Studies of Ligand and Solvent Effects in the Alternating Copolymerization of Carbon Monoxide and Ethene by Palladium-Diphosphine Catalysis

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The Pd(II) methyl complexes [Pd(Me)(MeCN)(P−P)]PF_6 are effective catalyst precursors for the alternating copolymerization of carbon monoxide with ethene in CH_2Cl_2 (P−P = 1,3-bis(diphenylphosphino)propane (dppp), *meso*-2,4-bis(diphenylphosphino)pentane (*meso*-bdpp), *rac*-2,4-bis(diphenylphosphino)pentane (*rac*-bdpp)). The productivity in high molecular weight polyketones within 30 min follows the ligand order dppp > *meso*-bdpp > *rac*-bdpp. All the methyl precursors exhibit comparable values of both intrinsic activity and energy barriers to migratory insertions [Pd(Me)(CO), Pd(COMe)(C_2H_4)] as well as opening of β-chelates [Pd($CH_2CH_2C(O)Me$)(P−P)]$^+$ by CO. It is concluded that the presence and/or stereochemistry of methyl groups in the 1,3-positions of dppp do not exert a significant influence on the propagation rate of the copolymerization reaction in CH_2Cl_2. High-pressure NMR studies under catalytic conditions show the occurrence of chain transfer by protonolysis with adventitious water to give μ-hydroxo compounds [Pd(μ-OH)(P−P)]$_2^{2+}$. With time, the bis-chelates [Pd(P−P)$_2$]$^{2+}$ are the only species visible on the NMR time scale. Independent copolymerization reactions in CH_2Cl_2 with either μ-OH or bis-chelate precursors show that both resting states can reenter the catalysis cycle to give alternating polyketones with productivities increasing in the orders [Pd(μ-OH)(*rac*-bdpp)]$_2^{2+}$ < [Pd(μ-OH)(*meso*-bdpp)]$_2^{2+}$ < [Pd(μ-OH)(dppp)]$_2^{2+}$, and [Pd(*rac*-bdpp)$_2$]$^{2+}$ < [Pd(dppp)$_2$]$^{2+}$ < [Pd(*meso*-bdpp)$_2$]$^{2+}$. On the basis of the batch reactions and in situ NMR experiments it is suggested that both μ-hydroxo and bis-chelate compounds contribute appreciably to determine the overall productivity of the methyl precursors [Pd(Me)(MeCN)(P−P)]$^+$ in CH_2Cl_2. The bis-chelates are also active catalysts for the CO/ethene copolymerization in MeOH with productivities that increase in the ligand order dppp ≪ *rac*-bdpp < *meso*-bdpp.

Introduction

The alternating copolymerization of carbon monoxide and ethene is a reaction of remarkable fundamental and industrial relevance that Pd(II) compounds stabilized by chelating diphosphine ligands catalyze in different phase variation systems.[1,2] Therefore, increasing research efforts are being paid to both design more efficient Pd-diphosphine catalysts and understand in depth the mechanism(s) by which the copolymerization proceeds.[2]

We have recently found that methyl substituents in the 1,3-positions of the ligand backbone affect remarkably the catalytic activity of Pd(OTs)$_2$(P−P) precursors in the copolymerization of CO and ethene in MeOH (P−P = 1,3-bis(diphenylphosphino)propane (dppp), *meso*-2,4-bis(diphenylphosphino)pentane (*meso*-bdpp), *rac*-2,4-bis(diphenylphosphino)pentane (*rac*-bdpp); OTs = *p*-toluenesulfonate). The precursor with *meso*-bdpp proved significantly more active than those containing dppp and *rac*-bdpp, yet all catalysts gave perfectly alternating polyketones (alt-E-CO) with relatively low molecular weight (M_n ranging from 10 to 20 kg mol^{-1}) (Scheme 1).[3]

In situ HPNMR studies of the three catalytic systems showed neither deactivation by autoionization of the precursors[4,5] nor different resting states on the NMR time scale. The greater productivity of the *meso*-bdpp catalyst was not rationalized but empirically related to two experimental observables: (i) Cyclic voltammetry

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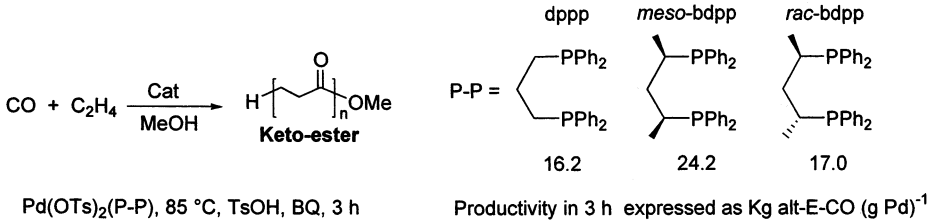
Scheme 1



showed the *meso*-bdpp precursor to undergo a chemically reversible Pd(II)/Pd(I) one-electron reduction prior to be reduced to Pd(0), whereas the dppp and *rac*-bdpp complexes were irreversibly reduced. Therefore, it was suggested that the oxidant cocatalyst 1,4-benzoquinone (BQ), necessary to oxidize inactive Pd(0) to Pd(II) sites,[2] could be more efficient for the *meso* precursor than for the dppp and *rac*-bdpp ones.[3a] (ii) NMR spectroscopy showed the *meso*-bdpp complex to adopt in solution a *chair* conformation with the four phenyl groups spatially disposed on either side of the PPdP coordination plane, while the dppp and *rac*-bdpp complexes exhibited a *skewphos* conformation with the phenyl groups diagonally positioned with respect to the same plane. Whether and to what extent this different steric situation might affect chain transfer and/or propagation was not clarified, however.[3a]

In this paper are reported the results obtained from an in-depth study of the catalytic performance of several Pd(II) complexes stabilized by dppp, *rac*-bdpp, and *meso*-bdpp. These include methyl precursors, resting states, and byproducts derived from chain transfer. Moreover, energy barriers associated with relevant propagation steps in model copolymerization intermediates have been determined. This study has allowed us to unravel the role of various Pd(II)-diphosphine compounds that may form during CO/ethene copolymerization reactions in either CH_2Cl_2 or MeOH as well as make a step forward in the design of more efficient catalysts.

