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Syndiotactic CO/Styrene Copolymerization Catalyzed by α-Diimine Pd(II) Complexes: Regio- and Stereochemical Control[†]

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Using the catalytic system $[(Pr^iDAB)Pd(Me)(NCMe)]^+[\{3,5\text{-}(CF_3)_2C_6H_3\}_4B]^-$, where Pr^iDAB = 1,4-diisopropyl-1,4-diaza-1,3-butadiene, it has been possible to obtain copolymers of styrene or *p*-methylstyrene with carbon monoxide, which have alternating, head-to-tail, syndiotactic structure and a stereochemical purity of 92%. To investigate the reaction mechanism, the first steps of the copolymerization were studied by isolating and characterizing the reaction intermediates. The reactivity of the catalyst toward carbon monoxide was studied, and the corresponding methyl carbonyl Pd initiator complex was isolated. The regiospecific 2,1-insertion of *p*-methylstyrene in the Pd−acyl bond was proved by NOE measurements performed on the first intermediate, a five-membered palladacycle, in which the acetylic oxygen is coordinated to the palladium. Moreover, the intermediate resulting after the second sequence of CO and styrene insertion unexpectedly showed a doubling of the signals, both in the proton and carbon-13 NMR spectra. This finding, attributed to the presence of two diastereoisomeric complexes, showed that the chain-end stereochemical control is not fully effective during the initial steps of the copolymerization. Last, the fluxional character of some examined complexes was studied and the relative activation energies were determined.

Introduction

Since the pioneering work of Drent,[1] the copolymerization of styrene or styrene analogues with carbon monoxide, catalyzed by palladium complexes, has been extensively investigated.[2] Pd(II) complexes containing nitrogen bidentate ligands and weakly coordinating anions have been used as active precatalysts, high values of CO pressure, fairly high temperature, and methanol as solvent generally being the reaction conditions. Copolymers have been produced at low pressure of CO (1 or 4 bar)[2b,3] only in a few cases. The copolymers obtained are characterized by *chemo*regularity, i.e. perfect alternation of the carbon monoxide and styrene comonomers, and by *regio*regularity, i.e. head-to-tail placement of the styrene monomeric units, the latter being a consequence of the secondary migratory insertion of the styrene units into the palladium−acyl bond of the catalytic system, as shown by studies of low molecular weight copolymers and oligomers[4] and model compounds.[2b,5] In the case of syndiotactic-specific catalysts, the stereochemical control of the copolymerization has been ascribed to the chirality of the polymer chain end,[1c,2a,2l] whereas in the case of isotactic-specific catalysts, it has been ascribed to the chirality of the ligands.[3a,b,5a,6]

From recent reports in the literature[1c] it appears that this field of polyketone chemistry is an opportunity for testing new catalytic systems and checking mechanism hypotheses. Prompted by this, we tried our approach:

[†] This paper is dedicated to Professor Alfredo Musco.

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[1] (a) Drent, E. *Eur. Pat. Appl.* **1986**, *229*, 408; *Chem. Abstr.* **1988**, *108*, 6617. (b) Drent, E.; van Broekhoven, J. A. M.; Doyle, M. J. *J. Organomet. Chem.* **1991**, *417*, 235. (c) Drent, E.; Budzelaar, P. H. M. *Chem. Rev.* **1996**, *96*, 663.

[2] (a) Corradini, P.; De Rosa, C.; Panunzi, A.; Petrucci, G.; Pino, P. *Chimia* **1990**, *44*, 52. (b) Brookhart, M.; Rix, F. C.; DeSimone, J. M.; Barborak, J. C. *J. Am. Chem. Soc.* **1992**, *114*, 5894. (c) Sen, A.; Jiang, Z. *Macromolecules* **1993**, *26*, 911. (d) Busico, V.; Corradini, P.; Landriani, L.; Trifuoggi, M. *Makromol. Chem. Rapid. Commun.* **1993**, *14*, 261. (e) Jiang, Z.; Adams, S. E.; Sen, A. *Macromolecules* **1994**, *27*, 2694. (f) Milani, B.; Alessio, E.; Mestroni, G.; Sommazzi, A.; Garbassi, F.; Zangrando, E.; Bresciani-Pahor, N.; Randaccio, L. *J. Chem. Soc., Dalton Trans.* **1994**, 1903. (g) Milani, B.; Anzilutti, A.; Vicentini, L.; Sessanta o Santi, A.; Zangrando, E.; Geremia, S.; Mestroni, G. *Organometallics* **1997**, *16*, 5064. (h) Nozaki, K.; Hiyama, T. *J. Organomet. Chem.* **1999**, *576*, 248. (i) Milani, B.; Corso, G.; Mestroni, G.; Carfagna, C.; Formica, M.; Seraglia, R. *Organometallics* **2000**, *19*, 3435. (j) Aeby, A.; Gsponer, A.; Sperrle, M.; Consiglio, G. *J. Organomet. Chem.* **2000**, *603*, 122.

[3] (a) Brookhart, M.; Wagner, M. I.; Balavoine, G. G. A.; Haddou, H. A. *J. Am. Chem. Soc.* **1994**, *116*, 3641. (b) Bartolini, S.; Carfagna, C.; Musco, A. *Macromol. Rapid Commun.* **1995**, *16*, 9. (c) Milani, B.; Alessio, E.; Mestroni, G.; Zangrando, E.; Randaccio, L.; Consiglio, G. *J. Chem. Soc., Dalton Trans.* **1996**, 1021. (d) Macchioni, A.; Bellachioma, G.; Cardaci, G.; Travaglia, M.; Zuccaccia, C.; Milani, B.; Corso, G.; Zangrando, E.; Mestroni, G.; Carfagna, C.; Formica, M. *Organometallics* **1999**, *18*, 3061.

[4] Barsacchi, M.; Consiglio, G.; Medici, L.; Petrucci, G.; Suter, U. W. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 989.

[5] (a) Aeby, A.; Bangerter, F.; Consiglio, G. *Helv. Chim. Acta* **1998**, *81*, 764. (b) Carfagna, C.; Formica, M.; Gatti, G.; Musco, A.; Pierleoni, A. *Chem. Commun.* **1998**, 1113.

[6] (a) Sperrle, M.; Aeby, A.; Consiglio, G.; Pfaltz, A. *Helv. Chim. Acta* **1996**, *79*, 1387. (b) Brookhart, M.; Wagner, M. I. *J. Am. Chem. Soc.* **1996**, *118*, 7219.

