Influence of pyridine-imidazoline ligands on the reactivity of palladium-methyl complexes with carbon monoxide

Abstract

New C_1-symmetrical pyridine-imidazoline ligands were synthesized and used in the preparation of neutral complexes [PdClMe(N-N')] and two series of monocationic complexes [PdMe(NCMe)(N-N')][X] (X = PF_6^-, BAr'_4^-). The pyridine-imidazoline ligands are modified with various R substituents at the aminic N atom of the imidazoline ring. These substituents make it possible to vary the electronic properties of the nitrogen-donor atoms. The crystal structures of two neutral palladium precursors [$PdCl_n(Me)_{2-n}$ (N-N')] (n = 1, 2) with different R substituents show different Pd-N coordination distances and geometrical distortions in the imidazoline ring. The characterization in solution of the neutral derivatives evidences the presence of the complex with the Pd-Me group cis to the imidazoline ring (*cis* isomer). For the cationic complexes, the number and the kind of stereoisomers present in solution depend on the nature of

both the ligand and the anion. The reactivity of the cationic complexes with carbon monoxide was studied in solution by multinuclear NMR spectroscopy, and it was shown that the Pd-acyl-carbonyl species was formed as the final product. The cationic complexes with BAr'_4^- behave as catalysts in the CO/4-*tert*-butylstyrene copolymerization and yield polyketones whose stereoregularity depends on the nature of the ligand. The stereocontrol in the copolymerization process is tentatively explained on the basis of the results of this mechanistic investigation.

5.1.1. Introduction

The insertion of unsaturated molecules into metal-carbon bonds is a fundamental step for C-C bond formation reactions catalyzed by organometallic compounds.[1] In the last fifteen years, the carbon monoxide/alkene copolymerization reaction has attracted much interest from both the academic and industrial scientific community. This reaction is homogeneously catalyzed by palladium(II) salts modified with P- or N-donor ligands and its products are perfectly alternating polyketones.[2] The study of the intimate mechanism of the copolymerization reaction started with the demonstration that the propagation step consists of two successive alternate migratory insertion reactions of Pd-alkyl to CO and of Pd-acyl to alkene.[3] While the reactions responsible for the growth of the polymeric chain are common to all catalytic systems, the initiation and termination steps depend on the nature of both the alkene and the palladium catalyst precursor. Most mechanistic investigations have been carried out in solution. Recently, however, there has been a study in the solid state.[4]

The various reactions involved in the initiation step are: (i) insertion of CO into the Pd-Me bond; (ii) insertion of CO into the Pd-OMe group; (iii) insertion of alkene into the Pd-H bond. Several groups have focused on the study of these insertion reactions and used Pd(II) systems containing bidentate nitrogen ligands. For the phenanthroline-based system $[PdMe(L)(phen)][BAr'_4]$ (L = solvent molecule; Ar' = 3,5-$(CF_3)_2C_6H_3$), a complete catalytic cycle has been constructed from kinetic and thermodynamic studies for the copolymerization of ethylene and CO.[5]

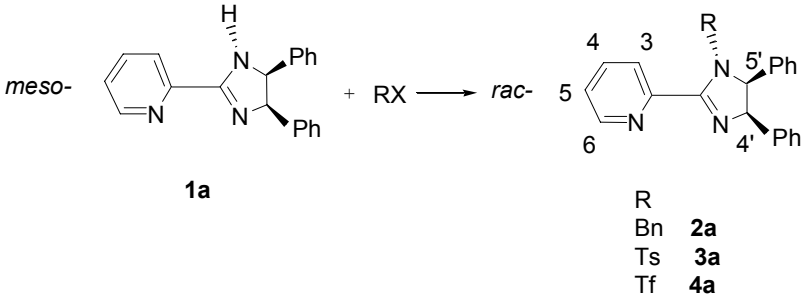
For unsymmetrical ligands, the insertion reactions may afford two different stereoisomers. The formation of one or both stereoisomers could influence the products of the copolymerization reaction. An intermediate resulting from the insertion of ethylene into a Pd-acyl bond has recently been isolated and characterized by X-ray for the first time for a complex containing the unsymmetrical 6-methyl-2,2'-bipyridine. A single stereoisomer was observed throughout the reaction sequence.[6]

When the copolymerization reaction involves styrene, the ligand can also play a role in controlling the stereoregularity of the synthesized polyketone. In the case of bisnitrogen planar ligands of C_{2v} or C_s symmetry (e.g. 2,2'-bipyridine, 1,10-phenanthroline, 5-NO_2-1,10-phenanthroline, 2,2'-bipyrimidine, diazabutadiene derivatives, pyridine-pyrazole) the syndiotactic polyketone is obtained.[7-12] C_2-symmetry chiral bidentate ligands (e.g. bisoxazoline, dioxazoline, diketiimines) provide good enantioface control and give isotactic copolymers.[10,13,14] Interestingly the C_1-symmetrical chiral ligands (e.g. N-N', P-N, P-OP) led to syndiotactic[15] or isotactic microstructures,[16] depending on the relative influence of the chain-end or the enantiomorphic control.

It has been reported that the site selective coordination of the alkene on the palladium complex determines its enantioface discrimination. In the case of palladium complexes modified with unsymmetrical N-N' ligands, the different *trans* effect of nitrogen atoms and the steric properties of the ligand seem to be responsible for the site-selective coordination.[15] Moreover, for P-N ligands, the isolation and characterization of some

insertion intermediates have always shown that a single stereoisomer is formed.[17-19]

We report on the synthesis of C_1-symmetrical pyridine-imidazoline ligands (N-N' = **1a-1d**) (Scheme 1) and their coordination to palladium. The modification of the R substituent on the imidazoline moiety leads to variation of the electronic properties of the nitrogen donors. The Pd(II) complexes of general formula [PdMe(NCMe)(N-N')][BAr'$_4$] (**4a-4d**) behave as catalyst precursors for the copolymerization of carbon monoxide and 4-*tert*-butylstyrene (TBS). By changing the electronic properties in the pyridine-imidazoline ligands the stereochemistry of these complexes, and therefore of the polyketones obtained, can be modified.



Scheme 1. Racemic (*R*,*S*) pyridine-imidazolines **1a-4a**

In order to learn more about the influence of our electronic tunable ligands, we studied the stereochemistry and the reactivity of intermediates involved in the mechanism. The X-ray structures of two neutral complexes [PdCl$_n$(Me)$_{2-n}$ (N-N')] (n = 1, 2; N-N' = **1d**, **1b**) were determined. The reactivity of the palladium-methyl precursors [PdMe(NCMe)(N-N')][PF$_6$]

(**3a-3d**) towards CO was investigated in depth by *in situ* ^{1}H and ^{13}C NMR experiments. The complete sequence of intermediates was established for complexes with ligands **1a** and **1b**. The [Pd(COMe)(CO)(**1a**)][PF_6] was isolated and characterized. Some correlations between NMR results and the catalytic activity of the precursors are also discussed.

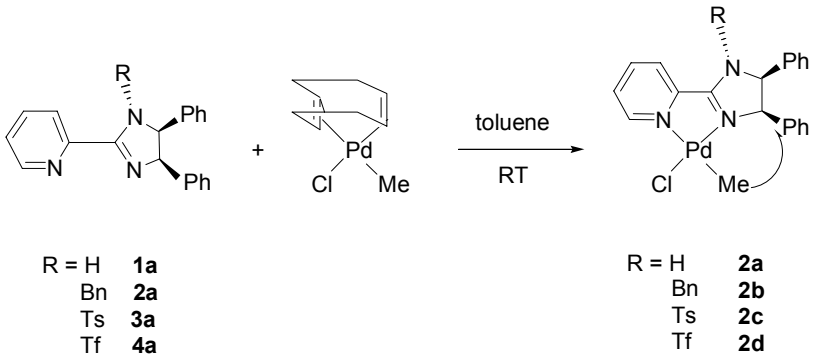
5.1.2. Results and discussion

5.1.2.1. Synthesis of ligands 1a-1d

Pyridine-imidazoline ligand **1a** was prepared similarly to the reported synthesis of oxazolines by reaction of 2-cyanopyridine with *meso*-1,2-diphenylethylenediamine but using $Yb(OTf)_3$ as catalyst.[20] Further reaction of **1a** with BnBr, TsCl or Tf_2O, provided the racemic *R*,*S*-(*S*,*R*)-1-substituted-4,5-dihydro-4,5-diphenyl-2-(2-pyridyl)-imidazoles **1b-1d**, respectively, in a racemic way (Scheme 1).

5.1.2.2. Synthesis and characterization of [PdClMe(N-N')] 2a-2d

Neutral [PdClMe(N-N')] **2a-2d** were isolated from the stoichiometric reaction of [PdClMe(cod)] (cod= 1,5-cyclooctadiene) and the ligands **1a-1d** in anhydrous toluene (Scheme 2).



R = H **1a**
Bn **2a**
Ts **3a**
Tf **4a**

R = H **2a**
Bn **2b**
Ts **2c**
Tf **2d**

Scheme 2. Synthesis of the neutral complexes **2a**-**2d**

Single crystals suitable for X-ray analysis were obtained for the neutral derivative **2d** with the ligand bearing the triflate substituent (Figure 1). Efforts to obtain single crystals of the neutral complex **2b**, with the ligand bearing an electron donating group, resulted in the dichloride species [$PdCl_2$(**1b**)], **2b'** being isolated, because the methyl group exchanged with the chloride in the chlorinated solvent (Figure 2). Figures 1 and 2 show the molecular structures of **2b'** and **2d** complexes together with the atom numbering scheme and Table 1 shows a selection of bond lengths and angles.

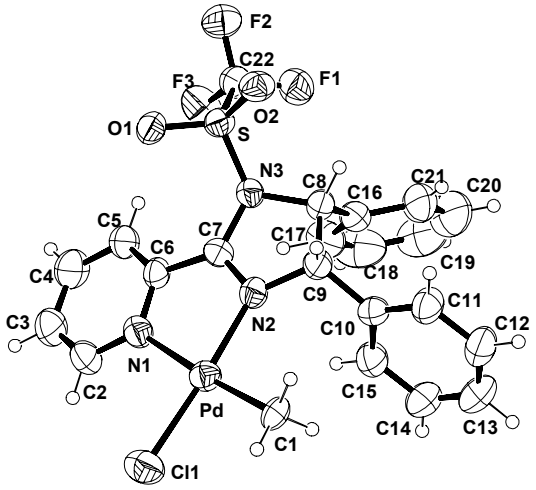


Figure 1. Molecular structure (ORTEP drawing, 50% thermal ellipsoids) with atom numbering scheme of **2d**

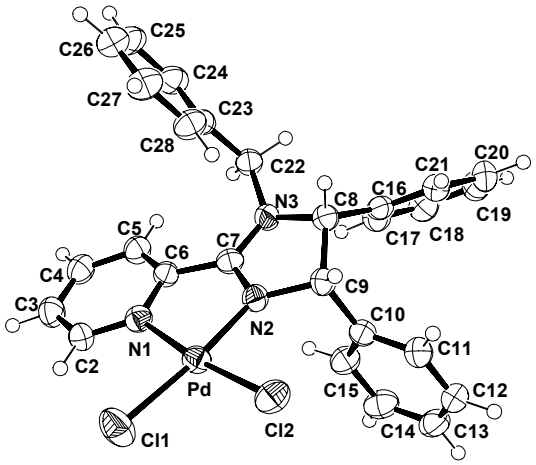


Figure 2. Molecular structure (ORTEP drawing, 40% thermal ellipsoids) with atom numbering scheme of **2b'**

Table 1. Selected bond lengths (Å) and angles (°) for complexes **2b'** and **2d**.

