Mechanistic Aspects of Isotactic CO/Styrene Copolymerization Catalyzed by Oxazoline Palladium(II) Complexes

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Received October 17, 2002

Catalytic systems of the type $[Pd(CH_3)(NCCH_3)(N{-}N)]^+[B\{3,5\text{-}(CF_3)_2C_6H_3\}_4]^-$, where N−N = (4*S*,4′*S*)-(−)-4,4′,5,5′-tetrahydro-4,4′-bis(1-methylethyl)-2,2′-bioxazole (BIOX) or N−N = (4*S*,4′*S*)-(−)-2,2′-(1-methylethylidene)bis[4,5-dihydro-4-(phenylmethyl)oxazole]) (BISOX), afford highly isotactic CO/styrene or *p*-methylstyrene copolymers. The reactivity of the catalyst with the BIOX ligand toward carbon monoxide was studied and the corresponding methyl carbonyl Pd complex was isolated and identified as the real catalytic species. Starting from this compound the first steps of the copolymerization process were investigated and particular attention was paid to the stereochemistry of the intermediates. Specifically, NOE experiments carried out on the five-membered palladacycle, obtained from the first insertion of *p*-methylstyrene, indicated that regiochemistry is of the 2,1 type and that one diastereoisomeric species is exclusively generated, with an *R* configuration of the new −CHAr− stereogenic center. Moreover, the investigation of the intermediate resulting after the second sequence of *p*-methylstyrene and CO insertion showed the presence of only one diastereoisomer. This evidence indicates that the stereocontrol of the isospecific catalyst is already very efficient at the first stages of copolymerization.

Introduction

The alternating copolymerization of olefins with carbon monoxide has been investigated in the past both for the practical application of the obtained polyketone products and for the interest in the mechanism of the process, and it is still the subject of extensive research.[1] Using styrene as olefin, suitable catalysts are mainly cationic Pd(II) complexes with nitrogen bidentate ligands and weakly coordinating anions.[2] The resulting alternating copolymers are characterized by structural features such as regioisomerism (either 1,2 or 2,1 monomer insertion) and stereoisomerism (iso- or syndio- or atactic structure). Catalytic systems containing achiral nitrogen ligands such as 2,2′-bipyridine and 1,10-phenanthroline in methanol or dichloromethane as solvent afford stereoregular syndiotactic copolymers[2a−g,j] by chain-end control. Moreover, an improvement in productivities and molecular weights of syndiotactic CO/styrene copolymers has been achieved by using 2,2,2-trifluoroethanol as solvent and bischelated Pd(II) catalyst[3] with a 3-alkyl-substituted phenanthroline ligand.[3c] Instead, chiral catalysts have been used for isotactic copolymerizations. Highly isotactic optically active polyketones have been obtained with bisoxazoline,[4] bioxazoline,[4b] diketimine,[5] or diphosphine[6] chiral ligands with C_2 symmetry. Alternatively a comparable degree of stereoregularity has been reached with catalysts based on either phosphine-oxazoline[7] or phosphine-phosphite[8] chiral ligands. The strong enantioface discrimination of

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10.1021/om0208669 CCC: $25.00
Publication on Web 01/25/2003

the incoming styrene unit, responsible for the high isotacticity of the obtained polyketones, has been ascribed to the steric constraint of the olefin at the coordination center.[4,7,8a] To collect additional experimental evidence supporting this assumption, we have undertaken a study of the first intermediates of isotactic copolymerization using bioxazoline complexes. Oxazoline ligands have been employed as chiral auxiliaries in several organic asymmetric syntheses catalyzed by transition metals. Easy modulation of the chiral centers located near the donor nitrogen atoms allows achieving high enantioselectivities in many processes.[9] Our group has previously reported that cationic bioxazoline and bisoxazoline Pd(II) complexes catalyze the alternating copolymerization of carbon monoxide with styrene and *p*-methylstyrene to yield highly isotactic, optically active, copolymer at 25 °C and low carbon monoxide pressure (1−4 atm).[4b] The crystal structure of the alternating styrene carbon monoxide copolymer has also been determined.[10] Moreover, we have recently described the results of the copolymerization reaction of styrene or *p*-methylstyrene and CO by using a syndiospecific α-diimine ligand, showing that the chain-end control is not fully effective during the initial steps of the copolymerization.[11] As far as we know, no detailed reports are available in the literature on analogous studies concerning the isotactic copolymerization using nitrogen chiral ligands.

The purpose of the present work is, first, to describe in detail the results of the preliminary communication concerning the isotactic copolymerization[4b] and, second, to elucidate its mechanism. This study was also undertaken with the aim of making a comparison with the syndiotactic copolymerization mechanism previously reported.[11,12]

Results and Discussion

A. Synthesis of Complexes 1 and 2. The complexes [Pd(CH_3)(Cl)(BIOX)] **1a** (BIOX = (4*S*,4′*S*)-(−)-4,4′,5,5′-tetrahydro-4,4′-bis(1-methylethyl)-2,2′-bioxazole) and [Pd(CH_3)(Cl)(BISOX)] **1b** (BISOX = (4*S*,4′*S*)-(−)-2,2′-(1-methylethylidene)bis[4,5-dihydro-4-(phenylmethyl)oxazole]) were synthesized by substitution of the diene in [Pd(CH_3)(Cl)(COD)] (COD = 1,5-cyclooctadiene) with the oxazoline ligands **a** or **b** in dichloromethane at 25 °C.[13] In the NMR spectra (20 °C) of complexes **1a** and **1b** the two halves of the ligand show separate sets of signals. Indeed, in complex **1a** the two isopropyl groups are nonequivalent, showing in both ^{1}H and ^{13}C spectra four distinct chemical shifts for the diastereotopic methyl groups and two resonances for the C*H* groups (the 2.80−2.60 ppm multiplet was assigned to the C*H cis* to the methyl coordinated to Pd by NOE experiments); a double pattern of signals is also observed for the two oxazoline rings. Likewise, the benzyl methylene groups of **1b** give four distinct proton chemical shifts and two resonances for the corresponding carbons; moreover, the two methyl groups on the bridging carbon are anisochronous and all the resonances of the two heterocycles are double. Another feature of the NMR spectra of these compounds is the considerable shielding of the Pd-CH_3 signals, observed at δ_H 0.79 and δ_C −9.0 for complex **1a** and at δ_H 1.00 and δ_C −4.6 for **1b**; this effect can be attributed to the coordination of CH_3 to the metal. In the IR spectrum two C═N stretching bands are detected at 1647 and 1627 cm^{-1} for **1a** and at 1659 and 1618 cm^{-1} for **1b**; the presence of two bands is due to the different *trans* effect of the chlorine and methyl group.

From the reaction of **1a** and **1b** with $Na^+[BAr'_4]^-$ (Ar′ = 3,5-$(CF_3)_2C_6H_3$) at −40 °C in a dichloromethane/acetonitrile (5:1 v/v) mixture, the cationic complexes [Pd(CH_3)($NCCH_3$)(N−N)]$^+$[BAr'_4]$^-$ **2a** and **2b** were formed in good yields (Scheme 1). Both complexes show the same NMR spectral pattern found for **1a** and **1b**, and the coordination of acetonitrile to palladium is confirmed by the chemical shifts of the CH_3CN group (δ_H 2.25, δ_C 3.0−3.1).

B. Copolymerization of Styrene or *p*-Methylstyrene with Carbon Monoxide. The precatalyst **2a** (or **2b**) was dissolved in dichloromethane presaturated with carbon monoxide; the solution was allowed to react with CO at 0 °C for 30 min, then styrene or *p*-methylstyrene was added (olefin/palladium molar ratio 400:1) (Scheme 1). The copolymerization was carried out at 25 °C and atmospheric pressure of CO; the reaction time was 7 h with **2a** and 21 h with the less reactive complex **2b**. The copolymers poly(1-oxo-2-phenyltrimethylene) **3** and poly(1-oxo-2-(4-methyl)phenyltrimethylene) **4**, obtained in moderate yields, were collected by precipitation with methanol. Despite the higher reaction time, using the BISOX ligand poorer yields were obtained with respect to the BIOX; indeed the productivities (express in g copolymer/g Pd) are 46 for **2a** and 38 for **2b**, with styrene as comonomer, and 82 for **2a** and 28 for **2b** with *p*-methylstyrene. This is most likely due to the different electronic properties of the ligands, bioxazoline being a better π-acceptor ligand than bisoxazoline. The molecular weights (M_w) are in the range 4500−7500 with a low polydispersity (1.2−1.4) (Table 1).