Experimental Section

All reactions and manipulations were carried out under an atmosphere of nitrogen by using Schlenk-type techniques. Diethyl ether and tetrahydrofuran (THF) were distilled from $LiAlH_4$. Reagent grade methanol or CH_2Cl_2 (CD_2Cl_2) freshly distilled from CaH_2 was used in the copolymerization reactions. All the other reagents and solvents were used as purchased from Aldrich, Fluka, or Strem. The ligand *meso*-bdpp[3a] and the palladium complexes $PdCl_2(COD)$,[6a] PdCl(Me)(COD)[6b] (COD = cycloocta-1,5-diene), [PdCl(Me)(dppp)][7] (**1**), [Pd(Me)(MeCN)(dppp)]BF_4[8] (**4BF$_4$**), [Pd(CH_2CH_2C(O)Me)(dppp)]SbF_6[8] (**7SbF$_6$**), and $PdCl_2$(dppp) (**10**)[9] were prepared following literature methods. All of the isolated solid samples were collected on sintered-glass frits and washed with appropriate solvents before being dried under a stream of nitrogen. Copolymerization reactions were performed with a 250 mL stainless steel autoclave, constructed at the ICCOM-CNR (Firenze, Italy), equipped with a magnetic drive stirrer and a Parr 4842 temperature and pressure controller. The autoclave was connected to a gas reservoir to maintain a constant pressure over the catalytic reactions. Deuterated solvents for routine NMR measurements were dried over molecular sieves. ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra were obtained on either a Bruker ACP 200 (200.13, 50.32, and 81.01 MHz, respectively) or a Bruker DPX 300 spectrometer (300.13, 75.49, and 121.51 MHz, respectively). All chemical shifts are reported in ppm (δ) relative to tetramethylsilane, referenced to the chemical shifts of residual solvent resonances (^{1}H, ^{13}C) or 85% H_3PO_4 (^{31}P). The 10 mm sapphire NMR tube was purchased from Saphikon (Milford, NH), while the titanium high-pressure charging head was constructed at the ISSECC−CNR (Firenze, Italy).[10] *Caution*: Since high gas pressures are involved, safety precautions must be taken at all stages of studies involving high-pressure NMR tubes. GC analyses of the solutions were performed on a Shimadzu GC-14 A gas chromatograph equipped with a flame ionization detector and a 30 m (0.25 mm i.d., 0.25 μm film thickness) SPB-1 Supelco fused silica capillary column. GC/MS analyses were performed on a Shimadzu QP 5000 apparatus equipped with a SPB-1 Supelco fused silica capillary column. Elemental analyses were performed using a Carlo Erba Model 1106 elemental analyzer. Infrared spectra were recorded on a Perkin-Elmer 1600 Series FT-IR spectrophotometer. Melting points were determined in glass capillaries under air. The intrinsic viscosity (η) for selected polyketone samples was obtained as the average value of Huggins and Kraemer inherent viscosities in 1,1,1,3,3,3-hexafluoropropan-2-ol (HFIP) at 25 °C using a standard capillary viscosity-measuring device. Thermogravimetric analyses (TGA) of selected polyketone samples were obtained with a Mettler Toledo (STARe Thermal Analysis) apparatus (STARe software) coupled to a TGA/SDTA 851e instrument. The analyses were run from 25 to 600 °C, with a scanning rate of 10 °C/min and a nitrogen flow of 60 mL/min. Materials and apparatus for electrochemistry have been described elsewhere.[11] Potential values are referred to the saturated calomel electrode (SCE). Under the present experimental conditions the one-electron oxidation of ferrocene occurs at $E^{\circ\prime} = +0.39$ V.

***rac*-CH_2(CH_3CHOTs)$_2$.** A solution of *p*-toluenesulfonic acid chloride (50 g, 262 mmol) in 80 mL of pyridine was slowly added to a solution of 2,4-pentanediol (mixture of isomers) (10 g, 96 mmol) in 20 mL of pyridine, cooled to 0 °C. The reaction mixture was stirred at 0 °C for 30 min and then at room temperature overnight. The excess of *p*-toluenesulfonic acid chloride was hydrolyzed by addition of 100 mL of water at 0 °C. A further 300 mL of CH_2Cl_2 and 200 mL of water were added. The organic layer was separated and washed with water, diluted hydrochloric acid and water, and dried over Na_2SO_4. The solvent was removed under reduced pressure to give a 2:1 (*meso*:*rac*) mixture of the tosylates. The *rac*-isomer (3 g) was obtained in >98% purity (^{1}H NMR integration) by treatment of the crude product with 4 × 20 mL of diethyl ether and 3 × 10 mL of acetone. Anal. Calcd for $C_{19}H_{24}O_6S_2$: C, 55.35; H, 5.82. Found: C, 56.00; H, 5.90. ^{1}H NMR ($CDCl_3$): 1.23 (d, ^3J(HH) = 6.3 Hz, 6H, CH_3CH), 1.87 (t, ^3J(HH) = 6.0

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Hz, 2H, CH_2), 2.45 (s, 6H, CH_3−Ar), 4.70 (m, 2H, *CH*CH_3), 7.34 (d, ^3J(HH) = 8.3 Hz, 4H, Ar), 7.80 (d, ^3J(HH) = 8.3 Hz, 4H, Ar).

***rac*-2,4-Bis(diphenylphosphino)pentane (*rac*-bdpp).**[3a] BuLi (7.80 mL, 12.5 mmol) was added to a solution of diphenylphosphine (2.18 mL, 12.5 mmol) in 50 mL of THF, cooled to 0 °C. The solution was stirred for 10 min, and then a solution of the *rac*-tosylate (2.46 g, 6 mmol) in 20 mL of THF was added and the reaction mixture was stirred at room temperature for 2 h. Water (2 mL) was added, and the solvent was removed under reduced pressure. CH_2Cl_2 and water were added (100 mL each), and the organic layer was separated. The water layer was extracted with 2 × 50 mL of CH_2Cl_2, and the combined organic layers were dried over Na_2SO_4. Evaporation of the solvent left a colorless oil, which contained exclusively *rac*-bdpp and impurities of phosphine oxides. Overall yield: 2.36 g (90%). All our attempts to crystallize the diphosphine were unsuccessful.