	2b'·$CDCl_3$	**2d**
	X = Cl(2) [a]	X = C(1)
Pd-N(1)	2.088(3)	2.149(5)
Pd-N(2)	2.000(3)	2.065(4)
Pd-Cl(1)	2.304(1)	2.282(2)
Pd-X	2.194(2)	2.071(4)
N(1)-C(2)	1.336(5)	1.325(7)
N(1)-C(6)	1.364(5)	1.352(7)
N(2)-C(7)	1.303(5)	1.279(6)
N(2)-C(9)	1.481(4)	1.480(7)
N(3)-C(7)	1.358(5)	1.423(6)
N(3)-C(8)	1.486(5)	1.503(6)
N(3)-C(22)	1.461(5)	-
N(3)-S	-	1.631(4)
N(1)-Pd-N(2)	78.6(1)	77.5(2)
N(1)-Pd-Cl(1)	96.62(9)	97.3(1)
N(1)-Pd-X	172.6(1)	175.7(2)
N(2)-Pd-Cl(1)	174.51(9)	174.7(1)
N(2)-Pd-X	94.0(1)	98.3(2)
Cl(1)-Pd-X	90.77(6)	86.9(1)

[a] The chloride is partially disordered with a methyl ligand (see Experimental)

The structural determination of complex **2b'** shows a significant difference in the Pd-Cl bond lengths (Pd-Cl(1) = 2.304(1), Pd-Cl(2) =

2.194(2) Å). This, together with the short Pd-N(py) bond distance *trans* to Cl(2) (2.088(3) Å), is further evidence for the previously mentioned exchange reaction at the methyl, and suggests that the Pd-Cl(2) bond length actually appears as an artifact arising from a mixed chloride/methyl ligand (see Experimental). The square planar geometry of palladium is slightly tetrahedrally distorted and the donor atoms deviate by ± 0.023 Å from the coordination mean plane. Both the Pd-N bond distances with pyridine and imidazoline, 2.088(3) and 2.000(3) Å, respectively, are significantly shorter than those measured in **2d** (see below). For purposes of comparison, the Pd-N(py) and Pd-N(imidazoline) bond lengths in the crystal structure of the bischelated head-tail $[Pd(\mathbf{1b})_2]^{2+}$ complex are similar (mean value 2.017(7) and 2.021(7) Å, respectively).[21]

In complex **2d** the square planar geometry around Pd involves the nitrogen atoms of the chelating ligand and, as expected, a chloride and a methyl group with donor atoms that are coplanar within ± 0.017 Å. The data in Table 1 indicates that the coordination distances for the chelating ligand are considerably different, Pd-N(1) = 2.149(5), Pd-N(2) = 2.065(4) Å, and longer than those found in **2b'**. In fact, the former is induced by the *trans* influence of the methyl, while the latter is affected by the strong electron withdrawing properties of the CF_3SO_2 group which provides a less basic iminic N donor. The Pd-Cl(1) and Pd-C(1) bond distances, 2.282(2) and 2.071(4) Å, respectively, fall in the range usually observed for Pd(II) complexes and follow the trend of those detected, for example, in the [PdClMe(2,9-dm-phen)] derivative (2,9-dm-phen = 2,9-dimethyl-1,10-

phenanthroline; Pd-Me = 2.015(6), Pd-Cl = 2.312(1), Pd-N(1) = 2.229(4), Pd-N(2) = 2.066(4) Å).[22]

In both complexes, the rings of the chelating ligand are not coplanar, but slightly tilted, as indicated by the N(1)-C(6)-C(7)-N(2) torsion angle of 9.0(4) (in **2b'**) and 11.2(7)° (in **2d**). On the other hand, the dihedral angles formed by the planes through the pyridine and imidazoline atoms are 13.0(2) and 18.1(1)°, respectively. The phenyl rings at C(8) and C(9) are oriented, as expected, on the same side of the imidazoline plane and avoid an eclipsed conformation through a torsion angle C(16)-C(8)-C(9)-C(10) of 20.3(5) (**2b'**) and 27.9(7)° (**2d**). This causes considerable distortions inside the five-membered ring of both complexes, and induces a certain degree of strain. The ring atoms (principally N(3), C(8), and C(9)) deviate by up ±0.15 Å from the mean plane. Moreover, in **2b'** the N(2)-C(7) and N(3)-C(7) bond distances, 1.303(5) and 1.358(5) Å, are consistent with a delocalization inside the N(2)-C(7)-N(3) fragment, as already observed in the molecular structure of two ruthenium derivatives where the pyridine-imidazoline ligand has a hydrogen or a methyl bound to the aminic nitrogen N(3).[23] In addition, in **2b'** the sum of the bond angles around N(3) is 353.9° (in **2d** 349.1°) which supports the degree of delocalization across the amidine.

On the other hand, the corresponding figures in **2d** agree with a double (N(2)-C(7) = 1.279(6) Å) and a single bond character (N(3)-C(7) = 1.423(6) Å), a feature that seems to be induced by the electronic properties of CF_3SO_2. Therefore, the Pd-N(2) and the N-C distances in the N(2)-C(7)-

N(3) fragment can be regarded as a proof of the electronic properties of the R substituent.

The analysis of the crystal packing in **2d** shows pairs of complexes arranged head-to-tail about a symmetry center with a short intermetallic Pd---Pd' distance of 3.440 Å (Figure 3), a feature often encountered in square planar Pd and Pt complexes.[24,25] Similar packing is also observed in the crystal structure of **2b'**, but the pair of complexes are related in such a way that Cl(2) lies almost at the metal apical position of the symmetry related molecule (Cl(2)---Pd' = 3.966 Å, Pd---Pd' = 4.980 Å). This arrangement prevents steric clashes between Cl(2) and the benzyl ring of the second molecule. The stacking of this latter ring with that of a nearby complex (shortest C---C distance 3.88 Å) accounts for the narrow torsion angle of 19.1 (5)° detected in the N(3)-C(22)-C(23)-C(28) fragment.

Finally in **2d**, it is worthwhile to point out the short intramolecular distance (3.81 Å) between the methyl carbon atom and the centroid of phenyl C(10-15) (see Figure 1).

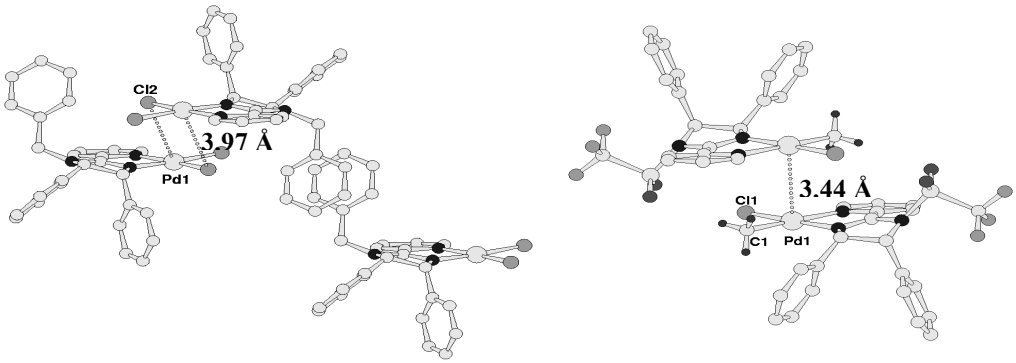
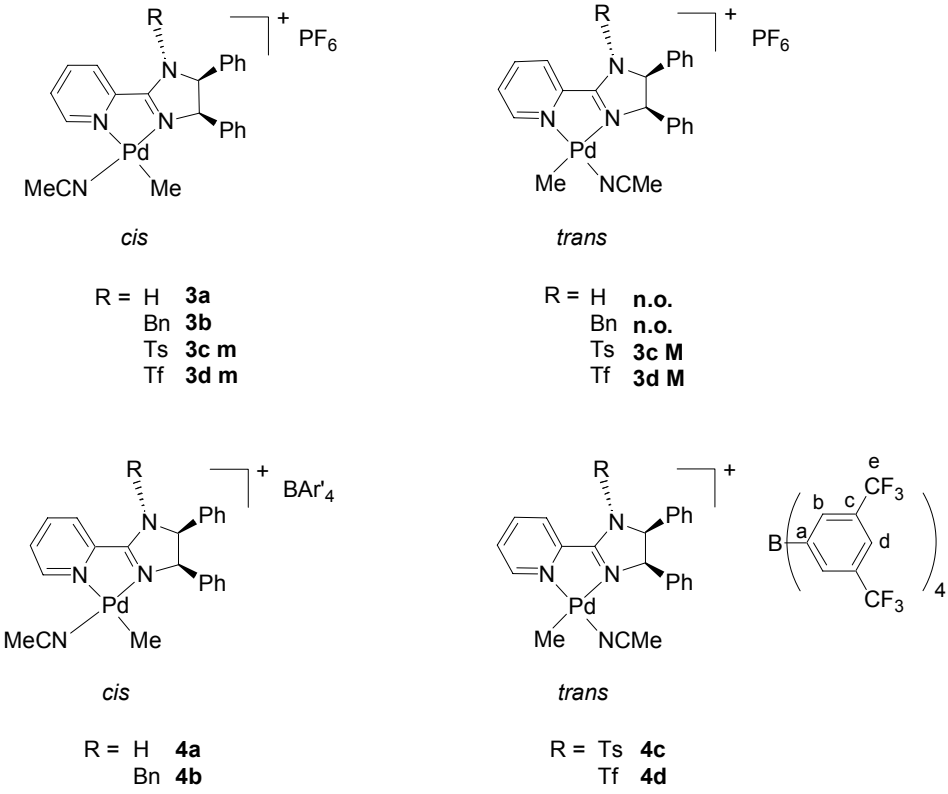


Figure 3. Crystal packing: head-to-tail arrangement of molecules related by a center of symmetry in compound **2b'** and in **2d**

The neutral derivatives **2a-2d** were characterized in solution by ^{1}H NMR spectroscopy. For all the complexes **2a-2d** in the aromatic region of the spectra, the H_6 signal (Scheme 1) is considerably downfield shifted with respect to the one in the free ligand ($\Delta\delta$ = 0.55 ppm), indicating that the chloride is *cis* coordinated to the pyridine moiety.[26] This coordination is confirmed by NOE experiments: irradiation of the Pd-Me protons show an NOE effect with the $H_{4'}$ of the imidazoline. The Pd-Me singlets are in the 0.50 - 0.25 ppm range, upfield shifted with respect to the same resonance in similar complexes [PdClMe(pzpy)] (pzpy = 2-(pyrazol-1-yl)pyridine).[27] This shift is related to the proximity of the shielding cone of the phenyl ring in position 4' on the imidazoline ring, as indicated by the X-ray analysis (Figure 1). For all the neutral derivatives, only the isomer that corresponds to the one found in the solid state is observed in solution, as found in the related pyridine-oxazoline (pyox) complexes [PdClMe(pyox)].[28]

5.1.2.3. Synthesis and characterization of [PdMe(NCMe)(N-N')][X] 3a-3d, 4a-4d

The cationic palladium complexes **3a-3d** [PdMe(NCMe)(N-N')][PF_6] and **4a-4d** [PdMe(NCMe)(N-N')][BAr_4'] were prepared starting from the corresponding neutral derivatives [PdClMe(N-N')], **2a-2d**, and reacting them with $AgPF_6$ or $NaBAr'_4$ to abstract the chloride ligand. No crystal suitable for structural determination was obtained for the cationic complexes **3a-3d** or **4a-4d** (Scheme 3). They were completely characterized in solution by recording the NMR spectra. The most significant signals are those related to H_6 (for the ligand), to the Pd-Me and to the Pd-NCMe fragments (Table 2). The signals were assigned to the protons on the basis of selective decoupling experiments and on the multiplicity of the signals.



