Modular pyridine-imidazolines as ligands for the CO/4-*tert*-butylstyrene copolymerization

Abstract

The modular nature of pyridine-imidazoline ligands allows to synthesize a series of C_1-symmetrical (*R*,*R*) pyridine-imidazolines to be compared with the previously reported racemic (*R*,*S*) ones. The different stereochemistry and substituents of the ligands, allow studying steric and electronic effects in the coordination to Pd(II) and Rh(I). Series of neutral complexes [PdMeCl(N-N')] and cationic ones [PdMe(NCMe)(N-N')][BAr'$_4$], [Rh(cod)(N-N')][BF_4] and [Rh(CO)$_2$(N-N')][BF_4] are prepared. The characterization in solution using ^{1}H NMR and IR techniques evidences the different basicity of the ligands. The crystal structures of two neutral palladium precursors [PdCl$_n$(Me)$_{2-n}$(N-N')] (n = 1, 2) and of two cationic rhodium complexes [Rh(cod)(N-N')][BF_4], with different R substituents in the imidazoline, show that larger distortions are induced in the imidazoline ring by the (*R*,*S*) and (*S*,*R*) configuration. Moreover depending on the R substituent in the imidazoline, the ligands show different coordination

distances and different degree of electronic delocalization across the imidazoline ring. The cationic complexes [PdMe(NCMe)(N-N')][BAr'$_4$] behave as precatalysts for the copolymerization of carbon monoxide and 4-*tert*-butylstyrene. The activity of the catalytic systems is shown to be largely dependent on the basicity and on the stereochemistry of the ligands. Moreover while using the racemic (*R*,*S*) pyridine-imidazolines, polyketones with different degree of stereoregularity may be obtained, using the (*R*,*R*) ligands the polyketones are always syndiotactic. The reactivity of the palladium precursors with carbon monoxide in solution is used to tentatively explain the catalytic results.

5.2.1. Introduction

The alternating copolymerization of carbon monoxide with alkenes is an attractive reaction because the polyketones it provides are low cost plastics with an environmentally friendly nature.[1-3] The use of homogeneous catalysts in the copolymerization reaction offers more control over the polymer properties than radical polymerization. Since the structures of the single-site catalysts are well defined, many research groups study the organometallic reactions involved in the mechanism.[4-9]

Nowadays Pd(II) complexes are the best choice for producing alternating copolymers of carbon monoxide with ethene, propene or styrene,[1] and they may be used for other unsaturated substrates like alkenes substituted with polar groups,[10] strained alkenes,[11] alkynes,[12] carbamates[13] and amines[14]. However, the commercialization of polyketones still raises many questions, the most important of which is the instability of the palladium precatalysts, which decompose to palladium metal during both the catalytic process and the copolymer workup. Therefore, the search for active catalysts in this process is of current interest.

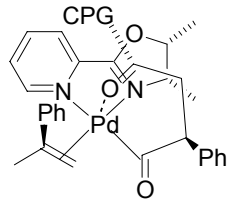
Palladium-bisnitrogen ligand (N-N) catalysts have been shown to be effective for CO/styrene copolymerization,[1,15] unlike palladium-diphosphine catalysts which, in general, form oligomers.[16] Therefore, bidentate nitrogen ligands have mainly been used,[7,16-23] although hemilabile P-N ligands have also shown activity.[6,24] The common feature, in all these nitrogen-containing ligands, is the sp^2 character of the coordinating nitrogen.

Oxazolines behave as effective ligands in several metal-catalyzed homogeneous reactions,[25] one of which is the CO/styrene copolymerization.[18,24] Imidazolines may be good alternatives since they are structurally analogous to oxazolines with different electronic properties. It has been shown that chelating ligands with a combination of a 6- and 5-membered N-containing heterocycles are good ligands for this process.[18,23] Therefore, we developed the racemic (*R,S*)-1-substituted-4,5-dihydro-4,5-diphenyl-2-(2-pyridyl)-imidazoles which have the advantage that the substituent in the aminic nitrogen N_1 can be easily modified and lead to a series of chiral ligands.[26] This substitution allows the electronic properties of the imidazoline ring to be tuned over a wide range without changing the chiral environment around the donor nitrogen (Scheme 1).[27,28] Recently some groups have also reported that 1-substitued-imidazolines can be used, as a possible alternative to oxazolines, for various catalytic processes.[29-31]

Scheme 1. General structure of pyridine-oxazoline and pyridine-imidazoline ligands

Modifying the electronic properties of the palladium center with different ligands may lead to variations not only in the activity of the catalysts but also in the selectivity of the copolymerization reaction, as has been shown for phosphorous-containing ligands.[32] The use of palladium(II) catalysts containing chiral C_1-symmetrical pyridine-oxazoline ligands in the

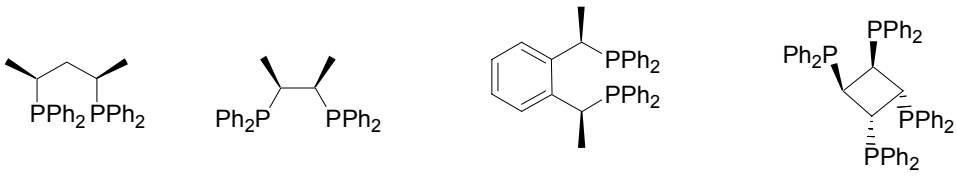
copolymerization of CO/styrene leads to syndiotactic polyketones, like the achiral ligands do.[18,24] The explanation is that because of the site-selective coordination of the styrene *cis* to the pyridine moiety the stereocontrol of the reaction is provided by the chain-end control and not by the chiral ligand (enantiosite control) (Scheme 2).[24] To increase the copolymer content on *l*-diads, using the similar pyridine-imidazolines, it seems that the styrene must be selectively coordinated *cis* to the chiral imidazoline. Therefore we decided to have take into account both steric and electronic factors in the ligand design.



GPC: growing polymer chain

Scheme 2. Model proposed by Consiglio et al. for styrene insertion to give prevailing syndiotactic copolymer

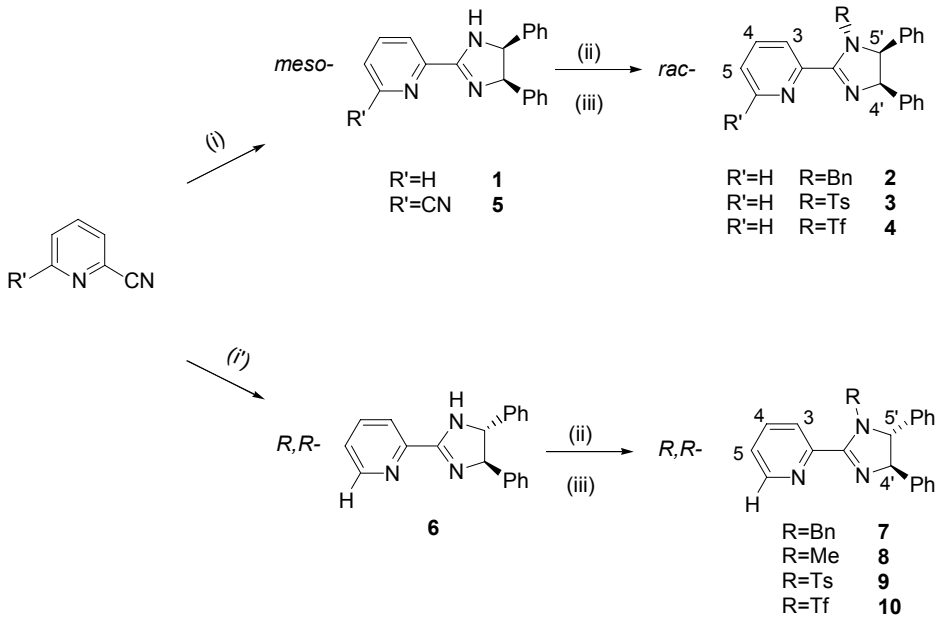
Recently some groups have reported that the activity in the alternating CO/ethene copolymerization of palladium catalysts containing (*R,S*) or (*S,R*) *meso*-diphosphines is higher than the activity of catalysts bearing the same ligands with (*R,R*) or (*S,S*) configuration (Scheme 3).[33,34]



meso-2,4-bdpp *meso*-2,3-dppb *meso*-$(C_6H_4)(CH(Me)PPh_2)_2$ *cyclo*-tetraphos

Scheme 3. *Meso*-diphosphines used as ligands in the CO/ethene copolymerization

Continuing our study of the pyridine-imidazoline ligands, we synthesized the (*R,R*)-1-substituted-4,5-dihydro-4,5-diphenyl-2-(2-pyridyl)-imidazoles with both phenyl rings of the imidazoline moiety in mutual *trans* position (Scheme 4). The "trans" pyridine-imidazoline ligands were coordinated to palladium neutral and cationic complexes. The palladium(II) cationic complexes were tested, as catalytic precursors, in the alternating copolymerization of CO/4-*tert*-butylstyrene and the results were compared with our previously reported data. The reactivity of the new palladium precursors towards carbon monoxide is also analyzed, trying to understand the stereocontrol obtained in copolymerization using these ligands.



(i) *meso*-(1*R*,2*S*)-1,2-diphenylethylenediamine; (i') (1*R*,2*R*)- 1,2-diphenylethylenediamine; (ii) 4-dimethylamino-pyridine for **3**, **4**, **9**, **10**; NaH for **2**, **7**, **8**; (iii) BnBr for **2**, **7**; TsCl for **3**, **9**; $(Tf)_2O$ for **4**, **10**; MeI for **8**.

Scheme 4. Synthesis of ligands **1-10** with their numbering scheme

5.2.2.Results and discussion

5.2.2.1. Synthesis and characterization of ligands

Pyridine-imidazoline ligands **1-4,** whose phenyl rings in the imidazoline moiety are in *cis* position (Scheme 4), were prepared and they enabled us to obtain a series of palladium(II) neutral [PdClMe(**1-4**)] (**1a-4a**) and cationic [PdMe(NCMe)(**1-4**)][BAr'$_4$] (BAr'$_4$= 3,5-$(CF_3)_2C_6H_3$) complexes (**1b-4b**). Modifying the R substituent in the imidazoline ring influenced the properties of the binding nitrogen and, therefore, the metal environment. This, in turn, led to palladium complexes with different stereochemistries. When the complexes **1b-4b** were used as precatalysts in the CO/4-*tert*-butylstyrene copolymerization, the degree of stereoregularity of the polyketones obtained depended on the R substituent.[26]

To get a better control of the stereoregularity, we tried to promote the coordination of styrene *cis* to the imidazoline through steric and electronic modifications. We first increased the steric hindrance near the pyridine nitrogen and simultaneously decreased the basicity of the pyridine ring. With this aim we synthesized the racemic *R,S-(S,R)*-4,5-dihydro-4,5-diphenyl-2-[2-(6-cyano)-pyridil]imidazol (**5**) (Scheme 4). The product was obtained in a low yield (20%) because the bis-anellation compound also formed.[35] Characterization by ^{1}H NMR shows the characteristic three aromatic signals related to the pyridinic protons $H_{3\text{-}5}$, the signal of the aminic proton at 6.5 ppm and a broad singlet at 5.6 ppm corresponding to protons $H_{4'}$ and $H_{5'}$ (Table 1). The relative integration of the pyridine to imidazoline proton signals together with the appearance in

the ^{13}C NMR spectrum of the signal at 117.0 ppm (CN) indicates the presence of the desired mono-imidazoline product.

Table 1. Selected ^{1}H NMR data for ligands **1-10**[a]

Ligand	R	$H_{4'}$, $H_{5'}$	$^{3}J_{4'-5'}$
1	H	5.51	-
2	Bn	5.44, 4.92	11.6
3	Ts	5.93, 5.80	10
4	Tf	5.98, 5.92	8.7
5	H	5.58	-
6	H	5.0	-
7	Bn	5.0, 4.42	9.2
8	Me	4.86, 4.25	10.5
9	Ts	5.36, 5.17	4.8
10	Tf	5.45, 5.37	3.8

[a] Spectra performed in $CDCl_3$ at room temperature. Coupling constants are given in Hz.