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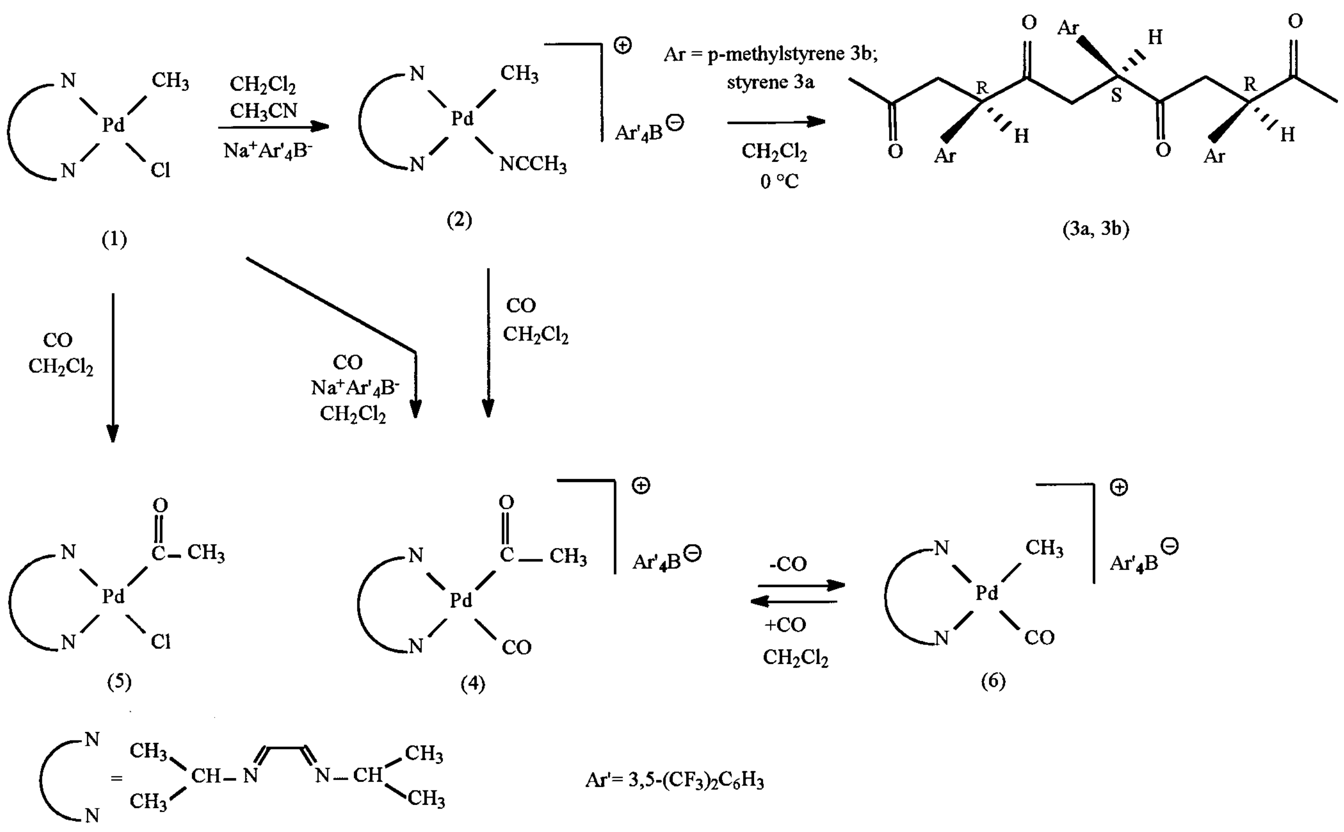
Scheme 1



by using precatalysts of the type $[(N{-}N)Pd(CH_3)(NCCH_3)]^+[\{3,5\text{-}(CF_3)_2C_6H_3\}_4B]^-$ we devised catalytic systems capable of producing both syndiotactic (in the case in which N−N = diazabutadienes)[5b] and isotactic (in the case in which N−N = bioxazolines)[3b] copolymers. The reaction conditions in both cases are very mild (P_{CO} = 1 bar and T = 0 °C, solvent = dichloromethane).

An appropriate ligand choice (1,4-diisopropyl-1,4-diazabuta-1,3-diene = Pr^{i}DAB) allowed us to monitor the first steps of polymer chain growth. Thus, with the aim of adding further knowledge to the syndiotactic propagation, we decided to investigate the stereochemistry of the intermediate complexes.

In this paper we report the results of the copolymerization reactions of styrene and *p*-methylstyrene with CO, using the syndiospecific precatalyst $[(Pr^iDAB)Pd(CH_3)(NCCH_3)]^+[\{3,5\text{-}(CF_3)_2C_6H_3\}_4B]^-$, where Pr^{i}DAB = 1,4-diisopropyl-1,4-diaza-1,3-butadiene. Moreover, we describe the full details of the synthesis and spectroscopic characterization of the catalyst and precursors. Last, but not least, we report on the reactivity of the catalyst with the comonomers and on the isolation and characterization of reaction intermediates, which was in part the subject of a preliminary note.[5b]

Results and Discussion

A. Synthesis of Complexes 1 and 2. The complex $(Pr^iDAB)Pd(CH_3)(Cl)$, **1**, was synthesized from the reaction of $(COD)Pd(CH_3)(Cl)$ (COD = 1,5-cyclooctadiene) with the α-diimine ligand in dichloromethane at room temperature;[7] the diene was substituted quantitatively by Pr^{i}DAB within a few hours. The ^{1}H NMR spectrum (20 °C) of **1** shows two characteristic broad singlets for the two nonequivalent imine ($CH{=}N$) protons, centered at 8.13 and 8.00 ppm, respectively, and in the ^{13}C NMR spectra the corresponding diimine carbons are at 160.0 and 155.2 ppm. This indicates that, at this temperature, the complex is in the regime of slow exchange on the NMR time scale. Moreover, the two isopropyl groups are not equivalent: the CH_3 signals are two doublets (J = 6.5 Hz) and the CH signals are two double septets (J = 6.5 Hz, and 1.2 Hz), the small splitting being due to long-range coupling with $CH{=}N$ protons. Last, $Pd{-}CH_3$ resonances are at δ_H 1.06 and at δ_C 0.1, the shielding being due to the coordination of the metal. In the IR spectrum of **1**, in a film, two (C=N) stretching bands at 1637.3 and 1582.2 cm^{-1} are found, due to the difference in *trans* effect exerted by the chlorine and the methyl group.

From the reaction of complex **1** with $Na^+BAr'_4{}^-$ (Ar′ = $3,5\text{-}(CF_3)_2C_6H_3$) at −40 °C in a CH_2Cl_2/CH_3CN (5:1 v/v) mixture, the cationic acetonitrile complex $[(Pr^iDAB)Pd(CH_3)(NCCH_3)]^+[\{3,5\text{-}(CF_3)_2C_6H_3\}_4B]^-$, **2**, was formed in good yields (Scheme 1), which is analogous to nitrile palladium adducts, containing α-diimine ligands with bulkier substituents, used by Brookhart as catalysts for olefin polymerizations[8a] and for the copolymerization of ethylene and α-olefins with methyl acrylate.[8b]

Complex **2** was characterized by ^{1}H and ^{13}C NMR spectra. It appears, from the ^{1}H NMR spectral pattern,

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(7) Rülke, R. E.; Ernsting, J. M.; Spek, A. L.; Elsevier, C. J.; van Leeuwen, P. W. N. M.; Vrieze, K. *Inorg. Chem.* **1993**, *32*, 5769.

(8) (a) Tempel, D. J.; Johnson, L. K.; Huff, R. L.; White, P. S.; Brookhart, M. *J. Am. Chem. Soc.* **2000**, *122*, 6686. (b) Mecking, S.; Johnson, L. K.; Wang, L.; Brookhart, M. *J. Am. Chem. Soc.* **1998**, *120*, 888.

similar to that of **1**, that **2**, at room temperature, is also in the regime of slow exchange. Moreover, the methyl resonance of the acetonitrile is shifted at δ 2.35, due to the coordination to palladium.

B. Copolymerization of Styrene or *p*-Methylstyrene with Carbon Monoxide. Styrene or *p*-methylstyrene was added to a dichloromethane solution of **2** presaturated with carbon monoxide (molar ratio olefin: palladium 250:1) at low temperature (0 °C) (Scheme 1). The solution was left for 24 h under CO atmosphere, and the copolymers poly(1-oxo-2-phenyltrimethylene), **3a**, or poly(1-oxo-2-(4-methyl)phenyltrimethylene), **3b**, were collected by precipitation with MeOH. Both copolymers were obtained in moderate yields: 98 g of copolymer **3a**/g Pd and 116 g of copolymer **3b**/g Pd were recovered. The molecular weight (M_w) was 8400 and 9200 amu, respectively, with a very low polydispersity (M_w/M_n) of 1.2−1.3. The stereoregularity of the copolymers was determined by ^{13}C NMR spectrometry (($(CF_3)_2CHOH/CDCl_3$ (50:50, v/v) at 45 °C): the carbons CO, C_{ipso}, CH_2, and CH show four strong signals, as well as small signals due to stereoisomeric impurities. The chemical shifts of the above carbons observed for **3a** and **3b** (see Experimental Section) correspond to the values reported in the literature[1,2,4,9] for the alternating head-to-tail syndiotactic copolymer. The stereoisomeric purity was estimated in the region of C_{ipso}, where the ratio of the *uu* triad to the *ul* and *lu* triads were 92% to 8% for **3a** and **3b**, while the *ll* triad was not detected.