PdCl(Me)(P−P) (P−P = *meso*-bdpp, 2; *rac*-bdpp, 3). To a stirred solution of PdCl(Me)(COD) (0.13 g, 0.50 mmol) in CH_2Cl_2 (20 mL) was added 1 equiv of diphosphine (0.50 mmol) at room temperature. After 2 h stirring, the solvent was reduced to 5 mL under reduced pressure, and 15 mL of 1:1 diethyl ether/petroleum ether was added to the reaction mixture to complete the precipitation of the product, which was filtered off, washed with petroleum ether, and dried in a nitrogen stream. Yield: 80−90%. **2**: $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 42.0 (d, J(PP) = 47.0 Hz), 15.5 (d). ^1H NMR (CD_2Cl_2): δ 0.41 (dd, ^3J(PH) = 3.5 Hz, ^3J(PH) = 7.7 Hz, 3H, PdC*H*$_3$), 0.95 (dd, ^3J(HH) = 7.1 Hz, ^3J(PH) = 10.4 Hz, 3H, CHC*H*$_3$), 1.05 (dd, ^3J(HH) = 7.3 Hz, ^3J(PH) = 12.6 Hz, 3H, CHC*H*$_3$), 1.85 (m, 2H, CH_2), 2.53 (m, 2H, C*H*CH$_3$), 7.3−8.0 (m, 20H, aromatic protons). Anal. Calcd for $C_{30}H_{33}ClP_2Pd$: C, 60.34; H, 5.52. Found: C, 60.60, 5.54. **3**: $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 39.6 (d, ^2J(PP) = 50.5 Hz), 7.1 (d).^1H NMR (CD_2Cl_2): δ 0.47 (dd, 3H, ^3J(PH) = 7.8 Hz, ^3J(PH) = 3.4 Hz, PdC*H*$_3$), 0.96 (dd, 3H, ^3J(PH) = 11.8 Hz, ^3J(HH) = 7.1 Hz, CHC*H*$_3$), 1.12 (dd, 3H, ^3J(PH) = 14.3 Hz, ^3J(HH) = 7.2 Hz, CHC*H*$_3$), 1.91 (m, 2H, CH_2), 2.64 (m, 1H, C*H*CH$_3$), 2.87 (m, 1H, C*H*CH$_3$), 7.25−7.94 (m, 20H, Ar). Anal. Calcd for $C_{30}H_{33}ClP_2Pd$: C, 60.34; H, 5.52. Found: C, 60.52; H, 5.70.

[Pd(Me)(MeCN)(P−P)]Y [P−P = *meso*-bdpp, Y = BF_4 (5BF_4), PF_6 (5PF_6); P−P = *rac*-bdpp, Y = BF_4 (6BF_4), PF_6 (6PF_6)]. A solid sample of either $AgBF_4$ or $AgPF_6$ (0.50 mmol) was added to a magnetically stirred solution of the appropriate PdCl(Me)(P−P) complex (0.45 mmol) in a 10:1 (v:v) mixture of CH_2Cl_2/MeCN. After 1 h stirring at room temperature, AgCl was removed by filtration on Celite. The resultant colorless solution was concentrated to ca. 2 mL under reduced pressure. Addition of a 1:10 (v:v) mixture of diethyl ether/*n*-hexane (20 mL) led to the precipitation of a brownish solid, which was filtered off, washed with petroleum ether, and dried in a nitrogen stream. Yield: 50−60%. **5BF_4**: $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 41.2 (d, ^2J(PP) = 51.1 Hz), 15.5 (d). ^1H NMR ($CDCl_3$): δ 0.46 (dd, 3H, ^3J(PH) = 2.3 Hz, ^3J(PH) = 7.2 Hz, PdC*H*$_3$), 1.08 (dd, 3H, ^3J(HH) = 7.2 Hz, ^3J(PH) = 14.3 Hz, CHC*H*$_3$), 1.10 (dd, 3H, ^3J(HH) = 7.2 Hz, ^3J(PH) = 11.8 Hz, CHC*H*$_3$), 1.90 (m, 2H, CH_2), 2.03 (s, 3H, MeCN), 2.70 (m, 1H, C*H*CH$_3$), 2.87 (m, 1H, C*H*CH$_3$), 7.3−7.9 (m, 20H, aromatic protons). IR (Nujol mull, KBr plates): (MeCN) 2318, 2290 cm^{-1}, (BF_4) 1060 cm^{-1}. Anal. Calcd for $C_{32}H_{36}BF_4NP_2Pd$: C, 55.75; H, 5.22; N, 2.03. Found: C, 55.90; H, 5.30; N, 2.20. **5PF_6**: $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 41.7 (d, ^2J(PP) = 50.8 Hz), 15.6 (d). ^1H NMR (CD_2Cl_2): δ 0.46 (dd, 3H, ^3J(PH) = 2.2 Hz, ^3J(HP) = 7.1 Hz, PdC*H*$_3$), 1.04 (dd, 3H, ^3J(PH) = 13.8 Hz, ^3J(HH) = 6.9 Hz, CHC*H*$_3$), 1.10 (dd, 3H, ^3J(PH) = 12.0 Hz, ^3J(HH) = 7.1 Hz, CHC*H*$_3$), 1.92 (s, 3H, MeCN), 1.85 (m, 2H, CH_2), 2.63 (m, 1H, C*H*CH$_3$), 2.78 (m, 1H, C*H*CH$_3$), 7.31−7.87 (m, 20H, Ar). IR (Nujol mull, KBr plates): (MeCN) 2317, 2290 cm^{-1}, (PF_6) 839 cm^{-1}. Anal. Calcd for $C_{32}H_{36}F_6NP_3Pd$: C, 51.41; H, 4.81; N, 1.87. Found: C, 51.60; H, 4.95; N, 1.90. **6BF_4**: $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 40.8 (d, ^2J(PP) = 53.2 Hz), 8.0 (d). ^1H NMR ($CDCl_3$): δ 0.58 (dd, 3H, ^3J(PH) = 7.1 Hz, ^3J(PH) = 2.15 Hz, PdC*H*$_3$), 1.09 (dd, 3H, ^3J(PH) = 12.2 Hz, ^3J(HH) = 7.1 Hz, CHC*H*$_3$), 1.21 (dd, 3H, ^3J(PH) = 15.5 Hz, J(HH) = 7.0 Hz, CHC*H*$_3$), 1.91 (m, 2H, CH_2), 2.05 (s, 3H, MeCN), 2.73 (m, 1H, C*H*CH$_3$), 2.88 (m, 1H, C*H*CH$_3$), 7.30−7.83 (m, 20H, Ar). IR (Nujol mull, KBr plates): (MeCN) 2317, 2289 cm^{-1}, (BF_4) 1055 cm^{-1}. Anal. Calcd for $C_{32}H_{36}BF_4NP_2Pd$: C, 55.74; H, 5.22; N, 2.03. Found: C, 55.85; H, 5.32; N, 2.15. **6PF_6**: $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 40.8 (d, ^2J(PP) = 52.7 Hz), 8.0 (d). ^1H NMR (CD_2Cl_2): δ 0.53 (dd, 3H, ^3J(PH) = 7.0 Hz, ^3J(PH) = 2.1 Hz PdC*H*$_3$), 1.05 (dd, 3H, ^3J(PH) = 11.8 Hz, ^3J(HH) = 7.0 Hz, CHC*H*$_3$), 1.18 (dd, 3H, ^3J(PH) = 15.7 Hz, ^3J(HH) = 7.1 Hz, CHC*H*$_3$), 1.89 (m, 2H, CH_2), 1.92 (s, MeCN), 2.70 (m, 1H, *CH*CH$_3$), 2.90 (m, 1H, C*H*CH$_3$), 7.33−7.80 (m, 20H, Ar). IR (Nujol mull, KBr plates): (MeCN) 2317, 2289 cm^{-1}, (PF_6) 839 cm^{-1}. Anal. Calcd for $C_{32}H_{36}F_6NP_3Pd$: C, 51.41; H, 4.81; N, 1.87. Found: C, 51.54; H, 4.90; N, 1.95.