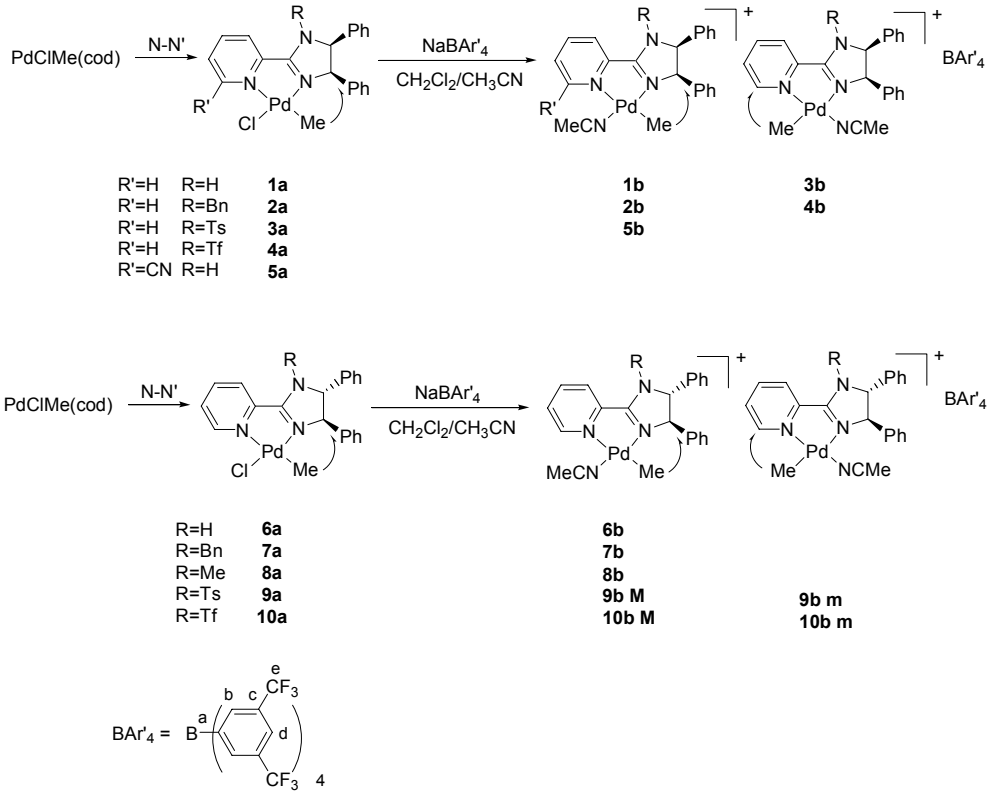
Trying to modify further the properties of the ligands, the stereochemistry of the imidazolines was changed. We prepared the enantiomeric pure (*R*,*R*) pyridine-imidazoline **6** quantitatively by reacting the corresponding diamine and 2-cyanopyridine, similarly to **1** (Scheme 4).

Reaction of **6** with different electrophiles (benzyl bromide, methyl iodide, *p*-toluenesulphonyl chloride and trifluoromethylsulphonyl anhydride), in the presence of a base, gave the (*R*,*R*) pyridine-imidazolines **7-10** (Scheme 4). The ^{1}H NMR spectra of the ligands show the signals of the pyridine ring and the two doublets (AB system) corresponding to $H_{4'}$ and $H_{5'}$ of the imidazoline (Table 1). In the case of **6**, the two doublets become a singlet at 5 ppm due to the tautomeric equilibrium. A comparison of the coupling constants within the compounds **1-10** shows that the nature of the R substituent has an effect on the coupling constant $^{3}J_{4'\text{-}5'}$, which decreases for the electron-withdrawing, bulkiest *p*-toluenesulphonyl (Ts) and trifluoromethylsulphonyl (Tf) groups (Table 1).[36] It is worth noting that in the case of the "trans" ligands **7-10** these variations are more noticeably than in the case of the "cis" ligands **2-4**.[26]

5.2.2.2. Synthesis, solution and solid state structures of neutral methylpalladium (II) complexes

When the ligands **5-10** were treated with [PdClMe(cod)] (cod = 1,5-cyclooctadiene) in toluene at room temperature the complexes [PdClMe(N-N′)] (**5a-10a**) precipitated (Scheme 5). The ^{1}H NMR spectrum of complex **5a** shows the signals corresponding to the ligand and the Pd-Me signal as a singlet at 0.72 ppm. In the spectra of complexes **6a-8a** the methyl group bonded to palladium appears as a singlet upfield shifted (average shift: 0.45 ppm) (Table 2). Since the methyl group σ-bonded to palladium normally appears at around 1 ppm,[37] the presence of the Pd-Me signals at lower frequencies may account for the unusual proximity between the

methyl group and the phenyl ring in 4' position. This proximity is observed in the solid state for complexes **4a**[38] and **8a** (see below).



Scheme 5. Synthesis of compounds **1a-10a** and **1b-10b**. The numbering scheme of BAr'_4 is included

Table 2. Selected ^{1}H NMR data for complexes **5a-10a** and **5b-10b** in $CDCl_3$ at room temperature

Compound	H_6	Pd-Me	Pd-NCMe
5a[a]	-	0.72	-
6a	8.82 (d)	0.34	-
7a	9.26 (d)	0.52	-
8a	9.28 (d)	0.48	-
9a	9.24 (d)	0.55	-
10a	9.29 (d)	0.75	-
5b	-	0.90	2.33
6b	8.34 (d)	0.56	2.30
7b	8.38 (d)	0.54	2.28
8b	8.38 (d)	0.48	2.30
9b[b]	M: 8.35 (dd) m: 8.50 (d)	0.57 0.97	2.20 1.61
10b[b]	M: 8.38 (d) m: 8.52 (d)	0.74 1.07	2.26 1.73

The signals are singlets unless another multiplicity is stated; (d): doublet; (t): triplet; (q): quadruplet; (m): multiplet. Coupling constants are omitted for clarity. [a] Spectrum made in $(CD_3)_2(CO)$. [b] M: major isomer; m: minor isomer.

As far as the pyridine-imidazoline signals are concerned, H_6 is sensitive to coordination being 0.5 ppm downfield shifted with respect to the free ligand. This indicates that H_6 feels the anisotropic effect of the neighboring chlorine.[39] Therefore the methyl group is *cis* to the imidazoline ring in all the neutral complexes. The chemical shift of both the methyl group and H_6 are useful for establishing the *cis* stereochemistry of complexes **6a**-**10a**. NOE experiments showed the interaction between the Pd-Me group and the $H_{4'}$ of the imidazoline ring which confirmed that all the neutral complexes **5a**- **10a** are the *cis* isomers. [To avoid confusion, *cis* and *trans* isomers indicate the stereochemical relationship between the methyl group and the imidazoline ring].

The *cis* stereochemistry was also observed in the solid state for complex **8a**, which contains the pyridine-imidazoline ligand **8** (R=Me) (Scheme 5). Suitable single crystals were obtained and analyzed by X-ray diffraction (Figure 1). Efforts to obtain single crystals of a neutral complex with the pyridine-imidazoline ligand bearing an electron-withdrawing group, resulted in the dichloro species **9a'**, [$PdCl_2$(**9**)] being isolated (Figure 2). Table 3 shows a selection of bond lengths and angles of the molecular structures for the neutral complexes **8a** and **9a'**.

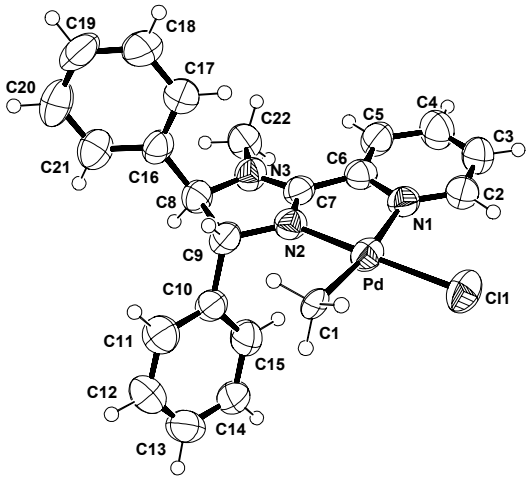


Figure 1. ORTEP drawing (thermal ellipsoids 50% probability) and atom numbering scheme of the molecular structure of **8a**

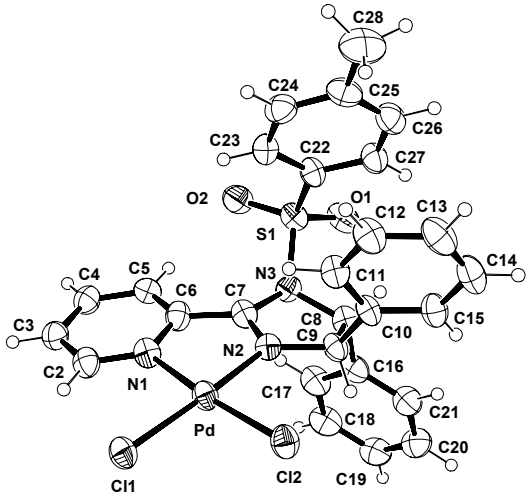


Figure 2. ORTEP drawing (thermal ellipsoids 40% probability) of the molecular structure of **9b'**

The Pd-N(py) distances are longer than those involving the iminic nitrogen of the imidazoline N2 (Table 3). The distance Pd-N(1) observed in **8a** is particularly long (2.121(6) Å) because the methyl group exerts *trans* influence. On the other hand, the Pd-N(2) bond length, 2.021(5) in **8a**, and 2.013(5) Å in **9a'**, seem to be slightly influenced by the different electron properties of the R group in the imidazoline ring.

Table 3. Selected bond distances (Å) and angles (°) and geometrical parameters (°) for **8a** and **9a'**

	8a X = C(1)	**9a'** X = Cl(2)
Pd-N(1)	2.121(6)	2.049(5)
Pd-N(2)	2.021(5)	2.013(5)
Pd-Cl(1)	2.303(2)	2.289(2)
Pd-X	2.181(4)	2.277(2)
N(2)-C(7)	1.293(9)	1.281(8)
N(2)-C(9)	1.462(8)	1.444(8)
N(3)-C(7)	1.330(8)	1.427(8)
N(3)-C(8)	1.467(9)	1.480(8)
N(3)-C(22)	1.477(9)	-
N(3)-S(1)	-	1.693(5)
N(1)-Pd-N(2)	78.4(2)	79.9(2)
N(1)-Pd-Cl(1)	96.00(16)	95.41(16)
N(1)-Pd-X	171.9(2)	172.57(15)
N(2)-Pd-Cl(1)	173.22(16)	175.15(14)
N(2)-Pd-X	94.5(2)	92.79(15)
Cl(1)-Pd-X	91.30(12)	91.81(6)
N(3)-S(1)-C(22)	-	108.2(3)
N(1)-C(6)-C(7)-N(2)	5.2(8)	2.1(9)
C(16)-C(8)-C(9)-C(10)	125.8(6)	139.7(6)
dihedral angle py/im	2.6(4)	17.9(3)

The Pd-Cl and Pd-C coordination distances fall in a range usually observed in other Pd(II) complexes.[38] In the chelating ligand the small N(1)-C(6)-C(7)-N(2) torsion angle of 5.2(8)° in **8a** and 2.1(9)° in **9a'** indicates a negligible tilt between the rings. However, the dihedral angle formed by the best fit planes through the rings are significantly distinct, being 2.6(4) and 17.9(3)°, respectively. The large angle in **9a'** might be ascribed to a distortion in the imidazoline plane to favour the intramolecular π stacking of the tosyl ring with the adjacent phenyl (distance between centroids 3.747 Å).

The electron withdrawing tosyl group in **9a'** causes the N(2)-C(7) and N(3)-C(7) distances to be different (1.281(8) and 1.427(8) Å, respectively), while in **8a** (R = Me) these bond lengths are comparable to 2σ. Correspondingly, the sum of the bond angles about the imidazoline N(3) is 360.0° in **8a** and 348.1° in **9a'**.

Analyzing the distance between the chloride ligand and the H_6 (2.80 Å for **8a** and 2.68 Å for **9a'**), a Cl-H interaction cannot be excluded. This may be the reason for the *cis* stereochemistry observed for all the neutral complexes **1a**-**10a**, since in view of the large *trans* influence of the methyl group it should be expected to be *trans* to the less basic ring (pyridine in **5a**-**8a** and imidazoline in **9a** and **10a**).

