76. Found: C, 48.32; H, 4.78; N, 7.65.

Synthesis of 1L

A mixture of **[L-H₃](I)₃** (100 mg, 0.07 mmol), NaH (6.5 mg, 0.27 mmol), sodium *tert*-butoxide (41 μ L of 2M solution in THF, 0.08 mmol), and **[IrCl(COD)]₂** (80.6 mg, 0.12 mmol) in THF (10 mL) was at -78 °C. The reaction mixture was maintained at -78 °C for 30 min. Then, it was warmed to room temperature and stirred overnight. After removal of the volatiles, the crude solid was purified by column chromatography using CH₂Cl₂ as eluent. Yield: 86.2 mg (58%). ¹H NMR (300 MHz, CDCl₃): δ 8.50 (s, 6H, CH_{Ar}), 5.13 (br s, 6H, CH_{COD}), 5.04 – 4.81 (m, 6H, NCH₂CH₂CH₂CH₃), 4.81 – 4.67 (m, 6H, NCH₂CH₂CH₂CH₃), 3.15 (br s, 6H, CH_{COD}), 2.48 – 2.15 (m, 24H, CH₂ COD), 2.15 – 1.82 (m, 12H, NCH₂CH₂CH₂CH₃), 1.82 – 1.63 (m, 12H, NCH₂CH₂CH₂CH₃), 1.16 (t, ³J_{H-H} = 7.2 Hz, 18H, NCH₂CH₂CH₂CH₃). ¹³C NMR (75 MHz, CDCl₃): δ 205.6 (Ir-C_{carbene}), 142.9 (C_{Ar}), 139.9 (C_{Ar}), 139.3 (C_{Ar}), 107.7 (CH_{Ar}), 88.1 (CH_{COD}), 57.0 (CH_{COD}), 49.0 (NCH₂CH₂CH₂CH₃), 33.1 (NCH₂CH₂CH₂CH₃), 30.7 (CH₂ COD), 30.3 (CH₂ COD), 20.8 (NCH₂CH₂CH₂CH₃), 14.0 (NCH₂CH₂CH₂CH₃). HRMS ESI-TOF-MS (positive mode): [M+H]⁺ monoisotopic peak 2123.5, calcd 2123.4, ϵ_r = 0.5 ppm. Anal. Calcd. for C₇₅H₉₆I₃Ir₃N₁₂ (2123.01): C, 42.43; H, 4.56; N, 7.92. Found: C, 42.44; H, 4.55; N, 7.93.

6.2.5 Synthesis and Characterization of ligand precursors of Chapter 5

Synthesis of [M-H₄]

[M-H₄]

To a solution of 1,2-diaminobutane (4 mL, 40 mmol) and a few drops of acetic acid in methanol at 0 °C was added dropwise formaldehyde (3.3 mL of a 37% aqueous solution, 44 mmol). Glyoxal (2.5 mL of a 40% aqueous solution, 22 mmol) was then added dropwise over 30 min,

while the temperature was kept at 0 °C. The solution was stirred for 7 days at room temperature. After this time, the solution was concentrated under reduced pressure, giving a red oil. The oil was then extracted 10 times with diethyl ether (10 $\times$ 10 mL). The combined organic layers were concentrated and washed with cold acetone, giving the desired product as a white crystalline solid. Yield: 2.2 g (50%). ¹H NMR (300 MHz, CDCl₃): δ 4.14 (s, 2H, CH_{bridge}), 3.43 (d, ²J_{H-H} = 3.0 Hz, 2H, NCH₂N), 3.27 (d, ²J_{H-H} = 3.0 Hz, 2H, NCH₂N), 2.78–2.74 (m, 4H, NCH₂), 2.63–2.60 (m, 4H, NCH₂), 1.74–1.73 (m, 8H, CH₂). ¹³C NMR (75 MHz, CDCl₃): δ 86.6 (CH_{bridge}), 74.4 (NCH₂N),

50.4 (NCH₂), 28.0 (CH₂). Electrospray MS (20 V, m/z): 223.4 [M + H]⁺. Anal. Calcd for C₁₂H₂₄N₄ (222.3): C, 64.83; H, 9.97; N, 25.20. Found: C, 65.30; H, 9.86; N, 25.53.

Figure 6.7 ¹H-¹H COSY spectrum of [M-H₄] in CDCl₃

Figure 6.8 ^{13}C - ^1H HSQC spectrum of $[\text{M-H}_4]$ in CDCl_3

Synthesis of $[\text{M-H}_2](\text{PF}_6)_2$

To a solution of $[\text{M-H}_4]$ (500 mg, 2.25 mmol) in 1,2-dimethoxyethane (DME, 10 mL) was added dropwise a solution of N-bromosuccinimide (800 mg, 4.5 mmol) in DME (5 mL). The reaction mixture was stirred at room temperature for 3 h under the exclusion of light. After this time, the white solid that formed was separated by filtration and solubilized in methanol (10 mL). NH_4PF_6 (734 mg, 4.5 mmol) was then added in one portion to the methanolic solution, and the resulting suspension was stirred for 30 min at room temperature. The white solid that formed was separated by filtration and subsequently washed with cold methanol, yielding the desired dicationic salt. Yield: 483 mg (42%). ^1H NMR (300 MHz, $\text{DMSO-}d_6$): δ 8.99 (s, 2H, NCHN), 6.66 (s, 2H, CH), 3.91–3.86 (m, 4H, 6 bridge NCH_2), 3.64–3.59 (m, 4H, NCH_2), 2.07–2.00 (m, 4H, CH_2), 1.92–1.85 (m, 4H, CH_2). ^{13}C NMR (126 MHz, $\text{DMSO-}d_6$): δ 160.4 (NCHN), 80.5 ($\text{CH}_{\text{bridge}}$), 48.1 (NCH_2), 25.4 (CH_2). Electrospray MS (20 V, m/z): 110.3 $[\text{M}]^{2+}$, 365.13 $[\text{M} + \text{PF}_6]^+$. Anal. Calcd for $\text{C}_{12}\text{H}_{20}\text{N}_4\text{P}_2\text{F}_{12}$: C, 28.25; H, 3.95; N, 10.98. Found: C, 28.53; H, 4.21; N, 10.65.

6.2.6 Synthesis and characterization of metal complexes of Chapter 5

Synthesis of isomers **1M'** and **1M''**

A mixture of [**M-H**₄] (82.6 mg, 0.37 mmol), [IrCl(COD)]₂ (250 mg, 0.37 mmol), and 1,5-cyclooctadiene (457 μ L, 3.7 mmol) was refluxed in dry toluene (10 mL) overnight. After removal of the volatiles, the crude solid was dissolved in CH₂Cl₂ and purified by column chromatography using silica gel. Using mixtures of CH₂Cl₂/acetone afforded the separation of two yellow bands that contained **1M'** (95:5) and **1M''** (75:25). Yield: 107.2 mg (33%) for **1M'** and 98.3 mg (30%) for **1M''**. Overall yield: 205.5 mg (63%).

Isomer 1M'. ¹H NMR (500 MHz, CDCl₃): δ 5.47 (s, 2H, CH_{bridge}), 4.87–4.82 (m, 4H, NCH₂), 4.49–4.47 (m, 4H, CH_{COD}), 3.50–3.45 (m, 2H, NCH₂), 3.34–3.29 (m, 2H, NCH₂), 2.94–2.93 (m, 4H, CH_{COD}), 2.10–2.08 (m, 8H, CH_{2 COD}), 2.01–1.94 (m, 4H, CH₂), 1.91–1.83 (m, 4H, CH₂), 1.71–1.65 (m, 4H, CH_{2 COD}), 1.62–1.53 (m, 4H, CH_{2 COD}). ¹³C NMR (126 MHz, CDCl₃): δ 208.5 (Ir-C_{carbene}), 208.3 (Ir-C_{carbene}), 86.6 (CH_{COD}), 85.9 (CH_{COD}), 81.5 (CH_{bridge}), 54.3 (CH_{COD}), 51.9 (CH_{COD}), 50.1 (NCH₂), 50.0 (NCH₂), 33.4 (CH_{2 COD}), 33.3 (CH_{2 COD}), 29.2 (CH_{2 COD}), 28.1 (CH₂), 26.8 (CH₂). Electrospray MS (20 V, m/z): 896.2 [M – Cl + CH₃CN]⁺.

Figure 6.9 ^1H - ^1H COSY spectrum of **1M'** in CDCl_3

Figure 6.10 ^{13}C - ^1H HSQC spectrum of **1M'** in CDCl_3

Isomer 1M''. ^1H NMR (500 MHz, CDCl_3) δ 5.55 (s, 2H, $\text{CH}_{\text{bridge}}$), 4.74–4.70 (m, 4H, NCH_2), 4.62–4.60 (m, 4H, CH_{COD}), 3.52–3.49 (m, 4H, NCH_2), 2.59–2.62 (m, 4H, CH_{COD}), 2.21–2.17 (m, 8H, CH_2_{COD}), 1.99–1.94 (m, 8H, CH_2), 1.81–1.78 (m, 4H, CH_2_{COD}), 1.71–1.65 (m, 4H, CH_2_{COD}). ^{13}C NMR (126 MHz, CDCl_3): δ 207.9 (Ir- $\text{C}_{\text{carbene}}$), 87.4 (CH_{COD}), 81.4 ($\text{CH}_{\text{bridge}}$), 52.9 (CH_{COD}), 50.2 (NCH_2), 50.1 (NCH_2), 33.4 (CH_2_{COD}), 29.2 (CH_2_{COD}), 27.8 (CH_2). Electrospray MS (20 V, m/z): 896.1 [$\text{M} - \text{Cl} + \text{CH}_3\text{CN}$] $^+$. Anal. Calcd for $\text{C}_{28}\text{H}_{42}\text{Cl}_2\text{Ir}_2\text{N}_4$ (890.00): C, 37.79; H, 4.76; N, 6.30. Found: C, 38.20; H, 4.65; N, 6.37.

Figure 6.11 ^1H - ^1H COSY spectrum of 1M'' in CDCl_3

Figure 6.12 ^{13}C - ^1H HSQC spectrum of **1M''** in CDCl_3

Synthesis of **2M**

CO gas was bubbled through a solution of isomer **1M'** (or **1M''**) in dichloromethane (5 mL) at 0 °C over 20 min. After the addition of hexanes, a light yellow solid precipitated. The solid obtained was composed by a mixture of complexes **2M'**, **2M''** in a 62:38 ratio. Yield: 19.0 mg (71%). ^1H NMR (500 MHz, CDCl_3): δ 5.82 (s, 2H), 5.79 (s, 2H), 4.75–4.64 (m, 4H), 3.60–3.48 (m, 4H), 2.09–1.97 (m, 8H). ^{13}C NMR (126 MHz, CDCl_3): δ 201.9, 200.7, 200.3, 181.1, 181.0, 180.9, 167.9, 167.2, 166.6, 82.2, 82.1, 51.1, 51.0, 50.9, 50.8, 26.9, 26.6. IR (KBr): $\nu(\text{CO})$ 2073, 1990 cm^{-1} . Electrospray MS (20 V, m/z): 824.9 [$\text{M} + \text{K}$] $^+$. Anal. Calcd for $\text{C}_{16}\text{H}_{22}\text{Cl}_2\text{Ir}_2\text{N}_4\text{O}_4$ (789.71): C, 24.33; H, 2.81; N, 7.09. Found: C, 24.76; H, 2.72; N, 7.26.

Synthesis of **3M**

A mixture of [**M-H**] $_2(\text{PF}_6)$ (202 mg, 0.396 mmol), $[\text{Pd}(\text{OAc})_2]$ (175 mg, 0.782 mmol), and KI (275 mg, 1.65 mmol) was refluxed in acetonitrile (10 mL) for 2 h. After removal of the volatiles, the crude solid was dissolved in $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$

(97/3) and purified by column chromatography using silica gel. Elution with $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ (97/3) afforded the separation of an orange band that contained compound **3M**. Yield: 76 mg (19%). ^1H NMR (300 MHz, CD_3CN): δ 5.88 (m, 2H, $\text{CH}_{\text{bridge}}$), 4.53–4.49 (m, 4H, NCH_2), 3.57–3.52 (m, 4H, NCH_2), 1.99–1.95 (m, 8H, CH_2). ^{13}C NMR (126 MHz, CD_3CN): δ 181.6 (Pd- $\text{C}_{\text{carbene}}$), 79.3 ($\text{CH}_{\text{bridge}}$), 51.2 (NCH_2), 25.8 (CH_2). Anal. Calcd for $\text{C}_{16}\text{H}_{24}\text{N}_6\text{Pd}_2\text{I}_4 \cdot \text{CHCl}_3$: C, 17.91; H, 2.21; N, 7.37. Found: C, 17.53; H, 2.23; N, 6.89.

