

Influence of Pyridine-Imidazoline Ligands on the Reactivity of Palladium-Methyl Complexes with Carbon Monoxide

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Two series of monocationic Pd-methyl complexes $[\text{Pd}(\text{Me})(\text{NCMe})(\text{N}-\text{N}')][\text{X}]$ ($\text{X} = \text{PF}_6^-$, BAR'_4^-) were synthesized, where N–N' are pyridine-imidazoline ligands of C_1 symmetry, electronically 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 $[\text{Pd}(\text{Me})_{2-n}\text{Cl}_n(\text{N}-\text{N}')] (n = 1, 2)$ 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. One isomer is always observed when the anion is BAR'_4^- : the *cis* when electron-donating substituents are present on the imidazoline ring and the *trans* when electron-withdrawing groups are present. Both *cis* and *trans* isomers were found for the latter kind of ligands, when PF_6^- was 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. For the complexes with electron-donating substituents, the intermediates of the insertion reaction were detected, namely, Pd-methyl-carbonyl and Pd-acyl-acetonitrile species. Moreover, only one stereoisomer was seen to form: the one with the Pd-acyl group *trans* to the imidazoline ring. For the other ligands, the final product is a mixture of *cis* and *trans* stereoisomers for both anions, and their distribution depends on the type of ligand. 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.

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/olefin 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 olefin.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 olefin 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)

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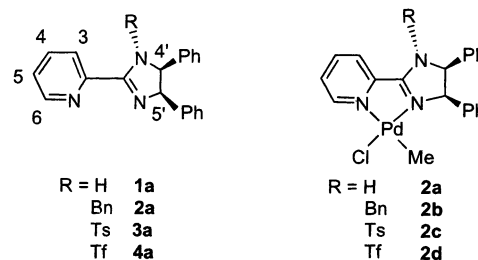
insertion of CO into the Pd–OMe group; (iii) insertion of olefin into the Pd–H bond. Several groups have focused on the study of these insertion reactions and used Pd(II) systems containing bidentate nitrogen ligands. For the phenanthroline-based system [Pd(Me)–(L)(phen)][BAR'₄] (L = solvent molecule; Ar' = 3,5-(CF₃)₂C₆H₃), 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

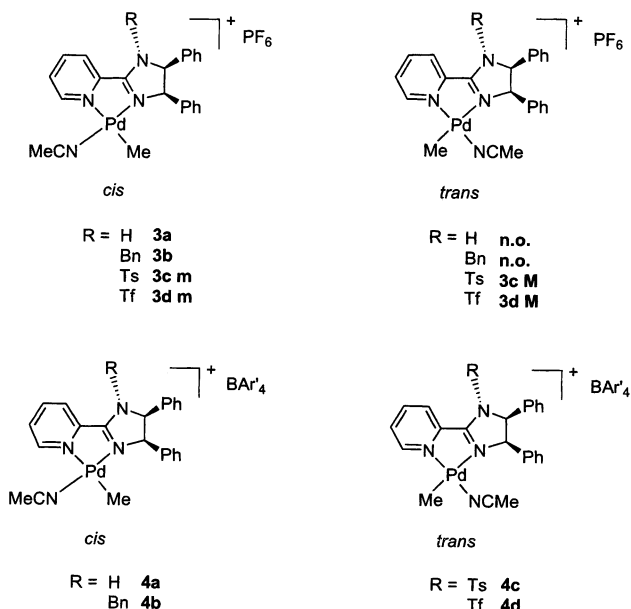
When the copolymerization reaction involves styrene, the ligand can also play a role in controlling the stereoregularity of the synthesized polyketone. In the case of bisnitrogen planar ligands of C_{2v} or C_s symmetry (e.g., 2,2'-bipyridine, 1,10-phenanthroline, 5-NO₂-1,10-phenanthroline, 2,2'-bipyrimidine, diazabutadiene derivatives, pyridine-pyrazole) the syndiotactic polyketone is obtained.^{7–12} C₂-symmetry chiral bidentate ligands (e.g., bisoxazoline, dioxazoline, diketimines) provide good enantioface control and give isotactic copolymers.^{10,13,14} Interestingly the C₁-symmetrical chiral ligands (e.g., N–N', P–N, P–OP) led to syndiotactic¹⁵ 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 olefin 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}

Scheme 1. Pyridine-Imidazoline Ligands Studied with Their Numbering Scheme and the Corresponding Palladium Neutral Complexes



Scheme 2. Cationic Palladium Complexes 3a–3d and 4a–4d (M = major isomer, m = minor isomer; n.o. = not observed)



We have recently reported the synthesis of C₁-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 [Pd(Me)(NCMe)(N–N')][BAR'₄] (**4a–4d**) (Scheme 2) 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.²⁰

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 [Pd(Me)₂–nCl_n(N–N')] (n = 1, 2; N–N' = **1d**, **1b**) were determined. The reactivity of the palladium-methyl precursors [Pd(Me)(NCMe)(N–N')][PF₆] (**3a–3d**) toward CO was investigated in depth by in situ ¹H and

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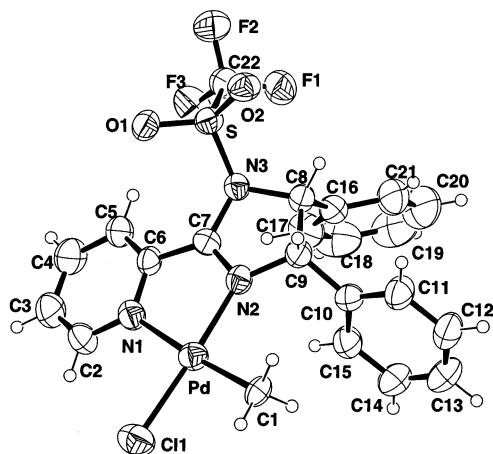


Figure 1. Molecular structure (ORTEP drawing, 50% thermal ellipsoids) with atom-labeling scheme of **2d**.