Scheme 3. The cationic palladium complexes **3a**-**3d** and **4a**-**4d** (M = major isomer, m = minor isomer; n.o. = not observed). The numbering scheme of BAr'_4 is included

Table 2. Selected ^{1}H NMR data for complexes **3a**-**3d**, **4a**-**4d** and free ligands **1a**-**1d**[a]

	H_6	Pd-Me	Pd-NCMe
1a	8.63 (d, ^3J = 5.0)	-	-
3a	8.59 (d, ^3J = 5.1)	0.54 (s)	2.41 (s)
4a	9.37 (d, ^3J = 5.8)	0.31 (s)	2.16 (s)
1b	8.69 (d, ^3J = 4.8)	-	-
3b	8.99 (d, ^3J = 4.4)	0.47 (s)	2.47 (s)
4b	8.44 (d, ^3J = 5.2)	0.56 (s)	2.27 (s)
1c	8.64 (d, ^3J = 5.0)	-	-
3c[b]	M 8.64[c]	M 1.10 (s)	M 1.59 (s)
	m 8.79 (d, ^3J = 4.4)	m 0.32 (s)	m 2.45 (s)
4c	8.52 (d, ^3J = 5.6)	0.99 (s)	1.40 (s)
1d	8.78 (d, ^3J = 4.8)	-	-
3d[b]	M 8.69 (d, ^3J = 5.7)	M 1.22 (s)	M 1.64 (s)
	m 8.88 (d, ^3J = 5.1)	m 0.46 (s)	m 2.47 (s)
4d	8.51 (d, ^3J =5.6)	1.06 (s)	1.50 (s)

[a] ^{1}H NMR spectra recorded in $CDCl_3$ at room temperature; (s)= singlet, (d)= doublet; δ values are in ppm, J in Hz; M = major isomer, m = minor isomer. [b] ^{1}H NMR spectra recorded in CD_2Cl_2 at room temperature. [c] Overlapped with signals of H_3, no multiplicity could be assigned.

For both complexes **3a** and **3b** one set of signals related to the N-N' ligand is evident at room temperature. All the signals are shifted with respect to the free ligand. By irradiating the signal of the methyl group bound to palladium, an NOE effect with $H_{4'}$ was evident. This indicates

that only one species was present in solution, whose Pd-Me bond was *cis* to the imidazoline ring (Scheme 3). This stereochemistry is analogous to that observed in the neutral derivatives and in the cationic species **4a**-**4b** with BAr'_4^- as anion.[f]

In the spectra of complexes with the electron-withdrawing substituents a different situation is found depending on the anion. For **3c** and **3d**, two sets of signals of different intensity are clearly evident (Table 2). In the aromatic region of the spectra the signals of each pyridine ring can be recognized through homonuclear COSY experiments. No signal belongs to the free N-N' ligand. In particular, for **3d** two H_6 signals are clearly evident. For **3c**, however, one of them overlaps the H_3 signals. In the aliphatic region of the spectra, there are also two sets of resonances for the Pd-Me group (minor species: 0.32 ppm for **3c** and 0.46 ppm for **3d**; major species: 1.10 ppm for **3c** and 1.22 ppm for **3d**) and the Pd-NCMe fragment (minor species: 2.45 ppm for **3c** and 2.47 ppm for **3d**; major species: 1.59 ppm for **3c** and 1.64 ppm for **3d**). For both complexes, in each species the ratio between Pd-Me and Pd-NCMe is 1. When NOE experiments were performed on **3c** or **3d** by irradiating the Pd-Me singlet of the minor species, the spectrum also shows a negative signal for the Pd-Me singlet of the major species, thus indicating that they are in equilibrium. This is confirmed because the signals broaden when the temperature is increased to 313 K. Moreover, an NOE effect is observed between the Pd-Me and $H_{4'}$

[f] Isomers are *cis* or *trans* depending on the position of the methyl group with respect to the imidazoline ring.

for the minor species in both the **3c** and **3d** complexes. On the basis of these NMR data, it is clear that the two species present in solution are the two stereoisomers [PdMe(NCMe)(N-N')][PF_6] (N-N' = **1c**, **1d**), which are differentiated by the *trans* or *cis* coordination of the methyl group to the imidazoline ring (Scheme 3). In particular, the Pd-Me fragment of the major species is *trans* to the imidazoline ring. The ratio between the *trans* and *cis* isomers is 2:1 for **3c** and 3:1 for **3d**. The chemical shifts for the Pd-Me protons in the *trans* isomer are very close to those observed for complexes [PdMe(NCMe)(N-N')][BAr'_4], **4c-4d**, which show only the *trans* isomer in solution even at low temperatures (Table 2).

In summary, for complexes **4a-4d** only one stereoisomer is observed in solution, regardless of the nature of the ligand. The stereoisomer formed depends on the R substituent on the imidazoline ring: it is the *cis*, when R is H or Bn (**4a** and **4b**) and the opposite for R = Ts, Tf (**4c** and **4d**) (Scheme 2). When the anion changes from BAr'_4^- to PF_6^-, there is no difference for complexes with the ligands **1a** or **1b**. With **1c** or **1d,** however, stereochemical control is partially lost, even though the preferential isomer has the same stereochemistry found in **4c** and **4d**. These results suggest that, in all cases, the methyl group of the stereoisomer that is preferentially formed is *trans* to the less basic nitrogen atom.

The effect of the anion on the stereochemistry of the complexes might be related to its position in solution with respect to the cation. Studies in solution on complexes [Pd(OMe-COD)(bipy)][Y] (OMe-COD = η^1,η^2-$C_8H_{12}OMe$; Y = BPh_4^-, $CF_3SO_3^-$, BF_4^-, PF_6^-, SbF_6^-, BAr'_4^-) showed

that the anion is preferentially located above or below the coordination plane and shifted towards the bipy ring *trans* to the Pd-C σ-bond. When BAr'_4^- changes to PF_6^- the strength of the interionic interactions increases and favours the dissociation of one N-arm of the bipy molecule.[29] Therefore, in the case of complexes **3c** and **3d**, this may be responsible for the *trans* to *cis* isomerization process.

The presence of stereochemical isomers in Pd(II) complexes of general formula [PdMe(NCMe)(L-L')][X], involved in the copolymerization process, has been observed in two other examples, where L-L' is 2-(1-(3,5-dimethyl)pyrazolyl)pyrimidine[12] or diphosphinoferrocene ligands derived from Josiphos.[30] In the first case, the presence of the less favored isomer, on the basis of electronic consideration, has been explained in terms of the steric hindrance of the ligand. In the diphosphine derivatives, a strict relationship was not found between the electronic effect of the ligand and the ratio of the stereoisomers mixture.

5.1.2.4. Copolymerization of carbon monoxide with 4-*tert*-butylstyrene using complexes 4a-4d

The new cationic Pd(II) complexes **4a-4d**, which have different stereochemistry depending on the R substituent of the imidazoline ring (Scheme 3), were tested as catalysts for the alternating CO/4-*tert*-butylstyrene (TBS) copolymerization. In a typical experiment **4a-4d** were placed in chlorobenzene under atmospheric pressure of CO and TBS was added. Table 3 shows the results of the catalytic experiments. There is a

clear effect of the R substituent on the productivity of the system. An improvement is observed when the catalyst contains a ligand with an electron-withdrawing substituent (entry 1 *vs.* entry 4). Regarding the molecular weights of the polyketones, they were high and similar in all the cases.

Table 3. Alternating CO/ TBS copolymerization catalyzed by **4a-4d**[a]

Entry	Precursor	Productivity[b] (gCP/gPd.h)	Stereoregularity (% *l* diads)	M_n (M_W/M_n)
1	**4a**	2	65	42200 (1.1)
2	**4b**	8.9	52	49750 (1.5)
3	**4c**	7	15	59250 (1.2)
4	**4d**	12.8	18	39700 (1.5)

[a] Reaction conditions: 0.0125 mmol catalyst, [TBS]/[cat] = 620, 5 mL chlorobenzene, p(CO) = 1 atm., 24h at room temperature. [b] Productivity calculated from the isolated copolymer.

Under copolymerization conditions the successive coordination of carbon monoxide to the palladium precursor and the migratory insertion of the methyl group take place to form an acyl species. This generates a vacant position which is filled by the coordination of styrene. As previously stated the site selective coordination of the alkene on the palladium complex may determine its enantioface discrimination, if unsymmetrical chiral ligands are used. The electronic determination caused by the pyridine-imidazoline ligands could therefore affect the stereoregularity of the copolymer obtained with the catalytic precursors **4a**-**4d**.

The degree of stereoregularity was evaluated from the ^{13}C NMR spectrum of the copolymers by integrating the signals in the region of the methylene carbon atom using an epimerized copolymer as reference (Figure 4). As Table 3 shows, introducing electron-withdrawing groups (entries 3 and 4) leads to a greater proportion of *u* diads giving highly syndiotactic copolymers. With the substituents H and Bn (entries 1 and 2 respectively) such a clear effect is not observed probably due to the smaller electronic differentiation of the two rings (pyridine and imidazoline) but there is a bigger proportion of *l* diads.

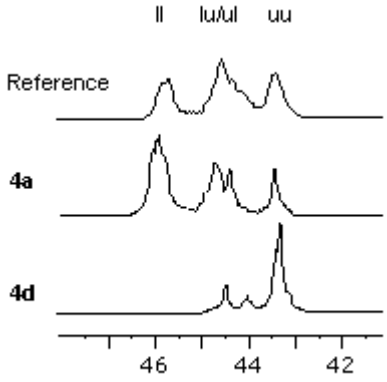


Figure 4. Comparative ^{13}C NMR spectrum of the copolymers, obtained with precatalysts **4a** and **4d,** in the region of the methylene carbon atom. An epimerized copolymer is used as reference

5.1.2.5. Reactivity of [PdMe(NCMe)(N-N')][X] complexes, 3a-3d and 4b, 4d with carbon monoxide

In order to simplify the ^{1}H and ^{13}C NMR spectra, the cationic palladium complexes with PF_6^- as counterion **3a-3d** were reacted with carbon monoxide and the reaction was studied by *in situ* NMR spectroscopy.

When carbon monoxide is bubbled for 5 minutes through a solution of [PdMe(NCMe)(**1a**)][PF_6], **3a**, or of [PdMe(NCMe)(**1b**)][PF_6], **3b**, in CD_2Cl_2, at 273 K, five new singlets (e.g., for **3a**+CO: 0.88 ppm, 1.52 ppm, 1.69 ppm, 2.10 ppm, 2.37 ppm) are present in the aliphatic region of the ^{1}H NMR spectra, recorded after 15 min, together with the resonance due to the methyl group of the precursor (Figure 5a-b) (Table 4). When labeled ^{13}CO is used, in the ^{1}H NMR spectrum two singlets (e.g., for **3a**+CO: 1.52 ppm and 1.69 ppm) become doublets, indicating that they belong to two acyl groups (Figure 5c). In the corresponding ^{13}C NMR spectra there are four signals (e.g., for **3a**+CO: 174.3 ppm, 176.6 ppm, 210.8 ppm, 220.9 ppm), the two at lower frequency are typical for Pd-CO fragments, while the other two are related to Pd-COMe species.[5b] When the concentration of CO in the same solution is increased, only two signals are still present in the ^{1}H NMR spectra: a doublet and a singlet (e.g., for **3a**+CO: 1.69 ppm, 2.10 ppm) (Figure 5d). The same is true of the ^{13}C NMR spectra (e.g., for **3a**+CO: 174.3 ppm, 210.8 ppm). The signal at 2.10 ppm in the ^{1}H NMR spectra is due to free acetonitrile.