Synthesis of **4M**

A mixture of **3M** (50 mg, 0.0489 mmol) and 3-chloropyridine (0.3 mL) was stirred at room temperature for 30 min. After this time, the solvent was evaporated under vacuum, giving a red solid. Compound **4M** was obtained as a red solid after precipitation in a mixture of dichloromethane and hexanes. Yield: 28 mg (82%). ^1H NMR (300 MHz, CDCl_3): δ 9.01 (s, 1H, CH_{py}), 8.90 (d, $^3J_{\text{H-H}} = 6$ Hz, 2H, CH_{py}), 7.73 (d, $^3J_{\text{H-H}} = 9$ Hz, 2H, CH_{py}), 7.27 (m, 2H, CH_{py}), 5.76 (s, 2H, $\text{CH}_{\text{bridge}}$), 4.86–4.78 (m, 4H, NCH_2), 3.73–3.68 (m, 4H, NCH_2), 2.32–2.21 (m, 4H, CH_2), 2.07–1.95 (m, 4H, CH_2). ^{13}C NMR (126 MHz, CDCl_3): δ 184.4 (Pd- $\text{C}_{\text{carbene}}$), 152.8 (CH_{py}), 151.8 (CH_{py}), 137.8 (C_{py}), 132.4 (CH_{py}), 124.7 (CH_{py}), 79.6 ($\text{CH}_{\text{bridge}}$), 51.6 (NCH_2), 26.4 (CH_2). Anal. Calcd for $\text{C}_{22}\text{H}_{26}\text{Cl}_2\text{I}_4\text{N}_6\text{Pd}_2$ (1165.58): C, 22.66; H, 2.25; N, 7.21. Found: C, 22.08; H, 1.91; N, 7.43. Although the results of the microanalytical analysis of the compound are outside the limit viewed as establishing analytical purity (% C deviates by 0.66%), they are provided to illustrate the best values obtained to date.

Figure 6.13 ^1H - ^1H COSY spectrum of **4M** in CDCl_3

6.3 Photophysical properties

6.3.1 UV-vis absorption and emission of azolium salts of Chapter 2

Figure 6.14 UV-Vis absorption spectra of [C-H](Br) and [C-H](PF₆) recorded using CH₃CN as solvent at room temperature

Figure 6.15 Emission spectra of [C-H](Br) and [C-H](PF₆) recorded using degassed CH₃CN. Exciting at 317 nm.

Figure 6.16 UV-Vis absorption spectra of [D-H](I), [E-H](I) and [F-H](I) recorded using CH_3CN as solvent at room temperature

Figure 6.17 Emission spectra of [D-H](I) and [E-H](I) recorded using degassed CH_3CN . Exciting at 350 nm.

6.4 ^1H NMR experiments

6.4.1 ^1H NMR experiments for the determination of the stoichiometry of the aggregates of Chapter 3

We prepared a series of solutions containing both the π -stacking additive (pyrene or C_6F_6) and the metal complex **3D** in varying proportions while maintaining the total concentration, $[\mathbf{3D}] + [\pi\text{-stacking additive}]$, constant for each solution. A 2:1 $\text{CDCl}_3/\text{CD}_3\text{OD}$ (0.6 mL) mixture was used to prepare the samples and record the ^1H NMR experiments. In the experiments carried out with pyrene and C_6F_6 , the doublet at 9.40 ppm corresponding to the two protons of the phenyl ring of the phenanthro[4,5-abc]phenazino[11,12-d]imidazol-2-ylidene ligand in complex **3D** was used to measure the change in chemical shift upon the addition of the corresponding additive ($\Delta\delta$).

^1H NMR experiments with pyrene

Table 6.1 Determination of the stoichiometry of the aggregates by means of the Method of Continuous Variations (Job's method)

$[\mathbf{3D}]$ (M)	$[\text{pyrene}]$ (M)	$[\mathbf{3D}] + [\text{pyrene}]$ (M)	χ (3D)	δ (ppm)	$\Delta\delta$ (ppm)	χ (3D) $\times$ $\Delta\delta$
1.8E-03	0.0E+00	1.8E-03	1.00	9.397	0.000	0.000
1.5E-03	2.9E-04	1.8E-03	0.83	9.415	0.018	0.015
1.2E-03	5.9E-04	1.8E-03	0.67	9.435	0.038	0.025
8.8E-04	8.8E-04	1.8E-03	0.50	9.456	0.059	0.029
5.9E-04	1.2E-03	1.8E-03	0.33	9.479	0.082	0.027
2.9E-04	1.5E-03	1.8E-03	0.17	9.504	0.107	0.018
0.0E-04	0.0E-04	0.0E-03	0.00	-	-	0.000

Figure 6.18 Job plot for the determination of the stoichiometry of the aggregates complex **3D**/pyrene

Figure 6.19 Aromatic region of the ^1H NMR spectra of complex **3D** in the presence of pyrene at different molar fractions. From top to bottom, molar fractions of **3D** are: 1 (a), 0.83 (b), 0.67 (c), 0.50 (d), 0.33 (e) and 0.17 (f).

^1H NMR experiments with C_6H_6

Table 6.2 Determination of the stoichiometry of the aggregates by means of the Method of Continuous Variations (Job's method)

[3D] (M)	[C_6F_6] (M)	[3D] + [C_6F_6] (M)	χ (3D)	δ (ppm)	$\Delta\delta$ (ppm)	χ (3D) x $\Delta\delta$
1.9E-03	0.0E+00	1.9E-03	1.00	9.397	0.000	0.000
1.6E-03	3.2E-04	1.9E-03	0.83	9.417	0.020	0.017
1.3E-03	6.3E-04	1.9E-03	0.67	9.441	0.044	0.029
9.5E-04	9.5E-04	1.9E-03	0.50	9.471	0.074	0.037
6.3E-04	1.3E-03	1.9E-03	0.33	9.482	0.085	0.028
3.2E-04	1.6E-03	1.9E-03	0.17	9.5	0.103	0.017
0.0E-04	0.0E-04	0.0E-03	0.00	-	-	0.000

Figure 6.20 Job plot for the determination of the stoichiometry of the aggregates complex **3D**/ C_6F_6

Figure 6.21 Aromatic region of the 1H NMR spectra of complex **3D** in the presence of C_6F_6 at different molar fractions. From top to bottom, molar fractions of **3D** are 1 (a), 0.83 (b), 0.67 (c), 0.50 (d), 0.33 (e) and 0.17 (f).

6.4.2 1H NMR experiments for the determination of the association constant (K_a) of Chapter 3

A NMR tube was charged with the corresponding amount of the π -stacking additive (pyrene or C_6F_6) and 0.1 μL of a 1.8 mM solution of complex **3D**. The total volume was then adjusted to 0.6 mL and the 1H NMR was acquired. A 2:1 $CDCl_3/CD_3OD$ mixture was used to prepare the samples and record the 1H NMR experiments. A large excess of the additives was used in the experiments, as this is the key feature of the Benesi-Hildebrand treatment for the determination of K_a .⁷

In the experiments carried out with pyrene, the signal at 9.40 ppm corresponding to two aromatic protons of the pyrene *core* in complex **3D** was used to measure the change in

chemical shift ($\Delta\delta$). In the experiments carried out with C_6F_6 , the signal at 8.33 ppm corresponding to two aromatic protons of the pyrene core in complex **3D** was used to measure the change in chemical shift ($\Delta\delta$).

¹H NMR experiments with pyrene

Table 6.3 Determination of the association constant of complex **3D** with pyrene

[3D] (M)	[pyrene](M)	Equivalents of pyrene	δ (ppm)	$\Delta\delta$ (ppm)	$1/\Delta\delta$ (ppm ⁻¹)	$1/[\text{pyrene}]$ (M ⁻¹)
3.06E-03	0.00	0.0	9.49	0.00	-	-
3.06E-03	0.05	161.7	9.41	0.08	12.8	20.20
3.06E-03	0.08	256.0	9.38	0.11	8.8	12.76
3.06E-03	0.11	350.3	9.34	0.15	6.6	9.32
3.06E-03	0.15	501.2	9.30	0.19	5.3	6.52
3.06E-03	0.22	706.0	9.22	0.28	3.6	4.63

Figure 6.22 Plot of the NMR titration data showing the relationship between the induced chemical shift change and the amount of pyrene added

Figure 6.23 Plot of $1/\Delta\delta$ vs. $1/[\text{pyrene}]$ for complex [**3D**]. The Benesi-Hildebrand data treatment gives

$$\Delta\delta_{\text{max}} = 0.79 \text{ ppm and } K_a = 2.21 \text{ M}^{-1}$$

Figure 6.24 Aromatic region of the ^1H NMR spectra of complex **3D** upon addition of different amounts of pyrene. From top to bottom, the equivalents of pyrene added are: 0.0 (a), 161.7 (b), 256.0 (c), 350.3 (d), 501.2 (e) and 706.0 (f).

^1H NMR experiments with C_6F_6

Table 6.4 Determination of the association constant of complex **3D** with C_6F_6

[3D] (M)	[C_6F_6] (M)	Equivalents of C_6F_6	δ (ppm)	$\Delta\delta$ (ppm)	$1/\Delta\delta$ (ppm^{-1})	$1/[\text{C}_6\text{F}_6]$ (M^{-1})
3.1E-04	0	0.0	8.33	0.00	-	-
3.1E-04	0.43	1414.9	8.35	-0.02	-47.6	2.31
3.1E-04	0.72	2358.2	8.37	-0.04	-28.6	1.38
3.1E-04	1.16	3773.1	8.40	-0.07	-14.3	0.87
3.1E-04	1.44	4716.3	8.42	-0.09	-10.9	0.69
3.1E-04	2.89	9432.7	8.48	-0.15	-6.5	0.35

Figure 6.25 Plot of the NMR titration data showing the relationship between the induced chemical shift change and the amount of C_6F_6 added

Figure 6.26 Plot of $1/\Delta\delta$ vs $1/[\text{C}_6\text{F}_6]$ for complex **3D**. The Benesi-Hildebrand treatment gives $\Delta\delta_{\text{max}} = 0.344$ ppm and $K_a = 0.13 \text{ M}^{-1}$

Figure 6.27 Aromatic region of the ^1H NMR spectra of complex **3D** with the addition of different amounts of C_6F_6 . From top to bottom the equivalents of C_6F_6 added are: 0.0 (a), 1414.9 (b), 2358.2 (c), 3773.1 (d), 4716.3 (e) and 9432.7 (f).

6.4.3 ^1H NMR titration of complex **7C** with pyrene

A NMR tube was charged with 0.015 mmol of complex **7C** and 0.7 mL of a 5:2 $\text{CDCl}_3/\text{CD}_3\text{OD}$ solution. Then, we gradually added pyrene (0.015, 0.030, 0.045, 0.15 mmol) and took the ^1H NMR spectra of the resulting solutions.

Figure 6.28 ^1H NMR titration of complex **7C** with pyrene in $\text{CDCl}_3/\text{CD}_3\text{OD}$ at 25°C . The mmol of pyrene from the top to bottom are a) 0, b) 0.015, c) 0.030, d) 0.045 and e) 0.150.

6.4.4 ^1H NMR experiments for the determination of the association constant (K_a) of Chapter 4

A NMR tube was charged with the corresponding amount of pyrene and 0.1 μL of 1.2 mM solution of complex **3K**. The total volume was then adjusted to 0.6 mL and the ^1H NMR was acquired. A 2:1 $\text{CDCl}_3/\text{CD}_3\text{OD}$ mixture was used to prepare the samples and record the ^1H NMR experiments. A large excess of pyrene was used in this experiment, as this is the key feature of the Benesi-Hildebrand treatment for the determination of K_a .⁷ The signal at 9.80 ppm, corresponding to the four protons of the quinoxalino groups in complex **3K**, was used to measure the change in chemical shift ($\Delta\delta$).