^{13}C NMR experiments. The complete sequence of intermediates was established for complexes with ligands **1a** and **1b**. The $[\text{Pd}(\text{COMe})(\text{CO})(\mathbf{1a})][\text{PF}_6]$ was isolated and characterized. Some correlations between NMR results and the catalytic activity of the precursors are also discussed.

Results and Discussion

Synthesis and Characterization of $[\text{Pd}(\text{Me})(\text{Cl})(\text{N}-\text{N}')] \mathbf{2a}-\mathbf{2d}$ and of $[\text{Pd}(\text{Me})(\text{NCMe})(\text{N}-\text{N}')][\text{X}] \mathbf{3a}-\mathbf{3d}$, and $\mathbf{4a}-\mathbf{4d}$. We have recently communicated the synthesis of complexes $[\text{Pd}(\text{Me})(\text{NCMe})(\text{N}-\text{N}')][\text{BAR}'_4]$, **4a-4d**, together with their catalytic behavior in the CO/TBS copolymerization reaction.²⁰ To simplify the ^1H NMR spectra, the related cationic palladium complexes with PF_6^- as the counterion have been synthesized in a similar way, starting from the corresponding neutral derivatives $[\text{Pd}(\text{Me})(\text{Cl})(\text{N}-\text{N}')] \mathbf{2a}-\mathbf{2d}$, by using AgPF_6 in place of BAR'_4 (Schemes 1 and 2).

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 $[\text{PdCl}_2(\mathbf{1b})]$, **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.

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

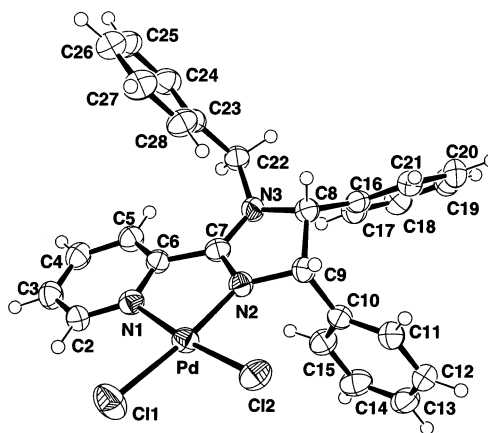


Figure 2. Molecular structure (ORTEP drawing, 40% thermal ellipsoids) with atom-labeling scheme of **2b'**.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for Complexes **2b' and **2d****

	2b' ·CDCl ₃ X = Cl(2) ^a	2d 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 Section).

comparison, the Pd–N(py) and Pd–N(imidazoline) bond lengths in the crystal structure of the bischelated head–tail $[\text{Pd}(\mathbf{1b})_2]^{2+}$ 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 indicate 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 $[\text{Pd}(\text{Me})(\text{Cl})(2,9\text{-dm-phen})]$ derivative (2,9-dm-phen = 2,9-dimethyl-1,10-phenanthroline; Pd–Me = 2.015(6) Å, Pd–Cl = 2.312(1) Å, Pd–N(1) = 2.229(4) Å, Pd–N(2) = 2.066(4) Å).²²

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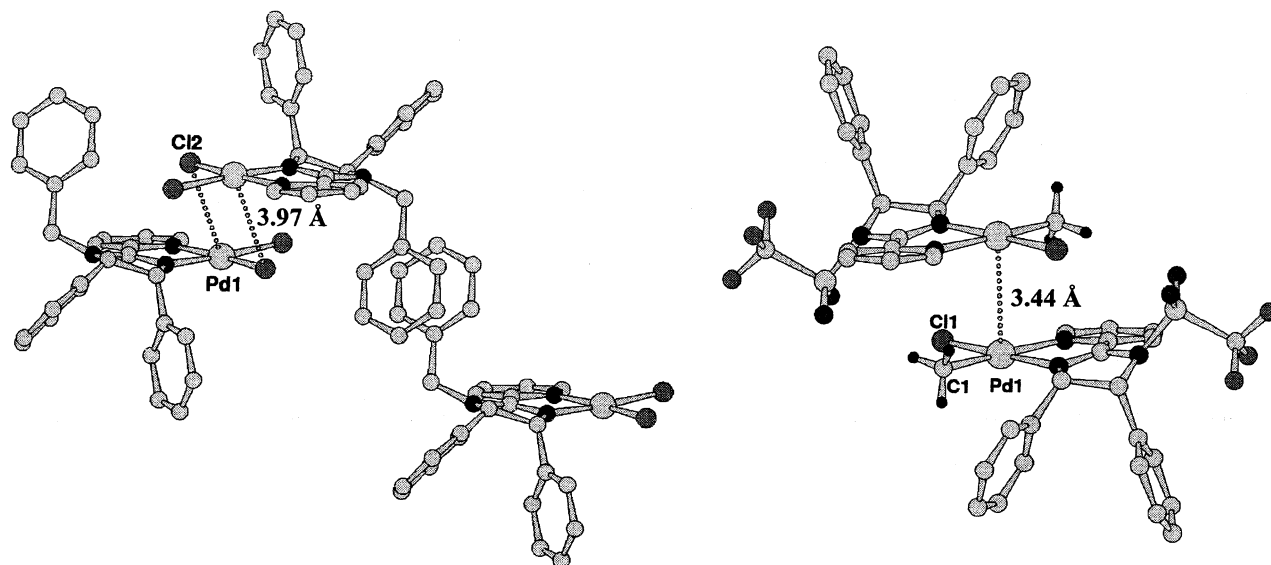


Figure 3. Crystal packing: head-to-tail arrangement of **2b'** and **2d** molecules related by a center of symmetry.