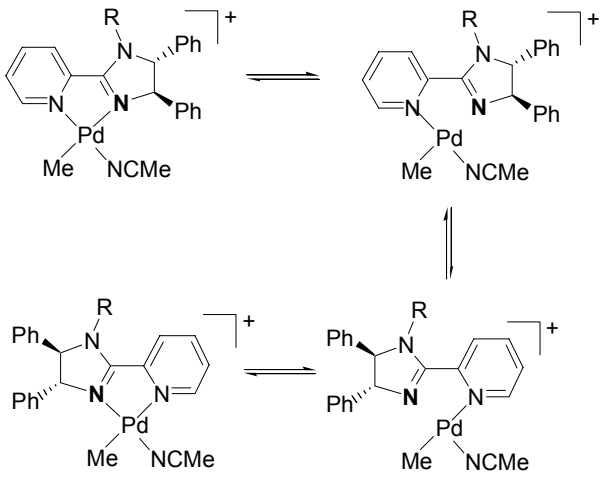
5.2.2.3. Synthesis and characterization of cationic palladium (II) complexes

The neutral complexes were treated with $NaBAr'_4$ in the presence of acetonitrile to obtain the cationic complexes $[PdMe(NCMe)(N\text{-}N')][BAr'_4]$ (**5b-10b**) (Scheme 5). ^1H and ^{13}C NMR analysis of the complexes at room temperature showed that both the Pd-Me and the Pd-NCMe signals were present, which confirmed the abstraction of the Cl ligand. For complexes **6b-8b** the signals of the methyl and the acetonitrile ligands, coordinated to palladium, appeared as singlets between 0.48-0.56 ppm and 2.28-2.30 ppm, respectively (Table 2). These shifts are indicative of *cis* stereoisomers.[26] For complex **5b**, however, the Pd-Me signal is downfield shifted because of the withdrawing effect of the substituted pyridine in *trans*. Irradiation of the protons of the Pd-Me group showed NOE interaction with $H_{4'}$ of the imidazoline ring, which confirmed the presence of *cis* stereoisomers as single products.

On the other hand, the characterization in solution of **9b** and **10b** showed two sets of resonances at room temperature, both in the aromatic and in the aliphatic part of the spectra (Table 2). COSY experiments together with selective irradiation of the aromatic signals confirmed the presence of *cis/trans* stereoisomers in a ratio of 3:1 for **9b** and 2:1 for **10b**. ^1H NMR spectra at higher temperatures (323 K in $CDCl_3$) showed broadening of the signals, which confirmed that both species are in equilibrium even though the process is in slow exchange regime at this temperature. Irradiation of the Pd-Me signal of the major isomer at room temperature

gave a NOE interaction with $H_{4'}$ but the Pd-Me signal of the minor species also appeared irradiated, thus confirming the *cis*/*trans* isomerization.

The equilibrium probably involves a process of Pd-N bond rupture, rotation of the ligand around the remaining Pd-N bond and reformation of the former Pd-N bond, as observed for similar compounds.[40] This behaviour may be attributed to the weaker donating ability of ligands **9** and **10**. The electron-withdrawing character of tosyl and trifil groups in the imidazoline ring lead to a weaker Pd-N (imidazoline) bond than the Pd-N (pyridine) one. Likewise, the methyl group *trans* to the less basic ring exerts a high *trans* influence and consequently facilitates the Pd-N(imidazoline) bond rupture (Scheme 6).



Scheme 6. Proposed isomer interconversion for complexes **9b** and **10b**

To sum up, for complexes **1b**-**5b**, bearing the pyridine-imidazoline ligands with the phenyl rings on the same side of the coordination plane, the coordination of the Me group to palladium is determined by the electronic properties of R substituents in the imidazoline. The methyl group is always *trans* to the less basic ring (pyridine for complexes **1b**, **2b**, **5b** and imidazoline for **3b** and **4b**). The behaviour of the complexes **6b**-**10b**, which have ligands with the phenyl rings up and down the coordination plane, depends also on the electron-donating or withdrawing character of the R substituent. However in the case of ligands **9** and **10** the electron-withdrawing substituent exerts a larger effect in the imidazoline (as seen also in the coupling constants in Table 1) and leads to a weaker coordination and therefore the mixture of stereoisomers is obtained (Schemes 5 and 6).

5.2.2.4. Synthesis of cationic rhodium complexes 1c-4c, 1d-4d

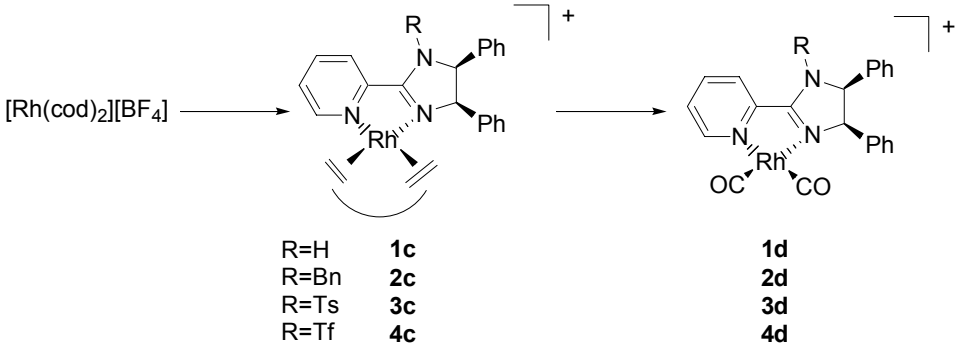
In order to get more information about the different basicities of the substituted pyridine-imidazoline ligands **1**-**4** (Scheme 4), which provide better electronic differentiation when coordinated to palladium cationic complexes, we synthesized a series of bis-carbonyl rhodium complexes and comparatively measured their CO frequencies by infrared spectroscopy.

The corresponding [Rh(cod)(N-N´)][BF_4] (**1c**-**4c**) were obtained by reacting [$Rh(cod)_2$][BF_4] with the pyridine-imidazoline ligands **1**-**4**. The ^1H NMR spectra show the expected signals for the nitrogen ligand and those corresponding to the diene (see Experimental). Considering that the symmetry of the rhodium(I) cation is C_1, four signals are expected although

fewer signals may be observed because the diene rotates easily around the coordination plane. In fact the number of signals observed at room temperature for the CH protons depends on the nitrogen ligand. For complexes **1c** and **2c** the four signals are observed (for **1c** two of them are partially overlapped), while for **3c** and for **4c** only one and two broad signals are present, respectively. Lower temperature experiments gave the four expected signals also for complexes **3c** and **4c**. These NMR data indicate that the rhodium complexes differentiate the ligands, which gives further proof of the influence of the R substituent in the pyrimidine-imidazoline properties.

Bubbling CO through the reddish solutions of the diolefinic derivatives displaces the coordinated cyclooctadiene and forms yellow solutions of the corresponding bis-carbonyl complexes **1d**-**4d** (Scheme 8).[41] As a reference the analogous complex containing 2,2'-bipyridine (bipy) as the nitrogen ligand has also been synthesized. This would let us compare with one of the best ligands for the CO/styrene copolymerization reaction.[42] The ^{1}H NMR spectra of the isolated complexes show the disappearance of the diene signals together with the shift of the pyridine-imidazoline signals, as expected for the change of the electronic properties of the ligands in *trans*.

Table 4 shows the data of the stretching frequencies, ν(CO), of the carbonyl complexes. All the complexes show two frequencies ($\Delta\delta$= 59 cm^{-1}) which we have assigned to *cis* bis-carbonyl complexes.[41] The frequencies vary and increase in the order **1** < **2** < bipy < **3** < **4**, indicating the decreasing order of basicity of the nitrogen ligands coordinated *trans* to the carbonyls.



Scheme 8. Synthesis of the Rh(I) complexes **1c**-**4c**, **1d**-**4d**

Table 4. Selected IR data for $[Rh(CO)_2(N\text{-}N')][BF_4]$ complexes[a]

Ligand	ν(CO) (cm^{-1})	Δδ
1	2093, 2030	63
2	2093, 2033	60
bipy	2099, 2042	57
3	2104, 2045	59
4	2106, 2050	56

[a] Measured in dichloromethane

5.2.2.5. X-ray crystal structures of 2c and 3c

The X-ray structural determination of **2c** and **3c** shows the rhodium atom in the expected square planar coordination through the N donors of the chelating pyridine-imidazoline ligand and the two double bonds of 1,5-cyclooctadiene. Figures 3 and 4 show perspective views of the complexes.

The Rh-C bonds (Table 5), which fall in a wide range (2.124(8) -

2.169(7) Å) and the alkene C-C bonds (1.38 Å mean value) agree with those detected in other Rh(cod) complexes.[43] Assuming C(1m) and C(5m) as the midpoint of the C-C alkene bonds, the calculated distances, *trans* to N(2) and to N(1), are Rh-C(1m) 2.008 and 2.009 Å, and Rh-C(5m) 2.033 and 2.047 Å, for **2c** and **3c**, respectively. These distances indicate a stronger *trans* influence of the ligand **3**. The coordination N(1)/N(2)/C(1m)/C(5m) mean plane forms an angle close to 88° with the plane calculated through the alkene C atoms.

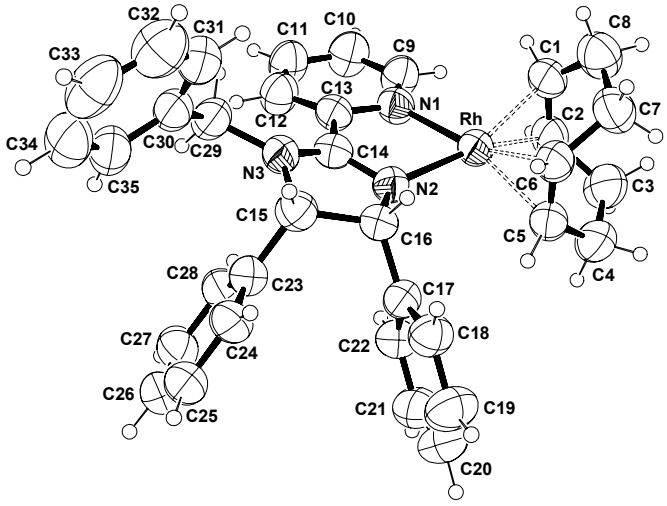


Figure 3. Molecular structure of **2c** cation. (ORTEP drawing, thermal ellipsoids at 40% probability level)

In both complexes the Rh-N1(pyridine) bond length is slightly longer than the Rh-N2(imidazoline) one. Moreover, the electronic effects exerted by the R group at N(3) are mainly evident in the imidazoline ring,

rather than in the metal coordination environment. In fact, in **2c** the N(2)-C(14) and N(3)-C(14) bond distances, 1.324(7) and 1.336(8) Å, are consistent with a delocalization inside the N(2)-C(14)-N(3) fragment, while the corresponding values in **3c** (1.283(8), 1.387(9) Å), induced by the tosyl group, indicate a double bond quite short. The degree of delocalization across the amidine is confirmed by the sum of the bond angles about N(3) of 359.5° in **2c** *vs*. 349.1° in **3c**.

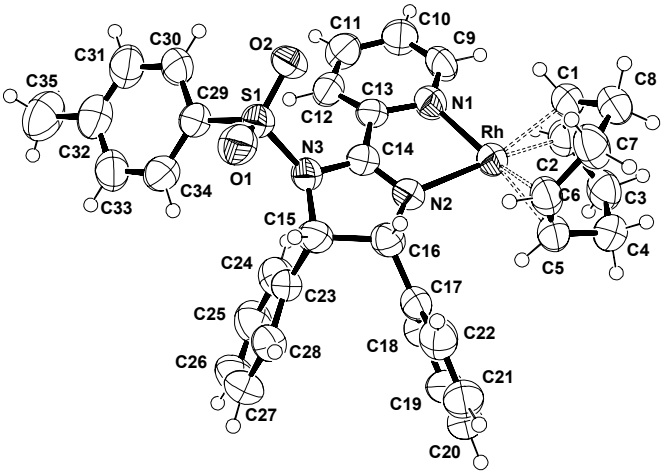


Figure 4. Molecular structure of **3c** cation. (ORTEP drawing, thermal ellipsoids at 50% probability level)

The chelating ligands are not coplanar, and the distortions are very similar to those found in the Pd derivatives with *cis* disposed phenyls.[38] The torsion angle N(1)-C(13)-C(14)-N(2) is -13.5(8) and -16.5(9)° in **2c** and **3c**, respectively, and the phenyls on the imidazoline ring avoid an eclipsed

conformation through a torsion angle C(16)-C(8)-C(9)-C(10) of 20.3(5) (**2c**) and 27.9(7)° (**3c**).