Table 6.5 Determination of the association constant of complex **3K** with pyrene

[3K] (M)	[pyrene] (M)	Equivalents of pyrene	δ (ppm)	$\Delta\delta$ (ppm)	$1/\Delta\delta$ (ppm ⁻¹)	$1/[\text{pyrene}]$ (M ⁻¹)
2.1×10^{-4}	0.00	0.0	9.799	0.000	-	-
2.1×10^{-4}	0.03	147.21	9.726	0.073	13.7	32.76
2.1×10^{-4}	0.06	286.46	9.685	0.114	8.8	16.83
2.1×10^{-4}	0.08	389.90	9.668	0.131	7.6	12.37
2.1×10^{-4}	0.10	489.36	9.644	0.155	6.5	9.85
2.1×10^{-4}	0.13	628.61	9.631	0.168	6.0	7.67

Figure 6.29 Plot of the NMR titration data showing the relationship between the induced chemical shift change and the amount of pyrene added **Figure 6.30** Plot of $1/\Delta\delta$ vs. $1/[\text{pyrene}]$ for complex **3K**. The Benesi-Hildebrand data treatment gives

$$\Delta\delta_{\text{max}} = 0.279 \text{ ppm and } K_a = 11.6 \text{ M}^{-1}$$

Figure 6.31 Aromatic region of the ^1H NMR spectra of complex **3K** upon addition of different amounts of pyrene. From top to bottom, the equivalents of pyrene added are: 0.0 (a), 147.21 (b), 286.46 (c), 389.90 (d), 489.36 (e) and 628.61 (f).

6.5 Electrochemical Studies

6.5.1 DPV experiments of Chapter 3

Figure 6.32 Differential pulse voltammetry diagrams of complex **2A**, with the addition of different amounts of pyrene (0 to 10 equivalents, from left to right)

Figure 6.33 Differential pulse voltammetry diagrams of complex **2B**, with the addition of different amounts of pyrene (0 to 10 equivalents, from left to right)

6.6 Catalytic Experiments

6.6.1 Catalytic experiments described in Chapter 3

α -arylation of ketones with aryl halides

A Schlenk tube was charged with NaOtBu (0.7 mmol) and the catalyst (1% mol). The Schlenk tube was evacuated and filled with nitrogen three times, and 1,4-dioxane (2 mL) was added. The resulting solution was stirred for 5 min. After this time, the corresponding aryl halide (0.6 mmol), ketone (0.5 mmol), and anisole (0.6 mmol) were subsequently added. The reaction mixture was heated at 80 °C. The evolution of the reactions and yields were determined by GC analysis, using anisole as standard.

Suzuki-Miyaura cross-coupling with palladium catalyst

A Schlenk tube was charged with the corresponding aryl boronic acid (0.35 mmol), Cs₂CO₃ (0.7 mmol) and the catalyst (2% mol). The Schlenk tube was sealed with a Teflon cap and purged with nitrogen three times. 1,4-Dioxane (2 mL) and the corresponding aryl halide (0.35 mmol) were subsequently added. The mixture was stirred and heated at 80 °C for 2 h. The yields of the reaction were calculated by GC using anisole as internal standard.

Suzuki-Miyaura cross-coupling with nickel catalyst

A Schlenk tube was charged with the corresponding aryl boronic acid (0.18 mmol), K_3PO_4 (0.47 mmol), and the catalyst (3% mol). The Schlenk tube was sealed with a Teflon cap and purged with nitrogen three times. Toluene (2 mL) and the corresponding aryl halide (0.18 mmol) were subsequently added. The mixture was stirred and heated at 90 °C for 50 min. The yields of the reaction were calculated by GC using anisole as internal standard.

6.6.2 Catalytic experiments described in Chapter 5

Acylation of aryl halides

In a 50 mL high-pressure Schlenk were added molecular sieves (1 g), tetrabutylammonium bromide (16 mg, 0.05 mmol), catalyst (2 mol %), aryl halide (0.5 mmol), hydrocinnamaldehyde (0.080 mg, 0.6 mmol), pyrrolidine (0.071 g, 1 mmol), and DMF (2 mL). The mixture was stirred and heated to 120 °C for 16 h. The yield of the reaction was calculated by GC, using anisole as internal standard.

6.7 X-Ray Crystallography

6.7.1 Crystal Structure of compounds of Chapter 2

Crystals suitable for X-ray study were obtained by slow diffusion of hexane into a concentrated solution of the complex in chloroform (**[C-H](Br)**, **1C**, **4C**), dichloromethane (**2B**, **6C**, **7C**, **10C**), or dichloromethane/methanol (**1D** and **1F**). Diffraction data was collected on a Agilent SuperNova diffractometer equipped with an Atlas CCD detector using Mo-K α radiation ($\lambda = 0.71073$ Å). Single crystals were mounted on a MicroMount® polymer tip (MiteGen) in a random orientation. Absorption corrections based on the multiscan method were applied.⁸ The structures were solved by direct methods in SHELXS-97 and refined by the full-matrix method based on F^2 with the program SHELXL-97⁹ using the OLEX software package.¹⁰ Key details of the crystal and structure refinement data are summarized in the following tables.

Table 6.6 Summary of crystal data, data collection, and structure refinement details

	Complex 2B	[C-H](Br)	Complex 1C
Empirical formula	C ₃₀ H ₃₁ BrN ₂ Ni	C ₂₅ H ₂₇ BrN ₂	C ₉₉ H ₁₁₄ Cl ₃ N ₆ Rh ₃
Formula weight	558.19	435.39	1803.04
Temperature	200	293(2)	199.95(10)
Crystal System	orthorhombic	monoclinic	monoclinic
Space group	Pbca	P2 ₁ /c	P2 ₁ /c
a/Å	7.83098(7)	8.2162(3)	18.20666(12)
b/Å	21.35005(18)	12.5197(4)	21.18239(13)
c/Å	30.0829(3)	19.5121(8)	21.55681(15)
α /°	90	90	90
β /°	90	93.037(4)	90.7989(6)
γ /°	90	90	90
Volume/Å ³	5029.62(8)	2004.27(14)	8312.80(9)
Z	8	4	4
Density (calculated)/ mg/mm ³	1.4742	1.443	1.441
Absorption coefficient/mm ⁻¹	3.121	2.064	6.045
F(000)	2279.5	904.0	3744.0
Crystal size/mm ³	0.312 × 0.09 × 0.059	0.055 × 0.135 × 0.239	0.238 × 0.149 × 0.116
Theta range for data collection	8.28 to 143.68°	5.936 to 58.934°	5.85 to 145.32°
Index ranges	-9 ≤ h ≤ 7, -26 ≤ k ≤ 25, -36 ≤ l ≤ 32	-10 ≤ h ≤ 11, -15 ≤ k ≤ 17, -26 ≤ l ≤ 26	-22 ≤ h ≤ 22, -25 ≤ k ≤ 26, -26 ≤ l ≤ 25
Reflections collected	23990	20273	7771
Independent reflections	4880 [R(int) = 0.0349]	5092 [R(int) = 0.0541]	16357 [R(int) = 0.0378]
Data / restraints / parameters	4880/0/308	5092/0/255	16357/2/1035
Goodness-of-fit on F ²	1.049	1.111	1.107
Final R indices [I > 2σ(I)]	R ₁ = 0.0356, wR ₂ = N/A	R ₁ = 0.0511, wR ₂ = 0.1311	R ₁ = 0.0546, wR ₂ = 0.1550
R indices (all data)	R ₁ = 0.0398, wR ₂ = 0.1059	R ₁ = 0.0765, wR ₂ = 0.1459	R ₁ = 0.0720, wR ₂ = 0.1691
Largest diff. peak and hole/ e.Å ⁻³	0.63/-0.36	0.81 and -0.52	2.37 and -1.36

Table 6.7 Summary of crystal data, data collection, and structure refinement details

	Complex 4C	Complex 6C	Complex 7C
Empirical formula	C ₃₃ H ₃₈ BrIrN ₂	C ₂₀ H ₂₇ BrN ₂ Ni	C ₃₀ H ₃₀ Cl ₃ N ₃ Pd
Formula weight	734.76	434.05	645.32
Temperature	200.00(10)	293	293(2)
Crystal System	monoclinic	monoclinic	monoclinic
Space group	P2 ₁ /c	P2 ₁	P2 ₁ /a
a/Å	9.3221(3)	9.6712(5)	7.8180(3)
b/Å	21.3617(5)	8.7098(4)	19.2890(6)
c/Å	14.4693(4)	11.7607(6)	20.7344(7)
α/°	90	90	90
β/°	101.674(3)	94.740(4)	97.032(3)
γ/°	90	90	90
Volume/Å ³	2821.75(14)	987.27(8)	3103.26(18)
Z	4	2	4
Density (calculated)/ mg/mm ³	1.730	1.460	1.381
Absorption coefficient/mm ⁻¹	6.172	3.010	0.879
F(000)	1448.0	448.0	1312.0
Crystal size/mm ³	0.3379 × 0.1486 × 0.1169	0.3682 × 0.1397 × 0.0903	0.073 × 0.117 × 0.506
Theta range for data collection	5.75 to 58.986°	5.828 to 58.914°	5.66 to 59.004°
Index ranges	-11 ≤ h ≤ 12, -29 ≤ k ≤ 28, -19 ≤ l ≤ 18	-13 ≤ h ≤ 12, -11 ≤ k ≤ 11, -14 ≤ l ≤ 15	-10 ≤ h ≤ 10, -24 ≤ k ≤ 26, -27 ≤ l ≤ 27
Reflections collected	22604	10926	35472
Independent reflections	6991 [R(int) = 0.0370]	4645 [R(int) = 0.0516]	7973 [R(int) = 0.0406]
Data / restraints / parameters	6991/0/336	4645/1/219	7973/0/336
Goodness-of-fit on F ²	0.928	1.060	0.727
Final R indices [I>2sigma(I)]	R ₁ = 0.0380, wR ₂ = 0.0891	R ₁ = 0.0434, wR ₂ = 0.0926	R ₁ = 0.0335, wR ₂ = 0.1018
R indices (all data)	R ₁ = 0.0598, wR ₂ = 0.1053	R ₁ = 0.0622, wR ₂ = 0.1208	R ₁ = 0.0455, wR ₂ = 0.1195
Largest diff. peak and hole/ e.Å ⁻³	1.42 to -1.29	0.72/-0.93	0.70/-0.62

Table 6.8 Summary of crystal data, data collection, and structure refinement details

	Complex 10C	Complex 1D	Complex 1F
Empirical formula	C ₄₃ H ₅₃ BrF ₆ IrN ₂ PRu	C ₃₉ H ₄₀ IIrN ₄	C ₃₆ H ₄₂ IIrN ₄ O
Formula weight	1116.02	883.90	865.83
Temperature	200.1(2)	200	293(2)
Crystal System	triclinic	triclinic	monoclinic
Space group	P-1	P-1	P2 ₁ /n
a/Å	11.8980(3)	10.7342(3)	14.6533(5)
b/Å	12.2223(4)	11.9737(5)	11.2029(4)
c/Å	17.2260(4)	13.7298(6)	19.8539(7)
α /°	96.493(3)	82.045(4)	90
β /°	101.866(2)	70.514(3)	92.917(3)
γ /°	118.496(3)	79.321(3)	90
Volume/Å ³	2088.52(12)	1629.18(12)	3254.98(19)
Z	2	2	4
Density (calculated)/ mg/mm ³	1.775	1.8017	1.767
Absorption coefficient/mm ⁻¹	4.599	5.080	5.085
F(000)	1100.0	860.9	1696.0
Crystal size/mm ³	0.1472 × 0.1353 × 0.0549	0.42 × 0.1383 × 0.0705	0.106 × 0.155 × 0.400
Theta range for data collection	5.424 to 59.05°	5.74 to 58.42°	5.568 to 58.736°
Index ranges	-15 ≤ h ≤ 16, -16 ≤ k ≤ 16, -23 ≤ l ≤ 23	-14 ≤ h ≤ 14, -15 ≤ k ≤ 16, -18 ≤ l ≤ 18	-20 ≤ h ≤ 19, -15 ≤ k ≤ 15, -27 ≤ l ≤ 21
Reflections collected	45967	34739	36346
Independent reflections	10643 [R(int) = 0.0519]	8079 [R(int) = 0.0541]	8208 [R(int) = 0.0283]
Data / restraints / parameters	10643/0/512	8079/0/407	8208/0/392
Goodness-of-fit on F ²	1.082	1.056	1.165
Final R indices [I>2sigma(I)]	R ₁ = 0.0433, wR ₂ = 0.0890	R ₁ = 0.0350, wR ₂ = N/A	R ₁ = 0.0288, wR ₂ = 0.0592
R indices (all data)	R ₁ = 0.0753, wR ₂ = 0.1069	R ₁ = 0.0436, wR ₂ = 0.0882	R ₁ = 0.0350, wR ₂ = 0.0620
Largest diff. peak and hole/ e.Å ⁻³	2.40 to -1.42	2.33/-1.07	1.24/-1.09