C. Syntheses of Complexes 4−7. The key steps of the copolymerization process are the insertion reactions of CO in the palladium−alkyl bond and of alkene in the palladium−acyl bond.[10] To investigate the mechanism of the copolymerization promoted by our catalytic system **2**, we first studied the reaction of **2** toward carbon monoxide under the same conditions used for the synthesis of polyketones **3a** and **3b** (Scheme 1).

By exposure of **2** to CO atmosphere, the corresponding acetyl carbonyl complex **4** was obtained. A convenient alternative route to complex **4**, acetonitrile free, was realized by addition of $Na^+[\{3,5\text{-}(CF_3)_2C_6H_3\}_4B]^-$ to **1** at low temperature under CO atmosphere in dichloromethane previously saturated with CO. The mixture was slowly warmed to 0 °C, and after NaCl filtration, followed by solvent evaporation, an oil was obtained; washing with hexane produced a yellow powder corresponding to complex **4**.

Complex **1** also turned out to be very reactive with respect to carbon monoxide insertion. Indeed, by dissolving complex **1** in dichloromethane previously saturated with CO at −20 °C and slowly warming the solution to 20 °C, the pure acetylchloropalladium complex **5** was obtained as an orange solid after filtration, evaporation of the solvent, and washing with hexane. The CO insertion into the Pd−Me bond was confirmed from the spectroscopic data: high-frequency shift of the methyl resonance in the ^1H NMR spectrum from 1.06 to 2.62 ppm, the presence of the characteristic CO stretching in the IR spectrum (1700 cm^{-1}), and last, the chemical shift values for the CO (229 ppm) and for the methyl group (36.2 ppm) in the corresponding ^{13}C spectrum. The acetyl complex **5** is thermally stable as a solid and also in solution if stored at − 20 °C and does not show any tendency to decarbonylate. Indeed, if nitrogen is bubbled through a chloroform solution of **5** up to complete evaporation of the solvent, **5** is recovered unchanged.

Instead, bubbling nitrogen through a dichloromethane solution of **4** at −15 °C resulted in the formation of **6**, upon releasing of one molecule of CO. Exposure of the solution of **6** to CO atmosphere led to the regeneration of **4**. This observation shows that this carbonylation reaction is reversible.

Finally the five-membered palladacycle **7** was synthesized by reaction of **6** with *p*-methylstyrene in CH_2Cl_2 as preliminarily reported[5b](Scheme 2).

D. Fluxional Behavior. The ^1H and ^{13}C NMR spectra of the complexes **1**, **2**, **4**, **5**, and **6** are temperature dependent. By lowering the temperature of the samples, the resonances of the Pr^iDAB ligand become broad and then split in two different sets of chemical shifts. This observation can be rationalized by assuming a fluxional interconversion between two forms (as shown in Scheme 3), which is fast at high temperature and slow at low temperature. However, the temperature of coalescence appears to be quite different in the series of complexes. Moreover, measuring the spectrum of **2** upon addition of 1 equiv of CH_3CN and, likewise, measuring the spectrum of **4** and **5** under CO atmosphere results in a considerable lowering of the coalescence temperature. To obtain a quantitative evaluation of the process, the chemical shift difference, measured in the slow interconversion regime, was used to estimate the interconversion frequency with the relationship $k = \pi\Delta\nu/\sqrt{2}$. The Gibbs free energy of activation for the process at the coalescence temperature was then calculated using the Eyring equation. The results of this analysis, performed on the proton signals of the fragment $-N{=}CH{-}CH{=}N-$, are shown in Table 1. It appears that the activation energy barrier depends strongly on the substituent pattern of the Pd center. Moreover the addition of free ligands such as CO and CH_3CN results in a lower energy barrier.

E. Mechanistic Studies: Alkene and CO Insertions. Several examples are described in the literature of reactions resulting from the insertion of various alkenes into metal acyl bonds, either preexistent or formed after α-migration of the alkyl,[11] but the olefin employed is styrene or substituted styrenes in only a few cases.[2b,12] The chain propagation has been observed by Brookhart, at low temperature, by using the 2,2′-bipyridine ligand.[2b]

We used complex **2** as the initiator of the syndiotactic copolymerization but, by studying its evolution under

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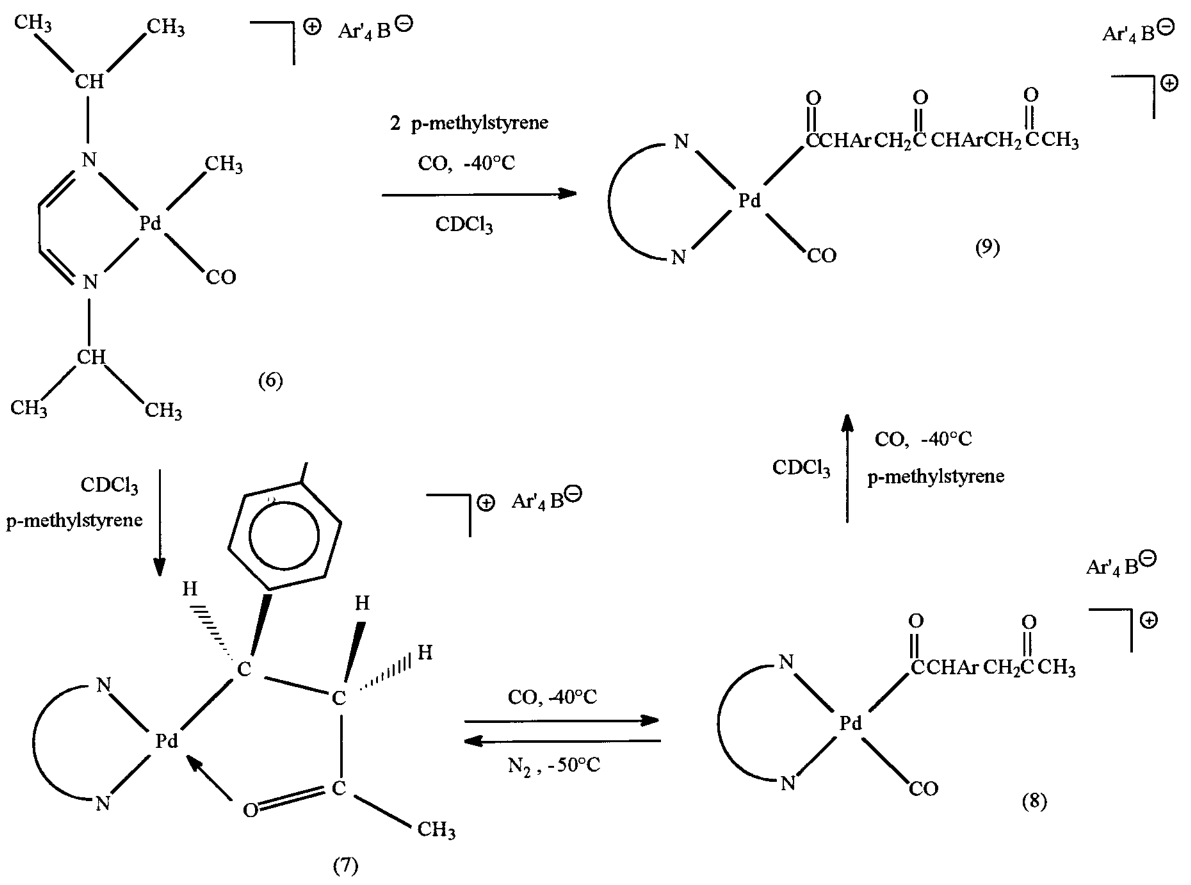
(9) Barsacchi, M.; Batistini, A.; Consiglio, G.; Suter, U. W. *Macromolecules* **1992**, *25*, 3604.