Table 5. Selected bond distances (Å) and angles (°) and geometrical parameters for **2c** and **3c**[a]

	2c	**3c**
Rh-N(1)	2.099(5)	2.112(6)
Rh-N(2)	2.078(5)	2.090(6)
Rh-C(1)	2.124(8)	2.125(7)
Rh-C(2)	2.139(7)	2.131(7)
Rh-C(5)	2.139(6)	2.169(7)
Rh-C(6)	2.147(6)	2.152(7)
Rh-C(1m)	2.008	2.009
Rh-C(5m)	2.033	2.047
N(2)-C(14)	1.324(7)	1.283(8)
N(2)-C(16)	1.484(7)	1.502(8)
N(3)-C(14)	1.336(8)	1.387(9)
N(3)-C(15)	1.483(8)	1.496(8)
N(3)-C(29)	1.480(8)	-
N(3)-S(1)	-	1.692(5)
C(1)-C(2)	1.393(10)	1.375(10)
C(5)-C(6)	1.378(10)	1.363(11)
N(1)-Rh-N(2)	78.2(2)	77.9(2)
C(1m)-Rh-C(5m)	87.41	87.32
N(3)-C(29)-C(30)	112.0(5)	-
N(3)-S(1)-C(29)	-	105.7(3)
N(1)-C(13)-C(14)-N(2)	–13.5(8)	–16.5(9)

C(23)-C(15)-C(16)-C(17)	–16.9(7)	–26.9(9)
C(29)-N(3)-C(15)-C(23)	62.8(7)	-
S(1)-N(3)-C(15)-C(23)	-	110.4(6)
dihedral angle py/im	16.2(3)	14.9(4)

[a] C(1m) and C(5m) are the midpoints of the C(1)-C(2) and C(5)-C(6) bond, respectively.

The X-ray structural results show that: i) significant distortions in the imidazoline ring are induced by *cis* disposed phenyl rings; ii) the nitrogen in the imidazoline substituted with a benzyl group is planar and shows a delocalization inside the amidine fragment, as was found with the methyl substituent (see **8a**, Figure 1); iii) the R substituent influences the coordination of the cyclooctadiene *trans* to the pyridine-imidazoline and not the direct coordination of the imidazoline to the rhodium. This is in agreement with the different behaviour found in solution for **2c** and **3c**.

5.2.2.6. Copolymerization of carbon monoxide and 4-*tert*-butylstyrene

Compounds **5b-10b** (Scheme 5) have been tested as catalyst precursors in the copolymerization of CO and 4-*tert*-butylstyrene and in the same experimental conditions as those used for precatalysts **1b-4b**.[26] Table 6 shows that **6b-10b** give rise to efficient catalysts while **5b** is inactive. In ligand **5**, the cyano substituent (Scheme 4) is *ortho* to the coordinating nitrogen, and this probably causes enough steric hindrance as to interfere the chain growth sequence. In the copolymerization reaction, 2,9-substituted phenantrolines and 6-substituted bipyridines have been

reported to behave in a similar fashion,[44] although in ligand **5** some activity was expected due to the presence of a five membered ring in the backbone.

Interestingly complexes **6b-10b** are more stable in solution, during copolymerization, than the corresponding **1b-5b**. This may be because of the relative disposition of both phenyl rings, which seems to stabilize the cationic intermediates. The most surprising feature of these catalysts is their disparate productivity. The catalysts containing the less basic ligands **4b**, **9b** and **10b**, are more productive than the more basic catalysts **1b**, **2b**, **6b-8b**. It is worth noting that the productivity observed for complex **9b** is high, ten times higher than the productivity obtained with other pyridine-imidazoline derived catalysts (entry 9 versus 1). The amount of copolymer produced by this system falls in the range of the productivities obtained with the most active systems reported for CO/styrene copolymerization at mild conditions.

For those precatalysts containing the more basic ligands (R = H, Bn, Me) the arrangement of both phenyl rings in the imidazoline moiety also affects the copolymer production. The racemic (*R*,*S*)-pyridine-imidazoline ligands (**1**, **2**), which show more significant distortions and create a larger steric hindrance than the related (*R*,*R*)-ligands (**6-8**), lead to more active catalysts (entries 1, 2 *versus* entries 6-8). This behaviour seems related to the *meso* effect reported for basic diphosphine-containing catalysts in the polymerization of ethene and/or propene with CO (Scheme 3).[33,34]

Table 6. CO/4-*tert*-butylstyrene copolymerization using complexes **1b-10b** at room temperature and 1 atm of CO pressure

Entry	Complex	Prod (gr CP/grPd.h)	M_n (M_w/M_n)	%*l* diads
1[a,b]	**1b**	2	42200 (1.1)[c]	65
2[b]	**2b**	8.9	49750 (1.5)[c]	52
3[b]	**3b**	7	59250 (1.2)[c]	15
4[b]	**4b**	12.8	39700 (1.5)[c]	18.4
5[b]	**5b**	-	-	-
6	**6b**	3.4	17200 (1.2)[d]	37.3
7	**7b**	4	n.d.	26.4
8	**8b**	5	13500 (1.3)[d]	34.5
9	**9b**	27.2	54700 (1.4)[d]	30.2
10	**10b**	14.6	26200 (2.0)[d]	23

Reaction conditions: sust/cat= 620; 1atm CO; 5 mL of chlorobenzene; t = 24h. [a] nPd= 0.083 mmol; [b] See Chapter 5.1; [c] Determined by SEC-MALLS in THF; [d] Determined by GPC in THF, relative to polystyrene standards.

The productivity of the different systems can be rationalized in terms of the basicity of the pyridine-imidazoline ligands. The catalysts containing the less basic ligands show higher productivity than the more basic ones. This seems to be consistent with the need to use π acidic imine donors instead of phosphines for the CO/styrene copolymerization.

The size of the polyketones obtained using the precursors with the new ligands **6-10** are related to the productivity of the catalytic systems

(Table 6). The molecular weights (M_n) of the polyketones obtained using the precursors **9b** and **10b** are high (up to 54700), while those obtained with the more basic catalysts **6b** and **8b** are lower. Comparing the two series of ligands (phenyl rings in *cis* and *trans* arrangement) (Scheme 4) structural factors and electronic effects again seem to be involved. On the one hand, there is no clear relationship between size of the polyketones obtained with the precursors containing the ligands **1-4** and the R substituent. On the other, the polyketones obtained with the precursors **6b-10b** had molecular weights that varied considerably according to the nature of the R substituent of the ligand used.

The tacticity of the polyketones was analyzed by integrating the ^{13}C NMR spectra in the $CH(Ph)CH_2$ region (Figure 5). It is interesting to note that the structure of the pyridine-imidazoline ligand used has a considerable effect on the stereoregularity of the polymer. While using the ligands **1-4**, the different substitutions of the imidazoline influenced the stereoregularity (see **1b** *vs.* **4b** in Figure 5), using the ligands **6-10** this effect was overridden. In fact, when precatalysts **6b-10b** were used, a prevailing syndiotactic microstructure was observed in all the cases as previously reported for the similar pyridine-oxazoline ligand.[18,24] The polyketone content of *l*-diads ranges between 23-37% (Table 6).

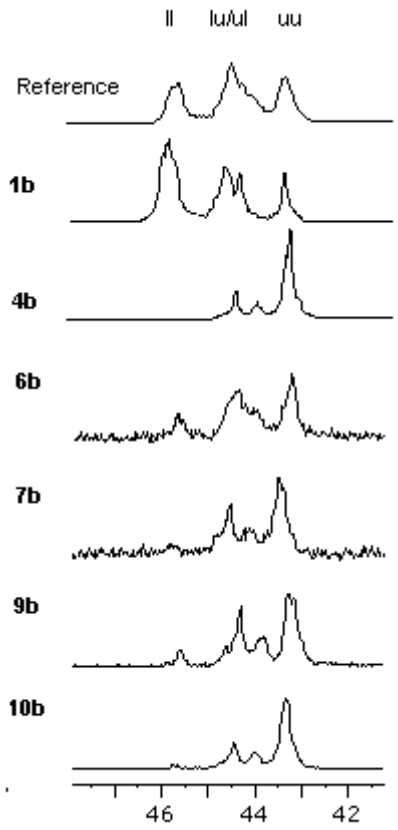


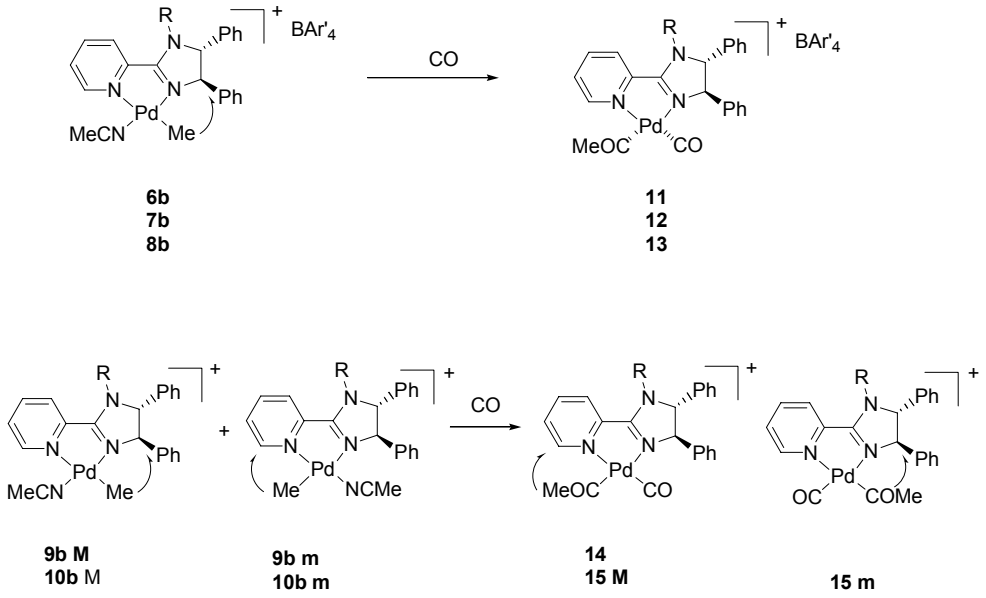
Figure 5. Comparative ^{13}C NMR spectrum of the copolymers, obtained using the complexes indicated, in the region of the methylene carbon atom. The reference is an epimerized copolymer

According to the results previously reported,[24] the syndiotacticity observed should be produced by the chain-end control, which overcomes the enantiosite control created by the chiral ligand. The reason for this may be that: 1) the styrene coordinates selectively *cis* to pyridine and prevents the alkene from being influenced by the chiral part of the ligand; 2) the chiral environment created by the pyridine-imidazoline ligand is not

enantioselective enough to force stereoregular styrene insertions. In an attempt to have more information of the role played by the pyridine-imidazoline ligands **6-10**, we monitored by NMR spectroscopy the reactivity of the palladium precursors with carbon monoxide.

5.2.2.7. Insertion of carbon monoxide in the palladium cationic complexes

The cationic complexes **6b-10b** were carbonylated in CD_2Cl_2 solution by bubbling CO for five minutes at 273 K. Selected ^{1}H and ^{13}C NMR data are given in Table 7 and indicate the formation of acyl-carbonyl complexes [Pd(COMe)(CO)(N-N')][BAr'$_4$], which result from inserting CO into the Pd-Me bond (**11-15**) (Scheme 8). The ^{1}H NMR spectra at 273 K show only two new singlets (e.g. for **7b** + CO: 1.72 ppm and 1.97 ppm) in the aliphatic part. When labeled ^{13}CO is used, in the ^{1}H NMR spectra one of these singlets become a doublet indicating that it corresponds to an acyl group. In the case of complex **15**, however, the acyl appears as a broad signal. The other singlet is due to free acetonitrile. The ^{13}C NMR spectra at 273 K, after the CO bubbling show two signals (e.g. for **7b** + CO: 174 ppm and 210.5 ppm), the one at lower frequency is typical for a Pd-CO fragment, while the other belongs to a Pd-COMe species.[17]



Scheme 8. Carbonylation of the cationic palladium compounds **6b-10b**. M: major isomer; m: minor isomer

Table 7. Selected ^{1}H and ^{13}C NMR resonances for the reaction of complexes **6b-10b** with ^{13}CO[a]

^{1}H NMR					
Compound	T	Me / Pd / NCMe	Me / Pd / CO	COMe / Pd / NCMe	COMe / Pd / CO
6b+CO	273	0.51	n.o.	n.o.	1.72
	183				1.53
7b+CO	273	0.49	n.o.	n.o.	1.72
	183				1.54
8b+CO	273	0.44	0.86	1.52 (d)	1.70 (d)
	183				1.52 (d)

9b+CO	273	M: 0.52 m: 1.04	0.90	1.46 (d)	1.62
	183				1.36 (d)
10b+CO	273	M: 0.72 m: 1.15	n.o.	n.o.	2.05
	183				M: 1.56 (d) m: 2.69 (br)
^{13}C NMR					
6b+CO	183		n.o.	n.o.	173.2, 211.6
7b+CO	273				174.0, 210.5
	183				173.1, 213.3
8b+CO	273		176.3	219.9	174.1, 210.3
	183				173.4, 212.7
9b+CO	273		175.0	215.4	173.2, 206.6
	183				172.5, 208.2
10b+CO	273		n.o.	n.o.	173.2, 207.2
	183				M:172.3, 208.2 m: 170.3, 212.9

[a] NMR spectra recorded in CD_2Cl_2; δ values are in ppm; d= doublet; br = broad; n.d.: not determined; n.o.: not observed. M: major isomer; m: minor isomer.