The stereoregularity of the copolymers was proved by ^{13}C NMR spectroscopy (in 1:1 $(CF_3)_2CHOH/CDCl_3$ (v/v) at 45 °C): strong signals of *C*O, C_{ipso}, CH_2, and *C*H carbons were detected together with small peaks due to stereoisomeric impurities. The carbon chemical shifts of **3** and **4** correspond to the typical values of the alternating head-to-tail isotactic copolymers reported in the literature.[4,6,7b,8] The polyketones **3** and **4** exhibit a high specific rotation, with $[\alpha]^{25}_{589}$ values between −354° and −411°, which further confirms the isotactic microstructure: the latter could correspond to either the ...*RRRRRR*... or ...*SSSSSS*... sequence of the stereogenic centers in the polymer backbone, which at this stage cannot be assigned. The stereoisomeric purity was determined in the region of C_{ipso}, where the intensity

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Scheme 1

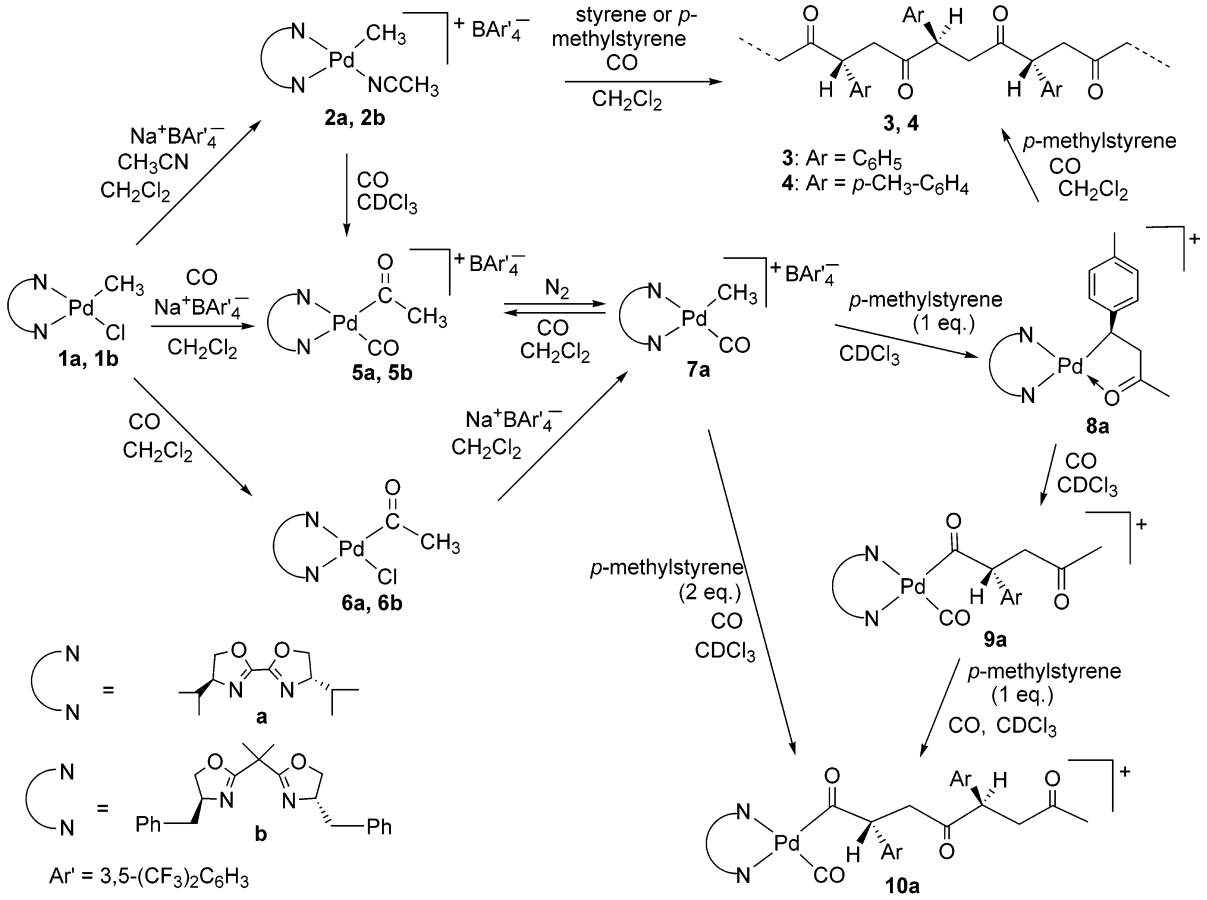

Table 1. CO/Styrene and CO/*p*-Methylstyrene Copolymerization Results[a]

catalyst	olefin	reaction time (h)	g copolymer/ g Pd	M_w (M_w/M_n)[b]	$[\alpha]^{25}_{589}$[c]
2a	styrene	7	46	4600 (1.4)	−411°
2a	*p*-methylstyrene	7	82	7000 (1.3)	−371°
2b	styrene	21	38	7300 (1.4)	−394°
2b	*p*-methylstyrene	21	28	6700 (1.2)	−354°
7a	*p*-methylstyrene	7	122	6800 (1.4)	−369°

[a] Reaction conditions: $n_{Pd} \cong 100 \times 10^{-6}$ mol; olefin/palladium molar ratio 400:1; $P_{CO} = 1$ atm; solvent CH_2Cl_2 $V = 4$ mL; $T = 25$ °C. [b] Determined by GPC vs polystyrene standards. [c] Optical rotations were measured in CH_2Cl_2 solution for CO/*p*-methylstyrene copolymers and in $CHCl_2CHCl_2$ solution for CO/styrene copolymers.

ratio of the *ll* triad signals to the sum of the *uu*, *ul*, and *lu* signals resulted in being 96% to 4% for both **3** and **4**, obtained with either BIOX or BISOX ligands. In the ^{13}C NMR spectra, measured with a high number of scans, it was also possible to determine chain-end groups: in particular, regarding copolymer **3**, one CH_3 resonance at 29.7 ppm was detected corresponding to the acetyl fragment generated in the initiation step (vide infra, section D), while the presence of small signals at 203.0 (*C*O), 147.0 (Ph-*C*H), and 125.8 (*C*H-CO) ppm, compatible with the unsaturated end group Ph−CH═CH-CO−,[2f] suggests that β-hydride elimination is the major termination event.[2c,f] The so-formed Pd(II)-H species seems to have a low tendency to restart the copolymerization process in the operating conditions; indeed, considering the yield and the molecular weight of each polyketone, the result is that the reaction is nearly stoichiometric, producing a maximum of two polymeric chains for each metal center.

C. Reactivity of Complexes 1 and 2 with CO and Synthesis of 5, 6, and 7. It is well known that the copolymerization process takes place through the alternating insertion reactions of CO in the palladium−alkyl bond and of alkene in the palladium−acyl bond.[14] Thus, to investigate the mechanism of the isotactic copolymerization promoted by our catalytic systems, we have first studied the reaction of the precatalysts **2a** and **2b** with carbon monoxide under the same conditions above-reported for the synthesis of polyketones **3** and **4** (Scheme 1).

Exposure of deuteriochloroform solutions of **2a** or **2b** to CO atmosphere resulted in the formation of the corresponding acetyl carbonyl complexes **5a** and **5b**, easily detected by NMR. It is also possible to synthesize complexes **5a** and **5b** directly by the reaction of **1a** and **1b** with $Na^+[BAr'_4]^-$ under CO atmosphere, in dichloromethane previously saturated with CO. In the ^{13}C NMR spectra two CO resonances were found, at 207.7 and 172.9 ppm for **5a**, and 214.6 and 176.6 ppm for **5b**.

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While the signals above 200 ppm are typical of acetyl groups, the resonances below 180 ppm can be assigned to the carbonyl CO, confirming the proposed structure. Furthermore, the IR spectra show two bands around 2130 and 1750 cm^{-1}, due to Pd-CO and Pd-$COCH_3$ groups, respectively.

The acetyl carbonyl complexes **5a** and **5b** have a tendency to decarbonylate, in solution after few hours and even in the solid state at −20 °C after months. A complete decarbonylation was obtained by bubbling nitrogen through a dichloromethane solution of **5a** at −5 °C for 6 h, resulting in the formation of **7a**. Conversely, exposure of the solution of **7a** to CO atmosphere leads to the regeneration of **5a**, indicating a reversible process.

The formation of **7a** was evidenced by the presence, in the ^{13}C NMR spectrum, of the Pd-*C*O and Pd-*C*H_3 resonances at 174.1 and −0.01 ppm, respectively, while the acetyl signals disappeared; in the IR spectrum the characteristic CO stretching was found at 2125 cm^{-1}.