(10) Parshall, G. W.; Ittel, S. D. *Homogeneous Catalysis*, 2nd. ed.; Wiley: New York, 1992.

(11) (a) Brumbaugh, J. S.; Whittle, R. R.; Parvez, M.; Sen, A. *Organometallics* **1990**, *9*, 1735. (b) Ozawa, F.; Hayashi, T.; Koide, H.; Yamamoto, A. *J. Chem. Soc., Chem. Commun.* **1991**, 1469. (c) Markies, B. A.; Verkerk, K. A. N.; Rietveld, M. H. P.; Boersma, J.; Kooijman, H.; Spek, A. L.; van Koten, G. *J. Chem. Soc., Chem. Commun.* **1993**, 1317. (d) Sen, A. *Acc. Chem. Res.* **1993**, *26*, 303. (e) van Asselt, R.; Gielsens, E. E. C. G.; Rülke, R. E.; Vrieze, K.; Elsevie, C. J. *J. Am. Chem. Soc.* **1994**, *116*, 977. (f) Rülke, R. E.; Kaasjager, V. E.; Kliphuis, D.; Elsevier, C. J.; van Leeuwen, P. W. N. M.; Vrieze, K. *Organometallics* **1996**, *15*, 668. (g) Rix, F. C.; Brookhart, M.; White, P. S. *J. Am. Chem. Soc.* **1996**, *118*, 4746.

(12) (a) Dekker, G. P C. M.; Elsevier, C. J.; Vrieze, K.; van Leeuwen, P. W. N. M.; Roobeek, C. F. *J. Organomet. Chem.* **1992**, *430*, 357. (b) Aeby, A.; Consiglio, G. *J. Chem. Soc., Dalton Trans.* **1999**, 655.

Scheme 2



Scheme 3

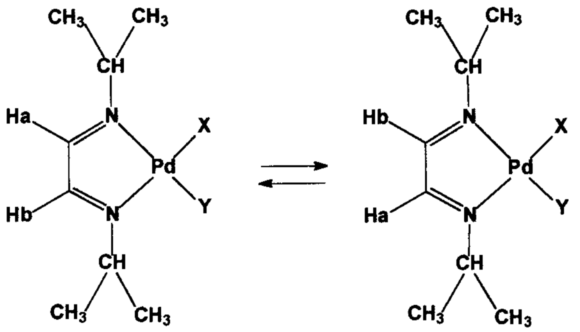


Table 1. Kinetic Parameters of Fluxionality

	1	2	2 +CH$_3$CN	4	4 +CO	5	5 +CO	6
T_{coalesc} (K)	335	336	271	213	196	278	240	288
k (s^{-1})	56	33	33	24	24	44	40	19
$\Delta G^{\ddagger} \pm 2$ kJ mol^{-1}	72	73	58	45	42	59	51	63

similar conditions used for the reaction, the real catalytic species was identified in complex **6**. It is isolable and adequately stable and is a useful starting point to follow the stoichiometric insertion of the unsaturated molecules step by step. In fact, the catalytic site of the metal center is easily obtainable by means of the alpha migration of the methyl. While the alkene insertion in complex **4** was very slow, the five-membered palladacycle **7** was smoothly obtained from **6** in good yield (Scheme 2).

The next step of the copolymerization reaction was investigated by cooling a CDCl$_3$ solution of complex **7** to −40 °C in an NMR tube and bubbling CO through the solution for 4 min. The conversion to the acyl carbonyl complex **8** was monitored by NMR, because it is stable only in solution at low temperature. This CO insertion is reversible, since by bubbling nitrogen through the solution for 4 min, at −50 °C, complex **7** was regenerated quantitatively. Last, one molecule of *p*-methylstyrene and one of carbon monoxide were inserted in complex **8** in order to determine the stereochemistry of complex **9**, in which two styrene units are present. Complex **9** can also be obtained directly from complex **6**, by adding 2 equiv of *p*-methylstyrene and bubbling CO (Scheme 2).

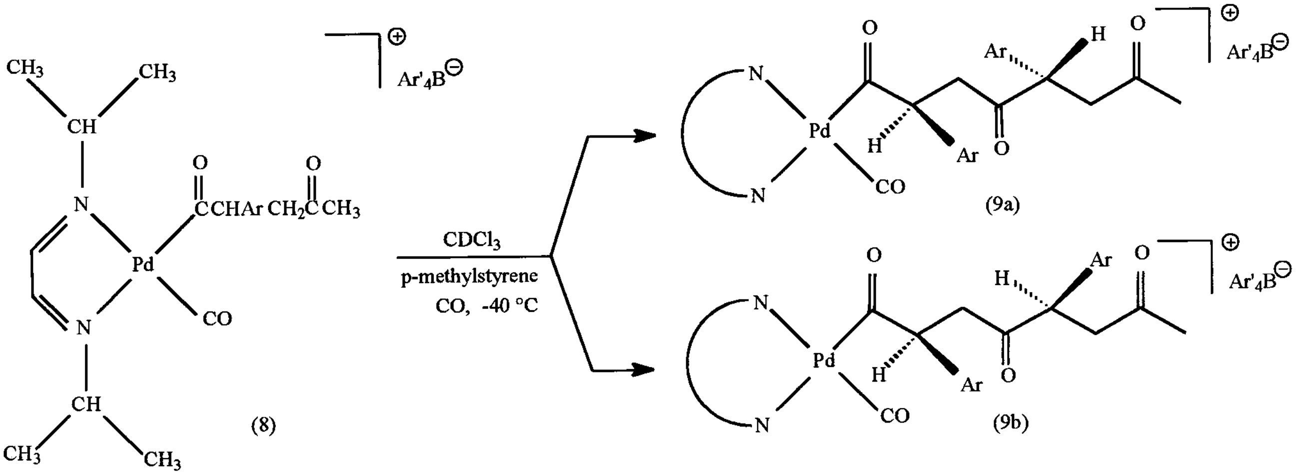
The structures of complex **7** and of the rather unstable species **8** and **9**, prepared with the aim of investigating the initial steps of the copolymerization reaction, were determined by ^{13}C, ^{1}H NMR, and IR spectroscopy. To allow comparison, the ^{13}C chemical shifts of Pd−(CO) and of the growing polymeric chain are shown in Table 2.