Low temperature NMR experiments were performed, by decreasing the temperature from 263 K to 183 K, with all the acyl-carbonyl complexes. Complexes **11-14** showed sharp singlets in all the temperature range, probing to be single isomers. In the case of **15**, the signal at 2.05 ppm

disappeared at 233 K. Two doublets became evident at 183 K (1.56 and 2.69 ppm; **15** major and minor isomer, respectively). In ^{13}C NMR the initial two signals at 273 K (at 173.2 and 207.2 ppm) became four at 183 K (172.3 and 208.2 for **15** major, 170.3 and 212.9 for **15** minor) as expected for the presence of two acyl-carbonyl species. This indicates the presence of *cis*/*trans* equilibrium in the case of complex **15** (Scheme 8).

The intermediates of the carbon monoxide migratory insertion reaction were detected in two additional experiments with complexes **8b** and **9b** (Table 7). After CO bubbling at 273 K the tube was carefully placed in the probe without shaking, so that the carbon monoxide could slowly diffuse into the solution. Three more signals in ^{1}H NMR and two more in ^{13}C NMR were observed. For example, complex **8b** showed two singlets at 0.86 and 2.35 ppm, and a doublet at 1.52 ppm in ^{1}H NMR together with two new signals at 176.3 and at 219.9 in ^{13}C NMR. These two new species were unequivocally assigned to the methyl-carbonyl (0.86 and 176.3 ppm) and acyl-acetonitrile species (1.52, 2.35 and 219.9 ppm).[17]

The stereochemistry of the acyl-carbonyl complexes **13**, **14** and **15** (major isomer) was assigned by NOE experiments. Irradiation of H_6 gave interaction with the Pd-COMe signal indicating that they are *trans* isomers (Scheme 8). In the case of complexes **11** and **12** the stereochemistry could not be unequivocally assigned by NOE experiments. Nevertheless as the signals of the Pd-COMe group for complexes **11**-**14** and **15** major appear, in ^{1}H NMR, at similar shifts (ca. 1.5 ppm) and the signal of **15** minor appears at 2.96 ppm, it could be state that also **11** and **12** are the *trans* isomers.

5.2.3. Conclusions

Modular pyridine-imidazoline ligands (**1-10**) allow studying structural influences of the ligands in the palladium-catalyzed copolymerization reaction. The modification of the ligand stereochemistry, racemic (*R*,*S*) or enantiomerically pure (*R*,*R*), leads to imidazolines with different degree of distortion. Variation of the R substituents on the imidazoline allows tuning their basicity. A larger effect of the R substituent is observed in the (*R*,*R*) imidazolines. Both structural changes are reflected in the coordination to Pd(II) and Rh(I) complexes.

All the neutral [PdClMe(N-N')] complexes have the methyl group *cis* with respect to the imidazoline ring, while the cationic complexes [PdMe(NCMe)(N-N')][BAr'$_4$] present different situations depending on the R substituent in the imidazoline ring, as we observed for ligands **1-4**. Ligands **5-8** with electron-donating substituents lead to the *cis* isomers **5b-8b**. Ligands **9** and **10** feel stronger the effect due to the electron-withdrawing R and therefore have less coordinating ability. This leads to a *cis*/*trans* equilibrium due to ligand fluxionality.

Differences are observed when the cationic palladium complexes are used as catalyst in copolymerization of CO/4-*tert*-butylstyrene: complexes **6b-10b** show higher stability in solution during the copolymerization reaction than the corresponding **1b-4b** and, in most of the cases, lower activity. For the first time a ligand effect that is similar to the *meso*-effect is observed using nitrogen ligands. Concerning the productivity of the systems there is a clear influence of the substituent R, being it more

evident for the precatalysts **6b-10b**. Higher productivities are observed using less basic ligands, probably because the insertion reactions are more favored. The special structural disposition of ligand **9**, when it is coordinated to palladium, may account for its outstanding performance.

While the polyketones obtained with the complexes **1b-4b** have different degree of stereoregularity depending on the R substituent, using complexes **6b-10b** always syndiotactic polyketones are obtained. The study of the insertion reaction of CO to form the species [Pd(COMe)(CO)(N-N')][BAr'$_4$] shows the selective formation of the *trans* stereoisomer using ligands **6-9**. This seems to indicate that using complexes **6b-9b** we are able to induce a site-selective coordination of the styrene *cis* to the chiral part of the ligand. Both low enantiomorphic control of the (*R*,*R*) ligands or isomerization processes during chain growth, may be responsible for the synthesis of syndiotactic polyketones.

5.2.4. Experimental

5.2.4.1. General procedure

All reactions were carried out under nitrogen atmosphere, at room temperature, using standard Schlenk techniques. Solvents for synthetic purposes were distilled and deoxygenated prior to use unless otherwise stated. Solvents for spectroscopy were used without further purification. Carbon monoxide (labeled and unlabeled, CP grade, 99 %) was supplied by Aldrich. The palladium precursor [PdClMe(cod)][39] and the salt NaBAr'$_4$ (Ar' = 3,5-(CF$_3$)$_2$-C$_6$H$_3$)[45] were prepared according to the reported methods. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Gemini spectrometer with

a ^{1}H resonance frequency of 300 MHz and a ^{13}C frequency of 75.4 MHz and on a Varian Mercury VX spectrometer with a ^{1}H resonance frequency of 400 MHz and a ^{13}C frequency of 100.5 MHz. The resonances were referenced to the solvent peak versus TMS ($CDCl_3$ at 7.26 δ for ^{1}H and 77.23 δ for ^{13}C, CD_2Cl_2 at 5.32 δ for ^{1}H and 54.0 δ for ^{13}C). The NOE experiments were run with a ^{1}H pulse of 12 μs (300 MHz) and 13.3 μs (400 MHz). Two-dimensional correlation spectra (gCOSY) were obtained with the automatic program of the instrument. Elemental analyses were carried out on a Carlo Erba Microanalyser EA 1108. MS (FAB positive) were obtained on a Fisons V6-Quattro instrument. The molecular weights of the copolymers and the molecular weight distributions were determined by size exclusion chromatography on a Waters 515-GPC device using a lineal Waters Ultrastyragel column with a Waters 2410 refractive index detector *versus* polystyrene standards.

5.2.4.2. Synthesis of ligands

5: The 2,6-dicyanopyridine (100 mg, 0.77 mmol) was reacted with the *meso*-1,2-diphenylethylenediamine (164 mg, 0.77 mmol) in chlorobenzene (5 mL) in the presence of $Yb(OTf)_3$ (46 mg, 0.14 mmol). The mixture was stirred for 24 hours under reflux. The desired product was separated from the bis-imidazoline product by column chromatography with hexane/ ethyl acetate (1:2) as eluent.[35] Rf = 0.41. Yield = 20%. Anal. Found: C, 77.52; H, 4.73; N, 17.21%. Calc. for $C_{21}H_{16}N_4$: C, 77.76; H, 4.97; N, 17.27%. ^{1}H NMR (300 MHz, $CDCl_3$, RT): δ 8.58 (d, ^{3}J = 7.8 Hz, 1H, H_5), 7.99 (t, ^{3}J = 7.8 Hz, 1H, H_4), 7.83 (d, ^{3}J = 7.8 Hz, 1H, H_3). 7.04- 6.95 (m, 10H, Ph), 6.49 (s, 1H, NH), 5.58 (br, 2H, $H_{4'}$ + $H_{5'}$). ^{13}C NMR (75.4 MHz, $CDCl_3$, RT): δ

162.5 (s, C_2), 150.0 (s, $C_{2'}$), 138.4 (s, C_6), 130.2 (s, $C_{3\text{-}5}$), 130.0 (s, $C_{3\text{-}5}$), 127.9 (s, Ph), 127.1 (s, Ph), 126.2 (s, $C_{3\text{-}5}$), 117.0 (s, C≡N), 67 (br, $C_{4'}$+$C_{5'}$).

6: 2-cyanopyridine (500 mg, 2.36 mmol) was reacted with (1*R*,2*R*)-1,2-diphenylethylenediamine (228 mg, 2.21 mmol) in chlorobenzene (10 mL) in the presence of $Yb(OTf)_3$ (50 mg, 0.16 mmol). The mixture was stirred for 72 h under reflux. The resulting mixture was evaporated to dryness, dissolved in CH_2Cl_2 and washed with three portions of H_2O (15 mL). The organic layers were extracted, dried over $MgSO_4$ and evaporated to give a light-coloured solid. Recrystallisation from CH_2Cl_2/ hexane afforded white crystals. Yield: 84%. Anal. Found: C, 80.09; H, 5.30; N, 13.77%. Calc. for $C_{20}H_{17}N_3$: C, 80.2; H, 5.4; N, 14%. ^{1}H NMR (300 MHz, $CDCl_3$, RT): δ 8.64 (d, ^3J = 5.4 Hz, 1H, H_6), 8.35 (d, ^3J = 8 Hz, 1H, H_3), 7.85 (t, ^3J = 8 Hz, 1H, H_4), 7.44 (dd, ^3J = 8, ^3J = 5.4 Hz, 1H, H_5), 7.36 - 7.31 (m, 10H, Ph), 5 (s, 2H, $H_{4'}$ + $H_{5'}$). ^{13}C NMR (75.4 MHz, $CDCl_3$, RT): δ 162.7 (s, C_2), 149 (s, C_6), 148.5 (s, $C_{2'}$), 143.3 (s, Ph), 136.9 (s, C_4), 128.9 (s, Ph), 127.7 (s, Ph), 126.8 (s, Ph), 125.6 (s, C_5), 123 (s, C_3), 75.6 (s, $C_{4'}$+$C_{5'}$).

7: Compound **6** (100 mg, 0.33 mmol) was dissolved in THF (3 mL) and reacted with NaH in excess for about an hour. To the reaction mixture, benzyl bromide (42.5 µL) was added dropwise at room temperature. After reacting for 5 hours, evaporation gave a brown paste which was purified by column chromatography using a hexane/ethyl acetate mixture (1:1) as eluent. Rf = 0.10. Yield: 71%. Anal. Found: C, 83.02; H, 5.82; N, 10.74%. Calc. for $C_{27}H_{23}N_3$: C, 83.26; H, 5.95; N, 10.79%. ^{1}H NMR (400 MHz, $CDCl_3$, RT): δ δ 8.72 (ddd, ^3J = 5.5 Hz, ^4J = 1.6 Hz, ^5J = 1 Hz, 1H, H_6), 8.17 (dt, ^3J = 8 Hz, ^4J = 1.4 Hz, 1H, H_3), 7.83 (td, ^3J = 5.5 Hz, ^4J = 1.4 Hz, 1H, H_4), 7.4 (m, 1H, H_5),

7.35- 6.97 (m, 15H, Ph), 5.63 (d, ^3J = 15.6 Hz, 1H, CH_2), 5.0 (d, ^3J = 9.6 Hz, 1H, $H_{4'}$ or $H_{5'}$), 4.42 (d, ^3J = 9.6 Hz, 1H, $H_{5'}$ + $H_{4'}$), 3.95 (d, ^3J = 15.6 Hz, 1H, CH_2). ^{13}C NMR (100.5 MHz, $CDCl_3$, RT): 148.9 (s, C_6), 137.1 (s, C_4), 129.1 (s, Ph), 128.6 (s, Ph), 128.3 (s, Ph), 128.0 (s, Ph), 127.7 (s, Ph), 127.5 (s, Ph), 127.3 (s, Ph), 127.2 (s, Ph), 125.4 (s, C_3 or C_5), 124.9 (s, C_5 or C_3), 77.9 (s, $C_{4'}$ or $C_{5'}$), 73.6 (s, $C_{5'}$ or $C_{4'}$), 49.1 (s, CH_2).

8: This compound was prepared in a similar way to **7** but with methyl iodide as the electrophile.[29] ^{1}H NMR (300 MHz, $CDCl_3$, RT): δ 8.59 (d, ^3J = 3.6 Hz, 1H, H_6), 7.99 (d, ^3J = 7.9 Hz, 1H, H_3), 7.70 (td, ^3J = 7.9 Hz, ^4J = 1.5 Hz, 1H, H_4), 7.28- 7.15 (m, 11H, H_5 + 10Ph), 4.86 (d, ^3J = 10.5 Hz, 1H, $H_{4'}$ or $H_{5'}$), 4.25 (d, ^3J = 10.5 Hz, 1H, $H_{4'}$ or $H_{5'}$), 2.88 (s, 3H, CH_3-N).