Complexes **1a** and **1b** resulted in being very reactive toward carbon monoxide even without the addition of $Na^+[BAr'_4]^-$. Indeed, simply by dissolving **1a** and **1b** in dichloromethane presaturated with CO at low temperature and then warming the solution up to 25 °C, the acetylchloropalladium complexes **6a** and **6b** were obtained. The following spectral data confirm CO insertion into the Pd−CH_3 bond: (i) in the ^1H NMR spectrum a high-frequency shift for the methyl resonance from 0.79 ppm for **1a** to 2.37 ppm for **6a**, and from 1.00 ppm for **1b** to 2.74 ppm for **6b** was found; (ii) characteristic CO stretching absorptions were found around 1700 cm^{-1} in the IR spectra; (iii) the ^{13}C NMR chemical shift values of *C*O (222.4 ppm for **6a** and 230.0 ppm for **6b**) and of CO*C*H_3 (36.8 ppm for **6a** and 36.9 for **6b**) are typical of acetyl groups. Complexes **6a** and **6b** are stable as solids and in solution when stored at −20 °C and do not show any tendency to decarbonylate. Indeed, if nitrogen is bubbled through a chloroform solution of **6a** up to complete evaporation of the solvent, it is recovered unchanged. From complex **6a**, **7a** is easily obtained by the addition of $Na^+[BAr']_4^-$: this represents a convenient and quick way to synthesize **7a** in good yield.

Finally, the NMR spectra of complexes **5a**, **5b**, **6a**, **6b**, and **7a** are temperature dependent: at low temperature (−60 °C) the two halves of the BIOX or BISOX ligand show two different sets of chemical shifts, which broaden by raising the temperature and then coalesce into a single set of signals. This feature is accounted for by the interconversion between two fluxional forms, as previously described for the corresponding complexes with the 1,4-diisopropyl-1,4-diaza-1,3-butadiene ligand.[11]

D. Mechanistic Studies, Alkene and CO Insertions. The insertion of various alkenes into metal acyl bonds, either preexistent or formed after α-migration of the alkyl, has been described in the literature,[8a,15] but the olefin employed is styrene or substituted styrene in only a few cases.[2d,7a,8b,16] The chain propagation of the CO/styrene copolymerization has been observed by Brookhart at low temperature using the 2,2′-bipyridine ligand[2d] and by us in a previous work using an α-diimine ligand.[11] However, these studies deal only with syndiospecific catalysts. In the following we report the results of a similar investigation concerning our isospecific catalyst. As shown in the previous section, complex **2a**, used as initiator of the isotactic copolymerization, is transformed, in reaction conditions analogous to those used for the copolymerization, in the acetyl carbonyl complex **5a**. To examine step by step the intermediates of the copolymerization, we first studied the insertion of *p*-methylstyrene in complex **5a**. The reaction resulted in being very slow, and it took place through the formation of the decarbonylated complex **7a**, which appears to be an essential species in the catalytic process. Indeed, **7a** reacts at −20 °C in a few minutes with an equimolecular amount of *p*-methylstyrene, giving the five-membered palladacycle **8a** in good yield (Scheme 1).

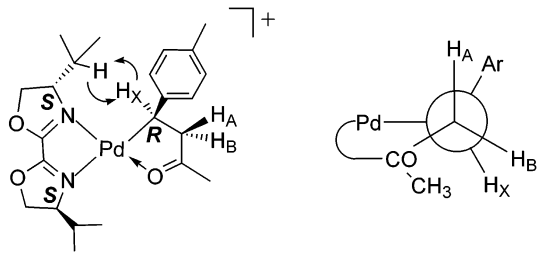

Figure 1. Stereochemistry and Newmann projection of the palladacycle **8a**.

Moreover, performing the CO/*p*-methylstyrene copolymerization using **7a** a better yield than with precatalyst **2a** was achieved. In particular the reaction was carried out allowing a dichloromethane solution of **7a** to react first with the olefin and then with carbon monoxide. After 7 h 1.28 g (122 g of copolymer/g Pd) of polyketone was obtained (Table 1).

Regarding complex **8a**, spectroscopic evidence is in agreement with the structure shown in Figure 1, corresponding to a 2,1 insertion of styrene, analogous to that obtained with the previously reported α-diimine ligand.[12] With that achiral ligand, the *R* or *S* configuration of the new chiral center −CHAr− can be generated by styrene insertion, but the resulting two enantiomeric products of course cannot be differentiated by NMR. For complex **8a**, due to the *SS* configuration of the bioxazoline ligand, one could in principle expect two possible alternative diastereoisomers: actually, the number of signals detected in both the ^1H and ^{13}C NMR spectra, between −50 and 50 °C, suggests the existence of just one form. This observation shows that the configuration of the styrene monomer unit is strictly controlled by the chiral ligand; moreover it confirms that enantiomerically pure ligands generate optically active isotactic copolymers.[4a] Since the five-membered ring is

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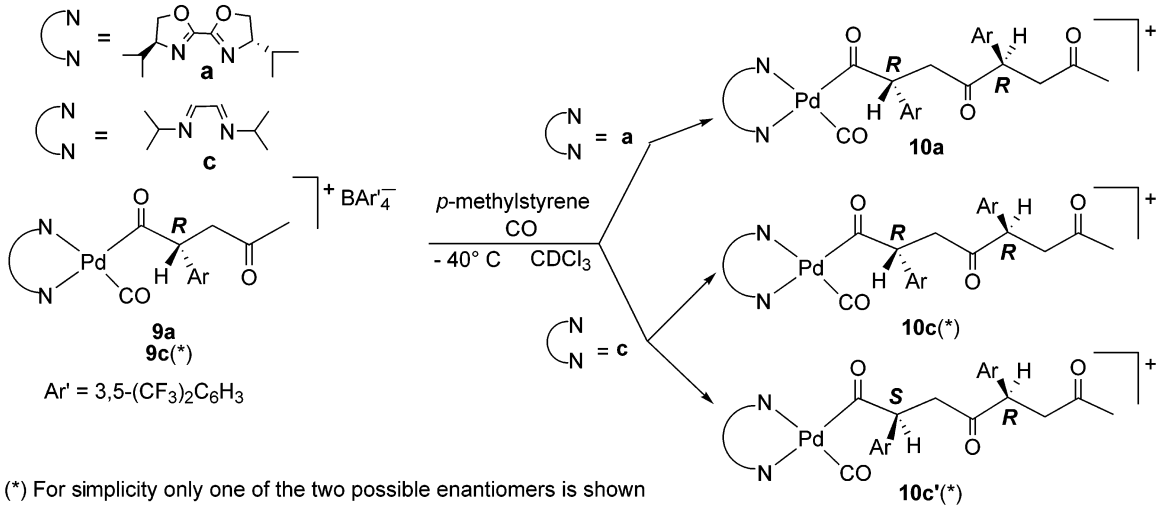
Scheme 2



(*) For simplicity only one of the two possible enantiomers is shown

the key step for each subsequent styrene insertion in the copolymerization reaction, it was appropriate to determine experimentally whether the configuration of intermediate **8a** is *SSR* or *SSS*. In a previous paper[4b] it had been postulated that the styrene phenyl ring and the nearest ligand isopropyl group are above and below the Pd coordination plane, respectively, corresponding to the *SSR* form. However, this assumption was based purely on the criterion of minimum steric repulsion between the two groups. To check this hypothesis, we have carried out nuclear Overhauser experiments on **8a**: in fact, presaturation of the CH_X resonance of the palladacycle resulted in an 8% enhancement of the C*H* signal of one isopropyl group, and, conversely, presaturation of the C*H* resonance of the isopropyl group resulted in a 5% enhancement of the CH_X signal of the palladacycle. This finding, together with the lack of NOE between the isopropyl C*H* and the aromatic ring signals, is in favor of the *SSR* configuration (Figure 1). The vicinal coupling constants of the three-spin system of the $CH_XC(H_A)H_B$ fragment in the five-membered cycle of **8a** are different from those observed in the corresponding complex with the 1,4-diisopropyl-1,4-diaza-1,3-butadiene ligand:[12] J_{AX} changes from 8.3 to 6.8 Hz and J_{BX} from 3.5 to 6.1 Hz. These values suggest the quasi eclipsed conformation shown in the Newmann projection of Figure 1, for which dihedral angles were estimated by the Karplus relationship. In agreement with this steric arrangement, H_B but not H_A shows the NOE with H_X.