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 CF₃SO₂. 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).

The neutral derivatives **2a–2d** were characterized in solution by ¹H NMR spectroscopy. For all the complexes **2a–2d** in the aromatic region of the spectra, the H⁶ 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 shows an NOE effect with the H⁵ 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 [Pd(Me)(Cl)(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 5' 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 [Pd(Me)(Cl)(pyox)].²⁸

No crystal suitable for structural determination was obtained for the cationic complexes **3a–3d** or **4a–4d** (Scheme 2). They were completely characterized in

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Table 2. Selected ^1H 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 8.79 (d, $^3J = 4.4$)	M 1.10 (s) m 0.32 (s)	M 1.59 (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 8.88 (d, $^3J = 5.1$)	M 1.22 (s) m 0.46 (s)	M 1.64 (s) m 2.47 (s)
4d	8.51 (d, $^3J = 5.6$)	1.06 (s)	1.50 (s)

^a ^1H 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 ^1H NMR spectra recorded in CD_2Cl_2 at room temperature. ^c Overlapped with H^3 signals, no multiplicity could be assigned.

solution by recording the ^1H NMR spectra in CDCl_3 or in CD_2Cl_2 (Table 2). The most significant signals are those related to H^6 for the ligand and to the Pd-Me and the Pd-NCMe fragments. The signals were assigned to the protons on the basis of selective decoupling experiments and on the multiplicity of the signals.

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^5 was evident. This indicates that only one species was present in solution, whose Pd–Me bond was *cis* to the imidazoline ring (Scheme 2). This stereochemistry is analogous to that observed in the neutral derivatives and in the cationic species **4a–4b** with BAR'_4^- as anion.²⁰ (Isomers are *cis* or *trans* depending on the position of the methyl group with respect to the imidazoline ring.)

In the spectra of complexes with the electron-withdrawing substituents **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^5 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 $[\text{Pd}(\text{Me})(\text{NCMe})(\text{N}-\text{N}')][\text{PF}_6]$ (N–N'

= **1c**, **1d**), which are differentiated by the *trans* or *cis* coordination of the methyl group to the imidazoline ring (Scheme 2). 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 $[\text{Pd}(\text{Me})(\text{NCMe})(\text{N}-\text{N}')][\text{BAR}'_4]$, **4c–4d**, which show only the *trans* isomer in solution (Table 2).²⁰

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).²⁰ When the anion changes from BAR'_4^- to PF_6^- , there is no difference for complexes with the ligand **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 $[\text{Pd}(\text{OMe}-\text{COD})(\text{bipy})][\text{Y}]$ ($\text{OMe}-\text{COD} = \eta^1, \eta^2\text{-C}_8\text{H}_{12}\text{OMe}$; 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 toward 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 favors 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 $[\text{Pd}(\text{Me})(\text{NCMe})(\text{L}-\text{L}')][\text{X}]$, involved in the copolymerization process, has been observed in two other examples, where L–L' is 2-(1-(3,5-dimethylpyrazolyl)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 stereoisomer mixture.

Reactivity of $[\text{Pd}(\text{Me})(\text{NCMe})(\text{N}-\text{N}')][\text{X}]$ Complexes, **3a–3d and **4b**, **4d** with Carbon Monoxide.** All the complexes **3a–3d** were reacted with carbon monoxide, and the reaction was studied by in situ ^1H and ^{13}C NMR spectroscopy.

When carbon monoxide is bubbled for 5 min through a solution of $[\text{Pd}(\text{Me})(\text{NCMe})(\text{1a})][\text{PF}_6]$, **3a**, or of $[\text{Pd}(\text{Me})(\text{NCMe})(\text{1b})][\text{PF}_6]$, **3b**, in CD_2Cl_2 , at 273 K, five new singlets (e.g., for **3a**+CO: 0.88, 1.52, 1.69, 2.10, 2.37 ppm) are present in the aliphatic region of the ^1H NMR spectra, recorded after 15 min, together with the resonance due to the methyl group of the precursor (Figure 4a,b) (Table 3). When labeled ^{13}CO is used, in