9: To a solution of ligand **6** (100mg, 0.33 mmol) and 4-(dimethylamino)pyridine (73.1 mg, 0.6 mmol) in dichloromethane (3 mL) at 273 K, a solution of *p*-toluenesulphonylchloride (75.7 m, 0.4 mmol) was added dropwise. The reaction mixture was allowed to warm to room temperature and stirred for 5 hours. Evaporation of the mixture gave a yellow solid that was purified by column chromatography using a hexane/ethyl acetate mixture (1:1) as eluent to obtain a white solid. Rf = 0.54. Yield: 77%. Anal. Found: C, 9.24; H, 70.88; N, 5.64%. Calc. for $C_{27}H_{23}N_3O_2S$: C, 9.26; H, 71.50; N, 5.11%. ^{1}H NMR (400 MHz, $CDCl_3$, RT): δ 8.62 (d, ^3J = 5 Hz, 1H, H_6), 7.96 (d, ^3J = 7.4 Hz, 1H, H_3), 7.84 (t, ^3J = 7.4 Hz, 1H, H_4), 7.43 (dd, ^3J = 7.4 Hz, ^3J = 5 Hz, 1H, H_5), 7.39- 7.09 (m, 14H, 10Ph + 4 Harom.-Ts-), 5.36 (d, ^3J = 4.8 Hz, 1H, $H_{4'}$ + $H_{5'}$), 5.17 (d, ^3J = 4.8 Hz, 1H, $H_{5'}$ + $H_{4'}$), 2.39 (s, 3H, CH_3). ^{13}C NMR (100.5 MHz, $CDCl_3$, RT): δ 158.5 (s, C_2), 148.6 (s, C_6), 136.5 (s, C_4), 129.1 (s, Ph), 128.9 (s, Ph), 128.3 (s, Ph), 128.1 (s,

Ph), 127.9 (s, Ph), 126.7 (s, Ph), 126.4 (s, Ph), 125.3 (s, C_5), 124.9 (s, C_3), 78.6 (s, $C_{4'}$ or $C_{5'}$), 72.1 (s, $C_{5'}$ or $C_{4'}$), 21.9 (s, CH_3).

10: Similar to the synthesis of **9** but using trifluoromethanesulfonic anhydride as the electrophile. Purification was done by column chromatography using ethyl acetate as eluent. Rf = 0.89. Anal. Found: C, 58.52; H, 3.39; N, 9.49%. Calc. for $C_{21}H_{16}N_3F_3O_2S$: C, 58.44; H, 3.71; N, 9.73%. ^{1}H NMR (400 MHz, $CDCl_3$, RT): δ 8.71 (ddd, ^3J = 4.8 Hz, ^4J = 1.7 Hz, ^5J = 0.8 Hz, 1H, H_6), 8.01 (d, ^3J = 7.7 Hz, 1H, H_3), 7.85 (td, ^3J = 7.7 Hz, ^4J = 1.7 Hz, 1H, H_4), 7.48- 7.31 (m, 11H, H_5+ 10Ph), 5.45 (d, ^3J = 3.8 Hz, 1H, $H_{4'}$ or $H_{5'}$), 5.37 (d, ^3J = 3.8 Hz, 1H, $H_{5'}$ or $H_{4'}$). ^{13}C NMR (100.5 MHz, $CDCl_3$, RT): 156.0 (s, C_2), 148.8 (s, C_6), 147.9 (s, $C_{2'}$), 139.9 (s, Ph), 139.4 (s, Ph), 136.7 (s, C_4), 129.3 (s, Ph), 129.3 (s, Ph), 128.9 (s, Ph), 128.6 (s, Ph), 126.2 (s, Ph), 126.2 (s, Ph), 125.8 (s, C_5), 124.5 (s, C_3), 78.9 (s, $C_{5'}$ or $C_{4'}$), 72.8 (s, $C_{4'}$ or $C_{5'}$).

5.2.4.3. Synthesis of [PdClMe(N-N')] (5a-10a)

The ligands (**5-10**) were added to a solution of [PdClMe(cod)] in toluene. The solution was stirred at room temperature for 1 hour yielding a yellow precipitate. After the solvent had evaporated, the compounds were washed with diethylether and filtered off.

[PdClMe(5)] (5a)

Yield: 61%. ^{1}H NMR (400 MHz, $(CD_3)_2CO$, RT): 8.55 (d, ^3J = 7.7 Hz, 1H, H_5), 8.46 (s, 1H, NH), 8.32 (t, ^3J = 7.7 Hz, 1H, H_4), 8.12 (d, ^3J = 7.7 Hz, 1H, H_3), 7.26-6.85 (m, 10H, Ph), 5.72 (d, ^3J = 11.2 Hz, 1H, $H_{5'}$), 5.53 (d, ^3J = 11.2 Hz, 1H, $H_{4'}$), 0.72 (s, 3H, Pd-CH_3).

[PdClMe(6)] (6a)

Yield: 81%. Anal. Found: C, 55.59; H, 4.67; N, 9.50%. Calc. for $C_{21}H_{20}N_3ClPd$: C, 55.28; H, 4.42; N, 9.21%. ^{1}H NMR (400 MHz, $CDCl_3$, RT): δ 8.82 (d, ^3J = 4.7 Hz, 1H, H_6), 8.60 (s, 1H, NH), 8.41 (d, ^3J = 7.8 Hz, 1H, H_3), 7.75 (td, ^3J = 7.8 Hz, ^4J = 1.9Hz, 1H, H_4), 7.41 (dd, ^3J = 7.8, ^3J = 4.7 Hz, 1H, H_5), 7.28-7.16 (m, 10H, Ph), 4.90 (d, ^3J = 6.8 Hz, 1H, $H_{4'}$), 4.83 (d, ^3J = 6.8 Hz, 1H, $H_{5'}$), 0.34 (s, 1H, Pd-CH_3). ^{13}C NMR (100.5 MHz, $CDCl_3$, RT): δ 149 (s, C_6), 138.6 (s, C_4), 129.2 (s, Ph), 129 (s, Ph), 128.1 (s, Ph), 127.9 (s, Ph), 126.6 (s, Ph), 126.2 (s, Ph), 128.4 (s, C_5), 124.3 (s, C_3), 76.6 (s, $C_{4'}$), 70.3 (s, $C_{5'}$), -8.6 (s, Pd-CH_3).

[PdClMe(7)] (7a)

Yield: 60%. Anal. Found: C, 60.50; H, 4.73; N, 7.48%. Calc. for $C_{28}H_{26}N_3ClPd$: C, 61.50; H, 4.80; N, 7.70%. ^{1}H NMR (400 MHz, $CDCl_3$, RT): δ 9.26 (d, ^3J = 5 Hz, 1H, H_6), 7.87 (t, ^3J = 7.8 Hz, 1H, H_4), 7.76 (d, ^3J = 7.8 Hz, 1H, H_3), 7.63 (dd, ^3J = 7.8 Hz, ^3J = 5 Hz, 1H, H_5), 5.15 (d, ^3J = 6.4 Hz, 1H, $H_{4'}$), 5.02 (d, ^2J = 17.2 Hz, 1H, CH_2), 4.64 (d, ^3J = 6.4 Hz, 1H, $H_{5'}$), 4.42 (d, ^2J = 17.2 Hz, 1H, CH_2), 0.52 (s, 3H, Pd-CH_3). ^{13}C NMR (100.5 MHz, $CDCl_3$, RT): 150.8 (s, C_6), 138.3 (s, C_4), 129.7, 129.4, 129.1, 128.4 (s, C_5), 127.2, 126.3, 126, 123.5 (s, C_3), 76.8 (s, $C_{5'}$), 74.3 (s, $C_{4'}$), 50.4 (s, CH_2), -3.4 (s, Pd-CH_3).

[PdClMe(8)] (8a)

Yield: 62%. Anal. Found: C, 56.30; H, 5.11; N, 8.67%. Calc. for $C_{22}H_{22}N_3ClPd$: C, 56.18; H, 4.71; N, 8.93%. ^{1}H NMR (400 MHz, $CDCl_3$, RT): δ 9.28 (d, ^3J = 4.8 Hz, 1H, H_6), 8.03 (m, 2H, H_3 + H_4), 7.67 (q, ^3J = 4.8 Hz, 1H, H_5), 7.46- 7.25 (m, 10H, Harom.), 5.04 (d, ^3J = 7 Hz, 1H, $H_{4'}$), 4.58 (d, ^3J = 7 Hz, 1H, $H_{5'}$), 3.26 (s, 3H, NCH_3), 0.48 (s, 3H, Pd-CH_3). ^{13}C NMR (100.5 MHz,

$CDCl_3$, RT): δ 150.8 (s, C_6), 138.1 (s, C_4), 129.7 (s, Ph), 129.3 (s, C_5), 129.0 (s, Ph), 128.1 (s, Ph), 126.8 (s, Ph), 126.2 (s, Ph), 123.5 (s, C_3), 79.5 (s, $C_{4'}$ or $C_{5'}$), 73.9 (s, $C_{5'}$ or $C_{4'}$), 35.5 (s, CH_3), -7.1 (s, Pd-CH_3).

[PdClMe(9)] (9a)

Yield: 75%. Anal. Found: C, 55.17; H, 4.32; N, 6.64%. Calc. for $C_{28}H_{26}N_3ClO_2PdS$: C, 55.04; H, 4.26; N, 6.88%. ^{1}H NMR (400 MHz, $CDCl_3$, RT): δ 9.24 (d, ^3J = 4 Hz, 1H, H_6), 8.72 (d, ^3J = 8 Hz, 1H, H_3), 8.09 (d, ^3J = 8 Hz, ^4J = 1.6 Hz 1H, H_4), 7.80 (m, 1H, H_5), 7.49- 6.91 (m, 14H, Harom.), 5.31 (d, ^3J = 5.6 Hz, 1H, $H_{4'}$), 5.19 (d, ^3J = 5.6 Hz, 1H, $H_{5'}$), 2.44 (s, 3H, CH_3-Ts-), 0.55 (s, 3H, Pd-CH_3). ^{13}C NMR (100.5 MHz, $CDCl_3$, RT): δ 150.4 (s, C_6), 138.3 (s, C_4), 130.6 - 125.5 (C_3 + C_5+ 8 Ph), 74.7 (s, $C_{4'}$ or $C_{5'}$), 73.7 (s, $C_{5'}$or $C_{4'}$), 22.1 (s, CH_3-Ts-), -4.9 (s, Pd-CH_3).

[PdClMe(10)] (10a)

Yield: 61%. Anal. Found: C, 44.80; H, 3.72; N, 7.50. Calc. for $C_{22}H_{19}N_3ClF_3O_2PdS$: C, 44.95; H, 3.26; N, 7.15. ^{1}H NMR (400 MHz, $CDCl_3$, RT): δ 9.29 (d, ^3J = 4.7 Hz, 1H, H_6), 8.22 (d, ^3J = 7.7 Hz, 1H, H_3), 8.10 (td, ^3J = 7.7 Hz, ^4J = 1.7 Hz, 1H, H_4), 7.84 (dd, ^3J = 7.7 Hz, ^3J = 4.7 Hz, 1H, H_5), 7.47 - 7.35 (m, 10H, Ph), 5.55 (d, ^3J = 1.8 Hz, 1H, $H_{4'}$), 5.43 (d, ^3J = 1.8 Hz, 1H, $H_{5'}$), 0.75 (s, 3H, Pd-CH_3). ^{13}C NMR (100.5 MHz, $CDCl_3$, RT): δ 150.5 (s, C_6), 138.4 (s, C_4), 130.1 (s, C_5), 130.0 (s, Ph), 129.6 (s, Ph), 129.5 (s, C_3), 125.8 (s, Ph), 125.4 (s, Ph), 75.8 (s, $C_{4'}$ or $C_{5'}$), 75.5 (s, $C_{5'}$ or $C_{4'}$), -3.7 (s, Pd-CH_3).

5.2.4.4. Synthesis of [PdMe(NCMe)(N-N′)][BAr′$_4$] (5b-10b)

To a solution of [PdClMe(N-N′)] in CH_2Cl_2, the stoichiometric amount of NaBAr′$_4$ (Ar′= 3,5-$(CF_3)_2C_6H_3$) was added together with 0.5 mL

of MeCN. The light yellow solution formed was stirred for about an hour, filtrated through Kieselghur and evaporated to dryness. The light-yellow compounds were crystallised from CH_2Cl_2/hexane.