Table 4. Selected NMR data for reactivity of complexes **3a** and **3b** with CO[a]

^{1}H NMR				
Compound	Me Pd NCMe	Me Pd CO	COMe Pd NCMe	COMe Pd CO
3a + CO	0.48	0.88	1.52	1.69
3b + CO	0.47	0.87	1.51	1.67
^{13}C NMR				
3a + CO	n.d.	176.6	220.9	174.3, 210.8
3b + CO	n.d.	176.7	222.3	174.3, 212.6

[a] NMR spectra recorded in CD_2Cl_2 at 273 K; δ values are in ppm; n.d.: not determined.

These NMR data indicate that the final product corresponds to the palladium-acyl-carbonyl species [Pd(COMe)(CO)(N-N')][PF_6] (N-N' = **1a**, **1b**), **7a** or **7b**, which is the result of inserting CO into the Pd-Me bond (Scheme 4). The other signals observed at lower CO concentrations are attributed to the intermediates of the insertion reaction. In particular, for the complex with ligand **1a**, the signal at 0.88 ppm, which is still a singlet in the presence of ^{13}CO, is due to the palladium-methyl-carbonyl derivative [PdMe(CO)(**1a**)][PF_6], **5a**, whose corresponding signal in the ^{13}C NMR spectrum is at 176.6 ppm. Finally, the resonance at 1.52 ppm, which becomes a doublet after bubbling ^{13}CO, and the singlet at 2.37 ppm belong to the acyl-acetonitrile intermediate [Pd(COMe)(NCMe)(**1a**)][PF_6], **6a**. The corresponding signal in the ^{13}C NMR spectrum is at 220.9 ppm.

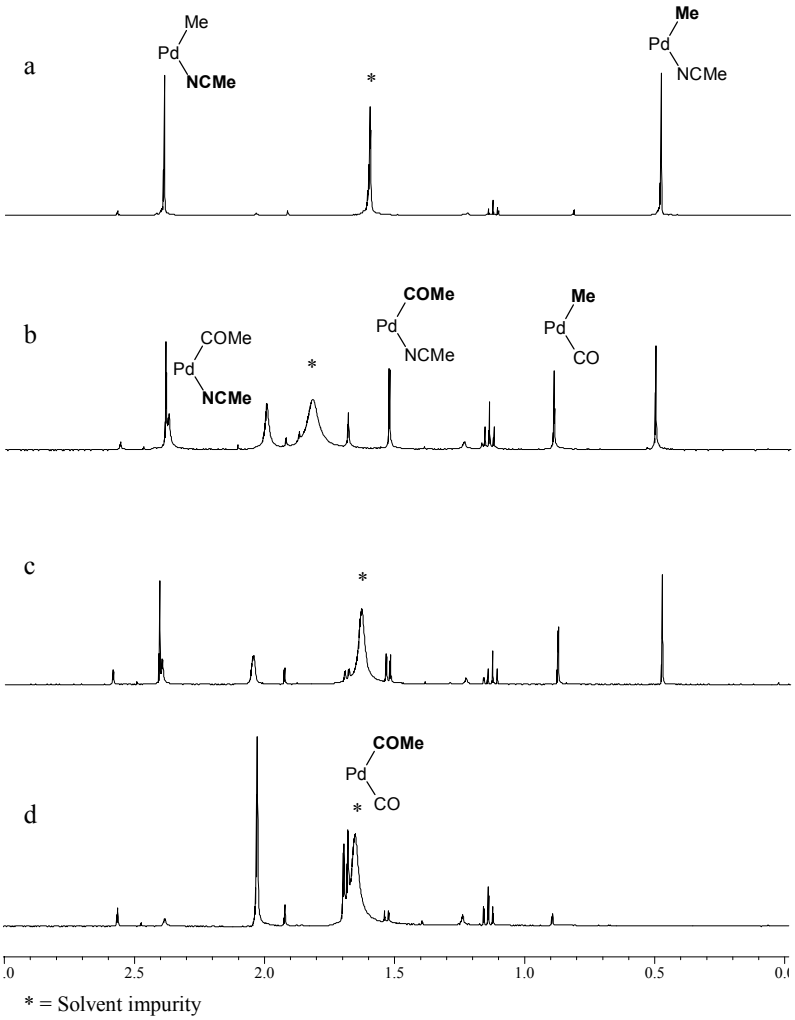
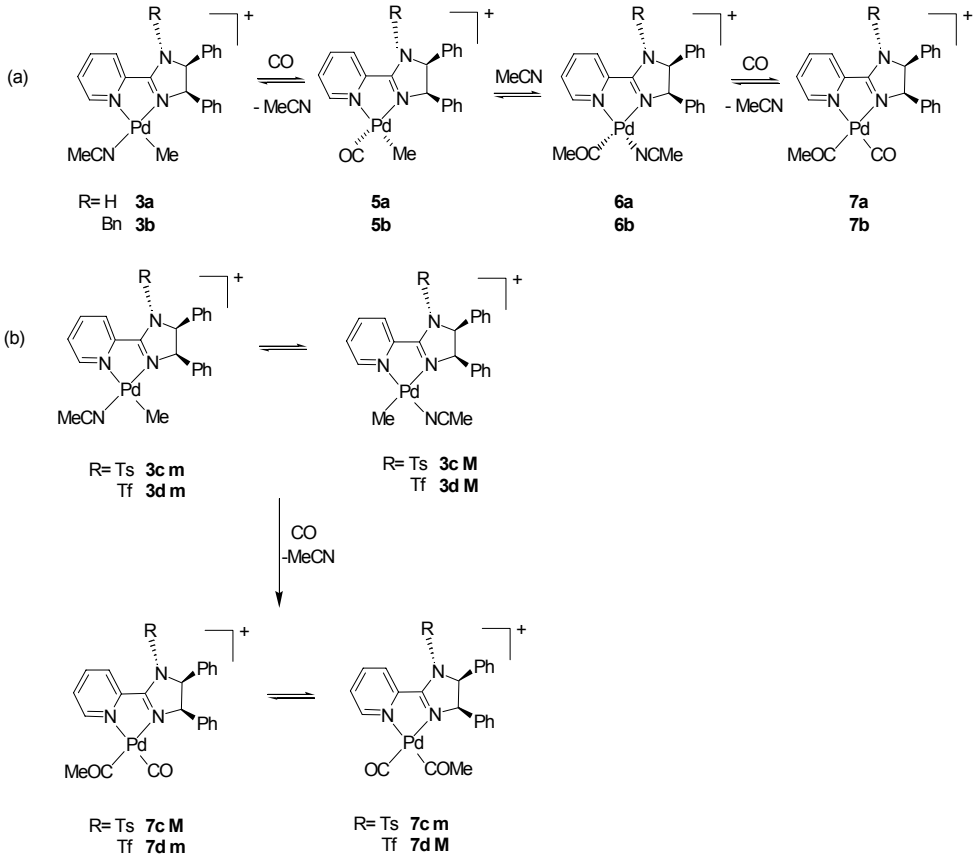


Figure 5. Reactivity of **3a** with carbon monoxide: ^{1}H NMR spectra recorded in CD_2Cl_2 at 273 K, region of aliphatic protons: a) spectrum of **3a**; b) spectrum of **3a** + CO; c) spectrum of **3a** + ^{13}CO; d) spectrum of **3a** + exc. of ^{13}CO



Scheme 4. Reactivity of complexes with carbon monoxide: a) **3a** and **3b**; b) **3c** and **3d**

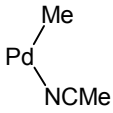
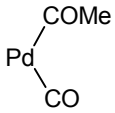
The most significant signal in the aromatic region of the spectra is the one related to the H_6 in the pyridine ring. For the intermediates, three signals are attributed to H_6, but they could not be clearly assigned to the corresponding species. In the final palladium-acyl-carbonyl species **7a**, H_6 gives a doublet at 8.48 ppm, upfield shifted with respect to the precursor. Thanks to the NOE effect between H_6 and the protons in the acyl group of

7a, it was possible to recognize this species as the *trans* isomer. The same situation is observed for **7b**. The ^{1}H NMR spectra of both **7a** and **7b** did not vary when the temperature was decreased by as much as 213 K, which confirmed the presence of a single stereoisomer. No direct experiment was performed on the stereochemistry of the intermediates.

The palladium-acyl-carbonyl derivative **7a** was also isolated by bubbling CO in a dichloromethane solution of [PdMe(NCMe)(**1a**)][PF_6] at 273 K. It was stored at 278 K without decomposition. Its ^{1}H NMR spectrum shows the same signals observed in the *in-situ* NMR experiments.

When carbon monoxide is bubbled for 5 min through a solution of [PdMe(NCMe)(**1c**)][PF_6], **3c**, or of [PdMe(NCMe)(**1d**)][PF_6], **3d**, in CD_2Cl_2, at 273 K, the ^{1}H NMR spectra, recorded after 15 min at 263 K, showed only two broad signals in the aliphatic region (e.g., for **3c**+CO: 1.65 ppm, 1.98 ppm) and the complete disappearance of the precursor's resonance (Table 5).

Table 5. Selected ^{1}H and ^{13}C NMR data for reactivity of complexes **3c** and **3d** with CO[a]

^{1}H NMR			
Compound	T		
3c + CO	263 K	M 1.10	1.65 (b)
		m 0.31	
	183 K	M 1.0	M 1.41
		m 0.16	m 2.74
3d + CO	263 K	M 1.18	2.33 (b)
		m 0.41	
	183 K	M 1.11	M 2.76
		m 0.23	m 1.52
^{13}C NMR			
3c + CO	263 K	n.d.	172.8, 211.5
	183 K	n.d.	M 172.4, 211
			m 170.7, 217.1
3d + CO	263 K	n.d.	171.9, 212.1
	183 K	n.d.	M 170.3, 216.4
			m 171.7, 210.2

[a] NMR spectra recorded in CD_2Cl_2; δ values are in ppm; b = broad.

When the labeled ^{13}CO was used, no variation was observed in the ^{1}H NMR spectrum. In the corresponding ^{13}C NMR spectrum two broad signals appeared (e.g. for **3c**+CO: 172.8 ppm, 211.5 ppm) (Figure 6a and Table 5) due to a Pd-CO and a Pd-COMe moiety, respectively. Low temperature NMR studies were performed by decreasing the temperature from 263 K to 183 K. In the case of **3c**, the signal at 1.65 ppm disappeared at 233 K. Two peaks became evident at 183 K (1.41 ppm and 2.74 ppm), and a sharp singlet appeared at 1.99 ppm. The two peaks were of different intensity, being the resonance at 1.41 ppm higher than that at 2.74 ppm in a ratio of 4.2:1. Moreover, the weighted sum of the two resonances corresponds to the chemical shift (1.66 ppm) of the signal observed at 263 K. At the same temperature in the ^{13}C NMR spectrum four signals appeared that can be grouped into two pairs on the basis of their intensities (170.7 and 217.1 ppm, 172.4 and 211 ppm) (Figure 5b). The reaction of **3d** with carbon monoxide was similar: the peak at 2.33 ppm at 263 K, which disappears at 233 K, splits into two peaks (2.76 ppm and 1.52 ppm) at 183 K. For this complex, the intensity of the signals was just the reverse of what was found for **3c**: in the ^{1}H NMR spectrum, the most intense peak was at the highest frequency (2.76 ppm), with a ratio of 1.7:1 (Table 4). The same inversion of intensity is observed in the corresponding ^{13}C NMR spectrum.