First of all, it appears that the spectral pattern of the chelated complex **7** is considerably different from the open chain complex **8**. Thus the CO signal of **7** is found at 224.9 ppm and is strongly deshielded when compared with the acetyl signal of **8**, which falls at 206.6 ppm, while the CH$_2$ signal of **7** appears, at 52 ppm, strongly deshielded in relation to the 45.9 ppm of **8**, which conforms to the presence of a chelating acetyl group in the cyclic structure **7**. These observations also give evidence in favor of the open chain structure of complex **8**, which was previously postulated to be cyclic.[5b] This assignment is further confirmed by the carbonyl signal

Table 2. Selected ^{13}C Chemical Shifts of the First Intermediates of Copolymerization (ppm from TMS)

complex	Pd−(CO)	−CO−	−CH−	$-CH_2-$	CH_3
7		224.9	47.0	52.0	29.2
8	171.5	211.2; 206.6	61.6	45.9	29.7
9	172.7; 171.9	209.2; 208.6; 208.2; 207.9; 207.8; 207.6	60.9; 52.5; 52.1	46.8; 46.3; 44.7; 44.3	29.9; 29.6

Scheme 4



at 171.5 ppm in the ^{13}C spectrum of **8** and by the presence in the IR spectrum of two bands at 2126 and 1718 cm^{-1}, the former being typical of a CO ligand bonded to a cationic palladium center. Moreover, in the ^{13}C NMR spectrum, the CH signal of **8** shifts at 61.6 ppm compared to 47 ppm in **7**, thereby proving the CO insertion in **8**. However, in the acetyl group, the chemical shift of methyl, is not strongly different between **7** and **8**.

As far as regards complex **9**, in which two styrene units are inserted, the number of resonances observed in each spectral region described above indicates the presence of two forms. In particular the resonance of the Pd−CO is split into two signals (172.7 and 171.9 ppm), and the resonances for the other three acyl CO groups are split into six signals (209.2, 208.6, 208.2, 207.9, 207.8, and 207.6 ppm), whereas three resonances for CH (52.5, 52.1, and two overlapping at 60.9 ppm), four resonances for CH_2 (46.8, 46.3, 44.7, and 44.3 ppm), and two for the terminal methyl group (29.9 and 29.6 ppm) were found. On the basis of the relatively small shifts observed, we suggest that the two forms are the two diastereoisomeric complexes **9a** and **9b**, as reported in Scheme 4. From the relative intensity of the split signals, it appears that the amount of one form is approximately double of the other.

The above picture is confirmed by ^{1}H NMR data. The analysis of the ABX pattern due to the $CH-CH_2$ fragment in the spectrum of **7** (previously reported)[5b] is additional evidence of styrene insertion. Moreover, the measurement of a strong NOE effect between the CH_3CO and the CH_2 proves the proximity of these groups and therefore the 2,1-regiochemistry of the styrene insertion. The NOE effect measurements allowed the assignment of regiochemistry; thus irradiation of CH_3CO resulted in enhancement of the CH_2 signal but not of the CH of the styrene unit. Furthermore, irradiation of the ortho proton of the phenyl ring resulted in enhancement of the proximal isopropyl CH. Both observations are in agreement with 2,1-insertion of the styrene monomer unit.

The neat ABX pattern of the $CH-CH_2$ present in the spectrum of **8** has different spectral parameters than that of **7**. The observed deshielding of the CH is in agreement with the vicinal CO insertion, while the changes of the vicinal coupling constants are due to the different conformation of the noncyclic form. The proton signal for the CH_3CO group, which is not bonded to the Pd center, is found at 2.15 ppm.

The ^{1}H spectrum of complex **9** contains a $CH-CH_2$ pattern of signals, which overlap in a complicated manner. However, in the CH region it is still possible to identify four quartets ($J_{vic} \approx 11$ Hz, $J_{vic} \approx 3$ Hz), two centered at 4.2, one at 4.1, and one at 4.05 ppm, while in the CH_2 region this distinction is not so easy. In any case, the remaining J value of ca. −18 Hz can be measured, which is diagnostic of geminal coupling of the CH_2 group linked to CO.

The above results suggest that the stereocontrol is not yet fully effective during the second sequence of CO and styrene insertion. To check this finding, we have examined the ^{13}C resonance of the terminal methyl of the copolymer by measuring long-term accumulations spectra with high signal to-noise ratio: it was possible to detect again two different resonances, at 29.6 and 30.3 ppm. The weakest signal at 29.6 was assigned to the isotactic chain end by comparison with an authentic sample of highly isotactic copolymer prepared with an isospecific catalyst.[3b] The intensity ratio of the two signals observed for the chain-end methyl groups of the copolymers is the same of that already observed in the complex **9**; therefore, the syndiotactic terminal configuration is, in both cases, more abundant than the isotactic configuration. All of this evidence suggests that in the case of our catalytic system the mechanism of chain-end stereocontrol is not fully working in the first steps of the copolymerization. However, considering the high stereoregularity of the obtained syndiotactic copolymer together with the absence of *ll* triads, undoubtedly such a mechanism becomes more effective in the next steps of the copolymerization. This might be ascribed to the increased length of the polymer chain on the last inserted chiral CH carbon, which enhances the asymmetric induction.

Conclusions

The catalytic system based on α-diimine Pd(II) complex **2**, in dichloromethane, affords regio- and stereoregular alternating copolymers of carbon monoxide with styrene or *p*-methylstyrene. The reaction can be carried out at low temperature and 1 bar carbon monoxide. The yield can be slightly enhanced by use of the *p*-methylstyrene comonomer. The structure of the copolymer resulted from NMR to be more than 92% syndiotactic.

Starting from our catalytic system we were able to identify the methyl carbonyl complex **6** as the active species for the initial olefin insertion. Moreover, it was possible to monitor the first steps of copolymerization through stoichiometric reactions. Insertion of the first olefin monomeric unit was observed by isolating a five-membered palladacycle, of which the fully characterized structure gave experimental support to the 2,1-mechanism of enchainment.

The intermediate **7** was proved, through spectroscopic evidence, to be able to insert carbon monoxide and a further olefin unit, thus resulting in the first dyad of the growing chain. Multiplicity of the NMR spectra, observed for complex **9**, was attributed to the presence of both *u* and *l* configurations. This unexpected finding suggests that the chain-end stereocontrol mechanism is not fully effective at this stage of the copolymerization reaction. However, considering the high stereoregularity of the syndiotactic copolymer, together with the absence of the *ll* triad, undoubtedly such a mechanism becomes effective in the next steps of copolymerization.

Last, all the examined complexes showed fluxional behavior with different free energy barriers depending on the pattern of the substituents. Moreover, in some cases it was possible to observe a definite lowering of the activation energy by addition of ligand excess to the solution, such as acetonitrile and carbon monoxide.

Experimental Section

All manipulations were carried out under a nitrogen atmosphere and 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. 1,4-Diisopropyl-1,4-diazabuta-1,3-diene[13] and $[\{3,5\text{-}(CF_3)_2C_6H_3\}_4B]^-Na^+$ [14] 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 solution in the range 4000−600 cm^{-1} on a Bruker IFS-48 FT-IR spectrometer. ^1H NMR spectra were measured on a Bruker AC200 spectrometer operating at 200.13 MHz with a selective 5 mm probehead. NOE measurements were performed using a Bruker noemult pulse program, with irradiation times of 2−4 s and power on the order of 32−36 dB (low scale). ^{13}C NMR spectra were measured at 50 MHz with a multinuclear 10 mm probehead. $_1H$ and ^{13}C NMR spectra chemical shifts are referred to the residual proton or carbon resonance of the deuterated solvents relative to TMS. Editing of ^{13}C NMR was obtained from DEPT spectra.

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 recorded 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). The CO/styrene copolymer was dissolved as follows: 3 mg of the sample was solubilized with 120 μL of 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) and chloroform was added up to 10 mL, while the CO/*p*-methylstyrene copolymer was directly soluble in chloroform. The statistical calculations were performed using the Bruker Chromstar software program.