[Pd(CH_2CH_2C(O)Me)(*meso*-bdpp)]BF_4 (8BF_4). A solution of **5BF_4** (70 mg, 0.1 mmol) in 2 mL of CH_2Cl_2 was transferred into a 10 mm o.d. sapphire tube which was pressurized to 20 bar of CO at room temperature. The gas was vented off, and the reaction mixture was cooled to − 20 °C. Acetonitrile (20 μL) was added, and the residual CO was removed from the solution by bubbling nitrogen for 2 min. The tube was pressurized with ethene (20 bar) at −20 °C. The gaseous phase was vented off, and the solution was transferred to a Schlenk tube. The solvent was evaporated under reduced pressure at −20 °C to leave a brownish oil. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 42.2 (d, J(PP) = 52.2 Hz), 15.8 (d). ^1H NMR (CD_2Cl_2): δ 1.05 (dd, 3H, ^3J(HP) = 12.07 Hz, ^3J(HH) = 7.06 Hz, CHC*H*$_3$), 1.11 (dd, 3H, ^3J(HP) = 15.14 Hz, ^{3}J(HH) = 8.17 Hz, CHC*H*$_3$), 1.34 (tdd, 2H, ^3J(HP) = 8.0 Hz, ^{3}J(HP) = 1.94 Hz, ^3J(HH) = 6.72 Hz, Pd*CH2*), 1.89 (m, 2H, CH_2), 2.26 (s, 3H, C*H*$_3$CO), 2.74 (m, 2H, C*H*CH$_3$), 3.08 (td, 2H, ^3J(HH) = 6.0 Hz, ^4J(PH) = 6.5 Hz, *CH*$_2$-CO), 7.37−7.93 (m, 20H, Ar). IR (Nujol mull, KBr plates): ν(C═O) 1626 cm^{-1}. Anal. Calcd for $C_{33}H_{37}BF_4OP_2Pd$: C, 56.26; H, 5.25. Found: C, 56.32; H, 5.30.

[Pd(CH_2CH_2C(O)Me)(*rac*-bdpp)]SbF_6 (9SbF_6). PdCl(Me)(*rac*-bdpp) (0.169 mmol) was dissolved in 2 mL of CH_2Cl_2 and transferred into a 10 mm sapphire tube, which was then pressurized to 20 bar of CO. After 3 min the tube was immersed into a cooling bath (at −20 °C) and the CO pressure was released. The residual CO was removed from the solution by bubbling a gentle stream of nitrogen through the solution for 7 min. The solution was transferred into a Schlenk tube cooled to −20 °C, and a stream of ethene was bubbled through the solution for 5 min. The reaction mixture was maintained at −20 °C while $AgSbF_6$ (0.186 mmol) was added. The silver chloride was separated by filtration through cotton wool. Removal of the solvent under reduced pressure at −10 °C left a brownish solid. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 39.6 (d, J(PP) = 54.5 Hz), 8.3 (d). ^1H NMR (CD_2Cl_2): δ 1.08 (dd, 3H, ^3J(PH) = 15.2 Hz, ^3J(HH) = 7.2 Hz, CHC*H*$_3$), 1.21 (dd, 3H, ^3J(PH) = 7.6 Hz, ^3J(HH) = 3.6 Hz, CHC*H*$_3$), 1.34 (tdd, 2H, ^3J(HH) = 6.4 Hz, ^3J(PH) = 2.2 Hz, ^3J(PH) = 7.3 Hz, PdC*H*$_2$), 1.8 (m, 2H, CH_2), 2.33 (s, 3H, C*H*$_3$CO), 2.90 (m, 2H, C*H*CH$_3$), 3.12 (td, 2H, ^3J(HH) = 6.4 Hz, ^4J(PH) = 6.8 Hz, *CH*$_2$CO), 7.11−8.10 (m, 20H, Ar). IR (Nujol mull, KBr plates): ν(C═O) 1632 cm^{-1}. Anal. Calcd for $C_{33}H_{37}F_6OSbP_2Pd$: C, 46.44; H, 4.33. Found: C, 46.52; H, 4.40.

$PdCl_2$(P−P) (P−P = *meso*-bdpp, 11; *rac*-bdpp, 12). $PdCl_2$(COD) (135 mg, 0.47 mmol) was added to a solution of the chelating diphosphine (0.47 mmol) in 20 mL of CH_2Cl_2. The solution was stirred at room temperature for 1 h and then reduced to 2 mL in vacuo. A 1:1 (v:v) mixture of diethyl ether and petroleum ether was added to the remaining solution, which separated a pale yellow microcrystalline product. This was filtered off, washed with a small amount of *n*-hexane, and dried under a stream of dry nitrogen. Yields: 85−90%. **11**: $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 29.7 (s). ^1H NMR ($CDCl_3$): δ 1.04 (dd,

6H, ^3J(PH) = 14.1 Hz, ^3J(HH) = 7.0 Hz, CHCH_3), 2.20 (m, 2H, CH_2), 2.60 (m, 2H, CHCH$_3$), 7.20−7.98 (m, 20H, Ar). Anal. Calcd for $C_{29}H_{30}Cl_2P_2Pd$: C, 56.40; H, 4.85. Found: C, 56.52; H, 4.80. **12**: $^{31}P\{^1H\}$ NMR ($CDCl_3$): 24.9 (s). ^1H NMR ($CDCl_3$): 1.09 (dd, 6H, ^3J(PH) = 14.2 Hz, ^3J(HH) = 6.9 Hz, CHCH_3), 2.23 (m, 2H, CH_2), 2.65 (m, 2H, CHCH$_3$), 7.27−7.96 (m, 20H, Ar). Anal. Calcd for $C_{29}H_{30}Cl_2P_2Pd$: C, 56.40; H, 4.85. Found: C, 56.50; H, 4.70.