The next step of the copolymerization, the insertion of CO into the Pd−alkyl bond of **8a**, was studied at low temperature, because of the instability of the resulting product **9a** (Scheme 1). The open chain structure of **9a** is evidenced by three *C*O chemical shifts observed in the ^{13}C NMR spectrum: δ 171.4, due to the *C*O coordinated to Pd, and δ 208.1, δ 206.9, due to the acyl *C*O of the growing chain. This assignment is further confirmed by the presence in the IR spectrum of three bands at 2129, 1718, and 1715 cm^{-1}, the former being typical of a CO ligand bonded to a metal center. Concerning the stereochemistry of **9a**, the observed patterns of ^{1}H and ^{13}C NMR spectra indicate the presence of only one diastereoisomer. Most likely this has the same *SSR* configuration as its precursor **8a**.

Finally, insertion of a second molecule of *p*-methylstyrene and carbon monoxide in **9a** gives complex **10a**, which can alternatively be obtained directly from complex **7a** by adding 2 equiv of *p*-methylstyrene and bubbling CO (Scheme 1). The latter procedure yields a 1:1 mixture of **9a** and **10a** after 36 h, while the former is much slower and results in a lower conversion. In any case, the resonances assigned in the NMR spectra to **10a** are in accordance with the presence of only one diastereoisomeric form. Specifically, in the ^{13}C NMR spectrum three resonances were detected for the acyl *C*O groups (208.4, 207.3, and 206.8 ppm), one resonance for the carbonyl Pd-*C*O (171.3 ppm), two resonances for the *C*H (61.4 and 51.6 ppm), two resonances for the CH_2 (47.4 and 44.3 ppm) and one for the terminal methyl group (30.0 ppm). This picture is confirmed by the ^{1}H NMR spectra, where just two neat ABX patterns, due to the C*H*-CH_2 fragments of **10a**, are easily recognized. The result is that **10a** is present in one configuration, as in the case of its precursors **8a** and **9a**. Moreover, considering the highly isospecific character of the operating catalytic system, one can assign the *SSRR* configuration to **10a**. All the above results lead to the necessary conclusion that the absolute configuration of the polymer chain must be ...*RRRRRR*....

The stereochemistry of the initial steps of the isotactic copolymerization, described in the present investigation, can be compared with that previously observed for the syndiotactic copolymerization.[11] As summarized in Scheme 2, the insertion of the second *p*-methylstyrene monomer unit into the growing chain appears to have a different steric course, depending on the ligand nature. Thus, complex **9a**, containing the enantiomerically pure C_2 symmetric ligand **a**, produces only diastereoisomer **10a**, as seen above. Instead, the corresponding complex **9c**, containing the achiral ligand **c**, gives a mixture of the two diastereoisomers **10c** and **10c′**. Evidently, the stereocontrol of the syndiospecific catalyst is not working fully in the first steps of the polymerization, while the stereocontrol of the isospecific catalyst is effective from the very beginning.

As a check of this finding, we have examined the ^{13}C resonance of the terminal methyl of the isotactic copolymer by measuring the spectrum of **4** with high signal-to-noise ratio: it was possible to detect just one

resonance at 29.7 ppm, differently from the corresponding methyl of the syndiotactic copolymer, showing two signals at 30.3 and 29.6 ppm.

Conclusions

The catalytic system based on cationic C_2 symmetric bisoxazoline or bioxazoline Pd(II) complexes **2a** and **2b** afforded regio- and stereoregular alternating isotactic optically active copolymers of carbon monoxide and styrene or *p*-methylstyrene. The reaction was carried out in dichloromethane at 25 °C and at a pressure of 1 bar of carbon monoxide. The yields could be enhanced by using the *p*-methylstyrene comonomer and the bioxazoline ligand **a**. Moreover a further increase in productivity was achieved performing the copolymerization with the preformed methyl carbonyl complex **7a**, which was shown to be an essential species in the catalytic process. The structure of the copolymers resulted in being 96% isotactic from ^{13}C NMR spectra.

Moreover, it has been possible to monitor the first steps of CO/*p*-methylstyrene copolymerization starting from **7a**. Insertion of the first olefin monomeric unit was observed by isolating a five-membered palladacycle, the structure which gave experimental support to the regio- and stereochemistry of the process: the mechanism of enchainment is of the 2,1 type, and the new chiral center −CHAr− has an *R* configuration (Figure 1). Apparently, the latter stereochemical feature is due to the constraint imposed by the chiral bioxazoline ligand, in such a way that just one of the styrene prochiral faces can be coordinated to the metal. This result, together with the isospecific nature of the catalyst, allowed us to assign the absolute configuration ...*RRRRRR*... to the isotactic polymer chain.

Finally, the investigation of the first and second *p*-methylstyrene and CO insertions showed that the stereocontrol of the isospecific catalyst **7a** is already very efficient at this stage, generating just one diastereoisomer. This behavior is substantially different from that observed for the corresponding intermediates of the syndiotactic copolymerization: in that case a mixture of two different diastereoisomers was detected. In this regard, it seems that the enantiomorphic site control of the process, provided by the chiral ligand of the isospecific catalyst, is more powerful than the chain-end control operating in the syndiotactic copolymerization.

Experimental Section

All manipulations were carried out under a nitrogen atmosphere by using Schlenk techniques. CP grade chemicals were used as received unless otherwise stated. Solvents were dried by standard methods and freshly distilled under nitrogen. $CDCl_3$ was degassed and stored over 3 Å molecular sieves. (4*S*,4′*S*)-(−)-4,4′,5,5′-tetrahydro-4,4′-bis(1-methylethyl)-2,2′-bioxazole (BIOX),[17] (4*S*,4′*S*)-(−)-2,2′-(1-methylethylidene)bis-[4,5-dihydro-4-(phenylmethyl)oxazole] (BISOX),[17c,18] $Na^+[BAr'_4]^-$ (Ar′ = 3,5-$(CF_3)_2C_6H_3$),[19] and $[Pd(CH_3)(Cl)(COD)]$[13] were synthesized as previously reported in the literature. Carbon monoxide (CP grade 99.99%) was supplied by Air Liquide.

Elemental analyses (C, H, N) were carried out with a Fisons Instruments 1108 CHNS-O elemental analyzer. Infrared spectra were measured as Nujols mulls between KBr disks or as films or in dichloromethane or $CDCl_3$ solution in the range 4000−600 cm^{-1} on a Bruker IFS-48 FT-IR spectrometer. NMR spectra were measured on a Bruker AC200 spectrometer with a multinuclear 5 mm probehead. ^{1}H and ^{13}C NMR chemical shifts are relative to TMS and were measured using the residual proton or carbon resonance of the deuterated solvents. NOE measurements were performed using the Bruker NOEDIFF pulse program, with irradiation times of 3 s and power of 40 L. Editing of ^{13}C NMR spectra was obtained from DEPT experiments.

The molecular weights (M_w) of copolymers and the molecular weight distributions (M_w/M_n) were determined by gel permeation chromatography versus polystyrene standards. The analyses were performed on a Bruker HPLC (model LC-22) with an Alltech macrosphere GPC 60 Å column and chloroform as solvent (flow rate 0.5 mL/min). Samples were prepared as follows: 3 mg of the CO/styrene copolymer was dissolved in 120 μL of 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP), and chloroform was added up to 10 mL; instead, the CO/*p*-methylstyrene copolymer was directly soluble in chloroform. The statistical calculations were performed using the Bruker Chromstar software program.

[Pd(CH$_3$)(Cl)(BIOX)] (1a). A solution of 0.191 g (0.83 mmol) of BIOX in 3 mL of dichloromethane was added to a solution of 0.201 g (0.76 mmol) of $[Pd(CH_3)(Cl)(COD)]$ in 2 mL of the same solvent. The reaction mixture was stirred overnight at 25 °C. The solution was evaporated in a vacuum after filtration through a pad of Celite, obtaining a brownish oil, which by washing with hexane crystallized as a yellow powder of compound **1a** (0.289 g, 0.76 mmol, 99%). IR (Nujol, cm^{-1}): 1647, 1627 (C═N). ^{1}H NMR (acetone-d_6): δ 5.00−4.63 (m, 4H, CH_2O); 4.43−4.24 (m, 2H, C*H*-N); 2.80−2.60, 2.26−2.10 (m, 1H each, C*H*$(CH_3)_2$); 0.96, 0.89, 0.88, 0.86 (d, J = 6.8 Hz, 3H each, CH(C$H_3)_2$); 0.79 (s, 3H, Pd-CH_3). ^{13}C NMR (acetone-d_6): δ 160.4, 158.0 (*C*═N); 73.4 (*C*H_2O); 69.9, 68.3 (*C*H-N); 30.3, 29.5 (*C*H$(CH_3)_2$); 18.7, 18.5, 15.0, 14.1 (CH(*C*$H_3)_2$); −9.0 (Pd-*C*H_3). Anal. Calcd for $C_{13}H_{23}ClN_2O_2Pd$: C, 40.96; H, 6.08; N, 7.35. Found: C, 41.12; H, 6.15; N, 7.56.