(*i*-C_3H_7-DAB)Pd(CH_3)Cl (1). To a solution of 0.348 g (2.49 mmol) of *i*-C_3H_7-DAB in 8 mL of dichloromethane was added a solution of 0.600 g (2.26 mmol) of (COD)Pd(CH_3)Cl in 6 mL of the same solvent. The solution was stirred overnight at room temperature. After filtration through Celite, the solution was evaporated in a vacuum and the brownish oil was washed with hexane, yielding **1** as a yellow powder (0.643 g, 2.16 mmol, 96%). IR (film, cm^{-1}): 1637.3, 1582.2 (C═N). IR (CH_2Cl_2, cm^{-1}): 1635.2, 1577.4 (C═N). ^1H NMR ($CDCl_3$): δ 8.13 (s br, 1H, C*H*═N), 8.00 (s br, 1H, C*H*═N), 4.37 (dsept, $^3J = 6.5$ Hz and $^4J = 1.2$ Hz, 1H, C*H*(CH_3)$_2$), 4.26 (dsept, $J = 6.5$ and 1.2 Hz, 1H, C*H*(CH_3)$_2$), 1.43 (d, $J = 6.5$ Hz, 6H, CH(CH_3)$_2$), 1.37 (d, $J = 6.5$ Hz, 6H, CH(CH_3)$_2$), 1.06 (s, 3H, Pd-CH_3). ^{13}C NMR ($CDCl_3$): δ 160.0, 155.2 (*C*═N); 59.1, 56.6 (*C*H(CH_3)$_2$); 22.7, 22.2 (CH(*C*H_3)$_2$), 0.1 (Pd-*C*H_3). Anal. Calcd for $C_9H_{19}ClN_2Pd$: C, 36.38; H, 6.45; N, 9.43. Found: C, 36.37; H, 6.59; N, 9.44.

[(*i*-C_3H_7-DAB)Pd(CH_3)$NCCH_3$]$^+$[BAr′$_4$]$^-$ (2). To a solution containing 0.247 g (0.83 mmol) of **1** in 7 mL of dichloromethane/acetonitrile (5:1) cooled to −40 °C was added a dichloromethane/acetonitrile (5:1) solution (7 mL) containing $[\{3,5\text{-}(CF_3)_2C_6H_3\}_4B]^-Na^+$ (0.738 g, 0.83 mmol). The reaction mixture was slowly warmed to 0 °C, stirred for 15 min, and filtered through Celite to remove NaCl. After evaporation in a vacuum a dark oil was obtained, which upon treatment with hexane (6 mL) at −80 °C gave **2** as a yellow powder (0.916 g, 0.79 mmol, 95%). IR (Nujol, cm^{-1}): 2330.7, 2302.9 (CH_3CN), 1610.1 (C═N). ^1H NMR ($CDCl_3$): δ 7.92 (s br, 1H, C*H*═N), 7.85 (s br, 1H, C*H*═N), 7.70 (double q of q, $^4J_{HH} = 2.5$ Hz $^4J_{HCF_3} = 2.5$ $^6J_{HCF_3} = 0.6$, 8H, Ar-H_0), 7.55 (m br, 4H, Ar-H_p), 4.07 (sept, $J = 6.6$ and 1.2 Hz, 1H, C*H*(CH_3)$_2$), 3.78 (sept, $J = 6.6$ and 1.2 Hz, 1H, C*H*(CH_3)$_2$), 2.35 (s, 3H, CH_3CN); 1.29 (d, $J = 6.5$ Hz, 6H, CH(CH_3)$_2$), 1.21 (d, $J = 6.5$ Hz, 6H, CH(CH_3)$_2$), 1.05 (s, 3H, Pd-CH_3). ^{13}C NMR ($CDCl_3$, −10 °C): δ 163.1, 157.0 (C═N), 161.6 (q, $^1J_{CB} = 49.9$ Hz, Ar-C_i), 134.8 (Ar-C_o); 128.8 (double q, $^2J_{CF} = 31.4$ Hz, $^4J_{CF} = 2.8$ Hz, Ar-*Cm*), 124.5 (q, $^1J_{CF} = 272.5$ Hz, *C*F_3), 122.6 (CH_3*C*N), 117.6 (Ar-*Cp*), 62.0, 57.4 (*C*H(CH_3)$_2$), 22.2, 21.8 (CH(*C*H_3)$_2$), 5.0 (Pd-*C*H_3); 3.3 (*C*H_3CN). Anal. Calcd for $C_{43}H_{34}BF_{24}N_3Pd$: C, 44.30; H, 2.94; N, 3.60. Found: C, 44.19; H, 3.03; N, 3.54.

Poly(1-oxo-2-phenyltrimethylene) (3a). 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 **2** (0.195 g, 0.167 mmol) was dissolved at 0 °C in dichloromethane saturated with CO, and it was allowed to react for 30 min. The color of the solution changed from pale yellow to orange-yellow, then styrene (4.8 mL, 41.7 mmol) was added (olefin/palladium molar ratio 250:1); the solution was kept under CO at 0 °C. Within 6 h the solution started to darken slightly; after 24 h the resulting gray polymer was precipitated by adding methanol (30 mL) and washed with methanol. To remove metallic palladium traces, it was redissolved in 1,1,1,3,3,3,-hexafluoro-2-propanol, diluted

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(13) Kliegman, J. M.; Barnes, R. K. *Tetrahedron* **1970**, *26*, 2555.

(14) (a) Bahr, S. R.; Boudjouk, P. *J. Org. Chem.* **1992**, *57*, 5545. (b) Brookhart, M.; Grant, B.; Volpe, A. F. *Organometallics* **1992**, *11*, 3920.

with dichloromethane, and filtered through Celite. After precipitation with methanol, washing with methanol and ether, and drying under vacuum, 1.75 g of copolymer (98 g of polymer/g Pd) was collected. This copolymerization reaction can also be carried out at room temperature (18 °C), but in this case the polymer yield decreases. IR (film, cm^{-1}): 1695 (CO). ^1H NMR ($CDCl_3$, 17 °C): δ 7.20−6.60 (m, 5H, Ph), 4.09 (t, J = 6.8 Hz, 1H, C*H*-CH_2); 3.08 (dd, J = 17.8 Hz e 7.3 Hz, 1H, CH-CH_2), 2.65 (dd, J = 17.8 Hz e 6.8 Hz, 1H,CH-CH_2). ^{13}C NMR ($CDCl_3$/$(CF_3)_2CHOH$, 50:50) 45 °C: δ 210.7 (*C*O); 136.2 (Ph-C_{ipso}); 129.9, 128.9, 128.5 (Ph-$C_{o,m,p}$); 54.6 (*C*H-CH_2); 43.5 (CH-*C*H_2). Anal. Calcd for $(C_9H_8O)_n$: C, 81.79; H, 6.10. Found: C, 81.51; H, 6.06.

Poly(1-oxo-2-(4-methyl)phenyltrimethylene) (3b). The copolymer **3b** was obtained according to the procedure described above. To a solution of **2** (0.176 g, 0.151 mmol) in 15 mL of dichloromethane saturated with CO, kept for 30 min at 0 °C, was added *p*-methylstyrene (5 mL, 38 mmol). The polymerization was carried out for 24 h. The resulting copolymer was precipitated by adding methanol (30 mL) and then washed with methanol. To remove Pd traces, the copolymer was redissolved in chloroform, filtered through Celite, precipitated with methanol, washed with methanol and ether, and dried under vacuum to yield 1.87 g of copolymer (116 g of polymer/g Pd). IR (film, cm^{-1}): 1707 (CO). ^1H NMR ($CDCl_3$, 17 °C): δ 6.75 (d, J = 7.9 Hz, 2H, Ph), 6.55 (d, J = 7.9 Hz, 4H, Ph), 4.05 (t, J = 6.8 Hz, 1H, C*H*-CH_2), 3.02 (dd, J = 17.6 Hz e 6.8 Hz, 1H, CH-CH_2), 2.60 (dd, J = 17.6 Hz e 6.8 Hz, 1H, CH-CH_2), 2.20 (s, 3H, Ph-CH_3). ^{13}C NMR ($CDCl_3$/$(CF_3)_2CHOH$, 50:50) 45 °C: δ 210.9 (*C*O), 138.5 (Ph-C_p), 133.0 (Ph-C_{ipso}), 130.4, 128.7 (Ph-$C_{o,m}$), 54.3 (*C*H-CH_2), 43.4 (CH-*C*H_2), 20.9 (Ph-*C*H_3). Anal. Calcd for $(C_{10}H_{10}O)_n$: C, 82.16; H, 6.89. Found: C, 82.46; H, 7.02.