6.7.2 Crystal Structure of compounds of Chapter 4

Suitable crystals for X-Ray study of complex **1K** were obtained by slow diffusion of chloroform into a concentrated solution of the complex in methanol. Diffraction data was collected on a Agilent SuperNova diffractometer equipped with an Atlas CCD detector using Mo-K α radiation ($\lambda = 0.71073$ Å). Single crystals were mounted on a MicroMount® polymer tip (MiteGen) in a random orientation. Absorption corrections based on the multiscan method were applied.⁸ Using Olex2,¹⁰ the structure of complex **1K** was solved using Charge Flipping^{11,12} in Superflip¹³ and refined with ShelXL refinement package using Least Squares minimisation.⁹

Disorder solvent is present in two voids per unit cell. Solvents used in synthesis and crystallization (methanol and chloroform) could not be recognized in the disordered electron density. The contribution of the disordered solvent to the diffraction pattern was therefore incorporated in the model using Squeeze in Platon v1.17.¹⁴ A total of 1171 electrons were found in two voids of 497 and 674 Å³, located at (0.000, 0.000, 0.000) and (0.054, 0.446, 0.500), respectively.

Key details of the crystals and structure refinement data are summarized in Table 6.9.

Table 6.9 Summary of crystal data, data collection, and structure refinement details

Complex 1K	
Empirical formula	C ₇₀ H ₈₆ I ₂ Ir ₂ N ₈
Formula weight	1677.66
Temperature	293(2)
Crystal System	triclinic
Space group	P-1
a/Å	14.4466(5)
b/Å	14.9597(9)
c/Å	20.8650(7)
α /°	82.666(4)
β /°	86.835(3)
γ /°	62.527(5)
Volume/Å ³	3968.0(3)
Z	2
Density (calculated)/ mg/mm ³	1.404
Absorption coefficient/mm ⁻¹	4.167

F(000)	1644.0
Crystal size/mm ³	0.217 × 0.164 × 0.095
Theta range for data collection	5.604 to 58.968°
Index ranges	-19 ≤ h ≤ 19, -19 ≤ k ≤ 19, -28 ≤ l ≤ 27
Reflections collected	70673
Independent reflections	19354[R(int) = 0.0559]
Data / restraints / parameters	19354/309/767
Goodness-of-fit on F ²	1.022
Final R indices [I > 2σ(I)]	R ₁ = 0.0696, wR ₂ = 0.1897
R indices (all data)	R ₁ = 0.1207, wR ₂ = 0.2295
Largest diff. peak and hole/ e.Å ⁻³	4.45/-2.50

6.7.3 Crystal Structure of compounds of Chapter 5

Suitable crystals for X-Ray study of complex **1M'** and **2M''** were obtained by slow diffusion of hexane into a concentrated solution of the complex in chloroform. Diffraction data was collected on a Agilent SuperNova diffractometer equipped with an Atlas CCD detector using Mo-K α radiation ($\lambda = 0.71073$ Å). Single crystals were mounted on a MicroMount® polymer tip (MiteGen) in a random orientation. Absorption corrections based on the multiscan method were applied.⁸ Using Olex2,¹⁰ the structure of complexes **1M** and **2M** was solved using Charge Flipping^{11,12} in Superflip¹³ and refined with ShelXL refinement package using Least Squares minimisation.⁹

Key details of the crystals and structure refinement data are summarized in Table 6.10

Table 6.10 Summary of crystal data, data collection, and structure refinement details

	Complex 1M'	Complex 2M''
Empirical formula	C ₅₉ H ₈₈ Cl ₁₂ Ir ₄ N ₈	C ₁₆ H ₁₈ Cl ₂ Ir ₂ N ₄ O ₄
Formula weight	2103.57	785.64
Temperature	200.00(10)	293(2)
Crystal System	monoclinic	monoclinic
Space group	I2/a	P2 ₁ /n
a/Å	15.1391(2)	9.2720(3)
b/Å	15.5045(3)	22.7873(8)

$c/\text{\AA}$	31.8334(5)	9.7352(3)
$\alpha/^\circ$	90	90.00
$\beta/^\circ$	98.9181(16)	94.710(3)
$\gamma/^\circ$	90	90.00
Volume/ $\text{\AA}^3$	7381.7(2)	2049.94(12)
Z	4	4
Density (calculated)/ mg/mm^3	1.893	2.546
Absorption coefficient/ mm^{-1}	7.664	13.261
$F(000)$	4040.0	1448.0
Crystal size/ mm^3	$0.1678 \times 0.1399 \times 0.0716$	$0.1364 \times 0.0821 \times 0.0971$
Theta range for data collection	5.86 to 58.392	5.68 to 58.08
Index ranges	$-19 \leq h \leq 20, -19 \leq k \leq 21, -41 \leq l \leq 42$	$-12 \leq h \leq 12, -30 \leq k \leq 30, -12 \leq l \leq 13$
Reflections collected	41054	22303
Independent reflections	9199 [$R_{\text{int}} = 0.0520, R_{\text{sigma}} = 0.0460$]	5062 [$R_{\text{int}} = 0.0668, R_{\text{sigma}} = 0.0611$]
Data / restraints / parameters	9199/48/388	5062/0/253
Goodness-of-fit on F^2	1.037	1.220
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0500, wR_2 = 0.1242$	$R_1 = 0.0663, wR_2 = 0.1539$
R indices (all data)	$R_1 = 0.0644, wR_2 = 0.1376$	$R_1 = 0.0798, wR_2 = 0.1604$
Largest diff. peak and hole/ $\text{e.\AA}^{-3}$	9.65/-1.59	3.59/-2.83

Molecular structure of **3M**

Although the data collected for complex did not allow the complete refinement of the structure, these data provide valuable information about its molecular structure. The molecular structure of **3M**, shown in Figure 6.34 confirms the formation of a dimetallic NHC complex. The tetracyclic bis(NHC) is bridging two palladium fragments, which complete their coordination sphere with two iodines and a CH_3CN ligand, as we observe by ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy. Table 6.11 shows the most representative bond lengths and angles. The $\text{Pd-C}_{\text{carbene}}$ distances are approximately 1.95 Å. Due to the angular nature of the bicyclic ligand, the through-space distance between the two metals is 7.14 Å.

Figure 6.34 Molecular structure of complex **3M**. Ellipsoids are at 50% probability. Hydrogen atoms have been omitted for clarity.

Table 6.11 . Selected bond lengths (Å) and angles (°) of complex **3M**

Bond	Length (Å)	Bond	(°)
Pd(3)-C(9)	2.02(1)	C(9)-Pd(3)-I(1)	87.76
Pd(3)-I(5)	2.60(1)	C(12)-Pd(2)-I(6)	86.96
Pd(3)-I(1)	2.60(1)	N(3)-C(5)-N(1)	113.15
Pd(3)-N(7)	2.06(1)	N(4)-C(7)-N(6)	108.98
Pd(2)-C(12)	1.90(1)		
Pd(2)-I(6)	2.60(1)		
Pd(2)-I(4)	2.59(1)		
Pd(2)-N(2)	2.12(1)		

6.8 References

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Chapter 7
**Compuestos metálicos con ligandos
poliaromáticos rígidos. Consecuencias
catalíticas**

En aplicación con la normativa de estudios de doctorado sobre la elaboración de Tesis Doctorales según el programa RD 99/2011, por la que establece que: *La tesis Doctoral escrita en una lengua diferente al valenciano o del castellano, en el momento de ser depositada, debe de contener un apartado suficientemente amplio en una de estas dos lenguas, y debe formar parte de la encuadernación final de la tesis*; el siguiente capítulo contiene un resumen en castellano del trabajo recogido en la presente Tesis Doctoral

7.1 Introducción

Desde que el primer complejo con un ligando carbeno N-heterocíclico (NHC por sus siglas en inglés) fue descrito simultáneamente por Öfele y Wanzlick en 1968;^{1,2} y Herrmann descubrió la primera aplicación catalítica de complejos basados en este tipo de ligandos en 1995,³ los ligandos NHC han sido ampliamente estudiados desde prácticamente todos los puntos de vista, incluyendo su preparación,⁴⁻⁷ estabilidad,⁸ propiedades estereoelectrónicas,⁹⁻¹¹ estrategias de coordinación,^{7,12,13} y su uso en catálisis homogénea¹⁴ y asimétrica.^{15,16} Incluso algunos libros han sido dedicados exclusivamente a la química de este tipo de ligandos.¹⁷⁻²⁰

Los ligandos NHC forman enlaces más fuertes con centros metálicos que la mayoría de los ligandos clásicos como, por ejemplo, las fosfinas. Esta cualidad explica que los complejos-NHC sean especialmente resistentes a la disociación, y permite la generación de centros metálicos con una alta densidad electrónica, lo que resulta beneficioso en el desarrollo de catalizadores altamente estables y activos.

Además de su estabilidad química, la amplia versatilidad coordinativa de los ligandos NHC ha ayudado a su gran desarrollo, proporcionando complejos con prácticamente todos los metales de transición en diferentes estados de oxidación. La relativa facilidad de preparación de los precursores de ligandos NHC (por lo general, sales de azolio) ha permitido el acceso a un elevado número de nuevas topologías. En el Esquema 7.1 se muestran solo algunas de las estructuras de ligandos NHC conocidas.

Esquema 7.1 Ejemplos de ligandos NHC

Recientemente, hemos centrado nuestro interés en ligandos NHC que incorporan anillos poliaromáticos fusionados en su estructura, ya que existe la posibilidad de generar interacciones π entre el ligando y compuestos aromáticos. De hecho las interacciones π - π han sido de gran interés desde el punto de vista de diseño de fármacos,²¹ estructuras de proteínas,^{22,23} ingeniería de cristales,^{24,25} reconocimiento molecular,²⁶⁻²⁸ entre otras. Además, es bien sabido que el apilamiento π puede proporcionar importantes ventajas en la inducción asimétrica en algunos procesos catalíticos.²⁹⁻³⁵

Hasta la fecha, se han descrito una serie de ligandos NHC poliaromáticos (Esquema 7.2) basados en naftaleno,³⁶⁻³⁸ fenantreno,³⁶⁻³⁸ acetanafteno,³⁹⁻⁴² piraceno^{43,44} y trifenileno.^{45,46} La aplicación de estos compuestos va desde el estudio de las propiedades fotofísicas de las respectivas sales de azolio, hasta la aplicación en catálisis de los complejo derivados de estos ligandos.

Esquema 7.2 Ligandos NHC basados en sistemas poliaromáticos

Debido a las propiedades fluorescentes del pireno, este ha sido el cromóforo más usado en el campo de la fotoquímica fundamental y aplicada.⁴⁷ Desde su descubrimiento por Laurent en 1837,⁴⁸ este compuesto poliaromático ha estado sujeto a numerosas

investigaciones. Por todo lo anterior, creemos que los derivados metálicos de un ligando NHC que incorpore pireno en su estructura pueden tener aplicaciones fotofísicas interesantes y, además, existe la posibilidad de generar interacciones- π entre el ligando y sustratos aromáticos, lo que puede ser beneficioso en muchos procesos catalíticos.