[Pd(OH)(P−P)]$_2$(PF$_6$)$_2$ (P−P = dppp, 13; *meso*-bdpp, *cis*-/*trans*-14; *rac*-bdpp, *cis*-/*trans*-15). Solid $AgPF_6$ (184.3 mg,0.729 mmol) was added to a CH_2Cl_2 (30 mL) solution of the appropriate $PdCl_2$(P−P) complex (0.33 mmol) at room temperature. After AgCl was removed by filtration, KOBu^t (40.5 mg, 0.33 mmol) dissolved in 1 mL of water was added under vigorous stirring. After 30 min, the solvent was removed under reduced pressure and the solid residue was treated with 20 mL of CH_2Cl_2. The CH_2Cl_2 phase was passed through Celite, and the resulting clear yellow solution was concentrated to 5 mL under reduced pressure. Addition of a 1:1 mixture of diethyl ether and *n*-hexane led to the precipitation of a microcrystalline solid, which was filtered off, washed with diethyl ether, and dried in a stream of nitrogen. Yield: 45−50%. **13**: $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 15.2 (s). ^1H NMR ($CDCl_3$): δ −2.42 (s, 2H, PdOH), 2.09 (m, 4H, CH_2), 2.68 (m, 8H, CH_2P), 7.33−7.50 (m, 40H, Ar). IR (Nujol mull, KBr plates): ν(OH) 3587 cm^{-1}. Anal. Calcd for $C_{54}H_{54}F_{12}O_2P_6Pd_2$: C, 47.65; H, 3.97. Found: C, 47.72; H, 3.93. ***cis*-/*trans*-14**: $^{31}P\{^1H\}$NMR (CD_2Cl_2): δ 29.5 (s, 70%), 32.8 (s, 30%). ^1H NMR (CD_2Cl_2): δ −2.52 (s, 2H, PdOH), −2.39 (s, 2H, PdOH), 1.11 (m, 12H, CH_3), 2.05 (m, 4H, CH_2), 2.84 (m, 4H, CHP), 7.11−7.68 (m, 40H, Ar). IR (Nujol mull, KBr plates): ν(OH) 3597 cm^{-1}. Anal. Calcd for $C_{58}H_{62}F_{12}O_2P_6Pd_2$: C, 49.16; H, 4.37. Found: C, 49.32; H, 4.44. ***cis*-/*trans*-15**: $^{31}P\{^1H\}$NMR (CD_2Cl_2): δ 27.3 (s, 40%), 27.7 (s, 60%). ^1H NMR (CD_2Cl_2): δ −2.46 (s, 2H, PdOH), −2.41 (s, 2H, PdOH), 1.19 (m, 12H, CH_3), 2.06 (m, 4H, CH_2), 2.77 (m, 4H, CHP), 7.24−7.66 (m, 40H, Ar). IR (Nujol mull, KBr plates): ν(OH) 3599 cm^{-1}. Anal. Calcd for $C_{58}H_{62}F_{12}O_2P_6Pd_2$: C, 49.16; H, 4.37. Found: C, 49.09; H, 4.40.

[Pd(P−P)$_2$](PF$_6$)$_2$ (P−P = dppp, 16; *meso*-bdpp, *cis*-/*trans*-17; *rac*-bdpp, *cis*-/*trans*-18). $PdCl_2$(P−P) (0.47 mmol) in 30 mL of a 10:1 mixture of CH_2Cl_2/MeCN was reacted with $AgPF_6$ (0.94 mmol). The resulting mixture was stirred for 1 h, then it was filtered through Celite. One equivalent of the appropriate diphosphine ligand was added to this solution, which was stirred at room temperature for 15 min. The solvent was removed under reduced pressure, leaving a solid product. This was recrystallized by CH_2Cl_2/*n*-hexane. Yields: 45−55%. **16**: $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −1.9 (s). Anal. Calcd for $C_{54}H_{52}F_{12}P_6Pd$: C, 53.13; H, 4.26. Found: C, 53.20; H, 4.30. ***cis*-/*trans*-17**: $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 14.2 (s, 13%), 12.2 (s, 87%). Anal. Calcd for $C_{58}H_{60}F_{12}P_6Pd$: C, 54.56; H, 4.70. Found: C, 54.50; H, 4.60. ***cis*-/*trans*-18**: $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 21.7 (s, 17%), 17.4 (s, 83%). Anal. Calcd for $C_{58}H_{60}F_{12}P_6Pd$: C, 54.56; H, 4.70. Found: C, 54.65; H, 4.55.

Copolymerization of Ethene and Carbon Monoxide Catalyzed by the Methyl Acetonitrile Complexes 4−6PF$_6$ in CH_2Cl_2. A. Autoclave Experiments. Typically, under a nitrogen atmosphere, a 100 mL solution of CH_2Cl_2 (freshly distilled under nitrogen from CaH_2) containing the catalyst precursor (0.01 mmol) was introduced into a 250 mL autoclave equipped with a magnetic drive stirrer and a temperature and pressure controller. The autoclave was charged with 20 bar of CO and 20 bar of ethene. After the contents of the autoclave had been brought to 70 °C, the pressure was maintained at ca. 40 bar by continuous feeding of an equimolar mixture of ethene and CO from a high-pressure gas reservoir connected to the autoclave. A pressure gauge connected to the gas reservoir was employed to determine the gas consumption during the reactions. The reaction mixture was then stirred (1400 rpm) for the desired time. The reaction was stopped by cooling the autoclave to room temperature using an ice−water bath. After the unreacted gases were released, the insoluble copolymer was filtered off, washed with CH_2Cl_2, and dried in a vacuum oven at 70 °C overnight. Anal. Calcd for $(COCH_2CH_2)_n$: C, 64.3; H, 7.2. Found: C, 64.1; H, 7.1. IR (powder sample in KBr pellet): 3391 (w), 2912 (m), 1694 (vs), 1408 (s), 1333 (s), 1259 (m), 1056 (s), 811 (m), 592 (m) cm^{-1}. ^1H NMR (HFIP-d_2): δ 2.85 (s, CH_2C(O)CH_2). $^{13}C\{^1H\}$ NMR (HFIP-d_2): δ 213.6 (CH_2C(O)CH_2), 36.0 (CH_2C(O)CH_2). Melting points: 260−263 °C (catalyst precursor **4PF$_6$**), 262−264 °C with decomposition (**5PF$_6$**), 258−260 °C (**6PF$_6$**). Intrinsic viscosity values for samples obtained in 30 min: 25.7 dL g^{-1} (catalyst precursor **4PF$_6$**), 5.0 dL g^{-1} (**5PF$_6$**), 7.3 dL g^{-1} (**6PF$_6$**).

B. HPNMR Experiments. The reactions were followed by variable-temperature $^{31}P\{^1H\}$ and ^1H NMR spectroscopy. Details of the procedure are exemplified for **4PF$_6$**. A 10 mm sapphire HPNMR tube was charged under nitrogen with a solution of the methyl acetonitrile complex (1.77×10^{-2} mmol) in CD_2Cl_2 (freshly distilled under nitrogen from CaH_2, 2 mL) and then placed into the NMR probe at room temperature. After $^{31}P\{^1H\}$ and ^1H NMR spectra were acquired, the tube was pressurized with a 1:1 mixture of CO/ethene to 40 bar at room temperature. NMR spectra were recorded at room temperature, 50 °C, and 70 °C. After 1 h at 70 °C, the probe-head was cooled to room temperature and the internal pressure was released. A gray precipitate of Pd metal was found in the NMR tube together with the copolymer. The solution was shown to contain the bis-chelate complex **16** together with traces of the binuclear μ-OH complex **13**.