[(*i*-C_3H_7-DAB)Pd($COCH_3$)CO]$^+$[BAr$'_4$]$^-$ (4). A 0.159 g (0.54 mmol) sample of **1** and 0.475 g (0.54 mmol) of $[\{3,5-(CF_3)_2C_6H_3\}_4B]^-Na^+$ were suspended at −40 °C under CO atmosphere in 8 mL of dichloromethane previously saturated with CO. The reaction mixture was slowly warmed at 0 °C, stirred for 1 h, and filtered through Celite to remove NaCl. After evaporation of the solvent by bubbling CO, an oil was obtained, which, upon treatment with hexane saturated with CO, gave **4** as a yellow powder (0.578 g, 0.49 mmol, 92%). IR (Nujol, cm^{-1}): 2137 (Pd-CO), 1750 ($COCH_3$), 1611 (C=N). ^1H NMR (CD_2Cl_2, −75 °C): δ 7.98 (s, 1H, C*H*=N), 7.92 (s, 1H, C*H*=N), 7.65 (s, 8H, Ar$'$-H_o), 7.47 (s, 4H, Ar$'$-H_p), 3.72 (m br, 2H, C*H*$(CH_3)_2$), 2.67 (s, 3H, COCH_3), 1.10 (d, J = 6.1 Hz, 12H, CH(CH_3)$_2$). ^{13}C NMR (CD_2Cl_2, −75 °C): δ 214.5 (*C*OCH_3), 172.9 (Pd-*C*O), 164.1, 160.5 (*C*=N), 162.1 (q, $^1J_{CB}$ = 49.4 Hz, Ar$'$-C_i), 134.9 (Ar$'$-C_o), 128.9 (q, $^2J_{CF}$ = 31.4 Hz, Ar$'$-C_m), 124.7 (q, $^1J_{CF}$ = 272.6 Hz, *C*F_3), 117.9 (Ar$'$-C_p), 63.8, 59.5 (*C*H$(CH_3)_2$), 41.6 (CO*C*H_3), 23.2, 22.0 (CH(*C*H_3)$_2$). Anal. Calcd for $C_{43}H_{31}BF_{24}N_2O_2Pd$: C, 43.73; H, 2.65; N, 2.37. Found: C, 43.54; H, 2.77; N, 2.23.

[(*i*-C_3H_7-DAB)Pd($COCH_3$)Cl] (5). A 0.201 g (0.68 mmol) sample of **1** was dissolved at −20 °C under CO atmosphere in 3 mL of dichloromethane previously saturated with CO. The solution was slowly warmed to 20 °C, stirred for 15 min, and then filtered through Celite to remove metallic Pd traces. After evaporation of solvent by bubbling CO at 0 °C, an orange solid was obtained, which was washed with hexane and dried and shown to be compound **5** (0.216 g, 0.66 mmol, 98%). IR (Nujol, cm^{-1}): 1700 (Pd-$COCH_3$). ^1H NMR ($CDCl_3$, −30 °C): δ 8.05 (s, 1H, C*H*=N), 7.95 (s, 1H, C*H*=N), 4.04 (sept, J = 6.4 Hz, 2H, C*H*$(CH_3)_2$), 2.62 (s, 3H, COCH_3), 1.38 (d, J = 6.4 Hz, 6H, CH(CH_3)$_2$), 1.29 (d, J = 6.4 Hz, 6H, CH(CH_3)$_2$). ^{13}C NMR ($CDCl_3$, −28 °C): δ 229.0 (*C*OCH_3), 158.8, 155.9 (*C*=N), 60.5, 59.4 (*C*H$(CH_3)_2$), 36.2 (CO*C*H_3), 22.1 (CH(*C*H_3)$_2$). Anal. Calcd for $C_{10}H_{19}ClN_2OPd$: C, 36.94; H, 5.89; N, 8.62. Found: C, 37.05; H, 6.08; N, 8.65.

[(*i*-C_3H_7DAB)Pd(CH_3)CO]$^+$[BAr$'_4$]$^-$ (6). Nitrogen gas was bubbled at −15 °C for 10 min in a dichloromethane solution (7 mL) of **4** (0.240 g, 0.20 mmol). After filtration through Celite and evaporation of the solvent at −15 °C in a vacuum a yellow solid was obtained, which was dissolved in dichloromethane, reprecipitated, and washed with hexane at −15 °C to yield **6** as a white powder (0.210 g, 0.18 mmol, 90%). IR (Nujol, cm^{-1}): 2130 (Pd-CO), 1610 (C=N). ^1H NMR ($CDCl_3$, −20 °C): δ 7.96 (s, 1H, C*H*=N), 7.92 (s, 1H, C*H*=N), 7.69 (s, 8H, Ar$'$-H_o); 7.54 (s, 4H, Ar$'$-H_p), 4.13 (sept, 1H, C*H*$(CH_3)_2$), 3.77 (sept, 1H, C*H*$(CH_3)_2$), 1.36 (s, 3H, Pd-CH_3), 1.25 (d, J = 6.7 Hz, 12H, CH(CH_3)$_2$). ^{13}C NMR (CD_2Cl_2, 0 °C): δ 174.8 (Pd-*C*O), 165.8, 160.1 (*C*=N), 161.5 (q, $^1J_{CB}$ = 49.6 Hz, Ar$'$-C_i), 134.6 (Ar$'$-C_o), 128.7 (q, $^2J_{CF}$ = 30.0 Hz, Ar$'$-C_m), 124.3 (q, $^1J_{CF}$ = 272.5 Hz, *C*F_3); 117.5 (Ar$'$-C_p); 63.4, 56.3 (*C*H$(CH_3)_2$), 22.7, 21.8 (CH(*C*H_3)$_2$), 5.7 (Pd-*C*H_3). Anal. Calcd for $C_{42}H_{31}BF_{24}N_2OPd$: C, 43.76; H, 2.71; N, 2.43. Found: C, 43.74; H, 2.62; N, 2.53.