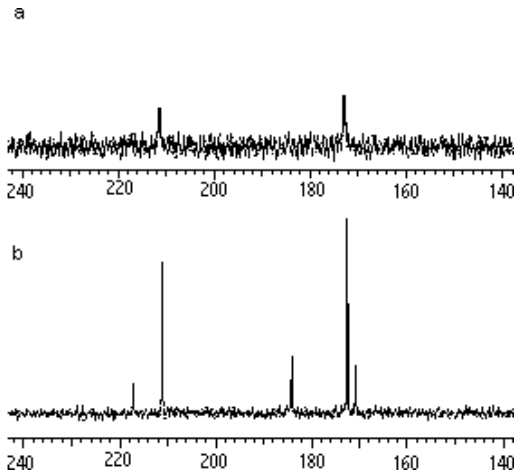


Figure 5. Reactivity of **3c** with ^{13}CO: ^{13}C NMR spectra recorded in CD_2Cl_2: a) at T = 273 K; b) at T = 183 K

The signal at 1.99 ppm in the ^1H NMR spectra is due to free acetonitrile. At the lowest temperature reached, the two resonances at 1.41 ppm and at 2.74 ppm, for the reactivity of **3c** with CO (or 1.52 ppm and 2.76 ppm for **3d** + CO), are attributed to two Pd-COMe groups. The resonances found in the ^{13}C NMR spectrum at the same temperature confirm that two Pd-COMe groups and two Pd-CO moieties are present. Therefore, these NMR data indicate that the final product is the palladium-acyl-carbonyl species [Pd(COMe)(CO)(N-N')][PF_6] (N-N' = **1c**, **1d**), **7c** or **7d**, which is present as a mixture of two isomers in equilibrium (Scheme 4). The rate of this equilibrium is intermediate on the NMR time scale at 263 K.

In the temperature range we investigated, the analysis of the H_6 signal for both complexes always reveals broad signals and, even at the

lowest temperature reached, no assignment was possible, since decoalescence was not complete. Therefore, the stereochemistry of the two isomers could not be determined. Finally, no signals from the intermediates were observed for either of the complexes, and the resonances of the precursors disappeared, indicating a higher reactivity with carbon monoxide than with **3a** and **3b**.

In view of the differences between complexes **3c**-**3d** and **4c**-**4d**, the reactivity with carbon monoxide was also investigated for two exponents of the series with BAr'_4^-, namely **4b** and **4d**. They behaved similarly to the corresponding PF_6^- derivatives: one isomer for the complex with ligand **1b** and two isomers for the species containing **1d**. Indeed, in the spectrum at 273 K, recorded after bubbling CO in a solution of **4b**, only the signal at 1.65 ppm is present in the aliphatic region. This indicates that *trans*-[Pd(COMe)(CO)(**1b**)][BAr'_4] (**8b**) has been formed. This signal is shifted at 1.50 ppm when the spectrum is recorded at 193 K. In the reaction of **4d** with CO, only one broad signal is present at 2.11 ppm at 273 K. It is split into two signals (2.72 ppm and 1.50 ppm) when the temperature was decreased down to 193 K. Therefore, both *cis* and *trans* [Pd(COMe)(CO)(**1d**)][BAr'_4] (**8d**) isomers are present in a ratio of 1:1.

No successful direct experiment was done to unambiguously assign the stereochemistry of the two isomers for complexes **7c**, **7d** and **8d**. However, comparing the chemical shifts at the lowest temperature reached, in particular for **8b** and **8d**, suggests that the resonance at 1.5 ppm is due to the Pd-acyl-carbonyl species with the acyl group *trans* to the imidazoline

ring. Finally, it should be noted that the stereocontrol observed in the BAr'_4 precursors **4a**-**4d** is partially lost after reaction of **4c** and **4d** with carbon monoxide.

Our study of the insertion of 4-*tert*-butylstyrene in the Pd-acyl-carbonyl species formed *in situ* (**7a-7d**) was unsuccessful, maybe due to the combined effect of decomposition and slow insertion of the alkene.

Complexes **4a-4d** have shown activity as catalyst precursors for the CO/4-*tert*-butyl-styrene copolymerization reaction. The nature of the ligand has an effect both on the productivity of the system and on the tacticity of the polyketones obtained. Complexes **4a-4b** show little activity and gave atactic polyketones with a slight prevalence of the isotactic triad. On the other hand, the syndiotactic polyketone is obtained with **4c** and **4d**. Moreover, the last precursor shows the highest catalytic activity. This catalytic behavior might be correlated with the different reactivity of these complexes with carbon monoxide. Only one stereoisomer is obtained for Pd-Me complexes with ligands **1a-1b**. It slowly reacts with carbon monoxide and yields only one Pd-acyl stereoisomer (Pd-acyl fragment *trans* to imidazoline). Both stereoisomers were found for Pd-Me complexes with ligands **1c-1d**. They react with CO faster than the complexes with **1a** and **1b**, to yield the corresponding Pd-acyl stereoisomers. The ratio between the stereoisomers depended on the ligand. The higher catalytic activity found for the precursor with **1d**, together with the prevailing presence of the opposite stereoisomer with respect to **1a** (or **1b**), might indicate that the Pd-acyl fragment *cis* to imidazoline is more reactive than the *trans* one.

It is well known that the insertion of the alkene is the rate determining step of the copolymerization reaction and that the enantioface selection during the alkene insertion is due to the chain end or to the enantiomorphic site control. The fact that the polyketone obtained with ligands **1a** and **1b** tends to isotacticity, together with the presence of a single stereoisomer (Pd-COMe *trans* to imidazoline), might indicate that there is site selective coordination of the alkene *cis* to the chiral moiety of the ligand. The enantioface selection of the ligand is nevertheless not efficient enough to completely overcome the chain end control, and the result is, therefore, the synthesis of an atactic copolymer. On the other hand, the synthesis of the syndiotactic copolymer, together with the presence of the two isomers in the case of **1c** and **1d** ligands, might indicate that isomerization takes place very easily by exchanging the coordination site of the polymer growing chain and the alkene. The greater reactivity of the stereoisomer with the Pd-COMe fragment *cis* to imidazoline might favour the insertion of the alkene preferentially under chain-end control and lead to a prevailing syndiotactic copolymer. However, due to the similarity of species **3a**-**3d**, two regioisomeric olefin intermediates might be present for all the complexes. As a consequence, the variation in the microstructure of the produced copolymers should arise from the different contribution of these regioisomers.

5.1.3. Conclusions

Pyridine-imidazoline ligands of C_1 symmetry, electronically modified with different R substituents, were prepared. Their coordination to palladium leads to efficient catalysts for the CO/4-*tert*-butylstyrene copolymerization. Depending on the electronic modification of the pyridine-imidazolines, polyketones with different degree of stereoregularity are obtained. Moreover these ligands provide information about the stereochemistry of the intermediates in the copolymerization reaction.

The neutral complexes [PdClMe(N-N')] have the same stereochemistry irrespectively of the N-N' ligand, with the methyl group *cis* to imidazoline. The behavior of the cationic complexes in solution depends on the ligand (**1a-1b** or **1c-1d**) as well as on the counterion (PF_6^- or BAr'_4^-). It is straightforward to note that the Pd-Me and the Pd-NCMe chemical shifts in the two isomers are very different and they can be considered as a probe for the stereochemistry of the resulting complexes.

All the intermediates of the reaction of the Pd-Me precursors with carbon monoxide, which yields the Pd-acyl-carbonyl final species, were detected in solution using ^1H and ^{13}C NMR spectroscopy. Depending on the R substituent of the ligand, one or both [Pd(COMe)(CO)(N-N')][X] stereoisomers were detected and characterized. Finally, the reactivity of the cationic Pd-Me complexes towards CO was seen to be related to the copolymerization results.

5.1.4. Experimental

5.1.4.1. General procedure

Commercial $Na_2[PdCl_4]$ and $[Sn(CH_3)_4]$ were purchased from Johnson Matthey and Aldrich, respectively, and used as received. 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 salt $NaBAr'_4$ (Ar' = 3,5-$(CF_3)_2$-C_6H_3) was prepared according to the reported method.[31] All reactions were carried out under nitrogen atmosphere, at room temperature, using standard Schlenk techniques.

^1H and ^{13}C NMR spectra were recorded on a Varian Gemini spectrometer with a ^1H resonance frequency of 300 MHz and a ^{13}C frequency of 75.4 MHz, on a Varian Mercury VX spectrometer with a ^1H resonance frequency of 400 MHz and a ^{13}C frequency of 100.5 MHz, and on a Jeol EX 400 spectrometer with a ^1H frequency at 400 MHz and a ^{13}C frequency of 100.5 MHz. The resonances were referenced to the solvent peak versus tetramethylsilane (TMS) ($CDCl_3$ at 7.26 δ for ^1H and 77.23 δ for ^{13}C, CD_2Cl_2 at 5.32 δ for ^1H and 54.0 δ for ^{13}C). The NOE experiments were run with a ^1H pulse of 12 μs (300 MHz) and of 13.3 μs (400 MHz). Two-dimensional correlation spectra (gCOSY) were obtained with the automatic program of the instrument. MS (FAB positive) were obtained on a Fisons V6-Quattro instrument. The molecular weight of the copolymers and molecular weight distributions were determined by gel permeation

chromatography (GPC - MALLS) measurements made in THF on a Waters 510 gel-permeation chromatography device using a three-serial column system (SHODEX K80M and PLGEL MIXED-D and MIXED-E linear columns) with a Wyatt mini-DAWN Light Scattering and a SHIMADZU RID-6A refractive index detector.

5.1.4.2. Synthesis of pyridine-imidazoline ligands 1a-1d

1a: 2-cyanopyridine (9 mmol) and *meso*-1,2-diphenylethylenediamine (9.5 mmol) were refluxed in chlorobenzene during 72 h using $Yb(OTf)_3$ (0.31 mmol) as catalyst. Recrystallisation from CH_2Cl_2/hexane afforded a white crystalline solid. Yield: 83%. Anal. Found: C, 79.25; H, 4.96; N, 13.78%. Calc. for $C_{20}H_{17}N_3$: C, 80.24; H, 5.39; N, 14.04%. ^{1}H NMR (400 MHz, $CDCl_3$, RT): δ 8.63 (ddd, ^3J = 5 Hz, ^4J = 1.8 Hz, ^5J = 1.1 Hz, 1H, H_6), 8.36 (dt, ^3J = 7.7 Hz, ^4J = 1.1 Hz, ^5J = 1.1 Hz, 1H, H_3), 7.81 (td, ^3J = 7.7 Hz, ^4J = 1.8 Hz, 1H, H_4), 7.40 (ddd, ^3J = 7.7 Hz, ^3J = 5 Hz, ^4J = 1.1 Hz, 1H, H_5), 7.02- 6.94 (m, 10H, Ph), 5.51 (s, 2H, $H_{4'}$ + $H_{5'}$). ^{13}C NMR (100.5 MHz, $CDCl_3$, RT): 164.3 (s, $C_{2'}$ or C_2), 149 (s, C_6), 148.4 (s, C_2 or $C_{2'}$), 138.8 (s, Ph), 136.9 (s, C_4), 127.7 (s, Ph), 127.6 (s, Ph), 126.9 (s, Ph), 125.6 (s, C_5), 122.8 (s, C_3), 71.0 (br, $C_{4'}$ + $C_{5'}$).