Reaction of the β-Chelates 7SbF$_6$, 8BF$_4$, and 9SbF$_6$ with Water Followed by Reaction of the Formed μ-OH Complexes with CO/Ethene. A 10 mm sapphire NMR tube was charged with a solution of a β-chelate complex (0.01 mmol) in 2 mL of CD_2Cl_2 under nitrogen. After the $^{31}P\{^1H\}$ NMR spectrum was acquired at room temperature, the tube was removed from the NMR probe and 20 μL of H_2O was syringed under nitrogen into it. The results of this investigation have been discussed in a previous section.

Copolymerization of Ethene and Carbon Monoxide Catalyzed by the μ-OH Complexes 13−15 and the Bis-chelate Complexes 16−18 in CH_2Cl_2 or MeOH. Autoclave Experiments. The catalytic activity of the μ-OH binuclear complexes was tested in 30 min experiments following a procedure analogous to that employed for the methyl acetonitrile complexes.

In Situ Carbonylation of the Methyl Acetonitrile Complexes 4−6BF$_4$. HPNMR Experiments. In a typical experiment, the methyl acetonitrile complex (0.035 mmol) was dissolved in 2 mL of deoxygenated CD_2Cl_2, and the resulting solution was then transferred into a 10 mm sapphire tube. After $^{31}P\{^1H\}$ and ^1H NMR spectra of this sample were acquired at room temperature, the NMR probe-head was cooled to −80 °C. $^{31}P\{^1H\}$ and ^1H NMR spectra were recorded at this temperature. The sapphire tube was removed from the spectrophotometer, immersed into an ethanol/liquid nitrogen thermostat bath (−117 °C), and charged with 15 bar of CO. After this procedure the tube was placed into the probe head precooled to −80 °C. Irrespective of the diphosphine ligand, the $^{31}P\{^1H\}$ and ^1H NMR spectra showed the quantitative conversion of the starting methyl acetonitrile complex into the corresponding methyl carbonyl derivative [Pd(Me)(CO)(P−P)]BF$_4$ (selected $^{31}P\{^1H\}$ and ^1H NMR data of the methyl carbonyl complexes **19**−**21** are reported in Tables 1 and 2, respectively). Afterward the probe temperature was gradually increased and $^{31}P\{^1H\}$ and ^1H NMR spectra were recorded at each intermediate temperature. Increasing the temperature converted each methyl carbonyl complex into the corresponding carbonyl acyl derivative [Pd(COMe)(CO)(P−P)]BF$_4$ (selected $^{31}P\{^1H\}$ and ^1H NMR data of the carbonyl acyl complexes **22**−**24** are reported in Tables 1 and 2, respectively). At the conversion temperature, the decrease in concentration of the methyl carbonyl complex was followed by $^{31}P\{^1H\}$ NMR spectroscopy. Spectra were

Table 1. $^{31}P\{^1H\}$ NMR Chemical Shifts (ppm), (Multiplicity), and [PP Coupling Constants] (Hz) for the Palladium Complexes $[Pd(X)(Y)(P-P)]^{0/+}$ in CD_2Cl_2 Solutions at {*T*} in °C

P−P	X = Me Y = CO	X = COMe Y = CO	X = COMe Y = Cl	X = $CO(CH_2)_2COMe$ Y = CO
dppp	17.0 (d) [61.0] −7.2 (d) {−80}	4.5 (d) [82.3] −6.2 (d) {22}	12.0 (d) [72.2] −9.0 (d) {22}	2.0 (d) [86.0] −9.0 (d) {−70}
meso-bdpp	32.2 (d) [56.2] 12.1 (d) {−80}	24.0 (d) [78.3] 11.5 (d) {22}	30.5 (d) [69.0] 12.4 (d) {22}	23.0 (d) [82.0] 7.8 (d) {−70}
rac-bdpp	30.0 (d) [58.0] 4.2 (d) {−80}	19.0 (d) [78.1] 6.2 (d) {22}	25.5 (d) [70.4] 4.4 (d) {22}	18.0 (d) [74.5] 6.0 (d) {22}

Table 2. ^1H NMR Chemical Shifts (ppm) and Multiplicity for Selected Resonances of the Palladium Complexes $[Pd(X)(Y)(P-P)]^{0/+}$ in CD_2Cl_2 Solutions at {*T*} in °C

P−P	X = Me Y = CO	X = COMe Y = CO	X = COMe Y = NCMe	X = COMe Y = Cl	X = $(CO)(CH_2)_2COMe$ Y = CO
dppp	0.48 (br s) Me {−80}	1.95 (s) COMe {22}	1.97 (s) COMe {22}	1.85 (s) COMe {22}	1.97 (s) COMe 2.14 (m) CH_2CO 2.56 (m) $Pd(CO)CH_2$ {−70}
meso-bdpp	0.50 (br s) Me {−80}	1.98 (s) COMe {22}	2.03 (s) COMe {22}	1.65 (s) COMe {−30}	1.97 (s) COMe 2.40 (m) CH_2CO 2.99 (m) $Pd(CO)CH_2$ {22}
rac-bdpp	0.60 (br s) Me {−80}	2.00 (s) COMe {0}	1.97 (s) COMe {0}	1.81 (s) COMe {22}	1.97 (s) COMe 2.60 (m) CH_2CO 2.91 (m) $Pd(CO)CH_2$ {22}

taken at intervals of 5−10 min, depending on conditions. The reaction was followed for 2−3 half-lives. The experiment was repeated with varying pressures of CO (5−25) to determine the dependence of the reaction rate on the CO concentration. The results indicated that the rate of the reaction is independent of CO. According to first-order kinetics, the free energy of activation was calculated as follows: $\Delta G^{\ddagger} = RT(\ln k_r - \ln kT/h)$ with $k_r = \ln 2/t_{1/2}$.