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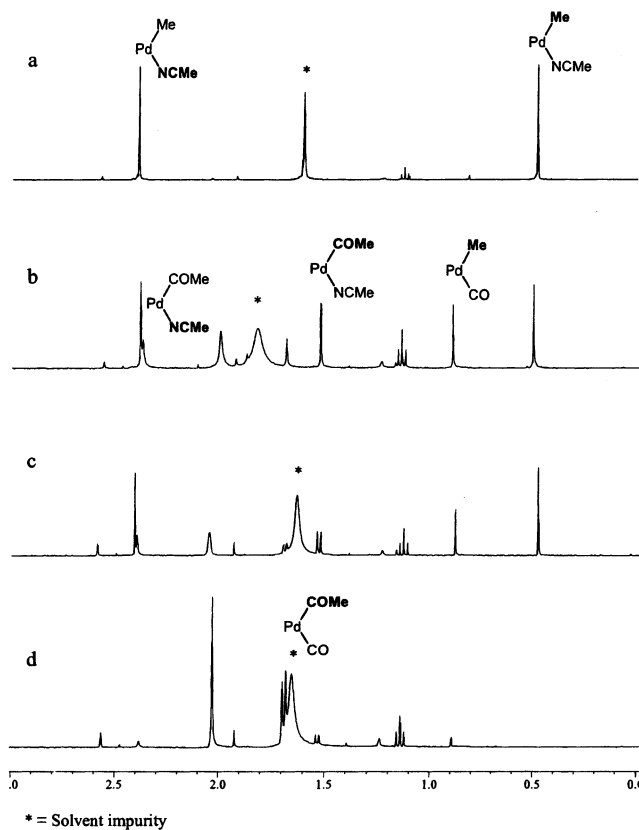


Figure 4. Reactivity of **3a** with carbon monoxide. ^1H NMR spectra recorded in CD_2Cl_2 at 273 K, region of aliphatic protons: (a) spectrum of **3a**; (b) spectrum of **3a** + CO; (c) spectrum of **3a** + ^{13}CO ; (d) spectrum of **3a** + excess of ^{13}CO .

Table 3. Selected ^1H and ^{13}C NMR Data for Reactivity of Complexes **3a and **3b** with CO^a**

^1H NMR				
Compound				
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.

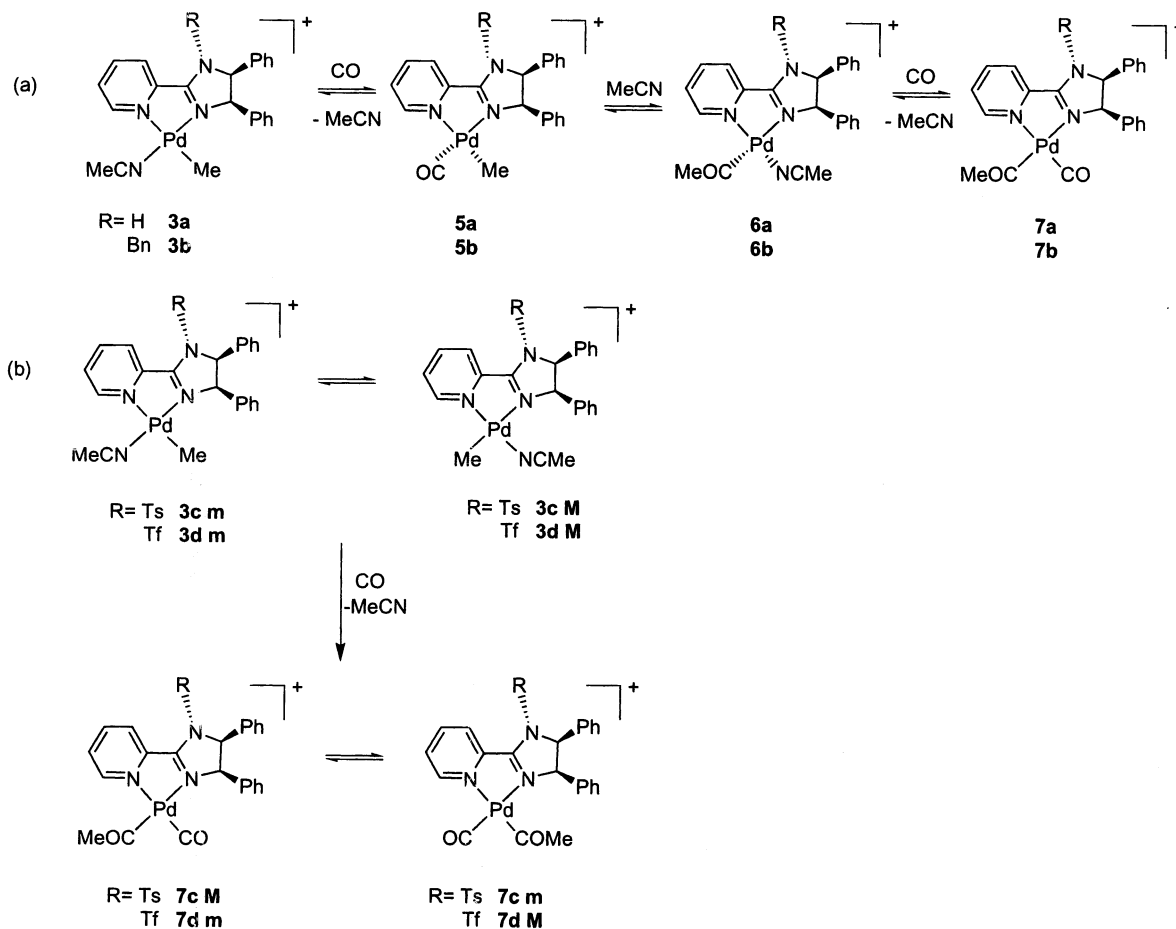
the ^1H NMR spectrum two singlets (e.g., for **3a**+CO: 1.52 and 1.69 ppm) become doublets, indicating that they belong to two acyl groups (Figure 4c). In the corresponding ^{13}C NMR spectra there are four signals (e.g., for **3a**+CO: 174.3, 176.6, 210.8, 220.9 ppm); the two at lower frequency are 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 ^1H NMR spectra: a doublet and a singlet (e.g., for **3a**+CO: 1.69, 2.10 ppm) (Figure 4d). The same is true of the ^{13}C NMR spectra (e.g., for **3a**+CO: 174.3, 210.8 ppm). The signal at 2.10 ppm in the ^1H NMR spectra is due to free acetonitrile.