7.2 Objetivos

Durante los últimos años, nuestro grupo de investigación ha estado interesado en desarrollar nuevos ligandos del tipo NHC para la preparación de catalizadores homogéneos. Siguiendo la misma línea de investigación, en esta tesis doctoral nos hemos enfocado en desarrollar nuevos complejos con ligandos del tipo NHC que incorporen sistemas poliaromáticos en su estructura, explorar la actividad catalítica de estos complejos y estudiar las propiedades electrónicas de los nuevos ligandos del tipo NHC. De manera más particular:

- Preparar una serie de sales de azolio con diferente número de anillos aromáticos fusionados y sus respectivos complejos metálicos.
- Preparar nuevas sales de azolio con dos o tres fragmentos NHC que se encuentren geométricamente separados uno de otro y su coordinación a diferentes centros metálicos.
- Estudiar las propiedades electrónicas de los nuevos ligandos del tipo NHC en la presencia de aditivos que favorezcan el apilamiento π , como pireno o hexafluorobenceno.
- Estudiar la interacción entre el ligando del tipo NHC y los aditivos de apilamiento π .
- Evaluar la actividad catalítica de los nuevos complejos en reacciones de acoplamiento cruzado. El objetivo principal en este punto es estudiar la influencia de aditivos que favorezcan el apilamiento π en la actividad catalítica de los nuevos complejos.

7.3 Resultados y discusión

7.3.1 Complejos metálicos basados en ligandos NHC con sistemas poliaromáticos

Este apartado está dividido en dos secciones. La primera versa sobre la síntesis de los precursores de ligando NHC con sistemas poliaromáticos. La preparación de los complejos metálicos derivados de estas sales se encuentra en el segunda sección.

I) Preparación de las sales de azolio basadas en sistemas poliaromáticos

Con el objetivo de preparar una lista sistemática de complejos que solo difieran en el número de anillos fusionados unido al ligando NHC, sintetizamos una serie de sales de imidazolio que no incorporen sistemas poliaromáticos y otras que si los contengan. Estos compuestos se muestran en el Esquema 7.3. Las sales de imidazolio **[A-H](X)**⁴⁹ y benzimidazolio **[B-H](X)**⁵⁰ fueron preparadas siguiendo los métodos descritos en la literatura, mientras que las sales de azolio **[C-H](X)**, **[D-H](X)**, **[E-H](X)** y **[F-H](X)** fueron sintetizadas y caracterizadas durante el desarrollo de este trabajo de investigación.

Esquema 7.3 Sales de azolio

La sal de azolio basada en pireno **[C-H](Br)** fue preparadas en dos pasos de reacción, empezando con la pireno-4,5-diona (Esquema 7.4), la cual fue sintetizada de acuerdo a un método descrito en la literatura.⁵¹ El primer paso consiste en la reacción de condensación entre la pireno-4,5-diona, formaldehído y acetato de amonio, siguiendo un procedimiento descrito en la bibliografía para compuestos similares.³⁸ El producto resultante del primer paso es puesto a reaccionar con un equivalente de bromuro de *n*-butilo en la presencia de KOH para dar el producto monoalquilado, el cual es puesto a reaccionar en puro bromuro de *n*-butilo a 130°C para dar **[C-H](Br)** como un sólido de color beige (57% de rendimiento). Para evitar posibles intercambios de halogenuros, el

contraíón fue reemplazado por hexafluorofosfato, mediante metátesis de anión con NH_4PF_6 en metanol. El compuesto $[\text{C-H}](\text{PF}_6)$ es obtenido casi cuantitativamente.

Esquema 7.4 Síntesis de $[\text{C-H}](\text{X})$

Las sales de azolio $[\text{D-H}](\text{X})$, $[\text{E-H}](\text{X})$ y $[\text{F-H}](\text{X})$ fueron preparadas mediante la reacción de condensación del yoduro de 1,3-dibutil-5,6-diaminobezimidazolio con la correspondiente dicetona (Esquema 7.5), se obtuvieron rendimientos que van desde el 70% hasta el 80%. Esta metodología para preparar sales de azolio con sistemas poliaromáticos extendidos fue recientemente descrita por la profesora Tapu⁵². Además, la profesora Tapu describió la síntesis del yoduro de 1,3-dibutil-5,6-diaminobezimidazolio, sin embargo nosotros encontramos un método más conveniente, el cual consiste en reducir los grupos nitro utilizando Pd/C e hidracina en etanol a 80°C, obteniéndose el producto deseado en un rendimiento del 90%. Esta metodología tiene la ventaja de que el catalizador de paladio puede ser removido fácilmente de la mezcla de reacción simplemente mediante filtración, después el producto puede ser obtenido fácilmente mediante la evaporación del disolvente, facilitando su purificación. Para evitar cambios de halogenuro en las siguientes reacciones de coordinación de los ligandos, las sales de yoduro $[\text{D-H}](\text{I})$, $[\text{E-H}](\text{I})$ y $[\text{F-H}](\text{I})$ se pusieron a reaccionar con NH_4PF_6 para obtener los productos de metátesis de anión $[\text{D-H}](\text{PF}_6)$, $[\text{E-H}](\text{PF}_6)$ y $[\text{F-H}](\text{PF}_6)$, respectivamente.

Esquema 7.5 Síntesis de **[D-H](X)**, **[E-H](X)** y **[F-H](X)**

Todas las nuevas sales de azolio fueron caracterizadas mediante técnicas espectroscópicas de RMN, espectrometría de masas y análisis elemental. La estructura de **[C-H](I)** fue confirmada de manera inequívoca mediante difracción de rayos X de monocristal. Además, las propiedades luminiscentes de los nuevos compuestos fueron estudiadas. Las sales basadas en pireno **[C-H](X)** mostraron emisión fluorescente en la región de 350-450 nm y un rendimiento cuántico de 0.31 y 0.28 para **[C-H](I)** y **[C-H](PF₆)**, respectivamente. Mientras que la emisión de los compuestos **[D-H](I)** y **[E-H](I)** se observó en la región de 450 -650 nm y el rendimiento cuántico calculado fue de 0.25 para **[D-H](I)** y de 0.32 para **[E-H](I)**. La sal **[F-H](I)** no exhibió emisión fluorescente.

II) Preparación de los complejos metálicos basados en ligandos NHC con sistemas poliaromáticos.

Con las sales de azolio mostradas en el Esquema 7.3, decidimos preparar los derivados metálicos de Ir, Rh, Ni y Pd. Nosotros pensamos que estos complejos metálicos pueden ayudarnos a estudiar las propiedades electrónicas de los ligandos NHC, y relacionar estos datos con su actividad catalítica.

a) Preparación de los complejos de Rh e Ir

Los complejos del tipo $[\text{MCl}(\text{NHC})(\text{CO})_2]$ ($\text{M} = \text{Rh}$ o Ir) han sido ampliamente usados para estudiar las propiedades electrónicas de los ligandos NHC.⁵³⁻⁵⁶ Nuestro principal

objetivo es preparar los derivados carbonílicos de todas las sales de azolio mencionadas anteriormente. Los complejos derivados de los ligandos imidazolilideno y benzimidazolilideno **1A** y **1B** fueron obtenidos siguiendo los métodos descritos en la literatura (Esquema 7.6).⁵⁷

Esquema 7.6 Síntesis de **1A** y **2B**

La coordinación del ligando pireno-imidazolilidene (**C**) a rodio e iridio es llevada a cabo mediante la desprotonación de la sal **[C-H](X)** con bis(trimetilsililamiduro) de potasio (KHMDS) en tetrahidrofurano (THF) a -78°C , seguida de la adición de $[\text{MCl}(\text{COD})]_2$ ($\text{M} = \text{Rh}$ o Ir). Las reacciones llevadas a cabo con la sal de hexafluorofosfato **[C-H](PF₆)**, dan lugar a los complejos clorados **1C** y **3C**. A las reacciones realizadas con la sal de bromuro **[C-H](Br)**, se les añadió NaBr al medio de reacción para favorecer la generación exclusiva de los complejos bromados **2C** y **4C**. Después de la purificación mediante columna cromatográfica, los complejos fueron obtenidos con un rendimiento que va desde moderado hasta alto (56-86%). La síntesis del complejo carbonílico derivado de iridio **5C** fue realizada mediante el intercambio del ligando COD con monóxido de carbono. Esta reacción se realiza burbujeando CO en una disolución del correspondiente complejo de iridio en diclorometano, tal cual se muestra en el Esquema 7.7.

Esquema 7.7 Síntesis de **1-5C**

La coordinación de **[D-H](X)**, **[E-H](X)** y **[F-H](X)** a iridio, fue llevada a cabo haciendo reaccionar $[\text{IrCl}(\text{COD})]_2$, KO^tBu y la sal de azolio correspondiente en THF a temperatura ambiente. Se le añadió un exceso de NaI a la mezcla de reacción cuando se utilizaron las sales de azolio que contienen yodo como contraión, con el fin de evitar mezclas de haluros en los complejos metálicos finales. Después de purificar los complejos mediante columna cromatográfica, se obtuvieron rendimientos que van de moderados a altos (46-78%). La síntesis de los complejos carbonílicos derivados de iridio **3D**, **3E** y **3F** fue llevada a cabo reemplazando el ligando COD por monóxido de carbono, burbujeando CO en una disolución de CH_2Cl_2 del correspondiente complejo de iridio a 0 °C, tal cual se muestra en el Esquema 7.8

Esquema 7.8 Síntesis de los complejos **1-3D**, **1-3E** y **1-3F**

b) Preparación de los complejos de Ni y Pd

Con el objetivo de determinar el efecto de la presencia de un fragmento poliaromático unido a la estructura del ligando NHC en la actividad catalítica de los complejos metálicos relacionados, y para tener un buen patrón de comparación, hemos decidido obtener los complejos a base de Ni (**2A**, **2B** y **6C**) y Pd (**3A**, **3B** y **7C**) tal cual se observa en el Esquema 7.9.

Los complejos de níquel fueron preparados siguiendo un protocolo para compuestos similares,⁵⁸ la reacción de la sal de azolio correspondiente (**[A-H](Br)**, **[B-H](Br)** o **[C-H](Br)**) con niqueloceno en una mezcla de DMF/THF, genera los complejos **2A**, **2B** y **6C** con rendimientos moderados (47-56%). Para la síntesis de los complejos que tienen la fórmula general $[\text{NiCpX}(\text{NHC})]$ es necesario que la sal de azolio contenga un

halogenuro como contraión, debido a que el enlace Ni-X formado en el producto final es muy fuerte, favoreciendo termodinámicamente la reacción.⁵⁹

Los complejos a base de paladio **3A**, **3B** y **7C**, fueron preparados siguiendo un protocolo para compuestos de paladio similares.⁶⁰ La reacción de la sal de azolio correspondiente ([**A-H**](PF₆), [**B-H**](PF₆) o [**C-H**](PF₆)) con PdCl₂ en la presencia de K₂CO₃ y utilizando 3-cloropiridina como disolvente a 90°C, genera los complejos del tipo [PdCl₂(NHC)(3-cloropiridina)] con rendimientos que van de moderados a altos (**3A**, 66%; **3C**, 50%; y **7C**, 31%).

Esquema 7.9 Síntesis de **2-3A**, **2-3B** y **6-7C**

Todos los nuevos complejos fueron caracterizados mediante técnicas espectroscópicas de RMN, espectrometría de masas y análisis elemental. Las estructuras de **1C**, **1D**, **1F**, **2B**, **4C**, **6C** y **7C** fueron confirmadas de manera inequívoca mediante difracción de rayos X de monocristal.

7.3.2 Preparación de complejos heterodimetálicos

Complejos basados en ligandos NHC que incorporen alguna funcionalización han atraído recientemente la atención, especialmente cuando un fragmento metálico es enlazado a un ligando que ya está coordinado a otro metal, es decir, que se incorpore un nuevo metal a un complejo.⁶¹⁻⁶³ En este sentido, Ganter fue capaz de enlazar un

fragmento $[\text{RuCp}^*]^+$ a un ligando benzimidazol-2-ilideno que ya contenía otro metal coordinado.⁶² Además, Ganter estudió las propiedades electrónicas del complejo dimetálico, y encontró que la incorporación del fragmento $[\text{RuCp}^*]^+$ en el ligando NHC produce un importante descenso de la fuerza electrón donadora del ligando NHC.