1b: Compound **1a** (0.33 mmol) was dissolved in THF (3 mL) and reacted with NaH (0.50 mmol) for about an hour. To the reaction mixture, benzyl bromide (0.35 mmol) 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: 67%. Anal. Found: C, 82.65; H, 6.17; N, 9.42%. Calc. for $C_{27}H_{23}N_3$: C, 83.26; H, 5.95; N, 10.78%. ^{1}H NMR (400 MHz, $CDCl_3$, RT): δ 8.69 (ddd, ^3J = 4.8 Hz, ^4J = 2 Hz, ^5J = 1 Hz, 1H, H_6), 8.08 (dt, ^3J = 7.9 Hz, ^4J = 1.1 Hz, ^5J = 1.1 Hz, 1H, H_3), 7.78 (td, ^3J = 7.7 Hz, ^4J = 1.9 Hz, 1H, H_4), 7.35 (ddd, ^3J = 7.7 Hz, ^3J = 4.8 Hz, ^4J = 1.1 Hz, 1H, H_5), 7.15- 6.9 (m, 15H, Ph), 5.58 (d, ^2J = 15.6 Hz, 1H, CH_2), 5.44 (d, ^3J = 11.6 Hz, 1H, $H_{4'}$), 4.92 (d, ^3J = 11.6 Hz, 1H, $H_{5'}$), 3.82 (d, ^2J = 15.6 Hz, 1H, CH_2). ^{13}C NMR (100.5 MHz, $CDCl_3$, RT): 164.7 (C_2), 149.1 (C_6), 137.5 (C_4), 132.2 (C_5), 128.8–126.8 (Ph), 125.7 (C_3), 71.5 ($C_{4'}$), 69.3 ($C_{5'}$), 48.6 (CH_2).

1c: To a solution of ligand **6** (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 (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 = 0.52. Yield: 42%. Anal. Found: C, 71.36; H, 5.37; N, 8.93; S, 6.90%. Calc. for $C_{27}H_{23}N_3O_2S$: C, 71.50; H, 5.11; N, 9.26; S, 7.06%. ^{1}H NMR (400 MHz, $CDCl_3$, RT): δ 8.67 (ddd, ^3J = 5 Hz, ^4J = 1.6 Hz, ^5J = 0.8 Hz, 1H, H_6), 7.97(dt, ^3J = 7.5 Hz, ^4J = 0.8 Hz, ^5J = 0.8 Hz, 1H, H_3), 7.86 (td, ^3J = 7.5 Hz, ^4J = 1.6 Hz, 1H, H_4), 7.5 (d, ^3J = 8.2 Hz, 2H, Harom.-Ts-), 7.47 (ddd, ^3J = 7.5 Hz, ^3J = 5 Hz, ^4J = 0.8 Hz, 1H, H_5), 7.11 (d, ^3J = 8.2 Hz, 2H, Harom.-Ts-), 7.12- 6.86 (m, 10H, Ph), 5.93 (d, ^3J = 10Hz, 1H, $H_{4'}$ or $H_{5'}$), 5.8 (d, ^3J = 10Hz, 1H, $H_{5'}$ or $H_{4'}$), 2.37 (s, 3H, CH_3). ^{13}C NMR (100.5 MHz, $CDCl_3$, RT): 148.8 (s, C_6), 136.9 (s, C_4), 129.1 – 127.2 (Ph) 125.6 (s, C_5), 124.9 (s, C_3), 75.3 ($C_{4'}$ or $C_{5'}$), 69.2 ($C_{5'}$ or $C_{4'}$), 21.8 (CH_3).

1d: Similar to the synthesis of **1d** but using trifluoromethanesulfonic anhydride as the electrofile. The purification was done by column chromatography using ethyl acetate as eluent. Rf = 0.89. Anal. Found: C, 58.85; H, 3.82; N, 9.42; S, 7.28%. Calc. for $C_{21}H_{16}N_3O_2SF_3$: C, 58.44; H, 3.71; N, 9.73; S, 7.42%. ^{1}H NMR (300 MHz, $CDCl_3$, RT): δ 8.78 (ddd, ^3J = 4.8 Hz, ^4J = 1.8 Hz, ^5J = 1 Hz, 1H, H_6), 7.96 (dt, ^3J = 7.7 Hz, ^4J = 1 Hz, ^5J = 1 Hz, 1H, H_3), 7.87 (td, ^3J = 7.7 Hz, ^4J = 1.8 Hz, 1H, H_4), 7.49 (ddd, ^3J = 7.7 Hz, ^3J = 4.8 Hz, ^4J = 1 Hz, 1H, H_5), 7.11- 6.99 (m, 10H, Ph), 5.98 (d, ^3J = 8.7 Hz, 1H, $H_{4'}$ or $H_{5'}$), 5.92 (d, ^3J = 8.7 Hz, 1H, $H_{5'}$ or $H_{4'}$). ^{13}C NMR (75.4 MHz, $CDCl_3$, RT): δ 149.3 (s, C_6), 136.9 (s, C_4), 128.2 - 127. 2 (Ph), 126.1 (s, C_5), 124.7 (s, C_3), 76.1 (s, $C_{4'}$ or $C_{5'}$), 70.5 (s, $C_{5'}$ or $C_{4'}$).

5.1.4.3. Synthesis of [PdClMe(N-N')] (2a-2d)

$Na_2[PdCl_4]$, used as starting material, was transformed into $[PdCl_2(cod)]$ (cod = 1,5-cyclooctadiene) according to the literature.[32] [PdClMe(cod)] was obtained from $[PdCl_2(cod)]$.[26] The neutral complexes **2a-2d** were synthesized by adding the ligand (**1a-1d**) to a solution of [PdClMe(cod)] in toluene, [ligand]/[Pd] = 1. The solution was stirred at room temperature for 1 hour yielding a yellow precipitate. After evaporation of the solvent, the compounds were washed with diethylether and filtered off.

[PdClMe(1a)] (2a)

Yield: 90%. ^{1}H NMR (400 MHz, $CDCl_3$, RT): δ 8.91 (ddd, ^3J = 5.1 Hz, ^4J = 1.7 Hz, ^5J = 0.6 Hz, 1H, H_6), 8.05 (ddd, ^3J = 7.8 Hz, ^4J = 1.2 Hz, ^5J = 0.6 Hz, 1H, H_3), 7.90 (td, ^3J = 7.8 Hz, ^4J = 1.7 Hz, 1H, H_4), 7.52 (ddd, ^3J = 7.8 Hz,

^{3}J = 5.1 Hz, ^{4}J = 1.2 Hz, 1H, H_5), 6.89-6.75 (m, 10H, Ph), 5.60 (d, ^{3}J = 11.4 Hz, 1H, $H_{5'}$), 5.4 (d, ^{3}J = 11.4 Hz, 1H, $H_{4'}$), 0.36 (s, 3H, Pd-CH_3). ^{13}C NMR (100.5 MHz, $CDCl_3$, RT): δ 149.2 (s, C_6), 138.4 (s, C_4), 128 (s, C_5), 127.7- 126.2 (Ph), 123.2 (s, C_3), 71.3 (s, $C_{4'}$), 66.8 (s, $C_{5'}$), -8.5 (s, Pd-CH_3). MS (FAB positive) *m/z*: 404 $[M\text{-}Cl]^+$.

[PdClMe(1b)] (2b)

Yield: 75%. Anal. Found: C, 60.50; H, 4.73; N, 7.48%. Calc. for $C_{28}H_{26}N_3ClPd$: C, 61.55; H, 4.80; N, 7.69%. ^{1}H NMR (400 MHz, $CDCl_3$, RT): δ 9.22 (d, ^{3}J = 4.8 Hz, 1H, H_6), 7.86 (m, 2H, H_3 + H_4), 7.59 (q, ^{3}J = 5.2 Hz, ^{4}J = 5.2 Hz, 1H, H_5), 7.25-6.76 (m, 15H, Ph), 5.46 (d, ^{3}J = 11.6 Hz, 1H, $H_{5'}$), 5.37 (d, ^{3}J = 11.6 Hz, 1H, $H_{4'}$), 5.03 (d, ^{2}J = 17.2 Hz, 1H, CH_2), 4.33 (d, ^{2}J = 17.2 Hz, 1H, CH_2), 0.49 (s, 3H, Pd- CH_3). ^{13}C NMR (75.4 MHz, $CDCl_3$, RT): δ 168 (s, C_2 or $C_{2'}$), 150.7 (s, C_6), 145. 3 (s, $C_{2'}$ or C_2), 138.4 (s, C_4), 136.3 (s, Ph), 134.8 (s, Ph), 133.4 (s, Ph), 129.5 (s, Ph), 128.8 (s, Ph), 128.5 (s, Ph), 128.34 (s, Ph), 128.3 (s, C_5), 128 (s, Ph), 127.7(s, Ph), 127.5 (s, Ph), 127 (s, Ph), 124 (s, C_3), 72.9 (s, $C_{4'}$), 69.6 (s, $C_{5'}$), 50.3 (s, CH_2), -6.6 (s, Pd-CH_3).

[PdClMe(1c)] (2c)

Yield: 69%. Anal. Found: C, 52.82; H, 4.29; N, 6.40; S, 5.35%. Calc. for $C_{28}H_{26}N_3ClO_2PdS$: C, 55.04; H, 4.26; N, 6.88; S, 5.24%. ^{1}H NMR (400 MHz, $CDCl_3$, RT): δ 9.20 (ddd, ^{3}J = 5.1 Hz, ^{4}J = 2.7 Hz, ^{5}J = 1.2 Hz, 1H, H_6), 8.64 (dt, ^{3}J = 7.9 Hz, ^{4}J = 1.3 Hz, ^{5}J = 1.3 Hz, 1H, H_3), 8.16 (td, ^{3}J = 7.9 Hz, ^{4}J = 2.7 Hz, 1H, H_4), 7.82 (ddd, ^{3}J = 7.9 Hz, ^{3}J = 5.1 Hz, ^{4}J = 1.3 Hz, 1H, H_5), 7.75 (d, ^{3}J = 7.5 Hz, 2H, Harom.-Ts-), 7.51 (d, ^{3}J = 7.5 Hz, 2H, Harom.-Ts-), 7.07- 6.71 (m,

10H, Ph), 5.67 (d, ^3J = 9Hz, 1H, $H_{5'}$), 5.05 (d, ^3J = 9Hz, 1H, $H_{4'}$), 2.55 (s, 3H, CH_3 -Ts-), 0.28 (s, 3H, Pd-CH_3).

[PdClMe(1d)] (2d)

Yield: 84%. Anal. Found: C, 45.42; H, 3.84; N, 6.45%. Calc. for $C_{22}H_{19}ClF_3N_3O_2PdS$: C, 44.95; H, 3.26; N, 7.15%. ^{1}H NMR (400 MHz, $CDCl_3$, RT): δ 9.27 (ddd, ^3J = 5.1 Hz, ^4J = 1.7 Hz, ^5J = 0.8 Hz, 1H, H_6), 8.32 (ddd, ^3J = 7.9 Hz, ^4J = 1.2 Hz, ^5J = 0.8 Hz, 1H, H_3), 8.15 (dt, ^3J = 7.9 Hz, ^4J = 1.7 Hz, 1H, H_4), 7.83 (ddd, ^3J = 7.9 Hz, ^3J = 5.1 Hz, ^4J = 1.2 Hz, 1H, H_5), 7.24 - 6.69 (m, 10H, Ph), 6.11 (s, 2H, $H_{4'}$ + $H_{5'}$), 0.45 (s, 3H, Pd-CH_3). ^{13}C NMR (100.5 MHz, $CDCl_3$, RT): δ 150.5 (s, C_6), 138.9 (s, C_4), 129.7 (s, C_5), 129.1-127 (Ph), 126.7 (s, C_3), 74.8 (s, $C_{4'}$or $C_{5'}$), 72.5 (s, $C_{5'}$ or $C_{4'}$), - 4.5 (s, Pd-CH_3).