Generation and Carbonylation of the *β*-Chelate Complexes 7−9SbF$_6$. HPNMR Experiments. In a typical experiment, the chloride methyl complex PdCl(Me)(P−P) (0.035 mmol) was dissolved in 2 mL of deoxygenated CD_2Cl_2, and the resulting solution was first transferred into a 10 mm sapphire tube and then pressurized to 20 bar of CO at room temperature. Irrespective of the diphosphine, the quantitative formation of the corresponding chloride acyl complex PdCl(COMe)((P−P) occurred at room temperature (selected $^{31}P\{^1H\}$ and ^1H NMR data of the chloride acyl complexes **25**−**27** are reported in Tables 1 and 2, respectively). Once the chloride acyl complex was obtained, the tube was removed from the spectrometer and the excess CO was released. The tube was then immersed into a thermostat bath at −20 °C, and nitrogen was bubbled through the solution for 15 min to eliminate any trace of CO. Ethene was bubbled through the solution maintained at −20 °C for 5 min, and then a solid sample of $AgSbF_6$ (0.04 mmol) was added to the solution. The immediately formed AgCl settled on the bottom of the tube. Irrespective of the diphosphine ligand, the $^{31}P\{^1H\}$ and ^1H NMR spectra of this sample showed the quantitative conversion of the chloride acyl complex into the corresponding *β*-chelate complex. Afterward, the NMR probe-head was cooled to −90 °C, and $^{31}P\{^1H\}$ and ^1H NMR spectra were recorded at this temperature. The sapphire tube was removed from the probe, and nitrogen was bubbled through the solution at room temperature to eliminate any trace of ethene. The sapphire tube was immersed into an ethanol/liquid nitrogen thermostat bath (−117 °C) and charged with 20 bar of CO. After this procedure the tube was placed into the probe-head precooled to −90 °C. $^{31}P\{^1H\}$ and ^1H NMR spectra showed that the *β*-chelate complexes were still present. Afterward the probe temperature was gradually increased, and $^{31}P\{^1H\}$ and ^1H NMR spectra were recorded at each intermediate temperature. Increasing the temperature caused the conversion of the *β*-chelate complex into the corresponding carbonyl acyl derivative $[Pd(COCH_2CH_2C(O)Me)(CO)(P-P)]SbF_6$ to occur (selected $^{31}P\{^1H\}$ and ^1H NMR data of the carbonyl acyl complexes **28**−**30** are reported in Tables 1 and 2, respectively). At the conversion temperature the decrease in concentration of the methyl carbonyl complex was followed by $^{31}P\{^1H\}$ NMR spectroscopy. Spectra were taken at intervals of 5−10 min, depending on conditions. The reaction was followed for 2−3 half-lives.

[Pd(CH$_2$CH$_2$C(O)Me)(P−P)]SbF$_6$/[Pd(COCH$_2$CH$_2$C(O)Me)(CO)(P−P)]SbF$_6$ Equilibria. Solutions of the carbonyl acyl complexes **28**−**30**, prepared as reported above in HPNMR tubes, were immersed in a thermostat bath at −20 °C. CO was released, and then couples of vacuum−nitrogen cycles were applied. $^{31}P\{^1H\}$ and ^1H NMR spectra of these samples acquired at −20 °C allowed us to follow the transformation of the carbonyl acyl complexes into the corresponding *β*-chelates **7**−**9SbF$_6$**.

Attempted Determination of the Migratory Insertion Barriers of [Pd(COMe)(C$_2$H$_4$)(P−P)]SbF$_6$. Solid samples of the chloride acyl complexes **25**−**27** (0.035 mmol) were prepared by a procedure analogous to that reported above in an HPNMR tube followed by evaporation of the solvent under vacuum. $AgSbF_6$ and $CDCl_2F/CD_2Cl_2$ (1:1) were added to the tube cooled to −130 °C under N_2, immediately followed by pressurization with ethene (15 bar) again at −130 °C. The tube was introduced into a precooled NMR probe-head. Only the *β*-chelates **7**−**9SbF$_6$** were seen in the first NMR spectrum at −117 °C.

Results

Synthesis of the Methyl Acetonitrile Complexes [Pd(Me)(MeCN)(P−P)]Y [P−P = dppp, Y = BF$_4$ (4BF$_4$), PF$_6$ (4PF$_6$); P−P = *meso*-bdpp, Y = BF$_4$ (5BF$_4$), PF$_6$ (5PF$_6$); P−P = *rac*-bdpp, Y = BF$_4$ (6BF$_4$), PF$_6$ (6PF$_6$)]. Methyl acetonitrile palladium complexes with *meso*-bdpp and *rac*-bdpp were synthesized following a procedure analogous to that previously reported for the dppp derivatives.[7] This involves the treatment of the neutral complexes PdCl(Me)(*meso*-bdpp) (**2**) and PdCl(Me)(*rac*-bdpp) (**3**) dissolved in a CH_2Cl_2/MeCN solution (10:1, v:v) with either $AgBF_4$ or $AgPF_6$ as chloride scavenger. Concentration under

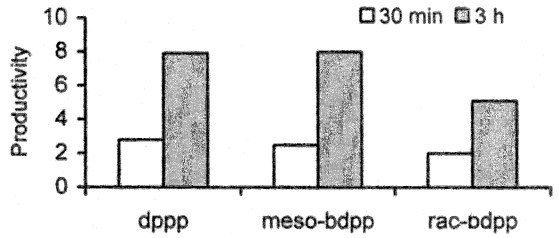

Figure 1. Productivity expressed as kg of polyketone (g of Pd)$^{-1}$ vs chelating diphosphine ligand for the series of precursors [Pd(Me)(MeCN)(P−P)]PF_6 (P−P = dppp, *meso*-bdpp, *rac*-bdpp).

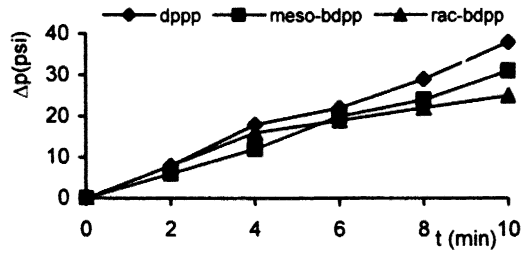

Figure 2. Plot of gas uptake vs time for copolymerization reactions catalyzed by **4PF$_6$**, **5PF$_6$**, and **6PF$_6$**.

reduced pressure and addition of diethyl ether/*n*-hexane gave analytically pure samples of [Pd(Me)(MeCN)(P−P)]Y (Y = BF_4, PF_6), whose unambiguous identification was achieved by both $^{31}P\{^1H\}$ (AM patterns) and ^1H NMR spectroscopy.[7]

A cyclic voltammetry study was carried out on CH_2Cl_2 solutions of **4PF$_6$**, **5PF$_6$**, and **6PF$_6$** using $[NBu_4]PF_6$ as supporting electrolyte. Both **4PF$_6$** and **6PF$_6$** underwent an irreversible two-electron reduction at E_p = −1.21 and −1.01 V, respectively. In contrast, the *meso* complex **5PF$_6$** showed two separate, irreversible reduction processes at E_p = −1.15 and −1.39 V.

Alternating Copolymerization of Ethene and Carbon Monoxide Catalyzed by [Pd(Me)(MeCN)(P−P)]PF$_6$ Precursors in CH_2Cl_2. Complexes **4PF$_6$**, **5PF$_6$**, and **6PF$_6$** were employed as catalyst precursors for the copolymerization of CO and ethene in freshly distilled CH_2Cl_2 at 70 °C under a constant CO/ethene pressure of 40 bar. The results of reactions lasting 30 min and 3 h are reported in Figure 1. The initial copolymerization rates were estimated over three runs measuring the gas uptake within the first 10 min (Figure 2).