En base a estos precedentes, y tomando en cuenta la presencia del fragmento pireno en el nuevo ligando NHC y la alta afinidad del fragmento $[\text{RuCp}^*]^+$ para coordinarse a grupos arenos, decidimos preparar complejos heterodimetálicos. La reacción de **2C**, **3C** y **4C** con $[\text{RuCp}^*(\text{CH}_3\text{CN})_3](\text{PF}_6)$ en diclorometano da lugar a la formación de los complejos de Rh/Ru (**8C**) e Ir/Ru (**9C** y **10C**) en rendimientos muy altos (Esquema 7.10). El compuesto carbonílico **11C**, fue preparado burbujeando CO a través de una disolución de **9C** en CH_2Cl_2 . El complejo **11C** fue aislado en un rendimiento alto (82%).

Esquema 7.10 Síntesis de los complejos **8-11C**

Con fines comparativos, los espectros de FT-IR de los complejos **5C** y **11C** fueron obtenidos en diclorometano. El promedio de las bandas de vibración de los grupos CO para el complejo **5C** es 2026.3 cm^{-1} , mientras que para **11C** es 2031.5 cm^{-1} . Es decir, la incorporación del grupo $[\text{RuCp}^*]^+$ genera un desplazamiento de 5.2 cm^{-1} hacia mayor longitud de onda. Lo que indica que el ligando NHC en **11C** es menos electrón dador que en **5C**. Anteriormente, el mismo comportamiento había sido observado para compuestos similares.⁶¹⁻⁶³

También hemos llevamos a cabo la voltamperometría cíclica (CV) y voltametría diferencial de pulsos (DPV) de los compuestos **4C** y **10C**. En la CV ambos compuestos mostraron dos ondas de oxidación; la primera onda de oxidación irreversible fue asignada al iridio y la segunda al ligando pireno. El valor del potencial de media onda para ambos complejos fue calculado a partir de la DPV. El potencial calculado para la

oxidación de iridio fue de 0.831 V para **4C** y de 0.891V para **10C**. Este desplazamiento anódico $\Delta E_{1/2}$ de 60 mV observado después de la coordinación del fragmento $[\text{RuCp}^*]^+$ al ligando pireno-imidazolilideno es menor que el descrito anteriormente para el caso del ligando benzimidazolilideno (167 mV).⁶² Un desplazamiento anódico similar es observado para la banda de oxidación del fragmento pireno, el cual ocurre de 1.098 a 1.143 V para **4C** y **10C**, respectivamente, en este caso el desplazamiento es menor (45 mV). Este desplazamiento hacia mayores potenciales indica que el ligando NHC disminuye su capacidad dadora. Estos resultados concuerdan perfectamente con los obtenidos en los estudios de FT-IR de **5C** y **11C**, ya que con ambos experimentos se puede concluir que la fuerza electrón dadora del ligando pireno-imidazolilideno disminuye después de la coordinación del fragmento $[\text{RuCp}^*]^+$.

7.3.3 Modificación de la propiedades electrónicas de los ligandos NHC mediante interacciones no covalentes

Con los compuestos basados en iridio y níquel descritos anteriormente (Esquema 7.11), nos propusimos estudiar las propiedades electrónicas de los nuevos ligandos NHC, y observar si estas son modificadas en la presencia de aditivos que favorezcan el apilamiento π , como pireno y hexafluorobenceno. Esta sección la hemos dividido en tres partes. La primera describe los estudios de FT-IR de los compuestos carbonílicos de iridio. Después, los cálculos teóricos DFT con respecto a las modificaciones de la propiedades electrónicas y la energía de la interacción no covalente entre el ligando NHC y los aditivos apiladores π son presentados, estos cálculos fueron realizado por el Profesor Dmitri Gusev de la Universidad de Wilfrid Laurier, en Ontario, Canadá. Por último, realizamos estudios electroquímicos de los compuestos de níquel **2A**, **2B** y **6C**, en la presencia de diferentes cantidades de pireno.

Complejos carbonílicos de iridio

Complejos de níquel

Esquema 7.11 Complejos de iridio, níquel y paladio

I) Estudios FT-IR

Los espectros de FT-IR correspondientes a los complejos **1A-B**, **5C** y **3D-F**, fueron obtenidos en disolución de CH₂Cl₂, en ausencia y en presencia de pireno o hexafluorobenceno. Los complejos **1A** y **1B**, que no contienen sistemas poliaromáticos, no presentan cambios significativos en el promedio de la frecuencia de vibración de CO ($\nu_{av}CO$) cuando está presente el pireno o el hexafluorobenceno. Sin embargo, la $\nu_{av}CO$ de los cuatro complejos que incorporan ligandos NHC con sistemas poliaromáticos (**5C** y **3D-F**) en presencia de pireno disminuyen alrededor de 1.4 cm⁻¹. El efecto opuesto es observado cuando en lugar de pireno el hexafluorobenceno es el que está presente en la disolución de CH₂Cl₂, en este caso, el aumento es de aproximadamente 1.4 cm⁻¹. Estos resultados sugieren que, el carácter electrón dador de los ligandos NHC con sistemas poliaromáticos puede ser modificado mediante la adición del adecuado aditivo de apilamiento π . En este sentido, la adición de pireno disminuye la fuerza electro dadora del ligando NHC, mientras que el efecto opuesto es obtenido con hexafluorobenceno.

II) Cálculos DFT

Con el fin de esclarecer las variaciones de $\nu_{av}CO$ en la presencia de pireno o hexafluorobenceno, nosotros calculamos la $\nu_{av}CO$ a partir del modelo de LNi(CO)₃, donde L corresponde al ligando pireno-imidazolilideno (Esquema 7.12). La $\nu_{av}CO$ calculada en la ausencia de aditivos es de 2056.1 cm⁻¹, mientras que en la presencia de pireno es de 2052.3 cm⁻¹, lo que significa una disminución de 3.8 cm⁻¹. Cuando el

hexafluorobenceno está presente la $\nu_{\text{av}}\text{CO}$ se incrementa en 2.3 cm^{-1} (2058.4 cm^{-1}). A pesar de que los resultados de los cálculos teóricos indican que los desplazamientos de la $\nu_{\text{av}}\text{CO}$ deberían ser mayores a los observados experimentalmente, cabe destacar que los resultados teóricos están de acuerdo con los datos experimentales en el sentido de que la adición de pireno produce un ligero incremento en la fuerza electrón dador del ligando NHC, mientras que el hexafluorobenceno produce exactamente el efecto contrario.

Además, los cálculos teóricos sugieren que los aductos más favorecidos energéticamente son aquellos en los cuales hay una interacción π - π entre el pireno (o hexafluorobenceno) y el fragmento pireno del ligando NHC. La geometría favorecida para esta interacción es 'face-to-face' (cara-a-cara), la cual, ha sido observada para aductos formados de hexafluorobenceno y moléculas poliaromáticas.⁶⁴

Esquema 7.12 Cálculos teóricos sobre la variación de la frecuencia de vibración de CO y de la energía de los aductos formados por el apilamiento π

II) Estudios electroquímicos

Realizamos los experimentos de voltamperometría cíclica (CV por sus siglas en inglés) y de voltametría diferencial de pulsos (DPV por sus siglas en inglés) de los complejos **2A**, **2B** y **6C** en disolución de diclorometano. Escogimos estos tres complejos ya que en la CV mostraron una onda reversible de oxidación de un electrón. Mediante la DPV de los tres complejos, pudimos calcular su respectivo potencial de media onda ($E_{1/2}$). Los complejos **2A** y **6C** mostraron el mismo valor de $E_{1/2}$, mientras que el valor calculado **2B** fue ligeramente mayor. Lo que sugiere que la fuerza electrón donadora de **2B** es ligeramente menor en comparación con **2A** y **6C**.

Como nosotros queríamos estudiar como influye la presencia de un aditivo apilador π en las propiedades electrónicas de los ligandos NHC, llevamos acabo los experimentos de DPV de los complejos **2A**, **2B** y **6C** en la presencia de cantidades crecientes de pireno. Los tres compuestos aumentan su $E_{1/2}$, sin embargo el aumento producido en el complejo **6C** es mayor que el producido en **2A** o en **2B**. Nosotros, hemos atribuido ese mayor aumento a la presencia del grupo pireno en el ligando NHC del complejo **6C**, ya que este facilita las interacciones π - π entre el pireno y el ligando NHC.

7.3.4 Cuantificación de las interacciones no covalentes entre el ligando NHC y aditivos apiladores π . Cálculo de la constante de asociación.

En los siguientes apartados se describen los experimentos realizados para estudiar las interacciones no covalentes entre complejos basado en ligandos poliaromático-imidazolilidenos y aditivos apiladores π . Estos estudios fueron realizados mediante espectroscopia de ^1H de RMN, absorción de UV-vis, y mediante cálculos DFT. Utilizamos los complejos **3D** y **7C** como modelos para nuestros estudios.

*1) Estudios de ^1H de RMN del complejo **3D***

Una de las técnicas más comunes para estudiar las interacciones no covalentes es mediante espectroscopia de RMN, ya que la formación de la especie huésped/hospedero (o mas comúnmente conocido en inglés como host/guest) produce cambios en el desplazamiento químico de varios núcleos atómicos que se encuentran presentes.⁶⁵⁻⁶⁷ Como resultado de esta variación es posible establecer la regioselectividad de la unión del “guest” y su respectiva constante de asociación (K_a).^{66,68}

Nosotros hemos encontrado que la interacción entre el complejo **3D** y pireno (o hexafluorobenceno) tiene una estequiometría de 1:1. La constante de asociación entre **3D** y pireno es de 2.21 M^{-1} , mientras que la K_a de **3D** y hexafluorobenceno es menor (0.13 M^{-1}). Esto quiere decir que el pireno interacciona más fuertemente con **3D**. Como se muestra en la Figura 7.1, el pireno interacciona con el fragmento de pirazina presente en ligando NHC del complejo **3D**, mientras que el hexafluorobenceno lo hace sobre el fragmento de pireno.

Figura 7.1 Posible interacción entre **3D** y pireno (o hexafluorobenceno)

II) Cuantificación de la interacción entre pireno y **7C**

Como hemos dicho anteriormente las propiedades electrónicas del ligando pireno-imidazolilideno (**C**) pueden ser modificadas mediante la adición de pireno o hexafluorobenceno. Para entender más sobre la naturaleza de esta interacción, hemos realizado experimentos de absorción de UV-vis, RMN de ^1H y cálculos teóricos basados en DFT. Los cálculos teóricos fueron realizado por el Dr. Gregori Ujaque en la Universitat Autònoma de Barcelona. Para realizar estos estudios hemos seleccionado el pireno y el complejo **7C** como modelos.

a) Estudios de absorción de UV-vis

Los compuestos que contienen grupos orgánicos conjugados usualmente absorben fuertemente en la región del ultravioleta o en la correspondiente al visible del espectro electromagnético. Cuando estos grupos se encuentran formando interacciones π - π o host/guest, las bandas de absorción son desplazadas como respuesta a dicha unión.⁶⁹ Nosotros realizamos los estudios de absorción de UV-vis del complejo **7C** y pireno en metanol a temperatura ambiente. Este estudio consiste en mantener la concentración fija de pireno mientras la concentración de **7C** es aumentada gradualmente, esta metodología ha sido usada anteriormente para estudios similares.⁶⁸ Lo que se observa es un ligero aumento en la intensidad de las bandas conforme aumenta la concentración de **7C**. Este efecto es típicamente observado para la formación de aductos π - π ,^{68,70-74} para nuestro caso involucra la formación de agregados de pireno y **7C**. Llegado a este punto, creemos que el pireno interacciona con el fragmento de pireno del ligando NHC. Para corroborar esta hipótesis realizamos experimentos de RMN de ^1H .

b) Titración de RMN de ^1H

La titración consiste en mantener fija la concentración de **7C** en una disolución de 1:1 de $\text{CDCl}_3/\text{CD}_3\text{OD}$, mientras se va aumentando gradualmente la concentración de pireno. Este experimento fue realizado con el fin de establecer en que parte del complejo **7C** se lleva acabo la interacción con el pireno. Como lo muestra la Figura 7.2, nosotros determinamos que el pireno interacciona con el fragmento poliaromático del ligando NHC presente en el complejo **7C**.