[Pd(CH$_3$)(Cl)(BISOX)] (1b). Complex **1b** was synthesized according to the procedure described for **1a** using 0.301 g (1.12 mmol) of $[Pd(CH_3)(Cl)(COD)]$ and 0.440 g (1.22 mmol) of BISOX, yielding a pale yellow powder (0.55 g, 1.06 mmol, 95%). IR (Nujol, cm^{-1}): 1659, 1618 (C═N). IR (CH_2Cl_2, cm^{-1}): 1658, 1622 (C═N). ^{1}H NMR ($CDCl_3$): δ 7.46−7.19 (m, 10H, Ph-*H*); 4.92−4.78, 4.65−4.50 (m, 1H each, C*H*-N); 4.43 (dd, J = 8.9 and 3.2 Hz, 1H, CH_2-O); 4.35 (dd, J = 8.7 and 3.7 Hz, 1H, CH_2-O); 4.20 (dd, J = 8.7 and 8.7 Hz, 1H, CH_2-O); 4.12 (dd, J = 8.9 and 8.9 Hz, 1H, CH_2-O); 3.54 (dd, J = 13.4 and 3.2 Hz, 1H, CH_2-Ph); 3.20 (dd, J = 13.8 and 3.0 Hz, 1H, CH_2-Ph); 2.79 (dd, J = 13.4 and 8.9 Hz, 1H, CH_2-Ph); 2.73 (dd, J = 13.8 and 8.6 Hz, 1H, CH_2-Ph); 1.47, 1.30 (s, 3H each, C(C$H_3)_2$); 1.0 (s, 3H, Pd-CH_3). ^{13}C NMR ($CDCl_3$): δ 172.2, 169.1 (*C*═N); 136.9, 135.4 (Ph-C_i); 130.1, 129.8, 128.6, 128.3 (Ph-C_o, Ph-C_m); 127.2, 126.6 (Ph-C_p); 72.1, 71.1 (*C*H_2O); 66.3, 65.7 (*C*H-N); 39.8, 39.5 (*C*H_2-Ph and *C*$(CH_3)_2$); 26.1, 23.6 (C(*C*$H_3)_2$); −4.6 (Pd-*C*H_3). Anal. Calcd for $C_{24}H_{29}ClN_2O_2Pd$: C, 55.5; H, 5.63; N, 5.39. Found: C, 55.51; H, 5.86; N, 5.25.

[Pd(CH$_3$)(NCCH$_3$)(BIOX)]$^+$[BAr′$_4$]$^-$ (2a). A dichloromethane/acetonitrile (5:1 v/v) solution (4 mL) containing 0.46 g (0.52 mmol) of $Na^+[BAr'_4]^-$ was added to a solution containing 0.20 g (0.52 mmol) of **1a** in 3 mL of dichloromethane/acetonitrile (5:1 v/v) cooled to −40 °C. The reaction mixture was slowly warmed to 0 °C in 2 h, stirred for 1 h, and then filtered through

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Celite to remove NaCl. After evaporation in a vacuum a dark oil was obtained, which upon treatment with hexane (4 × 6 mL) at −80 °C gave 0.62 g (0.50 mmol, 95%) of **2a** as a yellow powder. IR (Nujol, cm^{-1}): 2331, 2306 (CH_3CN); 1641, 1610 (C═N). ^1H NMR ($CDCl_3$, −20 °C): δ 7.70 (s, 8H, Ar′-H_o); 7.54 (s, 4H, Ar′-H_p); 4.82−4.47 (m, 4H, CH_2-O); 4.23−4.09 (m, 2H, CH-N); 2.25 (s, 3H, CH_3CN); 2.03, 1.92 (sept, J = 7.0 Hz, 1H each, CH(CH_3)$_2$); 1.01 (s, 3H, Pd-CH_3); 0.90, 0.85, 0.78 (d, J = 7.0 Hz, 12H, CH(CH_3)$_2$). ^{13}C NMR ($CDCl_3$, −33 °C): δ 161.4 (q, $^1J_{CB}$ = 49.9 Hz, Ar′-C_i); 160.4, 157.6 (C═N); 134.6 (Ar′-C_o); 128.6 (q, $^2J_{CF}$ = 31.4 Hz, Ar′-C_m); 124.3 (q, $^1J_{CF}$ = 272.5 Hz, CF_3); 121.0 (CH_3CN); 117.4 (Ar′-C_p); 73.5, 72.8 (CH_2O); 69.1, 67.1 (CH-N); 30.4, 29.2 (CH(CH_3)$_2$); 18.2, 18.0, 15.4, 13.4 (CH-(CH_3)$_2$); 3.1 (CH_3CN); −2.5 (Pd-CH_3). Anal. Calcd for $C_{47}H_{38}BF_{24}N_3O_2Pd$: C, 45.16; H, 3.06; N, 3.36. Found: C, 45.31; H, 2.98; N, 3.25.

[Pd(CH$_3$)(NCCH$_3$)(BISOX)]$^+$[BAr′$_4$]$^-$ (2b). Compound **2b** was synthesized with the same procedure described for **2a** starting from 0.250 g (0.48 mmol) of **1b** and 0.421 g (0.48 mmol) of $Na^+[BAr'_4]^-$. A 0.65 g (0.47 mmol, 98%) sample of **2b** was obtained as a pale yellow powder. IR (Nujol, cm^{-1}): 2328, 2300 (CH_3CN); 1653, 1610 (C═N). ^1H NMR ($CDCl_3$): δ 7.72 (s, 8H, Ar′-H_o); 7.54 (s, 4H, Ar′-H_p); 7.40−7.15 (m, 10H, Ph-H); 4.55−4.38 (m, 2H, CH-N); 4.35−4.20 (m, 4H, CH_2-O); 3.12−2.68 (m, 4H, CH_2-Ph); 2.25 (s, 3H, CH_3CN); 1.48, 1.18 (s, 3H each, C(CH_3)$_2$); 0.93 (s, 3H, Pd-CH_3). ^{13}C NMR ($CDCl_3$): δ 174.2, 171.9 (C═N); 161.7 (q, $^1J_{CB}$ = 48.8 Hz, Ar′-C_i); 134.8 (Ar′-C_o); 134.3, 134.2 (Ph-C_i); 129.5, 129.3, 129.0, 128.7 (Ph-C_o, Ph-C_m); 128.9 (q, $^2J_{CF}$ = 30 Hz Ar′-C_m); 127.7 (Ph-C_p); 124.6 (q, $^1J_{CF}$ = 272.8 Hz, CF_3); 121.4 (CH_3CN); 117.5 (Ar′-C_p); 72.7, 71.9 (CH_2O); 66.2, 64.7 (CH-N); 39.8, 39.5 (CH_2-Ph and C(CH_3)$_2$); 27.4, 22.1 (C(CH_3)$_2$); 3.0 (CH_3CN); −0.9 (Pd-CH_3). Anal. Calcd for $C_{58}H_{44}BF_{24}N_3O_2Pd$: C, 50.2; H, 3.19; N, 3.03. Found: C, 50.07; H, 3.11; N, 3.18.

Poly(1-oxo-2-phenyltrimethylene) (3). The copolymerization reaction was carried out in a thermostated Schlenk flask equipped with a carbon monoxide gas line and a tank for the CO. The complex **2a** (0.120 g, 0.096 mmol) was dissolved at 0 °C in 4 mL of dichloromethane saturated with CO, and it was allowed to react for 30 min. Then styrene (4.4 mL, 38.4 mmol) was added (olefin/palladium molar ratio 400:1). The reaction was carried out at 25 °C for 7 h, and then the resulting gray polymer was precipitated with methanol (20 mL) and washed with methanol. To remove metallic palladium traces, it was redissolved in chloroform (30 min at 35 °C) and filtered through Celite. After evaporation of solvent the resulting white solid was purified by suspending it overnight in ethyl acetate. The following day the solvent was evaporated and the product dried under vacuum, obtaining 0.47 g (46 g of polymer/g Pd) of copolymer **3**. IR (film, cm^{-1}): 1711 (CO). ^1H NMR ($CDCl_3$): δ 7.30−6.90 (m, 5H, Ph); 3.90 (dd, J = 10.2 and 3.5 Hz, 1H, CH-CH_2); 3.14 (dd, J = 18.0 and 10.2 Hz, 1H, CH-CH_2); 2.60 (dd, J = 18.0 and 3.5 Hz, 1H, CH-CH_2). ^{13}C NMR ($CDCl_3$/$(CF_3)_2CHOH$, 1:1 (v/v), 45 °C): δ 210.8 (C═O); 137.3 (Ph-C_i); 129.9, 128.9 (Ph-C_o, Ph-C_m); 128.7 (Ph-C_p); 53.8 (CH-CH$_2$); 45.5 (CH-CH_2). Anal. Calcd for $(C_9H_8O)_n$: C, 81.79; H, 6.10. Found: C, 81.62; H, 6.17. M_w = 4600; M_w/M_n = 1.4. $[\alpha]^{25}_{589}$ −411° (1.80 mg/mL, $CHCl_2CHCl_2$).