[PdMe(NCMe)(5)][BAr'$_4$] (5b)

Yield: 61%. ^{1}H NMR (400 MHz, $CDCl_3$, RT): δ 9.05 (s, 1H, NH), 7.91 (m, 2H, H_4 + H_5), 7.79 (s, ^3J = 7.6 Hz, 1H, H_3), 7.69 (s, 8H, H_b), 7.51 (s, 4H, H_d), 7.13- 6.79 (m, 10H, Ph), 5.70 (d, ^3J = 11.2 Hz, 1H, $H_{5'}$), 5.50 (d, ^3J = 11.2 Hz, 1H, $H_{4'}$), 2.33 (s, 3H, Pd-NCCH_3), 0.90 (s, 3H, Pd-CH_3).

[PdMe(NCMe)(6)][BAr'$_4$] (6b)

Yield: 78%. Anal. Found: C, 50.02; H, 2.60; N, 4.04%. Calc. for $C_{55}H_{35}N_4BF_{24}Pd$: C, 49.85; H, 2.66; N, 4.23%. ^{1}H NMR (400 MHz, $CDCl_3$, RT): δ 8.34 (d, ^3J = 4.8 Hz, 1H, H_6), 7.84 (t, ^3J =8 Hz, 1H, H_4), 7.7 (s, 8H, C_b), 7.64 (d, ^3J = 8 Hz, 1H, H_3), 7.45 (s, 4H, C_d), 7.43-7.2 (m, 11H, H_5 + 10Ph), 6.31 (s, 1H, NH), 5.05 (d, ^3J = 7 Hz, 1H, $H_{4'}$), 4.96 (d, ^3J = 7 Hz, 1H, $H_{5'}$), 2.30 (s, 3H, Pd-NCCH_3), 0.56 (s, 3H, Pd-CH_3). ^{13}C NMR (100.5 MHz, $CDCl_3$, RT): δ 161.6 (q, $^1J_{C\text{-}B}$ = 197.2 Hz, 4C, C_a), 149.2 (s, C_6), 139.9 (s, C_4), 134.8 (s, C_b), 129.8 (s, Ph), 129.7 (s, Ph), 129.5 (s, Ph), 129.4 (s, Ph), 129.2 (m, C_e), 128.9 (s, C_5), 126.1 (s, Ph), 123.3 (s, C_3), 117.6 (s, C_d), 76.6 (s, $C_{4'}$), 70.7 (s, $C_{5'}$), 3.4 (s, Pd-NCCH_3), -3.1 (s, Pd-CH_3). MS FAB(*m/z*): 703.2 [M – Me, -NCMe, + **6**]$^{2+}$, 404.1 [M – Me, -NCMe]$^+$, 298.1 [**6**]$^+$.

[PdMe(NCMe)(7)][BAr'$_4$] (7b)

Yield: 81%. Anal. Found: C, 51.95; H, 3.20; N, 3.83%. Calc. for $C_{62}H_{41}N_4BF_{24}Pd$: C, 52.62; H, 2.92; N, 3.96%. ^{1}H NMR (400 MHz, $CDCl_3$, RT): δ 8.38 (d, ^3J = 4Hz, 1H, H_6), 7.84 (m, 2H, H_4 + H_5), 7.70 (s, 8H, H_b), 7.51

(s, 4H, H_d), 7.45-7.02 (m, 16H, H_3 + 15Ph), 5.05 (d, ^3J = 5.6 Hz, 1H, $H_{4'}$), 5.02 (d, ^3J = 17.2 Hz, 1H, CH_2), 4.72 (d, ^3J = 5.6 Hz, 1H, $H_{5'}$), 4.46 (d, ^3J = 17.2 Hz, 1H, CH_2), 2.28 (s, 3H, Pd-NCCH_3), 0.54 (s, 3H, Pd-CH_3). ^{13}C NMR (100.5 MHz, $CDCl_3$, RT): δ 161.7 (q, $^1J_{C\text{-}B}$ = 197.2 Hz, C_a), 149.6 (s, C_6), 139.9 (s, C_4), 134.8 (s, C_b), 130.0 (s, Ph), 129.6 (s, Ph), 129.5 (s, Ph), 129.0 (s, C_5), 128.8 (m, C_e), 127.0 (s, Ph), 126.1 (s, Ph), 125.6 (Ph) 124.9 (s, C_3), 117.6 (s, C_d), 76.8 (s, $C_{4'}$ or $C_{5'}$), 73.6 (s, $C_{5'}$ or $C_{4'}$), 50.1 (s, CH_2), 3.4 (s, Pd-NCCH_3), -2.2 (s, Pd-CH_3). MS FAB(*m/z*): 883.3 [M – Me, -NCMe, + **7**]$^{2+}$, 494.1 [M – Me, -NCMe]$^+$, 390.2 [**7**]$^+$.

[PdMe(NCMe)(8)][BAr′$_4$] (8b)

Yield: 82%. Anal. Found: C, 49.35; H, 3.03; N, 3.99%. Calc. for $C_{56}H_{37}N_4BF_{24}Pd$: C, 50.23; H, 2.78; N, 4.18%. ^{1}H NMR (400 MHz, $CDCl_3$, RT): δ 8.38 (d, ^3J = 4 Hz, 1H, H_6), 8.03 (d, ^3J = 8 Hz, 1H, H_3), 7.86 (t, ^3J = 8 Hz, 1H, H_4), 7.69 (s, 8H, H_b), 7.5 (s, 4H, H_d), 7.46- 7.19 (m, 11H, H_5 + 10Ph), 4.92 (d, ^3J = 7.2 Hz, 1H, $H_{5'}$), 4.64 (d, ^3J = 7.2 Hz, 1H, $H_{4'}$), 3.25 (s, 3H, NCH_3), 2.30 (s, 3H, Pd-NCCH_3), 0.48 (s, 3H, Pd-CH_3). ^{13}C NMR (100.5 MHz, $CDCl_3$, RT): δ 161.6 (q, $^1J_{C\text{-}B}$ = 197.2 Hz, C_a), 149.6 (s, C_6), 139.7 (s, C_4), 134.8 (s, C_b), 130.0 (s, Ph), 129.8 (s, Ph), 129.4 (s, Ph), 129.2 (m, C_e), 128.9 (s, Ph), 128.7 (s, C_5), 126.6 (s, Ph), 125.9 (s, Ph), 124.7 (s, C_3), 117.6 (s, C_d), 79.3 (s, $C_{4'}$), 73.5 (s, $C_{5'}$), 35.1 (s, CH_3-N), 3.5 (s, 1C, Pd-NCCH_3), -2.5 (s, 1C, Pd-CH_3). MS FAB(*m/z*): 731.2 [M – Me, -NCMe, + **8**]$^{2+}$, 418.1 [M – Me, -NCMe]$^+$, 314.2 [**8**]$^+$.

[PdMe(NCMe)(9)][BAr′$_4$] (9b)

Yield: 83%. Anal. Found: C, 50.21; H, 2.68; N, 3.66. Calc. for $C_{62}H_{41}N_4BClF_{24}O_2PdS$: C, 50.34; H, 2.79; N, 3.79. Ratio M:m = 3:1. ^{1}H NMR (400 MHz, $CDCl_3$, RT): Major: δ 8.62 (d, ^3J = 8 Hz, 1H, H_3), 8.35 (dd, ^3J = 5

Hz, ^4J = 1.3 Hz, 1H, H_6), 8.05 (td, ^3J = 8 Hz, ^4J = 1.3 Hz, 1H, H_4), 7.71 (s, 8H, H_b), 7.52 (s, 5H, H_5 + 4H_d), 7.50-6.80 (m, 14H, Ph), 5.36 (d, ^3J =3.2 Hz, 1H, $H_{5'}$), 5.06 (d, ^3J =3.2 Hz, 1H, $H_{4'}$), 2.41 (s, 3H, CH_3-Ts-), 2.20 (s, 3H, Pd-NCCH_3), 0.57 (s, 3H, Pd-CH_3). ^{13}C NMR (100.5 MHz, $CDCl_3$, RT): δ 161.7 (q, $^1J_{C-B}$= 198.1 Hz, C_a), 149.3 (s, C_6), 140.1 (s, C_4), 134.8 (s, C_b), 130.8- 123.2 (C_3 + C_4 + Ph), 117.6 (s, C_d), 74.3 (s, $C_{5'}$), 74.1 (s, $C_{4'}$), 22.0 (s, CH_3), 3.2 (s, Pd-NCCH_3), -0.03 (s, Pd-CH_3). Minor: δ 8.63 (d, ^3J = 8.2 Hz, 1H, H_3), 8.50 (d, ^3J = 4.4 Hz, 1H, H_3), 8.17 (td, ^3J = 8.2 Hz, ^4J = 1.6 Hz, 1H, H_4), 7.71 (s, 9H, H_5 + 8H_b), 7.52 (s, 4H, H_d), 7.50-6.80 (m, 14H, Ph), 5.24 (d, ^3J =4.8 Hz, 1H, $H_{5'}$), 5.08 (d, ^3J =4.8 Hz, 1H, $H_{4'}$), 2.45 (s, 3H, CH_3-Ts-), 1.61 (s, 3H, Pd-NCCH_3), 0.97 (s, 3H, Pd-CH_3). ^{13}C NMR (100.5 MHz, $CDCl_3$, RT): δ 161.7 (q, $^1J_{C-B}$= 198.1 Hz, C_a), 147.2 (s, C_6), 137.8 (s, C_4), 134.8 (s, 8C, C_b), 130.8- 123.2 (C_3 + C_4 + Ph), 117.6 (s, 4C, C_d), 76.4 (s, $C_{4'}$), 74.1 (s, $C_{5'}$), 22.0 (s, CH_3), 5.67 (s, Pd-CH_3), 2.44 (s, Pd-NCCH_3).

[PdMe(NCMe)(10)][BAr'$_4$] (10b)

Yield: 68%.Anal. Found: C, 46.36, H, 2.60, N, 3.10%. Calc. for $C_{56}H_{34}N_4BF_{27}O_2PdS$: C, 46.16; H, 2.35; N, 3.84%. ^{1}H NMR (400 MHz, $CDCl_3$, RT): Ratio M:m = 2:1. Major: δ 8.38 (d, ^3J = 5.2 Hz, 1H, H_6), 8.28 (d, ^3J = 7.9 Hz, 1H, H_3), 8.04 (td, ^3J = 7.9 Hz, ^4J = 1.6 Hz, 1H, H_4), 7.70 (s, 8H, H_b), 7.51 (s, 4H, H_d), 7.48-7.14 (m, 11H, H_5 + 10Ph), 5.55 (d, ^3J = 2.2 Hz, 1H, $H_{5'}$), 5.28 (d, ^3J = 2.2 Hz, 1H, $H_{4'}$), 2.26 (s, 3H, Pd-NCCH_3), 0.74 (s, 3H, Pd-CH_3). ^{13}C NMR (100.5 MHz, $CDCl_3$, RT): δ 161.7 (q, $^1J_{C-B}$= 198.1 Hz, C_a), 149.6 (s, C_6), 140.1 (s, C_4), 134.8 (s, C_b), 130.7 – 123.2 (C_5 + C_3 + C_e + Ph), 117.6 (s, C_d), 77.4 (s, $C_{4'}$ or $C_{5'}$), 75.5 (s, $C_{5'}$ or $C_{4'}$), 3.3 (s, Pd-CH_3), 0.9 (s, Pd-NCCH_3). Minor: δ 8.52 (d, ^3J = 5.8 Hz, 1H, H_6), 8.29 (m, 1H, H_3), 8.18 (td, ^3J = 7.9 Hz, ^4J = 1.3 Hz, 1H, H_4), 7.74 (dd, ^3J = 7.9 Hz, ^3J = 5.8 Hz, 1H, H_5), 7.70 (s, 8H, H_b), 7.51 (s, 4H, H_d),

7.48-7.14 (m, 10H, Ph), 5.53 (d, ^3J = 3.4 Hz, 1H, $H_{5'}$), 5.32 (d, ^3J = 3.4 Hz, 1H, $H_{4'}$), 1.73 (s, 3H, Pd-NCCH$_3$), 1.07 (s, 3H, Pd-CH$_3$). ^{13}C NMR (100.5 MHz, $CDCl_3$, RT): 161.7 (q, $^1J_{C\text{-}B}$= 198.1 Hz, C_a), 150.4 (s, C_6), 140.4 (s, C_4), 134.8 (s, C_b), 130.7 – 123.2 (C_5 + C_3 + C_e + Ph), 117.6 (s, C_d), 75.7 (s, $C_{4'}$ or $C_{5'}$), 75.2 (s, $C_{4'}$ or $C_{5'}$), 6.8 (s, Pd-CH$_3$), 2.6 (s, Pd-NCCH$_3$).