Figura 7.2 Posible interacción entre **7C** y pireno

c) Estudios teóricos

Las interacciones π - π han sido muy estudiadas mediante aproximaciones teóricas.⁷⁵⁻⁷⁷ Nosotros analizamos la interacción entre el pireno y los complejos basados en pireno **3A**, **3B** y **7C**. Para realizar los cálculos teóricos, consideramos que el pireno puede interactuar con cualquier ligando aromático presente en el complejo, incluyendo a la 3-cloropiridina. Para los complejos que no contienen el fragmento poliaromático (**3A** y **3B**) la interacción del pireno con el ligando 3-cloropiridina está más favorecida que con el ligando NHC. En el complejo **7C** la situación es diferente, ya que la unión de pireno y el fragmento poliaromático del ligando NHC está más favorecida que la interacción con el ligando 3-cloropiridina. Los cálculos teóricos demuestran que la interacción de pireno con los complejos depende fuertemente de la naturaleza del ligando NHC, entre más extendido sea el sistema poliaromático presente en la estructura del ligando NHC más favorecida estará la interacción con pireno.

7.3.5 Estudios catalíticos. Reacciones de acoplamiento cruzado.

La preparación de los complejos de níquel y paladio que incorporan una familia relacionada de ligandos NHC, ofrecen una oportunidad única para comparar su actividad catalítica, y además, para determinar si las reacciones son afectadas por la presencia de un aditivo apilador π . Entre todas la reacciones de acoplamiento cruzado

descritas hasta hoy en día, seleccionamos las reacciones de acoplamiento de Suzuki-Miyaura (Esquema 7.13) y la α -arilación de cetonas (Esquema 7.14) para evaluar la actividad catalítica de los complejos a base de níquel (**2A**, **2B** y **6C**) y paladio (**3A**, **3B** y **7C**).

Esquema 7.13 Reacción de Suzuki-Miyaura

Esquema 7.14 Reacción de α -arilación de cetonas

1) Reacción de Suzuki-Miyaura

Las reacciones de acoplamiento de Suzuki-Miyaura utilizando los complejos de níquel, fueron llevadas a cabo con ácido fenilborónico, el halogenuro de arilo correspondiente, K_3PO_4 y 3% del respectivo catalizador, en tolueno a 90°C durante 50 min. Estas condiciones de reacción son similares a las descritas por otros autores.⁷⁸⁻⁸⁰ En general los rendimientos obtenidos del producto final fueron bajos. Solamente utilizando el complejo **2B** como catalizador y halogenuros de arilo activados se obtienen rendimientos moderados.

Las condiciones de reacción para estudiar la actividad catalítica de los complejos a base de paladio (**3A**, **3B** y **7C**) son: ácido fenilborónico, el halogenuro de arilo correspondiente, Cs_2CO_3 y 2% del respectivo catalizador, en 1,4-dioxano. Se optimizaron las condiciones de reacción variando la temperatura y el tiempo de reacción, llegando a la conclusión de que a 80°C durante 2 horas eran las mejores para evaluar el efecto de la presencia aditivos apiladores π . La presencia de pireno no

modificó la actividad catalítica de ningún complejo. Sin embargo estos resultados contrastaban con los descritos previamente por nuestro grupo, los cuales han demostrado que la presencia de pireno modifica la actividad catalítica de los complejos que contienen algún fragmento poliaromático en su estructura,⁷⁰ por lo cual pensamos que los resultados obtenidos estaban afectados por otros factores. El factor más común es la posibilidad de que las reacciones sean catalizada heterogéneamente, para comprobar esta hipótesis realizamos la prueba de la gota de mercurio,⁸¹ la cual demostró que las reacciones están catalizada heterogéneamente y por lo tanto es insensible a la adición de pireno.

II) Reacción de α -arilación de cetonas

Esta reacción fue descrita en el mismo año por tres autores distintos Miura,⁸² Buchwald⁸³ y Hartwig.⁸⁴ Consiste en el acoplamiento cruzado C-C de una cetona y un halogenuro de arilo en la presencia de una base y un catalizador metálico. En nuestro caso particular, las reacciones fueron llevadas acabo en 1,4-dioxano, usando 2% mol del catalizador correspondiente, calentando a 80°C durante 1 hora. Utilizamos yodobenceno y bromobenzenos sustituidos en la posición *para*, y cetonas alifáticas y aromáticas como sustratos. La actividad catalítica de los complejos **3A** y **3B**, los cuales no incorporan un fragmento poliaromático, no es afectada en ningún caso cuando se introduce 10% mol de pireno al medio de reacción. Por el contrario, en el caso del complejo basado en el ligando pireno-imidazolilideno **7C** y en la presencia de 10% de pireno, la actividad catalítica disminuye considerablemente solo cuando utilizamos cetonas aromáticas, en el caso de cetonas alifáticas la reacción no es afectada. Este resultado soporta la idea de que la reactividad asociada a los diferentes sustratos es influenciada por la capacidad de interaccionar *via* apilamiento π con el catalizador (cetonas aromáticas), mientras que no afecta aquellos sustratos que no son capaces de formar interacciones π - π (cetonas alifáticas).

7.3.6 Complejos dimetálicos y trimetálicos basados en sistemas poliaromáticos

Entre todos los ligandos NHC descritos en la literatura, aquellos que poseen fragmentos de carbenos aislados, de tal manera que se evite la formación de quelatos, han sido de gran utilidad en numerosos campos.^{44,45,85-89} Los ejemplos descritos en la literatura de ligandos bis(NHC) en los cuales los fragmentos carbenos se encuentren linealmente

opuestos (ligandos conocidos como *Janus*) son muy escasos (Esquema 7.15). El primer ejemplo de un ligando tipo *Janus* fue descrito por Bielawski,⁹⁰ para el cual utilizó el ligando benzobis(imidazolilideno) (**2**). En particular, nuestro grupo de investigación ha aportado ejemplos muy relevantes de complejos dimetálicos basados en ligandos del tipo *Janus*. Nuestro grupo ha empleado el ligando 1,2,4-trimetiltiazol-3,5-diilideno (**1**) para preparar complejos dimetálicos,^{89,91-96} los cuales han mostrado una excelente actividad catalítica en numerosos procesos, y más recientemente hemos descrito ejemplos de complejos que incorporan ligandos bis(NHC) basados en pireno (**3**)⁹⁷ y en piraceno (**4**).⁴⁴

Esquema 7.15 Ligandos bis(NHC) tipo *Janus*

Junto con estos bis(carbenos) lineales, una serie de tris(carbenos) con un *core* de naturaleza rígida y con simetría D_{3h} , han sido descritos recientemente (Esquema 7.16).^{45,88,98,99} El primer tris(NHC) de este tipo fue descrito por Bielawski en 2010 y es un derivado de triptíceno (**5**), más recientemente nuestro grupo describió dos tris(NHC); uno basado en trifenileno (**6**) y el otro tribenzotriquinaceno (**7**).

Esquema 7.16 Ligandos tris(NHC) con simetría D_{3h}

Basados en lo anteriormente dicho, y en la experiencia del grupo de investigación en desarrollar nuevos ligandos NHC politópicos con sistemas poliaromáticos, decidimos preparar dos nuevos ligandos NHC (Esquema 7.17); uno tipo *Janus* (**H**) y uno con forma de “estrella” (**I**), ambos incorporan sistemas poliaromáticos más extendidos que los anteriormente descritos. La preparación de estos nuevos sistemas involucran la incorporación de fragmentos de pirazina en sus estructuras. La introducción de pirazina es una ventaja para una posterior aplicación de nuestros ligandos, ya que este fragmento se encuentra en un gran número de compuestos naturales¹⁰⁰⁻¹⁰⁴ y farmacéuticos.¹⁰⁵⁻¹⁰⁹ Además, la pirazina es un excelente bloque de construcción para el diseño de numerosas estructuras moleculares, las cuales han sido empleadas en diferentes áreas de ciencias de materiales; como materiales electroluminiscentes,¹¹⁰ colorantes,¹¹¹ semiconductores orgánicos¹¹²⁻¹¹⁹ e interruptores químicos.^{120,121}

Esquema 7.17 Ligandos bis(NHC) y tris(NHC)

7.3.6.1 Preparación de los complejos dimetálicos y trimetálicos basados en NHC con sistemas poliaromáticos

La síntesis de los precursores de ligandos NHC, se realizó tal cual se muestra en el Esquema 7.18. Las sales de azolio [**G-H₂**](**I**)₂, [**H-H₂**](**I**)₂ y [**I-H₃**](**I**)₃ fueron preparadas mediante la reacción de condensación de yoduro de 1,3-dibutil-5,6-diaminobezimidazolio con la respectiva policetona. Para el caso de las sales de azolio [**G-H₂**](**I**)₂ y [**H-H₂**](**I**)₂ utilizamos derivados de pireno-tetraona, y metanol a reflujo, obteniendo las sales con un rendimiento del 75 y 73 %, respectivamente. La presencia de los grupos *tert*-butilos en la estructura de [**H-H₂**](**I**)₂ es muy importante, ya que

aumenta su solubilidad en disolventes orgánicos, haciendo que esta sal sea más adecuada para su posterior coordinación a dos centros metálicos que $[\mathbf{G-H_2}](\mathbf{I})_2$. Para evitar posibles cambios de halogenuros en los productos metálicos finales, decidimos obtener la sal $[\mathbf{H-H_2}](\mathbf{PF_6})_2$ mediante la reacción de metátesis de anión entre $[\mathbf{G-H_2}](\mathbf{I})_2$ y NH_4PF_6 en una mezcla de metanol/diclorometano. Para la preparación de la sal de tris(azolío) $[\mathbf{I-H_3}](\mathbf{I})_3$ utilizamos hexacetociclohexano y ácido acético glacial como disolvente, calentando a 140 °C. Después del trabajo de purificación $[\mathbf{I-H_3}](\mathbf{I})_3$ fue obtenida con un rendimiento del 84%.

Debido a que las sales que contienen los grupo *tert*-butilos $[\mathbf{H-H_2}](\mathbf{I})_2$ y $[\mathbf{H-H_2}](\mathbf{PF_6})_2$ son más solubles, consideramos que estas sales son mas adecuadas para la preparación de los derivados dimetálicos que $[\mathbf{G-H_2}](\mathbf{I})_2$. Como se muestra en el Esquema 7.19, la reacción de $[\mathbf{H-H_2}](\mathbf{PF_6})_2$ con $[\text{IrCl}(\text{COD})]_2$ en THF en la presencia de *tert*-butóxido de sodio, genera el complejo dimetálico **2H** en un rendimiento del 39%. Siguiendo un procedimiento similar, pero utilizando la sal de azolio $[\mathbf{H-H_2}](\mathbf{I})_2$ y un exceso de KI, se genera el análogo **1H** con un rendimiento del 42%. El complejo dicarbonílico **3H** es generado mediante burbujear CO a través de una disolución de **2H** en diclorometano, obteniéndose un rendimiento cuasi cuantitativo.

La coordinación de $[\mathbf{I-H_3}](\mathbf{I})_3$ a iridio fue realizada mediante la desprotonación de sal de tris(azolío) con una mezcla de hidruro de sodio y *tert*-butóxido de sodio en THF a -78°C (Esquema 7.19). Para mezclas de halogenuros en el producto final, un exceso de NaI fue añadido. Después de purificar el compuesto trimetálico mediante columna cromatográfica, este fue obtenido con un rendimiento del 58%.

Todos los complejos fueron caracterizados mediante técnicas espectroscópicas de RMN, espectrometría de masas y análisis elemental. La estructura del complejo dimetálico **2H** fue confirmada de manera inequívoca mediante difracción de rayos X de monocristal.

a) Síntesis de las sales de bis(azolio)

b) Síntesis de la sal de tris(azolio)

Esquema 7.18 a) Síntesis de $[\text{G-H}_2](\text{I})_2$ y $[\text{H-H}_2](\text{X})_2$. b) Síntesis de $[\text{I-H}_3](\text{I})_3$

a) Síntesis de los complejos dimetálicos

b) Síntesis del complejo trimetálico

Esquema 7.19 a) Síntesis de 1-3H. b) Síntesis de 1I

7.3.6.2 Complejos dimetálicos basados en sistemas poliaromáticos y aditivos apiladores π

Las propiedades electrónicas del ligando bis(NHC) (**H**) fueron estudiadas mediante espectroscopia de infrarrojo y cálculos teóricos. El primero está basado en determinar la frecuencia de vibración de CO del complejo **3H**. Además, estudiamos el efecto de apiladores π (pireno y hexafluorobenceno) en la frecuencia de vibración de CO de **3H**.