The copolymer **3** was also obtained with the same procedure by using 0.159 g (0.114 mmol) of the complex **2b** and 5.2 mL (45.7 mmol) of styrene (olefin/palladium molar ratio 400:1). The reaction was carried out at 25 °C for 21 h. The polymer was precipitated and purified as indicated above, yielding 0.46 g (38 g of polymer/g Pd) of white copolymer **3**. For IR, ^1H NMR, and ^{13}C NMR spectra, see above. Anal. Calcd for $(C_9H_8O)_n$: C, 81.79; H, 6.10. Found: C, 81.61; H, 6.06. M_w = 7300; M_w/M_n = 1.4. $[\alpha]^{25}_{589}$ −394° (3.33 mg/mL, $CHCl_2CHCl_2$).

Poly(1-oxo-2-(4-methyl)phenyltrimethylene) (4). The copolymer **4** was obtained according to the procedure described for compound **3** by using 0.144 g (0.115 mmol) of the complex **2a** and 6.3 mL (48.5 mmol) of *p*-methylstyrene (olefin/palladium molar ratio 400:1). The reaction was carried out at 25 °C for 7 h. The resulting gray polymer was purified by dissolving in chloroform, filtering through Celite, and suspending it overnight in ethyl acetate. A 1.01 g (82 g of polymer/g Pd) sample of white copolymer **4** was collected. IR (Nujol, cm^{-1}): 1711 (CO). ^1H NMR ($CDCl_3$): δ 7.02, 6.84 (d, J = 7.9 Hz, 4H, Ph); 3.88 (dd, J = 9.8 and 3.4 Hz, 1H, CH-CH_2); 3.13 (dd, J = 18.2 and 9.8 Hz, 1H, CH-CH_2); 2.57 (dd, J = 18.2 and 3.4 Hz, 1H, CH-CH_2); 2.27 (s, 3H, Ph-CH_3). ^{13}C NMR ($CDCl_3$/$(CF_3)_2CHOH$, 1:1 (v/v), 45 °C): δ 211.1 (C═O); 138.9 (Ph-C_p); 134.3 (Ph-C_i); 130.6, 128.8 (Ph-C_o, Ph-C_m); 53.4 (CH-CH$_2$); 45.5 (CH-CH_2); 20.9 (Ph-CH_3). Anal. Calcd for $(C_{10}H_{10}O)_n$: C, 82.16; H, 6.89. Found: C, 82.19; H, 7.03. M_w = 7000; M_w/M_n = 1.3. $[\alpha]^{25}_{589}$ −371° (4.60 mg/mL, CH_2Cl_2).

The copolymer **4** was also obtained with the same procedure by using 0.121 g (0.087 mmol) of the complex **2b** and 4.6 mL (34.9 mmol) of *p*-methylstyrene (olefin/palladium molar ratio 400:1). The reaction was carried out at 25 °C for 21 h. The polymer was precipitated and purified as indicated above, yielding 0.25 g (28 g of polymer/g Pd) of white copolymer **4**. For IR, ^1H NMR, and ^{13}C NMR spectra, see above. Anal. Calcd for $(C_{10}H_{10}O)_n$: C, 82.16; H, 6.89. Found: C, 82.01; H, 6.92. M_w = 6700; M_w/M_n = 1.2. $[\alpha]^{25}_{589}$ −354° (2.20 mg/mL, CH_2Cl_2).

[Pd(COCH$_3$)(CO)(BIOX)]$^+$[BAr′$_4$]$^-$ (5a). A 0.059 g (0.155 mmol) sample of **1a** and 0.189 g (0.155 mmol) of $Na^+[BAr'_4]^-$ were suspended at −40 °C under CO atmosphere in 4 mL of dichloromethane previously saturated with CO. The reaction mixture was slowly warmed at 0 °C, stirred for 2 h, and filtered through Celite to remove NaCl. An oil was obtained after evaporation of the solvent by bubbling CO, which upon treatment with hexane saturated with CO (2 × 4 mL) gave **5a** as a yellow powder (0.18 g, 0.143 mmol, 92%). IR (Nujol, cm^{-1}): 2133 (Pd-CO); 1735 (CO-CH_3); 1645, 1611 (C═N). IR ($CHCl_3$, cm^{-1}): 2130 (Pd-CO); 1764 (CO-CH_3); 1649, 1611 (C═N). ^1H NMR (CD_2Cl_2, −80 °C): δ 7.65 (s, 8H, Ar′-H_o); 7.47 (s, 4H, Ar′-H_p); 4.79−4.40 (m, 4H, CH_2O); 4.21−4.02 (m, 2H, CH-N); 2.61 (s, 3H, COCH_3); 1.88−1.74, 1.67−1.51 (m, 1 H each, CH(CH_3)$_2$); 0.72 (d, J = 6.5 Hz, 12H, CH(CH_3)$_2$). ^{13}C NMR (CD_2Cl_2, −80 °C): δ 207.7 ($COCH_3$); 172.9 (Pd-CO); 162.1 (q, $^1J_{CB}$ = 49.2 Hz, Ar′-C_i); 161.4, 158.9 (C═N); 134.9 (Ar′-C_o); 128.9 (q, $^2J_{CF}$ = 31.4 Hz, Ar′-C_m); 124.7 (q, $^1J_{CF}$ = 270.9 Hz, CF_3); 117.9 (Ar′-C_p); 74.8, 74.3 (CH_2O); 69.4, 67.4 (CH-N); 41.9 (COCH_3); 31.1, 29.8 (CH(CH_3)$_2$); 18.5, 15.8, 13.9 (CH(CH_3)$_2$). Anal. Calcd for $C_{47}H_{35}BF_{24}N_2O_4Pd$: C, 44.63; H, 2.79; N, 2.21. Found: C, 44.48; H, 2.87; N, 2.11.

[Pd(COCH$_3$)(CO)(BISOX)]$^+$[BAr′$_4$]$^-$ (5b). Complex **5b** was synthesized according to the procedure described for **5a** using 0.152 g (0.29 mmol) of **1b** and 0.281 g (0.29 mmol) of $Na^+[BAr'_4]^-$. A 0.403 g (0.28 mmol, 98%) sample of **5b** was collected as a yellow powder. IR (Nujol, cm^{-1}): 2124 (Pd-CO); 1746 ($COCH_3$); 1647, 1610 (C═N). IR (CH_2Cl_2, cm^{-1}): 2123 (Pd-CO); 1744 ($COCH_3$); 1646, 1610 (C═N). ^1H NMR (CD_2Cl_2, −56 °C): δ 7.65 (s, 8H, Ar′-H_o); 7.47 (s, 4H, Ar′-H_p); 7.43−7.05 (m, 10H, Ph-H); 4.55−4.07 (m, 6H, CH_2-O and CH-N); 2.88−2.23 (m, 4H, CH_2-Ph); 2.60 (s, 3H, CO-CH_3); 1.46, 1.40 (s, 3H each, (C(CH_3)$_2$). ^{13}C NMR (CD_2Cl_2, −50 °C): δ 214.6 ($COCH_3$); 176.6 (Pd-CO); 173.7, 171.8 (C═N); 162.0 (q, $^1J_{CB}$ = 49.6 Hz, Ar′-C_i); 135.2, 134.4 (Ph-C_i); 134.9 (Ar′-C_o); 129.8, 129.2 (Ph-C_o, Ph-C_m); 128.9 (q, $^2J_{CF}$ = 32.0 Hz, Ar′-C_m); 128.1, 128.0 (Ph-C_p); 124.7 (q, $^1J_{CF}$ = 272.8 Hz, CF_3); 117.8 (Ar′-C_p); 74.3, 73.4 (CH_2O); 68.5, 66.4 (CH-N); 42.6 (COCH_3); 41.4, 39.6 (CH_2-Ph); 40.4 (C(CH$_3$)$_2$); 25.8, 25.3 (C(CH_3)$_2$). Anal. Calcd for $C_{58}H_{41}BF_{24}N_2O_4Pd$: C, 49.65; H, 2.95; N, 2.0. Found: C, 49.44; H, 3.06; N, 1.95.