5.2.4.5. Synthesis of [Rh(cod)(N-N')][BF$_4$]

When the pyridine-imidazoline ligands **1**-**4** (0.12 mmol) were added to a solution of [Rh(cod)$_2$][BF$_4$] (0.12 mmol) in CH_2Cl_2 (2 mL) there was an instantaneous color change. After reacting for 5 minutes, diethylether was added to precipitate the complexes **1c**-**4c**.

[Rh(cod)(1)][BF$_4$] (1c)

Yield: 69%. Anal. Found: C, 56.14; H, 4.96; N, 6.70%. Calc. for $C_{28}H_{29}N_3BF_4Rh$: C, 56.29; H, 4.89; N, 7.03%. ^{1}H NMR (400 MHz, $CDCl_3$, RT): δ 8.57 (d, ^{3}J = 7.8 Hz, 1H, H_3), 8.39 (s, 1H, NH), 8.22 (dd, ^{3}J = 7.8 Hz, ^{3}J = 6.9 Hz, 1H, H_4), 7.78 (d, ^{3}J = 5.6 Hz, 1H, H_6), 7.67 (dd, ^{3}J = 6.9 Hz, ^{3}J = 5.6 1H, H_5), 7.08-6.83 (m, 10H, Ph), 5.74 (d, ^{3}J = 11.7 Hz, 1H, $H_{4'}$ or $H_{5'}$), 5.25 (d, ^{3}J = 11.7 Hz, 1H, $H_{5'}$ or $H_{4'}$), 4.44 (m, 1H, CH= cod), 4.17 (m, 2H, CH= cod), 3.51 (m, 1H, CH= cod), 2.51 – 2.37 (m, 4H, CH_2-cod), 1.90 – 1.68 (m, 4H, CH_2-cod).

[Rh(cod)(2)][BF$_4$] (2c)

Yield: 69%. Anal. Found: C, 61.03; H, 5.24; N, 5.56%. Calc. for $C_{35}H_{35}N_3BF_4Rh$: C, 61.15; H, 5.13; N, 6.11%. ^{1}H NMR (400 MHz, $CDCl_3$, RT): δ 8.37 (d, ^3J = 8 Hz, 1H, H_3), 8.27(t, ^3J = 8 Hz, 1H, H_4), 7.91 (d, ^3J = 5.5 Hz, 1H, H_6), 7.79 (dd, ^3J = 8 Hz, ^3J = 5.5 Hz, 1H, H_5), 5.47 (d, ^3J = 12 Hz, 1H, $H_{4'}$ or

$H_{5'}$), 5.32 (d, ^3J = 17.2 Hz, 1H, CH_2), 5.2 (d, ^3J = 12 Hz, 1H, $H_{5'}$ or $H_{4'}$), 4.55 (d, ^3J = 17.2 Hz, 1H, CH_2), 4.41 (m, 1H, CH= cod), 4.31 (m, 1H, CH= cod), 4.22 (m, 1H, CH= cod), 3.56 (m, 1H, CH= cod), 2.5 (m, 2H, CH_2-cod), 2.3 (m, 2H, CH_2-cod), 1.97 (m, 2H, CH_2-cod), 1.8 (m, 2H, CH_2-cod).

[Rh(cod)(3)][BF_4] (3c)

Yield: 83%. Anal. Found: C, 55.75; H, 3.78; N, 5.58%. Calc. for $C_{35}H_{35}N_3BF_4SO_2$: C, 55.9; H, 3.19; N, 5.59%. ^{1}H NMR (300 MHz, $CDCl_3$, RT): δ 8.56 (d, ^3J = 8.1 Hz, 1H, H_3), 8.34 (m, 1H, H_4), 8.04 (m, 2H, H_5 + H_6), 7.76 (d, ^2J = 8.3 Hz, 2H, Harom.-Ts), 7.45 (d, ^2J = 8.3 Hz, 2H, Harom.-Ts), 7.06-6.67 (m, 10H, Ph), 5.96 (d, ^3J = 9.5 Hz, 1H, $H_{4'}$ or $H_{5'}$), 5.37 (d, ^3J = 9.5 Hz, 1H, $H_{5'}$ or $H_{4'}$), 4.34 (m, 4H, CH= cod), 2.3 (m, 4H, CH_2-cod), 1.81 (m, 4H, CH_2-cod).

[Rh(cod)(4)][BF_4] (4c)

Yield: 73%. Calc. for $C_{29}H_{28}N_3BF_7SO_2$: C, 47.77; H, 3.87; N, 5.76 %. ^{1}H NMR (400 MHz, $CDCl_3$, RT): δ 8.30 (m, 2H, H_6+H_3), 8.14 (m, 1H, H_4 or H_5), 8.10 (m, 1H, H_5 or H_4), 7.15 (m, 6H, Ph), 7.00 (br, 1H, Ph), 6.72 (m, 2H, Ph), 6.52 (br, 1H, Ph), 6.12 (d, ^3J = 8.8 Hz, 1H, $H_{4'}$ or $H_{5'}$), 5.95 (d, ^3J = 8.8 Hz, 1H, $H_{5'}$ or $H_{4'}$), 4.56 (m, 2H, CH= cod), 3.96 (m, 2H, CH= cod), 2.43 (m, 2H, CH_2-cod), 2.31 (m, 2H, CH_2-cod), 1.85 (m, 4H, CH_2-cod).

5.2.4.6. Synthesis of [$Rh(CO)_2$(N-N')][BF_4] (1d-4d)

Bubbling carbon monoxide through solutions of **1c-4c** in CH_2Cl_2 leads to the formation of yellow solutions of the dicarbonyl complexes, which are precipitated by adding Et_2O.

$[Rh(CO)_2(1)][BF_4]$ (1d)

Yield: 98%. ^{1}H NMR (300 MHz, $CDCl_3$, RT): δ 9.08 (s, 1H, NH), 8.84 (d, ^3J = 8.4 Hz, 1H, H_3), 8.65 (d, ^3J = 5.3 Hz, 1H, H_6), 8.43 (dd, ^3J = 8.4 Hz, ^3J = 7.1 Hz, 1H, H_4), 7.82 (dd, ^3J = 7.1 Hz, ^3J = 5.3 Hz, 1H, H_5), 7.13- 6.92 (m, 10H, Ph), 5.83 (d, ^3J = 12.2 Hz, 1H, $H_{4'}$ or $H_{5'}$), 5.67 (d, ^3J = 12.2 Hz, 1H, $H_{5'}$ or $H_{4'}$).

$[Rh(CO)_2(2)][BF_4]$ (2d)

^{1}H NMR (400 MHz, $CDCl_3$, RT): δ 8.72 (d, ^3J = 4.8 Hz, 1H, H_6), 8.44 (d, ^3J = 8 Hz, 1H, H_3), 8.38 (t, ^3J = 8 Hz, 1H, H_4), 7.82 (dd, ^3J = 8 Hz, ^3J = 4.8 Hz, 1H, H_5), 7.37- 6.89 (m, 15 H, Ph), 5.72 (d, ^3J = 12.4 Hz, 1H, $H_{4'}$ or $H_{5'}$), 5.58 (m, 2H, $H_{5'}$ or $H_{4'}$ + CH_2), 4.64 (d, ^3J = 17.2 Hz, 1H, CH_2).

$[Rh(CO)_2(3)][BF_4]$ (3d)

Yield: 87%. ^{1}H NMR (400 MHz, $CDCl_3$, RT): δ 8.86 (m, 2H, H_6 + H_3), 8.49 (t, ^3J = 8 Hz, 1H, H_4), 8.04 (t, ^3J = 6.6 Hz, 1H, H_5), 7.78 (d, ^2J = 8.2 Hz, 2H, Harom.-Ts-), 7.41 (d, ^2J = 8.2 Hz, 2H, Harom.-Ts-), 7.16 – 6.74 (m, 10H, Ph), 5.98 (d, ^3J = 9.6 Hz, 1H, $H_{4'}$ or $H_{5'}$), 5.71 (d, ^3J = 9.6 Hz, 1H, $H_{5'}$ or $H_{4'}$).

$[Rh(CO)_2(4)][BF_4]$ (4d)

^{1}H NMR (400 MHz, $CDCl_3$, RT): δ 8.92 (d, ^3J = 5.3 Hz, 1H, H_6), 8.50 (d, ^3J = 7.8 Hz, 1H, H_3), 8.42 (td, ^3J = 7.8 Hz, ^4J = 1.2 Hz, 1H, H_4), 8.09 (ddd, ^3J = 7.8 Hz, ^3J = 5.3 Hz, ^4J = 1.2 Hz, 1H, H_5), 7.18 (m, 8H, Ph), 6.84 (m, 2H, Ph), 5.58 (m, 2H, $H_{4'}$ and $H_{5'}$).

5.2.4.7. X-Ray Crystallography

Crystal data, data collections and refinement parameters for the structures reported are summarized in Table 8. All the data sets were carried out on a Nonius DIP-1030H system with Mo-Kα radiation (λ = 0.71073 Å) graphite monochromatized. For each crystal a total of 30 frames were collected with an exposure time of 12 min, a rotation of 6° about φ and the detector at a distance of 90 mm from the crystal. Cell refinement, indexing and scaling of the data sets were carried out using Mosflm and Scala.[46]

Table 8. Crystal data and details of structure refinements for compounds **2c**, **3c**, **8a,** and **9a'**

	2c	**3c**	**8a**	**9a'**·CH_2Cl_2
Empirical formula	$C_{35}H_{35}BF_4N_3Rh$	$C_{35}H_{35}BF_4N_3O_2RhS$	$C_{22}H_{22}ClN_3Pd$	$C_{28}H_{25}Cl_4N_3O_2PdS$
Formula weight	687.38	751.44	470.28	715.77
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Triclinic
Space group	$P\,2_1/n$	$P\,2_1/c$	$P\,2_12_12_1$	$P\,\bar{1}$
a/Å	11.068(3)	15.071(3)	11.335(3)	9.481(3)
b/Å	25.636(5)	10.445(5)	13.280(4)	10.207(3)
c/Å	11.581(4)	20.830(4)	13.327(4)	16.059(4)
α/°				101.71(2)
β/°	105.25(2)	99.86(2)		95.82(2)
γ/°				108.38(2)
U/Å^3	3170.3(15)	3230.5(18)	2006.1(10)	1421.0(7)
*D*calcd/g cm^{-3}	1.440	1.545	1.557	1.673
Z	4	4	4	2

Temperature	293(2)	293(2)	150(2)	150(2)
μ (Mo-Kα) mm^{-1}	0.591	0.654	1.069	1.135
F(000)	1408	1536	952	720
θ range, deg	2.27 - 26.02	1.98 - 25.02	2.36 - 27.10	2.24 - 27.10
Reflections collected	9764	10603	4678	9780
Independent reflections	5285	5604	4252	5805
*R*int	0.0498	0.0709	0.0363	0.0707
Reflections $I > 2\sigma(I)$	3202	3483	3681	4239
Parameters	397	453	246	353
Flack parameter	-	-	-0.04(6)	-
Goodness-of-fit (F^2)	1.007	1.038	1.076	1.048
$R1$ ($I > 2\ \sigma\ (I)$) [a]	0.0594	0.0554	0.0539	0.0635
$wR2$ ($I > 2\ \sigma\ (I)$) [a]	0.1579	0.1402	0.1478	0.1914
residuals, e/Å3	0.942, –0.449	0.614, –0.540	1.137,[b] –1.011	1.407,[b] –1.043

[a] $R1 = \Sigma\ ||Fo| - |Fc||\ /\ \Sigma|Fo|$, $wR2 = [\Sigma\ w\ (Fo^2 - Fc^2)^2\ /\ \Sigma w\ (Fo^2)^2]^{1/2}$. [b] residual close to Pd ion.

All the structures were solved by Patterson and Fourier analyses[47] and refined by the full-matrix least-squares method based on F2 with all observed reflections.[47] The final cycles include the contribution of hydrogen atoms at calculated positions. In **3c** the BF_4^- anion was found to be disordered over two positions consequent to a rotation about a B-F bond with refined occupancies to 0.59(2)/0.41(2). A molecule of CH_2Cl_2 was detected in the ΔF map of **9a'**. All the calculations were performed using the WinGX System, Ver 1.64.02.[48]

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5.2.5. References

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