[(*i*-C_3H_7DAB)PdCH(*p*-CH_3-Ph)$CH_2C(O)CH_3$]$^+$[BAr$'_4$]$^-$ (7). To a solution of **6** (0.166 g, 0.144 mmol) in 2 mL of dichloromethane, cooled to −15 °C, was added *p*-methylstyrene (0.018 g, 0.151 mmol); the orange solution formed was slowly warmed at 25 °C and then 5 mL of *n*-hexane was added. The resulting oil was washed with *n*-hexane and then dried in a vacuum to yield **7** as a red powder (0.176 g, 0.138 mmol, 96%). IR (Nujol, cm^{-1}): 1721 (CO-CH_3), 1610 (C=N). ^1H NMR ($CDCl_3$, −3 °C): δ 7.80 (s, 1H, C*H*=N), 7.78 (s, 1H, C*H*=N), 7.71 (s, 8H, Ar$'$-H_o), 7.54 (s, 4H, Ar$'$-H_p), 7.2 (d, J = 7.9 Hz, 2H, Ph-H_o, Ph-H_m), 7.0 (d, J = 7.9 Hz, 2H, Ph-H_o, Ph-H_m), 3.88 (sept, 1H, C*H*$(CH_3)_2$), 3.68 (sept, 1H, C*H*$(CH_3)_2$), 3.76 (dd, J = 8.3 and 3.5 Hz, 1H, C*H*-CH_2), 3.04 (dd, J = 19.5 and 8.3 Hz, 1H, CH-CH_2), 2.70 (dd, J = 19.5 and 3.5 Hz, 1H, CH-CH_2), 2.39 (s, 3H, CO-CH_3), 2.19 (s, 3H, Ph-CH_3), 1.29, 1.17, 1.09 (3d, J = 6.4 Hz, 12H, CH(CH_3)$_2$). ^{13}C NMR ($CDCl_3$, −20 °C): δ 224.9 (*C*OCH_3), 161.7 (q, $^1J_{CB}$ = 49.2 Hz, Ar$'$-C_i), 161.2, 157.1 (*C*=N), 139.9 (Ph-C_i), 134.8 (Ar$'$-C_o), 132.1 (Ph-C_o), 130.8 (Ph-C_p), 128.8 (q, $^2J_{CF}$ = 31.5 Hz, Ar$'$-C_m), 124.5 (q, $^1J_{CF}$ = 272.4 Hz, *C*F_3), 119.9 (Ph-C_m), 117.6 (Ar$'$-C_p), 62.1, 59.5 (*C*H$(CH_3)_2$), 52.0 (CH-*C*H_2), 47.0 (*C*H−CH_2), 29.2 (CO*C*H_3), 22.8, 22.0, 21.4, 21.3 (CH(*C*H_3)$_2$), 21.9 (Ph-*C*H_3). Anal. Calcd for $C_{51}H_{41}BF_{24}N_2OPd$: C, 48.19; H, 3.25; N, 2.20. Found: C, 48.01; H, 3.22; N, 2.14.

[(*i*-C_3H_7-DAB)Pd(COCH(*p*-CH_3-Ph)CH_2COCH_3)CO]$^+$[BAr$'_4$]$^-$ (8). To a $CDCl_3$ solution (0.6 mL) of **6** (38 mg, 0.03296 × 10^{-3} mol), at −40 °C, was added 4.8 μL (0.03626 × 10^{-3} mol) of *p*-methylstyrene. After a few minutes, the solution was warmed to 0 °C, whereupon it changed color from yellow to red. Bubbling of CO at −40 °C for 4 min finally resulted in the yellow solution of **8**. Complex **8** was stable only in solution and for a few hours, which precludes elemental analysis. IR ($CDCl_3$, cm^{-1}): 2126 (Pd-CO); 1718.7 br (CO), 1610 (C=N). ^1H NMR ($CDCl_3$, −20 °C): δ 7.71 (s, 2H, C*H*=N), 7.63 (s, 8H, Ar$'$-H_o), 7.47 (s, 4H, Ar$'$-H_p), 7.10 (s, 4H, Ph-H_o, Ph-H_m), 4.54 (dd, J = 10.7 and 2.4 Hz, 1H, C*H*-CH_2), 3.67 (br s, 2H, C*H*$(CH_3)_2$), 3.50 (dd, J = 18.6 and 10.7 Hz, 1H, CH-CH_2), 2.67 (dd, J = 18.6 and 2.4 Hz, 1H, CH-CH_2), 2.19 (s, 3H, Ph-CH_3), 2.15 (s, 3H, CO-CH_3), 0.97 (d, J = 6.4 Hz, 12H, CH(CH_3)$_2$). ^{13}C NMR ($CDCl_3$, −48 °C): δ 211.2, 206.6 (*C*O-CH_3, *C*O-CH), 171.5 (Pd-*C*O), 163.2, 159.2 (*C*=N), 161.7 (q, $^1J_{CB}$ = 49.5 Hz, Ar$'$-C_i), 140.4 (Ph-C_p), 134.4 (Ar$'$-C_o), 130.9, 129.5 (Ph-$C_{o,m}$), 128.8 (q, $^2J_{CF}$ = 31.1 Hz, Ar$'$-C_m), 124.2 (q, $^1J_{CF}$ = 272.8 Hz, *C*F_3), 117.7 (Ar$'$-C_p), 62.9, 59.8 (*C*H$(CH_3)_2$), 61.6 (*C*H-CH_2), 45.9 (CH-*C*H_2), 29.7 (CO-*C*H_3), 22.1 (CH(*C*H_3)$_2$), 21.3 (Ph-*C*H_3).

[(*i*-C^3H_7-DAB)Pd((COCH(*p*-CH_3-Ph)CH_2)$_2$$COCH_3$)CO]$^+$[BAr$'_4$]$^-$ (9). To a $CDCl_3$ solution (0.8 mL) of **6**, [(*i*-C_3H_7DAB)Pd(CH_3)CO]$^+$[BAr$'_4$]$^-$ (84.2 mg, 0.0730959 × 10^{-3} mol), at −20 °C, was added 10.0 μL of *p*-methylstyrene (0.07675 × 10^{-3} mol). After bubbling CO and subsequent addition of *p*-methylstyrene (9.6 μL, 0.0730959 × 10^{-3} mol), and bubbling CO at −40 °C, the solution was left 16 h at −14 °C to yield compound **9**, which is stable only in solution. IR ($CDCl_3$, cm^{-1}): 2126 (Pd-CO), 1716 (br, CO), 1610 (C=N). ^1H NMR (CD_2Cl_2, −25 °C): δ 7.89 (s, 1H, C*H*=N), 7.82 (s, 1H, C*H*=N), 7.68 (s, 8H, Ar$'$-H_o), 7.50 (s, 4H, Ar$'$-H_p), 7.27−6.40 (m, 8H, Ph-H_o, Ph-H_m); 4.20 (dd, J ≈

11 and 3 Hz, 1H, CH-CH$_2$), 4.10, 4.05 (2 dd, $J \approx 11$ and 3 Hz, 1H, CH-CH$_2$), 3.85 (br, 2H, CH(CH$_3$)$_2$), 3.72−3.25 (m, 2H, CH-CH_2), 2.80−2.50 (m, 2H, CH-CH_2), 2.31, 2.25, 2.18, 2.10, 2.07 (5s, 9H, Ph-CH_3 and CO-CH_3), 1.30−0.99 (m, 12H, CH(CH_3)$_2$). ^{13}C NMR (CDCl$_3$, −20 °C): δ 209.2, 208.6, 208.2, 207.9, 207.8, 207.6 (CO-CH$_3$, CO-CH), 172.7, 171.9 (Pd-CO), 157.4, 156.8 (C═N), 161.4 (q, $^1J_{\mathrm{CB}} = 49.6$ Hz, Ar′-C_i); 140.1, 140.0, 139.8, 139.7 (Ph-C_p), 134.5 (Ar′-C_o), 130.6−129.5 (Ph-$C_{o,m,i}$), 128.6 (q, $^2J_{\mathrm{CF}} = 32.6$ Hz, Ar′-C_m), 124.3 (q, $^1J_{\mathrm{CF}} = 272.9$ Hz, CF$_3$), 117.4 (Ar′-C_p), 61.7, 59.8 (CH(CH$_3$)$_2$), 60.9, 52.5, 52.1 (CH-CH$_2$), 46.8, 46.3, 44.7, 44.3 (CH-CH$_2$), 29.9, 29.6 (CO-CH$_3$), 22.7, 22.1, 22.0, 21.6 (Ph-CH$_3$), 20.9 br (CH(CH$_3$)$_2$).

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