[Pd(COCH$_3$)(Cl)(BIOX)] (6a). A 0.683 g (1.79 mmol) sample of **1a** was dissolved at −20 °C under CO atmosphere, in 10 mL of dichloromethane previously saturated with CO. The solution was slowly warmed to 25 °C, stirred for 1 h, and then filtered through Celite to remove metallic Pd traces. A yellow-green solid was obtained after evaporation of the solvent under vacuum, washed with hexane (3 × 5 mL), dried,

and shown to be compound **6a (**0.671 g, 1.64 mmol, 92%). IR (Nujol, cm^{-1}): 1707 (C═O); 1684, 1652 (C═N). ^1H NMR (CD_2Cl_2, −50 °C): δ 4.67−4.32 (m, 4H, CH_2O); 4.22−4.01 (m, 2H, C*H*-N); 2.37 (s, 3H, CO-CH_3); 2.36−2.18, 1.79−1.49 (m, 1H each, C*H*(CH_3)$_2$); 0.73, 0.72 (d, J = 6.7 Hz, 6H each, CH(CH_3)$_2$). ^{13}C NMR (acetone-d_6, −50 °C): δ 222.4 (*C*O-CH_3); 160.1, 158.0 (*C*═N); 73.6 (*C*H_2-O); 69.5, 67.8 (*C*H-N); 36.8 (CO-*C*H_3); 29.8, 30.2 (*C*H(CH_3)$_2$); 18.6, 18.2, 15.5, 14.9 (CH(*C*H_3)$_2$). Anal. Calcd for $C_{14}H_{23}ClN_2O_3Pd$: C, 41.09; H, 5.67; N, 6.85. Found: C, 41.23; H, 5.88; N, 7.00.

[Pd(COCH$_3$)(Cl)(BISOX)] (6b). Compound **6b** was obtained with the same procedure described for **6a** starting from 0.212 g (0.41 mmol) of **1b**. A 0.21 g (0.38 mmol, 94%) sample of **6b** was collected. IR (Nujol, cm^{-1}): 1690 (CO-CH_3); 1653, 1618 (C═N). IR (CH_2Cl_2, cm^{-1}): 1692 (CO-CH_3); 1657, 1622 (C═N). ^1H NMR ($CDCl_3$): δ 7.40−7.13 (m, 10H, Ph-*H*); 4.88−4.72, 4.61−4.45 (m, 1H each, C*H*-N); 4.37 (dd, J = 9.1 and 3.3 Hz, 1H, CH_2-O); 4.29 (dd, J = 8.9 and 4.4 Hz, 1H, CH_2-O); 4.18 (dd, J = 8.9 and 8.9 Hz, 1H, CH_2-O); 4.12 (dd, J = 9.1 and 9.1 Hz, 1H, CH_2-O); 3.39 (dd, J = 13.4 and 3.2 Hz, 1H, CH_2-Ph); 2.92 (dd, J = 13.7 and 3.2 Hz, 1H, CH_2-Ph); 2.67 (dd, J = 13.4 and 8.6 Hz, 1H, CH_2-Ph); 2.48 (dd, J = 13.7 and 8.9 Hz, 1H, CH_2-Ph); 2.74 (CO-CH_3); 1.39, 1.35 (s, 3H each, C(CH_3)$_2$). ^{13}C NMR ($CDCl_3$): δ 230.0 (*C*═O); 172.5, 169.4 (*C*═N); 136.7, 135.1 (Ph-C_i); 130.0, 129.7, 128.7, 128.3 (Ph-C_o, Ph-C_m); 127.2, 126.6 (Ph-C_p); 72.1, 71.3 (*C*H_2O); 66.6, 65.6 (*C*H-N); 39.9, 39.0 (*C*H_2-Ph); 39.6 (*C*(CH$_3$)$_2$); 36.9 (CO-*C*H_3); 25.3, 24.5 (C(*C*H_3)$_2$). Anal. Calcd for $C_{25}H_{29}ClN_2O_3Pd$: C, 54.9; H, 5.34; N, 5.12. Found: C, 55.01; H, 5.50; N, 5.35.

[Pd(CH$_3$)(CO)(BIOX)]$^+$[BAr′$_4$]$^-$ (7a). Nitrogen gas was bubbled at −5 °C for 6 h in a solution of 0.358 g (0.28 mmol) of **5a** in 30 mL of dichloromethane (solvent was added up to 30 mL each hour). A solid was obtained after filtration through Celite and evaporation of the solvent in a vacuum, and washed with hexane to yield **7a** as a white powder (0.328 g, 0.26 mmol, 94%). Alternatively **7a** was synthesized by reaction of 0.408 g (1.00 mmol) of **6a** and 0.884 g (1.00 mmol) of $Na^+[BAr'_4]^-$ at −40 °C in 25 mL of dichloromethane. The reaction mixture was slowly warmed to 0 °C, and the solution was filtered through Celite to remove NaCl. Then solvent was evaporated in a vacuum, and the resulting solid was washed with hexane (3 × 5 mL). A 1.123 g sample of the white compound **7a** (0.91 mmol, 91%) was collected. IR (Nujol, cm^{-1}): 2125 (Pd-CO); 1649, 1611 (C═N). ^1H NMR ($CDCl_3$, −20 °C): δ 7.60 (s, 8H, Ar′-H_o); 7.54 (s, 4H, Ar′-H_p); 4.71−4.41 (m, 4H, CH_2O); 4.25−4.10 (m br, 2H, C*H*-N); 2.00−1.83 (m, 2H, C*H*(CH$_3$)$_2$); 1.27 (s, 3H, Pd-CH_3); 0.80, 0.77, 0.71, 0.62 (d, J = 6.5 Hz, 3H each, CH(CH_3)$_2$). ^{13}C NMR ($CDCl_3$, −20 °C): δ 174.1 (Pd-*C*O); 161.6 (q, $^1J_{CB}$ = 50.2 Hz, Ar′-C_i); 162.5, 159.6 (*C*═N); 134.8 (Ar′-C_o); 128.8 (q, $^2J_{CF}$ = 31.7 Hz, Ar′-C_m); 124.5 (q, $^1J_{CF}$ = 272.6 Hz, *C*F_3); 117.6 (Ar′-C_p); 74.3, 74.0 (*C*H_2O); 69.2, 67.1 (*C*H-N); 30.9, 29.7 (*C*H(CH$_3$)$_2$); 18.3, 18.2, 15.3, 13.6 (CH(*C*H$_3$)$_2$); −0.01 (Pd-*C*H_3). Anal. Calcd for $C_{46}H_{35}BF_{24}N_2O_3Pd$: C, 44.67; H, 2.85; N, 2.26. Found: C, 44.54; H, 3.00; N, 2.14.

[Pd(CH(*p*-CH$_3$-Ph)CH$_2$C(O)CH$_3$)(BIOX)]$^+$[BAr′$_4$]$^-$ (8a). *p*-Methylstyrene (28 μL, 0.212 mmol) was added to a solution of **7a** (0.257 g, 0.207 mmol) in 2.5 mL of chloroform cooled to −20 °C. After 20 min solvent was evaporated in a vacuum, and the resulting solid was washed with hexane (2 × 4 mL). A 0.253 g sample of the yellow compound **8a** (0.187 mmol, 90%) was collected. IR (Nujol, cm^{-1}): 1710 (CO−CH_3); 1622, 1610 (C═N). IR ($CDCl_3$, cm^{-1}): 1623.5 (CO-CH_3); 1637.2, 1610.0 (C═N). ^1H NMR ($CDCl_3$, −50 °C): δ 7.71 (s, 8H, Ar′-H_o); 7.54 (s, 4H, Ar′-H_p); 7.25, 7.03 (d, J = 8.0 Hz, 2H each, Ph-H_o, Ph-H_m); 4.72−4.25 (m, 4H, CH_2O and 1H, C*H*-N); 4.02 (dd, J = 6.8 and 6.1 Hz, 1H, C*H*-CH_2); 3.02 (dd, J = 20.5 and 6.8 Hz, 1H, CH-CH_2); 2.69 (dd, J = 20.5 and 6.1 Hz, 1H, CH-CH_2); 2.56−2.40 (m, 1H, C*H*-N); 2.42 (s, 3H, CO-CH_3); 2.14 (s, 3H, Ph-CH_3); 2.16−1.94, 1.81−1.59 (m br, 1H each, C*H*(CH$_3$)$_2$); 0.87, 0.83, 0.68, 0.64 (d, J = 7.4 Hz, 3H each, CH(CH_3)$_2$). ^{13}C NMR ($CDCl_3$, −20 °C): δ 232.8 (*C*OCH$_3$); 161.5 (q, $^1J_{CB}$ = 50.2 Hz, Ar′-C_i); 159.4, 158.0 (*C*═N); 140.2, 137.7 (Ph-C_i, Ph-C_p); 134.6 (Ar′-C_o); 130.3, 125.2 (Ph-C_o, Ph-C_m); 128.6 (q, $^2J_{CF}$ = 31.7 Hz, Ar′-C_m); 124.3 (q, $^1J_{CF}$ = 272.2 Hz, *C*F_3); 117.4 (Ar′-C_p); 73.7, 72.3 (*C*H_2O); 69.3, 64.8 (*C*H-N); 57.3 (CH-*C*H_2); 40.5 (*C*H-CH_2); 30.1, 29.3 (*C*H(CH$_3$)$_2$); 27.7 (CO*C*H$_3$); 21.3 (Ph-*C*H$_3$); 17.9, 15.6, 13.2 (CH(*C*H$_3$)$_2$). Anal. Calcd for $C_{55}H_{45}BF_{24}N_2O_3Pd$: C, 48.75; H, 3.35; N, 2.07. Found: C, 48.69; H, 3.35; N, 1.94.