5.1.4.4. Synthesis of [PdMe(NCMe)(N-N')][PF_6] (3a-3d)

To a solution of [PdClMe(N-N')] (0.18 mmol) in dichloromethane (3 mL), 1.2 equivalents of $AgPF_6$ (0.22 mmol) dissolved in acetonitrile (1 mL) were added. After stirring for 1 h in the absence of light, the AgCl formed was filtrated and, when diethyl ether was added, the solution concentrated under vacuum to yield a pale yellow solid. Average yield: 75 %.

[PdMe(NCMe)(1a)][PF_6] (3a)

^{1}H NMR (400 MHz, $CDCl_3$, RT): δ 8.59 (dd, ^3J = 5.1 Hz, ^4J = 0.6 Hz, 1H, H_6), 8.21 (td, ^3J = 8 Hz, ^4J = 0.7 Hz, 1H, H_4), 8.06 (dd, ^3J = 8 Hz, ^4J = 0.7 Hz, 1H, H_3), 7.83 (dd, ^3J = 8 Hz, ^3J = 5.1 Hz, 1H, H_5), 5.81 (d, ^3J = 11.2 Hz, 1H, $H_{5'}$), 5.48 (d, ^3J = 11.2 Hz, 1H, $H_{4'}$), 2.41 (s, 3H, Pd-$NCCH_3$), 0.54 (s, 3H, Pd-CH_3). MS (FAB positive) *m/z*: 461.2 $[M]^+$, 404 $[M - NCMe]^+$.

[PdMe(NCMe)(1b)][PF_6] (3b)

^{1}H NMR (400 MHz, $CDCl_3$, RT): δ 8.99 (d, ^3J = 4.4 Hz, 1H, H_6), 8.02 (m, 3H, H^3, H_4 + H_5), 7.35-6.80 (m, 10H, Ph), 5.50 (d, ^3J = 11.7 Hz, 1H, $H_{5'}$), 5.40 (d, ^3J = 11.7 Hz, 1H, $H_{4'}$), 5.19 (d, ^3J = 17.6 Hz, 1H, CH_2), 4.42 (d, ^3J = 17.6 Hz, 1H, CH_2), 2.47 (s, 3H, Pd-NCCH_3), 0.47 (s, 3H, Pd-CH_3).

[PdMe(NCMe)(1c)][PF_6] (3c)

Ratio of isomers in CD_2Cl_2 M:m = 2:1. Major: ^{1}H NMR (400 MHz, CD_2Cl_2, RT): δ 8.67 (m, ^3J = 7.9 Hz, 1H, H_3), 8.64 (m, 1H, H_6), 8.35 (td, ^3J = 7.9 Hz, ^4J = 1.1 Hz, 1H, H_4), 7.92 (dd, ^3J = 7.9 Hz, ^3J = 6Hz, 1H, H_5), 7.76-6.71 (m, 14H, Ph), 5.86 (d, ^3J = 8.8 Hz, 1H, $H_{5'}$), 5.44 (d, ^3J = 8.8 Hz, 1H, $H_{4'}$), 2.5 (s, 3H, CH_3 -Ts-), 1.59 (s, 3H, Pd-NCCH_3), 1.10 (s, 3H, Pd-CH_3); minor: 8.79 (d, ^3J = 4.6 Hz, 1H, H_6), 8.64 (m, 1H, H_3), 8.28 (td, ^3J = 7.7 Hz, ^4J = 1.2 Hz, 1H, H_4), 8.03 (dd, ^3J = 7.7 Hz, ^3J = 4.6 Hz, 1H, H_5), 7.76-6.71 (m, 14H, Ph), 5.85 (d, ^3J = 9.6 Hz, 1H, $H_{5'}$), 5.29 (d, ^3J = 9.6 Hz, 1H, $H_{4'}$), 2.50 (s, 3H, CH_3-Ts-), 2.45 (s, 3H, Pd-NCCH_3), 0.32 (s, 3H, Pd-NCCH_3). MS (FAB positive) *m/z*: 615.1 $[M]^+$, 558 $[M - Me, NCMe]^+$, 403 $[M – Me, NCMe, Ts]^{2+}$.

[PdMe(NCMe)(1d)][PF_6] (3d)

Ratio of isomers in CD_2Cl_2 M:m = 3:1. Major: ^{1}H NMR (400 MHz, CD_2Cl_2, RT): 8.69 (d, ^3J = 5.7 Hz, 3H, H_6), 8.44 (m, 1H, H_3), 8.38 (td, ^3J = 7.8 Hz, ^4J = 1.5 Hz, 1H, H_4), 7.97 (ddd, ^3J = 7.8 Hz, ^3J = 5.7 Hz, ^4J = 1.5 Hz, 1H, H_5), 6.17 (m, 2H, $H_{4'}$ + $H_{5'}$), 1.64 (s, 3H, Pd-NCCH_3), 1.22 (s, 3H, Pd-CH_3); minor: 8.88 (d, ^3J = 5.1 Hz, 1H, H_6), 8.44 (m, 1H, H_3), 8.30 (t, 1H, ^3J = 7.8 Hz, H_4), 8.10 (dd, ^3J = 7.8 Hz, ^3J = 5.1 Hz, 1H, H_5), 6.17 (m, 1H, $H_{4'}$ or $H_{5'}$), 6.03 (d, ^3J = 8.8 Hz, 1H, $H_{4'}$ or $H_{5'}$), 2.47 (s, 3H, Pd-NCCH_3), 0.46 (s, 3H, Pd-CH_3). MS

(FAB positive) *m/z*: 593.1 $[M]^+$, 536.0 [M - Me, NCMe]$^+$, 403.1 [M- Me, NCMe, Tf]$^{2+}$.

5.1.4.5. Synthesis of [PdMe(NCMe)(N-N')][BAr'$_4$] (4a-4d)

To a solution of [PdClMe(N-N')] (0.22 mmol) in dichloromethane (3 mL), 1 equivalent of NaBAr'$_4$ (0.22 mmol) dissolved in the minim volume of acetonitrile was added. After stirring for 1 hour, the NaCl formed was filtrated. The solution was concentrated under vacuum and hexane was added to yield pale yellow solids.

[PdMe(NCMe)(1a)][BAr'$_4$] (4a)

Yield: 80%. Anal. Found: C, 50.70; H, 2.99; N, 4.45%. 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 9.37 (d, ^3J = 5.8 Hz, 1H, H_6), 9.06 (m, 1H, H_4), 8. 12 (d, ^3J = 7.2 Hz, 1H, H_3), 8.04 (t, ^3J = 5.8 Hz, 1H, H_5), 7.71 (s, 8H, H_b), 7.52 (s, 4H, H_d), 7.11- 6.84 (m, 10 H, Ph), 5.72 (d, ^3J = 11.4 Hz, 1H, $H_{5'}$), 5.49 (d, ^3J = 11.4 Hz, 1H, $H_{4'}$), 2.16 (s, 3H, Pd-NCCH_3), 0.31 (s, 3H, Pd-CH_3). ^{13}C NMR (100.5 MHz, $CDCl_3$, RT): 161.9 (q, $J_{C\text{-}B}$= 198.1 Hz, C_a), 152.3 (s, C_6), 140.4 (s, C_5), 135 (s, C_b), 129.5 – 123.4 (Ph), 117.7 (C_d), 70.7 (s, $C_{4'}$), 67.3 (s, $C_{5'}$), 31.3 (s, Pd-NCCH_3), 1.3 (s, Pd-CH_3).

[PdMe(NCMe)(1b)][BAr'$_4$] (4b)

Yield: 85%. Anal. Found: C, 50.76; H, 2.88; N, 3.44%. Calc. for $C_{62}H_{41}BF_{24}N_4Pd$: C, 52.62; H, 2.92; N, 3.96%. ^{1}H NMR (300 MHz, $CDCl_3$, RT): δ 8.44 (dd, ^3J = 5.2 Hz, ^4J = 1.8 Hz, 1H, H_6), 7.98 (dd, ^3J = 8.1 Hz, ^4J = 1 Hz, 1H, H_3), 7.86 (td, ^3J = 8.1 Hz, ^4J = 1.8 Hz, 1H, H_4), 7.72 (s, 8H, H_b), 7.53 (s, 4H,

H_d), 7.43 (ddd, ^3J = 8.1 Hz, ^4J = 5.2 Hz, ^5J = 1Hz, 1H, H_5), 7.36- 6.77 (m, 15H, Ph), 5.54 (d, ^3J = 11.7 Hz, 1H, $H_{5'}$), 5.43 (d, ^3J = 11.7 Hz, 1H, $H_{4'}$), 5.11 (d, ^2J = 17.6 Hz, 1H, CH_2), 4.45 (d, ^2J = 17.6 Hz, 1H, CH_2), 2.27 (s, 3H, CH_3CN), 0.56 (s, 3H, Pd-CH_3). ^{13}C NMR (75.4 MHz, $CDCl_3$, RT): δ 161.9 (q, ^2J= 49.8 Hz, 4C, Ca), 149.9 (s, C_6), 140.0 (s, C_4), 135.0 (s, 8C, C_b), 133.7-125.3 (Ph + C_5), 122.9 (s, C_3), 117.7 (s, 4C, C_d), 73.0 (s, $C_{5'}$), 69.1 (s, $C_{4'}$), 49.9 (s, CH_2), 3.2 (s, Pd-$NCCH_3$), -1.9 (s, Pd-CH_3).

[PdMe(NCMe)(1c)][BAr'$_4$] (4c)

Yield: 79%. Anal. Found: C, 50.29; H, 2.81; N, 3.33; S, 1.73%. Calc. for $C_{62}H_{41}N_4BClF_{24}O_2PdS$: C, 50.34; H, 2.79; N, 3.79; S, 2.17%. ^{1}H NMR (300 MHz, $CDCl_3$, RT): δ 8.58 (d, ^3J = 7.7 Hz, H_3), 8.52 (dd, ^3J = 5.6 Hz, ^4J = 1.4 Hz, H_6), 8.24 (dt, ^3J = 7.7 Hz, ^4J = 1.4 Hz, H_4), 7.75 (dd, ^3J = 7.7 Hz, ^3J = 5.6 Hz, H_5), 7.72 (s, 8H, H_b), 7.53 (s, 4H, H_d), 7.4 - 6.6 (m, 14 H, Harom.), 5.82 (d, ^3J = 11.6 Hz, 1H, $H_{5'}$), 5.39 (d, ^3J = 11.6 Hz, 1H, $H_{4'}$), 2.41 (s, 3H, CH_3-Ts-), 1.4 (s, 3H, Pd-$NCCH_3$), 0.99 (s, 3H, Pd-CH_3). ^{13}C NMR (100.5 MHz, $CDCl_3$, RT): 161.9 (J_{C-B}= 198.3 Hz, C_a), 150.1 (C_6), 140.3 (C_4), 135 (C_b), 130.4 (s, C_3), 129.9 (s, C_5), 129-120.4 (Ph), 117.7 (C_d), 74.1 ($C_{4'}$), 71.6 ($C_{5'}$), 21.8 (CH_3-Ts-), 5.32 (s, Pd-CH_3), 1.8 (s, Pd-NCCH_3).