These NMR data indicate that the final product corresponds to the palladium-acyl-carbonyl species $[\text{Pd}(\text{COMe})(\text{CO})(\text{N}-\text{N}')][\text{PF}_6]$ ($\text{N}-\text{N}' = \mathbf{1a}, \mathbf{1b}, \mathbf{7a}$ or $\mathbf{7b}$), which is the result of inserting CO into the Pd-Me bond (Scheme 3). 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 $[\text{Pd}(\text{Me})(\text{CO})(\mathbf{1a})][\text{PF}_6]$, **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 palladium-acyl-acetonitrile intermediate $[\text{Pd}(\text{COMe})(\text{NCMe})(\mathbf{1a})][\text{PF}_6]$, **6a**. The corresponding signal in the ^{13}C NMR spectrum is at 220.9 ppm.

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 ^1H 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 $[\text{Pd}(\text{Me})(\text{NCMe})(\mathbf{1a})][\text{PF}_6]$ at 273 K. It was stored at 278 K without decomposition. Its ^1H 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 $[\text{Pd}(\text{Me})(\text{NCMe})(\mathbf{1c})][\text{PF}_6]$, **3c**, or of $[\text{Pd}(\text{Me})(\text{NCMe})(\mathbf{1d})][\text{PF}_6]$, **3d**, in CD_2Cl_2 , at 273 K, the ^1H 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, 1.98 ppm) and the complete disappearance of the precursor's resonance (Table 4). When the labeled ^{13}CO was used, no variation was observed in the ^1H NMR spectrum. In the corresponding ^{13}C NMR spectrum two broad signals appeared (e.g., for **3c**+CO: 172.8, 211.5 ppm) (Figure 5a and Table 4) due to a Pd-CO and a Pd-COMe moiety, respectively. Low-temperature NMR studies were performed by decreasing the temperature from 263 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 and 2.74 ppm), and there was a sharp singlet at 1.99 ppm. The two peaks were of different intensity, the resonance at 1.41 ppm being 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:

Scheme 3. Reactivity of Complexes with Carbon Monoxide: (a) 3a and 3b; (b) 3c and 3d

the peak at 2.33 ppm at 263 K, which disappears at 233 K, splits into two peaks (2.76 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 ^1H 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.

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 and 2.74 ppm, for the reactivity of **3c** with CO (or 1.52 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 $[\text{Pd}(\text{COMe})(\text{CO})(\text{N}-\text{N}')][\text{PF}_6]$ ($\text{N}-\text{N}' = \mathbf{1c}, \mathbf{1d}, \mathbf{7c}$ or $\mathbf{7d}$), which is present as a mixture of two isomers in equilibrium (Scheme 3). 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**.

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*- $[\text{Pd}(\text{COMe})(\text{CO})(\mathbf{1b})][\text{BAR}'_4]$ (**8b**) has been formed. This signal is shifted at 1.50 ppm

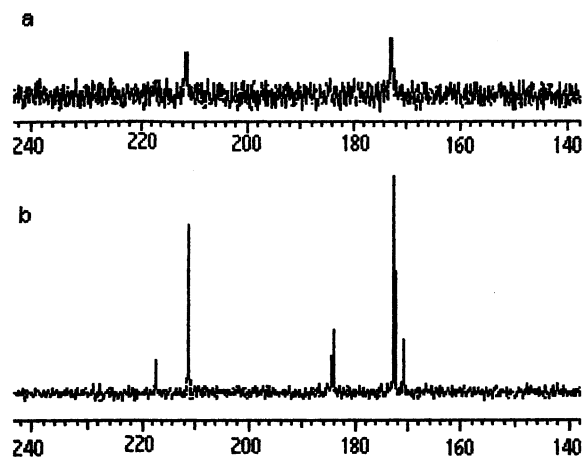




Figure 5. Reactivity of **3c** with ^{13}CO . ^{13}C NMR spectra recorded in CD_2Cl_2 : (a) at $T = 263$ K; (b) at $T = 183$ K.

Table 4. Selected ^1H 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 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 and 1.50 ppm) when the temperature was decreased down to 193 K. Therefore, both *cis* and *trans* $[\text{Pd}(\text{COMe})(\text{CO})(\mathbf{1d})][\text{BAR}'_4]$ (**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 is partially lost after the reaction 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 olefin.

Complexes **4a**–**4d** have been used as catalyst precursors for the CO/4-*tert*-butylstyrene copolymerization reaction. The nature of the ligand was found to have an effect both on the productivity of the system and on the tacticity of the polyketones obtained.²⁰ Complexes **4a**, **4b** showed little activity and gave atactic polyketones with a slight prevalence of the isotactic triad. On the other hand, the syndiotactic polyketone was obtained with **4c** and **4d**. Moreover, the last precursor showed 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 olefin is the rate-determining step of the copolymerization reaction and that the enantioface selection during the olefin insertion is due to the chain end or to the enantiomeric 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 olefin *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 olefin. The greater reactivity of the stereoisomer with the Pd-COMe fragment *cis* to imidazoline might favor the insertion of the olefin preferentially under chain-end control and lead to a prevailing syndiotactic copolymer. However, due to the similarity of species **3a**–**3d**, two regioisomeric intermediates might be present for all the complexes. As a consequence, the variation in the microstructure of the produced copolymers should arise from different contribution of these regioisomers.