CO/*p*-Methylstyrene Copolymerization Starting from 7a. The copolymer poly(1-oxo-2-(4-methyl)phenyltrimethylene) **4** was also obtained according to the following procedure: 0.122 g (0.099 mmol) of the complex **7a** was dissolved in 1.5 mL of dichloromethane under nitrogen atmosphere, then *p*-methylstyrene (11.6 mg, 0.099 mmol) was added at −20 °C. The reaction mixture was slowly warmed to 0 °C, then a solution of 5.2 mL of *p*-methylstyrene in 2.5 mL of dichloromethane was added (olefin/palladium molar ratio 400:1). The resulting solution was transferred into a thermostated Schlenk flask equipped with a carbon monoxide gas line and a tank for the CO, where the copolymerization was carried out at 25 °C for 7 h. The resulting gray polymer was precipitated with methanol, washed with methanol, and purified by dissolving in chloroform, filtering through Celite, and suspending it overnight in ethyl acetate. A 1.28 g (122 g of polymer/g Pd) sample of white copolymer **4** was collected. For IR, ^1H NMR, and ^{13}C NMR spectra, see Experimental Section of compound **4**. Anal. Calcd for $(C_{10}H_{10}O)_n$: C, 82.16; H, 6.89. Found: C, 82.37; H, 7.01. M_w = 6800; M_w/M_n = 1.4. $[\alpha]^{25}_{589}$ −369° (3.70 mg/mL, CH_2Cl_2).

[Pd(COCH(*p*-CH$_3$-Ph)CH$_2$COCH$_3$)(CO)(BIOX)]$^+$-[BAr′$_4$]$^-$ (9a). A 5.1 μL (0.0386 mmol) sample of *p*-methylstyrene was added to a $CDCl_3$ solution (0.6 mL) of **7a** (47.8 mg, 0.0386 mmol) at −40 °C. After a few minutes the reaction mixture was warmed to 0 °C, whereupon it changed from yellow to red. Bubbling of CO at −40 °C for 10 min finally resulted in the yellow solution of **9a**. This complex was stable only in solution and for a few hours, which precluded elemental analysis. IR ($CDCl_3$, cm^{-1}): 2129.7 (Pd-CO); 1718.0, 1715.1 (br, CO); 1635.5, 1609.5 (C═N). ^1H NMR ($CDCl_3$, −55 °C): δ 7.65 (s, 8H, Ar′-H_o); 7.48 (s, 4H, Ar′-H_p); 7.13, 7.05 (d, J = 7.8 Hz, 2H each, Ph-H_o, Ph-H_m); 4.99−4.83, 4.07−3.91 (m br, 1H each, C*H*-N); 4.69−4.35 (m, 4H, CH_2O and 1H, C*H*-CH_2); 3.52 (dd, J = 18.4 and 10.9 Hz, 1H, CH-CH_2); 2.62 (dd, J = 18.4 and 2.4 Hz, 1H, CH-CH_2); 2.22 (s, 3H, Ph-CH_3); 2.16 (s, 3H, CO-CH_3); 1.75−1.55 (m br, 2H, C*H*(CH$_3$)$_2$); 0.77, 0.73, 0.60 (d, J = 7.1, 6.8, 6.5 Hz, 12H, CH(CH_3)$_2$). ^{13}C NMR ($CDCl_3$, −50 °C): δ 208.1, 206.9 (*C*O-CH_3, *C*O-CH); 171.4 (Pd-*C*O); 161.7 (q, $^1J_{CB}$ = 50.2 Hz, Ar′-C_i); 161.2, 159.1 (*C*═N); 140.4 (Ph-C_p); 134.8 (Ar′-C_o); 134.0 (Ph-C_i); 131.0 129.6 (Ph-C_o, Ph-C_m); 128.8 (q, $^2J_{CF}$ = 30.1 Hz, Ar′-C_m); 124.5 (q, $^1J_{CF}$ = 272.6 Hz, *C*F_3); 117.7 (Ar′-C_p); 74.3, 74.1 (*C*H_2O); 69.1, 68.3 (*C*H-N); 61.9 (*C*H-CH_2); 46.3 (CH-*C*H_2); 30.9, 29.1 (*C*H(CH$_3$)$_2$); 30.1 (CO*C*H$_3$); 21.4 (Ph-*C*H$_3$); 18.3, 15.8, 13.6 (CH(*C*H$_3$)$_2$).

[Pd((COCH(*p*-CH$_3$-Ph)CH$_2$)$_2$COCH$_3$)(CO)(BIOX)]$^+$-[BAr′$_4$]$^-$ (10a). A 13 μL (0.0987 mmol) sample of *p*-methylstyrene was added to a $CDCl_3$ solution (1 mL) of **7a** (60,0 mg, 0.0485 mmol) at −30 °C. The reaction mixture was stirred at −30 °C for 30 min, then CO was bubbled for 10 min. The resulting solution was stirred for 4 h at −5 °C and then left for 36 h at −14 °C to yield a 1:1 mixture of compounds **9a** and **10a** stable only in solution. IR ($CDCl_3$,cm^{-1}): 2127.8 (Pd-CO); 1716.0 (br, CO); 1640.1, 1612.2 (C═N). ^1H NMR ($CDCl_3$): δ 7.62 (s, 8H, Ar′-H_o); 7.45 (s, 4H, Ar′-H_p); 7.25−6.92 (m, 8H, Ph-H_o, Ph-H_m); 4.59−4.47 (m, 4H, CH_2O and 1H, C*H*-CH_2); 4.47−4.25 (m br, 2H, C*H*-N); 4.04 (dd, J = 10.6 and 3.1 Hz 1H, C*H*-CH_2); 3.40 (dd, J = 18.7 and 10.9 Hz, 1H, CH-CH_2); 3.31 (dd, J = 18.4 and 10.6 Hz, 1H, CH-CH_2); 2.83 (dd, J = 18.7 and 2.4 Hz, 1H, CH-CH_2); 2.61 (dd, J = 18.4 and 3.1 Hz, 1H, CH-CH_2); 2.36, 2.33 (s, 3H each, Ph-CH_3); 2.13 (s, 3H, CO-CH_3); 1.89−1.69 (m br, 2H, C*H*(CH$_3$)$_2$); 0.77, 0.68 (2d, J = 7.1, 6.8 Hz, 12H, CH(CH_3)$_2$). ^{13}C NMR ($CDCl_3$, −50 °C): δ 208.4,

207.3, 206.8 (*C*O-CH_3, *C*O-CH); 171.3 (Pd-*C*O); 161.7 (q, $^1J_{CB}$ = 49.4 Hz, Ar′-C_i); 161.3, 159.0 (*C*═N); 140.3, 138.2 (Ph-C_p); 134.8 (Ar′-C_o); 134.0, 133.0 (Ph-C_i); 131.0, 130.1, 129.7, 128.0 (Ph-C_o, Ph-C_m); 128.5 (q, $^2J_{CF}$ = 31.7 Hz, Ar′-C_m); 124.5 (q, $^1J_{CF}$ = 272.6 Hz, *C*F_3); 117.7 (Ar′-C_p); 74.3, 74.0 (*C*H_2O); 69.1, 68.3 (*C*H-N); 61.4, 51.6 (*C*H-CH_2); 47.4, 44.3 (CH-*C*H_2); 30.9, 29.2 (*C*H(CH_3)$_2$); 30.0 (CO*C*H_3); 21.4, 21.3 (Ph-*C*H_3); 18.2, 15.8, 13.6 (CH(*C*H_3)$_2$).

Acknowledgment. This work was supported by the Ministero dell'Università e della Ricerca Scientifica (MURST-Rome) grant no. MM03027791. We would like to thank Ms. Anna Rita Pierleoni for her technical assistance.

OM0208669