El segundo estudio involucra cálculos de DFT. Estos cálculos fueron realizados por el profesor Dmitri Gusev (Wilfrid Laurier University).

a) Estudios de espectroscopia de FT-IR

Nosotros encontramos que el promedio de las frecuencias de vibración de CO ($\nu_{\text{av}}(\text{CO})$) de los complejos **3H** y de **3E** (análogo monometálico de **3H**) son exactamente iguales, lo que sugiere que ambos complejos son electrónicamente equivalentes. Al añadir pireno al complejo dimetálico **3H**, se observa una disminución de 1.9 cm^{-1} en el $\nu_{\text{av}}(\text{CO})$, mientras que la adición de hexafluorobenceno produce un aumento de 0.9 cm^{-1} del $\nu_{\text{av}}(\text{CO})$. Esto corrobora que las propiedades electrónicas de ligandos NHC a base de sistemas poliaromáticos se pueden modular de una forma predecible mediante la adición del adecuado aditivo apilador π .

b) Cálculos DFT

Las síntesis de los complejos dimetálicos con ligandos NHC derivados de sistemas poliaromáticos, ofrecen una oportunidad única para estudiar la comunicación electrónica entre ambos centros metálicos, debido a la deslocalización π del ligando puente. En este sentido, Gusev y Peris han sugerido que los cálculos DFT pueden ser usados para este propósito.¹²² Por lo que decidimos estudiar si existe una comunicación electrónica entre los centros metálicos unidos a **H**. De acuerdo a los cálculos DFT realizados para nuestro sistema, los centros metálicos unidos al ligando **H** se encuentran esencialmente desconectados, a pesar de estar unidos por un ligando que posee un sistema π muy deslocalizado.

7.3.6.3 Cuantificación de la interacción no covalente entre 3H y pireno. Cálculo de la constante de asociación

La cuantificación de la interacción (constante de asociación, K_a), y la regioselectividad, entre el pireno y el complejo **3H** fue estudiada mediante RMN de ^1H . El experimento consiste en mantener una concentración fija de **3H**, mientras la concentración de pireno se va incrementando gradualmente. El experimento de RMN de ^1H fue realizado en una mezcla 1:2 de $\text{CDCl}_3/\text{CD}_3\text{OD}$ a 28°C . Asumiendo una relación molar 1:1 entre **3H** y pireno y empleando el modelo de Benesi-Hildebrand, calculamos una K_a de 11.6 M^{-1} . Esta constante de asociación es mayor a la calculada para la interacción del complejo

monometálico **3E** con pireno (2.21 M^{-1}). Estos resultados pueden atribuirse a que el complejo **3H** tiene un sistemas π mas extendido que **3E**, por la tanto una mayor superficie para interaccionar con la molécula de pireno. Con respecto a la regioselectividad de la unión entre **3H** y pireno, los experimentos de RMN de ^1H sugiere que la interacción ocurre en la parte de la pirazina del ligando NHC (Figura 7.3).

3H + pireno

Figura 7.3 Posible regioselectividad entre **3H** y pireno

7.3.7 Preparación de una nueva bis(imidazolidina) tetracíclica para la preparación de complejos dimetálicos basados en ligandos NHC

Durante el desarrollo de esta tesis Doctoral, además de estar interesados en desarrollar ligandos mono(NHC), bis(NHC) y tris(NHC) basados en sistemas poliaromáticos, también hemos centrado nuestro interés en la síntesis de complejos dimetálicos que contengan los centros metálicos espacialmente cercanos. Es bien sabido que los catalizadores que contiene múltiples centros metálicos que se encuentren cercanos entre ellos, pueden mejorar la actividad catalítica que sus análogos monometálicos, especialmente cuando la cinética asociada al catalizador es de segundo orden,¹²³⁻¹²⁶ este efecto ha sido demostrado varias veces por nuestro grupo de investigación, utilizando complejos basados en ligandos poli(NHC).^{44,45,92-95,127,128}

Recientemente nuestro grupo de investigación, ha preparado complejos de rodio e iridio basados en bis(imidazolinilidenos), empleando el correspondiente tetraazobiciclooctano neutro (o bis(imidazolidina)) como precursor del bis(NHC).¹²⁹ En este caso particular, la formación del ligando bis(NHC) implica la doble activación C-H del grupo metileno de la bis(imidazolidina), lo cual es facilitado por la adición de una diolefina externa

(1,5-diciclooctadieno o norbornadieno) que actúan como aceptor de átomos de hidrógeno. Sin embargo, esta metodología está limitada, ya que únicamente se pueden preparar los complejos bis(NHC) derivados de iridio y rodio. Con el fin de extender la versatilidad coordinativa de este tipo de ligandos bis(NHC) a otros metales, y por la tanto ampliar su rango de aplicabilidad, en este apartado describimos la preparación de una nueva serie de complejos basados en bis(imidazolinilideno), para ello utilizamos dos protocolos: i) la metodología de la doble activación C-H, utilizando como compuesto de partida la bis(imidazolidina) neutra y ii) la activación de la sal de bis(azolío) con una base.

7.3.7.1 Preparación de los precursores de los ligandos bis(NHC)

La bis(imidazolidina) [**J-H₄**] fue preparada mediante la reacción de condensación de 1,4-diamonobutano, formaldehído y glicoxal, utilizando una gota de ácido acético y metanol como disolvente, la mezcla de reacción es agitada a temperatura ambiente durante 7 días (Esquema 7.20). Después del trabajo de purificación, la bis(imidazolidina) [**J-H₄**] es obtenida como un sólido blanco cristalino, con un rendimiento del 50%.

Esquema 7.20 Síntesis de [**J-H₄**]

La bis(imidazolidina) [**J-H₄**] puede ser oxidada utilizando N-bromosuccinamida (NBS), utilizando 1,4-dioxano como disolvente a temperatura ambiente (Esquema 7.21). Debido a que la sal de bis(azolío) obtenida en este paso de reacción es muy higroscópica, es necesario el intercambio de anión. Utilizando NH_4PF_6 en metanol, la reacción de metátesis de anión puede realizarse, obteniéndose la sal de bis azolío [**J-H₂**](PF_6)₂ como un sólido blanco, con un rendimiento del 64%.

Esquema 7.21 Síntesis de $[\text{J-H}_2](\text{PF}_6)_2$

Los precursores del ligando bis(NHC) $[\text{J-H}_4]$ y $[\text{J-H}_2](\text{PF}_6)_2$ fueron caracterizados por espectroscopia de RMN de ^1H , espectrometría de masas y análisis elemental.

7.3.7.2 Preparación de los complejos dimetálicos

Como mencionamos anteriormente, dos metodologías para la preparación de los complejos dimetálicos fueron empleadas:

- 1) Doble activación del enlace C-H de los grupos $\text{C}(\text{sp}^3)\text{H}_2$ del N-heterociclo neutro. Esta metodología fue usada por nuestro grupo de investigación en 2011,¹²⁹ permitiendo preparar complejos basados en NHC con estructuras sofisticadas no accesibles por otras vías. Esta metodología ha sido usada restrictivamente para preparar los complejos de iridio descritos en este apartado.
- 2) Activación de la sal de bis(imidazolinio) con una base débil. Esta “ruta tradicional” ha sido empleada para la preparación de complejos dimetálicos de paladio.

1) Preparación de los complejos de dimetálicos de iridio mediante la doble activación del enlace C-H.

La reacción de $[\text{J-H}_4]$ con $[\text{IrCl}(\text{COD})]_2$ en la presencia de un exceso de 1,5-ciclooctadieno en tolueno a reflujo, genera el complejo **1J**. Burbujeando CO a través de una disolución de **1J** en diclorometano, se obtiene **2J** (Esquema 7.22). Los complejos fueron caracterizados mediante espectroscopia de RMN de ^1H , espectrometría de masas y análisis elemental. Las estructuras de **1J** y **2J** fue confirmada de manera inequívoca mediante difracción de rayos X de monocristal.

Las propiedades electrónicas del ligando **J** fueron estudiadas mediante el análisis de FT-IR de la frecuencia de vibración de CO del complejo carbonílico **2J**. El promedio de la frecuencia de vibración de las bandas de CO ($\nu_{\text{av}}(\text{CO})$) de **2J** fue ligeramente mayor a su análogo tetrabencilado, el cual había sido descrito previamente por nuestro grupo de investigación.¹²⁹ Esto sugiere que la capacidad electrón donadora del ligando **J** es ligeramente menor que la de su análogo. La misma tendencia se observa cuando se cambia el grupo N-bencilo¹³⁰ por N-etilo¹³¹ en ligandos mono(imidazolinilidenos).

II) Preparación de los complejos dimetálicos de paladio

La preparación de los complejos dimetálicos de paladio, está basada en una ruta más “tradicional”, utilizando la sal de bis(imidazolinio) $[\text{J-H}_2](\text{PF}_6)_2$. Tal cual muestra el Esquema 7.23, la reacción de $[\text{J-H}_2](\text{PF}_6)_2$ con PdCl_2 , K_2CO_3 y KI en acetonitrilo a reflujo, genera el compuesto dimetálico **3J**, en un rendimiento del 33%. Haciendo reaccionar **3J** con 3-cloropiridina el ligando acetonitrilo puede ser intercambiado, dando lugar al compuesto **4J** en un rendimiento del 82%.

7.3.7.3 Estudios catalíticos. Acilación de halogenuros de arilo con hidrocinamaldehído

La reacción de acilación de halogenuros de arilo con hidrocinamaldehído fue inicialmente desarrollada por Xiao.¹³² Esta reacción consiste en el acoplamiento de un halogenuro de arilo con un aldehído (hidrocinamaldehído), para generar una aril alquil

cetona. Esta metodología representa una buena alternativa a la reacción de acilación de Fiedel-Craft (la cual falla para arenos electrón deficientes) ya que minimiza el uso de reactivos peligrosos. A pesar de este gran potencial, solo se han descritos pocos ejemplos hasta ahora,^{44,96,133-135} algunos de los cuales incluyen procesos intermoleculares.^{44,96,132,135}

Basados en estos precedentes, decidimos explorar la actividad catalítica de los complejos **3J** y **4J**. Las reacciones las llevamos a cabo con halogenuro de arilo (bromobenceno o yodobenceno), hidrocinamaldehído, pirrolidona y 2% mol del respectivo catalizador en DMF a 120°C, durante 16h (Esquema 7.24). Bajo estas condiciones de reacción ambos catalizadores mostraron rendimiento entre moderados a bajos, si comparamos con otros ejemplos descritos en la literatura.^{44,96,132,135} El complejo que incorpora el ligando 3-cloropiridina **4J** fue ligeramente más activo que el derivado de acetonitrilo **3J**. Los rendimientos más elevados se obtuvieron utilizando yodobenceno como sustrato. Cabe resaltar que este ejemplo es uno de los pocos que se encuentran descritos en la literatura.

Esquema 7.24 Acilación de halogenuros de arilo con hidrocinamaldehído

7.4 Conclusiones generales

A lo largo de esta Tesis Doctoral se han obtenido complejos que incorporan, principalmente, ligandos NHC con sistemas poliaromáticos. Las propiedades electrónicas de este tipo de ligandos puede ser modulada mediante la simple adición de una molécula orgánica que favorezca las interacciones del tipo π - π , como por ejemplo, pireno o hexafluorobenceno. Además, determinamos de manera inequívoca, la constante de asociación y la regioselectividad de la interacción entre los ligandos NHC con sistemas poliaromáticos y apiladores π , mediante técnicas experimentales y teóricas.

Demostramos que la actividad catalítica de un complejo que incorpore un fragmento poliaromático puede verse afectada por la presencia de un compuesto que favorezca el apilamiento π .

También hemos preparado una serie de complejos dimetálicos y trimetálicos basados en ligandos NHC, en los cuales, los fragmentos carbenos se encuentran unidos por sistemas poliaromáticos extendidos. Cabe destacar que en la literatura hay muy pocos ejemplos de este tipo complejos.

Por último, hemos ampliado la versatilidad coordinativa de los ligandos bis(NHC) basados en bis(imidazolilidinas). Para ello hemos utilizado dos estrategias sintéticas: i) la doble activación C-H de un grupo $C(sp^3)H_2$ y ii) la activación de la sal de azolio con una base débil.

7.5 Referencias

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