Conclusions

Pyridine-imidazoline ligands of C_1 symmetry, electronically modified with different R substituents, provide information about the stereochemistry of the intermediates in the copolymerization reaction.

The neutral complexes $[\text{Pd}(\text{Me})(\text{Cl})(\text{N}-\text{N}')]]$ have the same stereochemistry with all the ligands, and the methyl group is *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 $[\text{Pd}(\text{COMe})(\text{CO})(\text{N}-\text{N}')][\text{X}]$ stereoisomers were detected and char-

acterized. Finally, the reactivity of the cationic Pd-Me complexes toward CO was seen to be related to the copolymerization results. The catalytic activity of the hexafluorophosphate derivatives as well as of the stereochemistry of the synthesized polyketones is being evaluated at present.

Experimental Section

General Comments. Commercial $\text{Na}_2[\text{PdCl}_4]$ and $[\text{Sn}(\text{CH}_3)_4]$ 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. Ligands **1a–1d** were prepared according to published methods.²⁰ The salt BAR'_4 ($\text{Ar}' = 3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3$) 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 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. Elemental analyses were carried out on a Carlo Erba microanalyzer EA 1108. MS (FAB positive) were obtained on a Fisons V6-Quattro instrument.

Synthesis. $\text{Na}_2[\text{PdCl}_4]$, used as starting material, was transformed into $[\text{PdCl}_2(\text{COD})]$ ($\text{COD} = 1,5\text{-cyclooctadiene}$) according to the literature.³² $[\text{Pd}(\text{Me})(\text{Cl})(\text{COD})]$, obtained from $[\text{PdCl}_2(\text{COD})]$,²⁶ was transformed into $[\text{Pd}(\text{Me})(\text{Cl})(\text{N}-\text{N}')](\mathbf{2a}-\mathbf{2d})$ following the method already reported.²⁰ Abstraction of the chloride to synthesize the monocationic derivatives (**3a–3d** and **4a–4d**) was done both with AgPF_6 (see below) and with BAR'_4 .

$[\text{Pd}(\text{Me})(\text{Cl})(\text{N}-\text{N}')](\mathbf{2a}-\mathbf{2d})$. The synthesis has already been reported.²⁰ **2a:** ^1H 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, $^3J = 5.1$ Hz, $^4J = 1.2$ Hz, 1H, H^5), 6.89–6.75 (m, 10H, Ph), 5.60 (d, $^3J = 11.4$ Hz, 1H, H^5), 5.4 (d, $^3J = 11.4$ Hz, 1H, H^4), 0.36 (s, 3H, Pd-Me). **2b:** ^1H NMR (400 MHz, CDCl_3 , rt): δ 9.22 (d, $^3J = 4.8$ Hz, 1H, H^6), 7.86 (m, 2H, $\text{H}^3 + \text{H}^4$), 7.59 (q, $^3J = 5.2$ Hz, $^4J = 5.2$ Hz, 1H, H^5), 7.25–6.76 (m, 15H, Ph), 5.46 (d, $^3J = 11.6$ Hz, 1H, H^4), 5.37 (d, $^3J = 11.6$ Hz, 1H, H^5), 5.03 (d, $^2J = 17.2$ Hz, 1H, CH_2), 4.33 (d, $^2J = 17.2$ Hz, 1H, CH_2), 0.49 (s, 3H, Pd-Me). **2c:** ^1H NMR (400 MHz, CDCl_3 , rt): δ 9.20 (ddd, $^3J = 5.1$ Hz, $^4J = 2.7$ Hz, $^5J = 1.2$ Hz, 1H, H^6), 8.64 (dt, $^3J = 7.9$ Hz, $^4J = 1.3$ Hz, $^5J = 1.3$ Hz, 1H, H^3), 8.16 (td, $^3J = 7.9$ Hz, $^4J = 2.7$ Hz, 1H, H^4), 7.82 (ddd, $^3J = 7.9$ Hz, $^3J = 5.1$ Hz, $^4J = 1.3$ Hz, 1H, H^5), 7.75 (d, $^3J = 7.5$ Hz, 2H, H^{arom} , Ts), 7.51 (d, $^3J = 7.5$ Hz, 2H, H^{arom} , Ts), 7.07–6.71 (m, 10H, Ph), 5.67 (d, $^3J = 9$ Hz, 1H, H^5), 5.05 (d, $^3J = 9$ Hz, 1H, H^4), 2.55 (s, 3H, Me Ts), 0.28 (s, 3H, Pd-Me). **2d:** ^1H 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, $\text{H}^{4'} + \text{H}^5$), 0.45 (s, 3H, Pd-Me).

$[\text{Pd}(\text{Me})(\text{NCMe})(\text{N}-\text{N}')] [\text{PF}_6]$ (3a–d**).** To a solution of $[\text{Pd}(\text{Me})(\text{Cl})(\text{N}-\text{N}')] (0.18 \text{ mmol})$ in dichloromethane (3 mL) was added 1.2 equiv of $\text{AgPF}_6 (0.22 \text{ mmol})$ dissolved in acetonitrile (1 mL). After stirring for 1 h in the absence of light, the AgCl formed was filtrated, and when diethyl ether was added, the solution was concentrated under vacuum to yield a pale yellow solid. Average yield: 75%.