[PdMe(NCMe)(1d)][BAr'$_4$] (4d)

Yield: 75%. Anal. Found: C, 48.34; H, 2.35; N, 3.71, S, 2.34%. Calc. for $C_{44}H_{34}BF_9N_4O_2PdS$: C, 46.16; H, 2.35; N, 3.84, S, 2.20%. ^{1}H NMR (400 MHz, $CDCl_3$, RT): δ 8.51 (dt, ^3J = 5.6 Hz, ^4J = 0.8 Hz, 1H, H_6), 8.41 (ddd, ^3J = 7.8 Hz, ^4J = 1.4 Hz, ^5J = 0.8 Hz, 1H, H_3), 8.24 (td, ^3J = 7.8 Hz, ^4J = 1.5 Hz, 1H, H_4), 7.76 (ddd, ^3J = 7.8 Hz, ^3J = 5.6 Hz, ^4J = 1.4 Hz, 1H, H_5), 7.72 (s, 8H, H_b), 7.53 (s,

4H, H_d), 7.2- 6.64 (m, 10H, Ph), 6.09 (d, ^3J = 8 Hz, 1H, $H_{4'}$ + $H_{5'}$), 6.01 (d, ^3J = 8 Hz, 1H, $H_{5'}$ + $H_{4'}$), 1.5 (s, 3H, Pd-NCCH_3), 1.06 (s, 3H, Pd-CH_3). ^{13}C NMR (100.5 MHz, $CDCl_3$, RT): δ 150.6 (s, C_6), 140.7 (s, C_4), 135 (s, C_b), 130.5 (s, C_5), 129.4 (s, C_3), 129.3- 123.4 (Ph), 117.7 (s, C_d), 74.9 (s, $C_{4'}$or $C_{5'}$), 73.2 (s, $C_{5'}$ or $C_{4'}$), 6.5 (s, Pd-CH_3), 2.0 (s, Pd-NCCH_3).

5.1.4.6. X-ray structure determination for complexes 2b' and 2d. For both complexes crystals suitable for X-ray analysis were obtained. Efforts to crystallize **2b** from $CDCl_3/Et_2O$ gave suitable crystals of **2b'**. Complex **2d** was crystallized from a CH_2Cl_2 /Et_2O mixture.

Crystal and experimental data are summarized in Table 5. All the data were collected on a Nonius DIP-1030H system with Mo-Kα radiation. A total of 30 frames were collected, each with an exposure time of 15 min, over half of the reciprocal space with a rotation of 6° about φ. The detector was at a distance of 90 mm from the crystal. Cell refinement, indexing and scaling of the data sets were carried out using Mosflm[33] and Scala.[33] The structures were solved by Patterson and Fourier analyses[34] and refined by the full-matrix least-squares method based on F^2 with all observed reflections.[35] Anisotropic temperature factors for all non-H atoms of the two complexes were used. In **2b'** the methyl ligand was partially exchanged by a chlorine atom and the site was refined with a mixed Cl/C species (any attempt to refine two separate peaks was unsatisfactory). Since the relative occupancies indicate a slight excess of the chlorine, 0.53/0.47, the compound is reported as a dichloro species. Moreover, a $CDCl_3$ solvent molecule was located in the difference Fourier map. The contribution of the

hydrogen atoms (excluding those of the disordered methyl) was included at calculated positions in the final cycles of refinements. All the calculations were performed using the WinGX System, Ver 1.64.03.[36]

Table 5. Crystal data and details of structure refinements for compounds **2b'** and **2d**.

	2b'. $CDCl_3$	**2d**
formula	$C_{28}H_{23}DCl_5N_3Pd$	$C_{22}H_{19}ClF_3N_3O_2PdS$
fw	686.15	588.31
temperature, K	150(2)	298(2)
crystal system	monoclinic	monoclinic
space group	P $2_1/c$ (No. 14)	P $2_1/c$ (No. 14)
a, Å	13.186(3)	10.698(3)
b, Å	12.405(3)	10.368(4)
c, Å	17.813(5)	21.206(5)
β, deg	105.01(2)	99.84(2)
V, Å^3	2814.3(12)	2317.5(12)
Z	4	4
density (calcd), g cm^{-3}	1.619	1.686
μ (Mo-Kα), mm^{-1}	1.158	1.055
F(000)	1376	1176
ϑ range for data collection	2.38 – 28.62	2.19 – 29.06
no. reflns collected/unique	13441/ 6978	11040/ 5719
R(int)	0.0565	0.0547
refinement method	Full-matrix least-squares on F^2	

no. reflections $I > 2\sigma(I)$	4790	3296
no. of parameters	335	299
goodness-of-fit	1.034	1.0
$R1$ (Fo)	0.0424	0.05
$wR2$ (Fo^2)	0.1035	0.1319
residuals, e Å^{-3}	0.531, –0.639	0.713, –0.803

5.1.4.7. CO/TBS copolymerization experiments

The 4-*tert*-butylstyrene was passed through a small column of Al_2O_3 prior to use. Chlorobenzene was used as purchased from Aldrich. In a typical procedure, the cationic precursor **4a-4d** (0.0125 mmol) was dissolved in 5 mL of chlorobenzene in a previously purged Schlenk and placed under CO at atmospheric pressure. 4-*tert*-butylstyrene was then introduced and the reaction was allowed to take place at room temperature. Workup included filtration of the reaction mixture through Kieselghur and precipitation of the polymeric material by adding the reaction solution dropwise into 100 mL of rapidly stirring methanol. The off-white powder was collected by filtration, washed with methanol and dried under vacuum.

5.1.4.8. Reactivity of the complexes [PdMe(NCMe)(N-N')][PF_6] (3a-3d) and [PdMe(NCMe)(N-N')][BAr'_4] (4b, 4d) with carbon monoxide

The reactivity of all the complexes [PdMe(NCMe)(N-N')][PF_6] (**3a-3d**) and [PdMe(NCMe)(N-N')][BAr'_4] (**4b, 4d**) with carbon monoxide was

studied *in situ* by ^{1}H and ^{13}C NMR spectroscopy. CD_2Cl_2 (0.7 mL) was placed in a NMR tube charged with the complex (7 x 10^{-3} mmol). The solution was cooled at 273 K and CO was bubbled for 5 min. The NMR sample was placed in a precooled NMR probe and spectra were obtained after 15 min.

[Pd(COMe)(CO)(1a)][PF_6] (7a). ^{1}H NMR (400 MHz, 273 K, CD_2Cl_2): see synthesis of the complex. ^{13}C NMR (100.5 MHz, CD_2Cl_2): δ 174.3 (s, Pd-CO), 210.8 (s, Pd-COMe).

[Pd(COMe)(CO)(1b)][PF_6] (7b). ^{1}H NMR (400 MHz, 273 K, CD_2Cl_2): δ 8.63 (d, ^{3}J = 4.9 Hz, 1H, H_6), 8.23 (m, 2H, H_3 + H_4), 7.89 (dd, ^{3}J= 6.4 Hz, ^{3}J= 4.9 Hz, 1H, H_5), 7.37-6.86 (m, 15H, Ph), 5.54 (d, ^{3}J = 12.7 Hz, 1H, $H_{5'}$ or $H_{4'}$), 5.47 (d, ^{3}J = 12.7 Hz, 1H, $H_{4'}$ or $H_{5'}$), 5.29 (d, ^{3}J = 17.1 Hz, 1H, CH_2), 4.50 (d, ^{3}J = 17.1 Hz, 1H, CH_2), 1.67 (s, 3H, Pd-COMe). ^{13}C NMR (100.5 MHz, 273 K, CD_2Cl_2): δ 174.3 (s, Pd-CO), 212.5 (s, Pd-COMe).

[Pd(COMe)(CO)(1c)][PF_6] (7c). Ratio of isomers in CD_2Cl_2 M:m = 4.2:1. ^{1}H NMR (400 MHz, 183 K, CD_2Cl_2): δ 8.64 (broad), 8.36 (broad), 8.00 (broad), 7.65-6.31 (broad), 5.76 (d, ^{3}J = 9.6 Hz, $H_{5'}$ or $H_{4'}$), 5.08 (d, ^{3}J = 9.6 Hz, $H_{4'}$ or $H_{5'}$), 2.74 (s, Pd-$COMe_m$), 2.48 (s, Me), 1.41 (s, Pd-$COMe_M$). ^{13}C NMR (100.5 MHz, 183 K, CD_2Cl_2): δ 170.7 (s, Pd-CO_m), 172.4 (s, Pd-CO_M), 211 (s, Pd-$COMe_M$), 217.1 (s, Pd-$COMe_m$).

[Pd(COMe)(CO)(1d)][PF_6] (7d). Ratio of isomers in CD_2Cl_2 M:m = 1.7:1. ^{1}H NMR (400 MHz, 183 K, CD_2Cl_2): δ 8.67–6.21 (broad), 2.76 (s, Pd-

$COMe_M$), 1.53 (s, Pd-$COMe_m$). ^{13}C NMR (100.5 MHz, 183 K, CD_2Cl_2): δ 170.3 (s, Pd-CO_M), 171.7 (s, Pd-CO_m), 210.2 (s, Pd-C(O)Me_m), 216.4 (s, Pd-$COMe_M$).

[Pd(COMe)(CO)(1b)][BAr'$_4$] (**8b**)**.** ^1H NMR (400 MHz, 193 K, CD_2Cl_2): δ 8.49 (d, ^3J = 5.2 Hz, 1H, H_6), 8.07 (t, ^3J = 7.7 Hz, 1H, H_4), 7.98 (d, ^3J = 7.7 Hz, 1H, H_3), 7.72 (s, 8H, H_b), 7.35 (s, 4H, H_d), 7.33-6.64 (m, 16H, H_5 + Ph), 5.59 (d, ^3J = 13 Hz, 1H, $H_{5'}$ or $H_{4'}$), 5.45 (d, ^3J = 13 Hz, 1H, $H_{5'}$ or $H_{4'}$), 5.23 (d, ^3J = 17.6 Hz, 1H, CH_2), 4.47 (d, ^3J = 17.6 Hz, 1H, CH_2), 1.50 (s, 3H, Pd-COMe).

[Pd(COMe)(CO)(1d)][BAr'$_4$] (8d). Ratio of isomers in CD_2Cl_2 M:m = 1.2:1. ^1H NMR (400 MHz, 193 K, CD_2Cl_2): δ 8.50-7.90 (broad), 7.71 (s, H_b), 7.52 (s, H_d), 7.44-5.96 (broad), 2.72 (s, 3H, Pd-$COMe_m$), 1.50 (s, 3H, Pd-$COMe_M$).

Synthesis of [Pd(COMe)(CO)(1a)][PF$_6$] (7a). 3a was dissolved in the minimum amount of dichloromethane and the solution was cooled to 273 K. CO was bubbled through the solution for 20 minutes and the color changed from light to bright yellow. Addition of diethyl ether at room temperature resulted in the precipitation of the desired complex as a light yellow solid. Yield: 70 %. Anal. Calc. for $C_{23}H_{20}F_6N_3O_2PPd$: C, 44.43; H, 3.24; N, 6.75. Found: C, 43.56; H, 3.62; N, 6.50. ^1H NMR (400 MHz, CD_2Cl_2, RT): δ 8.50 (d, ^3J = 5.2 Hz, 1H, H_6), 8.33 (m, 2H, H_3 and H_4), 7.85 (m, 1H, H_5), 7.52 (s, 1H, Ph), 7.13-6.89 (m, 9H, Ph), 5.84 (d, 1H, ^3J = 12.2 Hz, $H_{5'}$ or $H_{4'}$), 5.49 (d, 1H, ^3J = 12.2 Hz, $H_{4'}$ or $H_{5'}$), 1.74 (s, 3H, Pd-COMe).

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5.1.5. References

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