$[\text{Pd}(\text{Me})(\text{NCMe})(\mathbf{1a})] [\text{PF}_6] \cdot 0.3\text{Et}_2\text{O}$ (3a**).** Anal. Calcd for $\text{C}_{24.3}\text{H}_{26.3}\text{F}_6\text{N}_4\text{O}_{0.3}\text{PPd}$: C, 42.99; H, 3.39; N, 8.88. Found: C, 42.75; H, 3.35; N, 8.66. ^1H NMR (400 MHz, CDCl_3): 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-NCMe), 0.54 (s, 3H, Pd-Me). MS (FAB positive) m/z 461.2 $[\text{M}]^+$, 404 $[\text{M} - \text{NCMe}]^+$.

$[\text{Pd}(\text{Me})(\text{NCMe})(\mathbf{1b})] [\text{PF}_6] \cdot 0.3\text{Et}_2\text{O}$ (3b**).** Anal. Calcd for $\text{C}_{31.3}\text{H}_{32.3}\text{F}_6\text{N}_4\text{O}_{0.3}\text{PPd}$: C, 47.90; H, 4.20; N, 7.26. Found: C, 48.00; H, 3.98; N, 7.46. ^1H NMR (400 MHz, CDCl_3): δ 8.99 (d, $^3J = 4.4$ Hz, 1H, H^6), 8.02 (m, 3H, H^3 , $\text{H}^4 + \text{H}^5$), 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-NCMe), 0.47 (s, 3H, Pd-Me).

$[\text{Pd}(\text{Me})(\text{NCMe})(\mathbf{1c})] [\text{PF}_6]$ (3c**).** Anal. Calcd for $\text{C}_{30}\text{H}_{29}\text{F}_6\text{N}_4\text{O}_2\text{PPdS}$: C, 47.35; H, 3.84; N, 7.36. Found: C, 46.99; H, 3.70; N, 7.34. Ratio of isomers in CD_2Cl_2 M:m = 2:1. Major: ^1H NMR (400 MHz, CD_2Cl_2): 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, $^3J = 6$ Hz, 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, Me Ts), 1.59 (s, 3H, Pd-NCMe), 1.10 (s, 3H, Pd-Me). 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, Me Ts), 2.45 (s, 3H, Pd-NCMe), 0.32 (s, 3H, Pd-NCMe). MS (FAB positive) m/z 615.1 $[\text{M}]^+$, 558 $[\text{M} - \text{Me}, \text{NCMe}]^+$, 403 $[\text{M} - \text{Me}, \text{NCMe}, \text{Ts}]^{2+}$.

$[\text{Pd}(\text{Me})(\text{NCMe})(\mathbf{1d})] [\text{PF}_6]$ (3d**).** Anal. Calcd for $\text{C}_{24}\text{H}_{22}\text{F}_6\text{N}_4\text{O}_2\text{PPd}$: C, 39.01; H, 3.00; N, 7.58. Found: C, 38.87; H, 2.94; N, 7.39. Ratio of isomers in CD_2Cl_2 M:m = 3:1. Major: ^1H NMR (400 MHz, CD_2Cl_2): δ 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, $\text{H}^{4'} + \text{H}^5$), 1.64 (s, 3H, Pd-NCMe), 1.22 (s, 3H, Pd-Me). 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, $\text{H}^{4'}$ or H^5), 6.03 (d, $^3J = 8.8$ Hz, 1H, $\text{H}^{4'}$ or H^5), 2.47 (s, 3H, Pd-NCMe), 0.46 (s, 3H, Pd-Me). MS (FAB positive) m/z 593.1 $[\text{M}]^+$, 536.0 $[\text{M} - \text{Me}, \text{NCMe}]^+$, 403.1 $[\text{M} - \text{Me}, \text{NCMe}, \text{Ts}]^{2+}$.

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 $\text{CDCl}_3/\text{Et}_2\text{O}$ gave suitable crystals of **2b'**. **2d** was crystallized from a $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ mixture.

Crystal and experimental data are summarized in Table 5. All the data were collected on a Nonius DIP-1030H system with Mo K α 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 Mosflm³³ and Scala.³³ The structures were solved by Patterson and Fourier analyses³⁴ and refined by the full-matrix least-squares

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Table 5. Crystal Data and Details of Structure Refinements for Compounds 2b' and 2d

	2b'·CDCl ₃	2d
formula	C ₂₈ H ₂₃ DCl ₅ N ₃ Pd	C ₂₂ H ₁₉ ClF ₃ N ₃ O ₂ PdS
fw	686.15	588.31
temp, K	150(2)	298(2)
cryst syst	monoclinic	monoclinic
space group	<i>P</i> 2 ₁ / <i>c</i> (No. 14)	<i>P</i> 2 ₁ / <i>c</i> (No. 14)
<i>a</i> , Å	13.186(3)	10.698(3)
<i>b</i> , Å	12.405(3)	10.368(4)
<i>c</i> , Å	17.813(5)	21.206(5)
β , deg	105.01(2)	99.84(2)
<i>V</i> , Å ³	2814.3(12)	2317.5(12)
<i>Z</i>	4	4
density (calcd), g cm ⁻³	1.619	1.686
μ (Mo K α), mm ⁻¹	1.158	1.055
<i>F</i> (000)	1376	1176
θ range for data collection	2.38–28.62	2.19–29.06
no. reflns collected/unique	13441/6978	11040/5719
<i>R</i> (int)	0.0565	0.0547
refinement method	full-matrix least-squares on <i>F</i> ²	
no. of reflns <i>I</i> > 2 σ (<i>I</i>)	4790	3296
no. of params	335	299
goodness-of-fit	1.034	1.032
<i>R</i> 1 (<i>F</i> _o)	0.0424	0.0509
<i>wR</i> 2 (<i>F</i> _o ²)	0.1035	0.1319
residuals, e Å ⁻³	0.531, –0.639	0.713, –0.803

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 CDCl₃ 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

Reactivity of the Complexes [Pd(Me)(NCMe)(N–N')][PF₆] (3a–3d) and [Pd(Me)(NCMe)(N–N')][BAR₄] (4b, 4d) with Carbon Monoxide. The reactivity of all the complexes [Pd(Me)(NCMe)(N–N')][PF₆] (**3a–3d**) and [Pd(Me)(NCMe)(N–N')][BAR₄] (**4b, 4d**) with carbon monoxide was studied in situ by ¹H and ¹³C NMR spectroscopy. CD₂Cl₂ (0.7 mL) was placed in a NMR tube charged with the complex (7 × 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)][PF₆] (7a). ¹H NMR (400 MHz, 273 K, CD₂Cl₂): see synthesis of the complex. ¹³C NMR (100.5 MHz, CD₂Cl₂): δ 174.3 (s, Pd–CO), 210.8 (s, Pd–COMe).

[Pd(COMe)(CO)(1b)][PF₆] (7b). ¹H NMR (400 MHz, 273 K, CD₂Cl₂): δ 8.63 (d, ³*J* = 4.9 Hz, 1H, H⁶), 8.23 (m, 2H, H³ + H⁴), 7.89 (dd, ³*J* = 6.4 Hz, ³*J* = 4.9 Hz, 1H, H⁵), 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, CH₂), 4.50 (d, ³*J* = 17.1 Hz, 1H, CH₂), 1.67 (s, 3H, Pd–COMe). ¹³C NMR (100.5 MHz, 273 K, CD₂Cl₂): δ 174.3 (s, Pd–CO), 212.5 (s, Pd–COMe).

[Pd(COMe)(CO)(1c)][PF₆] (7c). Ratio of isomers in CD₂Cl₂ M:m = 4.2:1. ¹H NMR (400 MHz, 183 K, CD₂Cl₂): δ 8.64 (br), 8.36 (br), 8 (br), 7.65–6.31 (br), 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). ¹³C NMR (100.5 MHz, 183 K, CD₂Cl₂): 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)][PF₆] (7d). Ratio of isomers in CD₂Cl₂ M:m = 1.7:1. ¹H NMR (400 MHz, 183 K, CD₂Cl₂): δ 8.67–6.21 (br), 2.76 (s, Pd–COMe_m), 1.53 (s, Pd–COMe_m). ¹³C NMR (100.5 MHz, 183 K, CD₂Cl₂): 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)][BAR₄] (8b). ¹H NMR (400 MHz, 193 K, CD₂Cl₂): δ 8.49 (d, ³*J* = 5.2 Hz, 1H, H⁶), 8.07 (t, ³*J* = 7.7 Hz, 1H, H⁴), 7.98 (d, ³*J* = 7.7 Hz, 1H, H³), 7.72 (s, 8H, H^{BAR₄}), 7.35 (s, 4H, H^{BAR₄}), 7.33–6.64 (m, 16H, H⁵ + Ph), 5.59 (d, ³*J* = 13 Hz, 1H, H^{5'} or H^{4'}), 5.45 (d, ³*J* = 13 Hz, 1H, H^{5'} or H^{4'}), 5.23 (d, ³*J* = 17.6 Hz, 1H, CH₂), 4.47 (d, ³*J* = 17.6 Hz, 1H, CH₂), 1.50 (s, 3H, Pd–COMe).

[Pd(COMe)(CO)(1d)][BAR₄] (8d). Ratio of isomers in CD₂Cl₂ M:m = 1.2:1. ¹H NMR (400 MHz, 193 K, CD₂Cl₂): δ 8.50–7.90 (br), 7.71 (s, H^{BAR₄}), 7.52 (s, H^{BAR₄}), 7.44–5.96 (br), 2.72 (s, 3H, Pd–COMe_m), 1.50 (s, 3H, Pd–COMe_m).

Synthesis of [Pd(COMe)(CO)(1a)][PF₆] (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 min, 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. Calcd for C₂₃H₂₀F₆N₃O₂PPd: C, 44.43; H, 3.24; N, 6.75. Found: C, 43.56; H, 3.62; N, 6.5. ¹H NMR (400 MHz, CD₂Cl₂, rt): δ 8.50 (d, ³*J* = 5.2 Hz, 1H, H⁶), 8.33 (m, 2H, H³ and H⁴), 7.85 (m, 1H, H⁵), 7.52 (s, 1H, Ph), 7.13–6.89 (m, 9H, Ph), 5.84 (d, 1H, ³*J* = 12.2 Hz, H^{5'} or H^{4'}), 5.49 (d, 1H, ³*J* = 12.2 Hz, H^{4'} or H^{5'}), 1.74 (s, 3H, Pd–COMe).

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Supporting Information Available: This material is available free of charge via the Internet at <http://pubs.acs.org>.

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