As illustrated in Figure 2, the initial rates were rather similar for the three catalysts with a prevalence for the dppp system; however, after only 6 min, the activity of the *meso* catalyst surpassed that of the *rac* catalyst and approached that of the dppp catalyst. Consistently, the productivities (kg of polyketone (g of Pd)$^{-1}$) of batch reactions lasting 30 min were in the order dppp (2.8) > *meso*-bdpp (2.5) > *rac*-bdpp (2.0), while after 3 h the dppp and *meso*-bdpp catalysts were equally active and produced much more polyketone (7.9−8.0 kg (g of Pd)$^{-1}$) than the *rac* complex (5.1) (Figure 1). A comparison of the productivities obtained after 30 min and 3 h showed that all catalytic systems underwent deactivation with time, yet the *meso*-bdpp catalyst proved to be the most robust, as in 3 h its productivity was slightly better than that of the dppp system.

A series of catalytic experiments lasting 30 min were carried out using "wet" CH_2Cl_2 obtained by adding a controlled amount of water (1%) to freshly distilled solvent. The productivity trend was the same as in the reactions performed in distilled CH_2Cl_2: dppp (2.6 kg (g of Pd)$^{-1}$) > *meso*-bdpp (2.4) ≫ *rac*-bdpp (1.4); yet a significant decrease in catalytic activity was observed for the *rac* complex.

Irrespective of the ligand, the molecular weights of the copolymers produced by the methyl acetonitrile precursors in CH_2Cl_2 were much larger than those obtained in MeOH with the bis-*p*-toluenesulfonate precursors Pd(OTs)$_2$(P−P) (Scheme 1).[3a] Indeed, we could not determine the nature of the end groups by ^1H NMR spectroscopy in HFIP-d_2.[2,4,12] It is very likely that all copolymers contain vinyl and ketone end groups due to by β-H chain transfer and Pd-H initiation, respectively,[2,4,12] yet other end groups produced by adventitious water (e.g., −COOH) might be present.[2] Unlike the polyketones obtained in MeOH (Scheme 1),[3] the materials produced in CH_2Cl_2 were significantly different from each other, as indicated by their intrinsic viscosities (η) of 25.7 (dppp), 5.0 (*meso*-bdpp), and 7.3 (*rac*-bdpp) dL g^{-1}, respectively.[2,12] Due to the limitations of our GPC instrumentation, we were unable to determine the molecular weights of these copolymers. These should have much longer polymer chains than those produced in MeOH (M_n = 10−20 kg mol^{-1}), which were featured by η values in the range 0.5−0.8 dL g^{-1}.[3a]

The polyketone samples subjected to viscosity measurements were also studied by thermogravimetric analysis (TGA) under inert atmosphere. All samples showed one degradation step with inflection points that, although very similar, increased in the ligand order *meso*-bdpp (389.9 °C) < *rac*-bdpp (400.6 °C) < dppp (402.2 °C). The amount of residue recovered at 600 °C was rather large for all samples (26% in weight for the dppp and *rac* catalysts and 38% for the *meso* catalyst), which reflects the occurrence of copolymer cross-linking via radical pathways promoted by residual palladium.[12a,13]

In Situ HPNMR Study of the Alternating Copolymerization of Ethene and Carbon Monoxide Catalyzed by [Pd(Me)(MeCN)(P−P)]PF$_6$ Precursors in CD_2Cl_2. The CO/ethene copolymerization reactions catalyzed by **4PF$_6$**, **5PF$_6$**, and **6PF$_6$** were studied in situ by means of HPNMR spectroscopy in 10 mm o.d. sapphire tubes under experimental conditions comparable to those of the batch reactions. In the NMR experiments was employed a palladium concentration higher than that in the batch reactions (ca. 10^{-2} vs 10^{-4} M) in order to acquire well-resolved NMR spectra in a short residence time.[3,4,14] The much higher concentration of Pd(II) precursor in the HPNMR studies as compared to the batch reactions may have relevant

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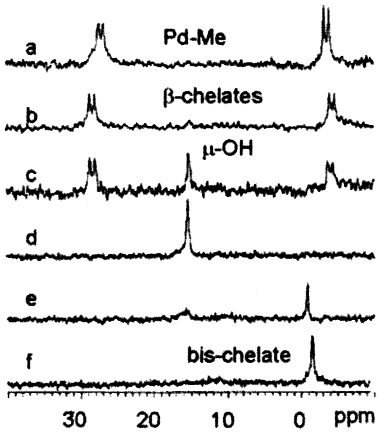

Figure 3. Variable-temperature $^{31}P\{^1H\}$ NMR study (sapphire tube, CD_2Cl_2, 81.01 MHz) of CO/ethene copolymerization assisted by **4PF$_6$**: (a) dissolving **4PF$_6$** in CD_2Cl_2 under nitrogen at room temperature; (b) after the tube was pressurized with 40 bar of CO/ethene (1:1) at room temperature; (c) after 15 min at 50 °C; (d) after 10 min at 70 °C; (e) after 60 min at 70 °C; (f) after the tube was depressurized at room temperature.

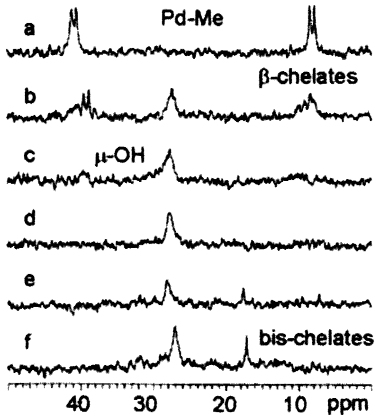

Figure 4. Variable-temperature $^{31}P\{^1H\}$ NMR study (sapphire tube, CD_2Cl_2, 81.01 MHz) of CO/ethene copolymerization assisted by **6PF$_6$**: (a) dissolving **6PF$_6$** in CD_2Cl_2 under nitrogen at room temperature; (b) after the tube was pressurized with 40 bar of CO/ethene (1:1) at room temperature; (c) after 10 min at 50 °C; (d) after 10 min at 70 °C; (e) after 60 min at 70 °C; (f) after the tube was depressurized at room temperature.

effects in the kinetics of formation of some palladium species during the catalysis (i.e., resting states and degradation products).[14] Nevertheless, the information obtained in the HPNMR studies is generally valuable for series of homologous compounds such as the present Pd-methyl complexes.

Selected $^{31}P\{^1H\}$ NMR spectra relative to the reactions catalyzed by **4PF$_6$** and **6PF$_6$** are reported in Figures 3 and 4.

The $^{31}P\{^1H\}$ NMR spectrum of **4PF$_6$** at room temperature is shown in Figure 3 (trace a). Immediately after pressurizing the tube to 40 bar with a 1:1 CO/ethene mixture at room temperature, polyketone formation occurred, while the methyl complex was converted first to the known[8,15] β-chelate $[Pd(CH_2CH_2C(O)Me)(dppp)]^+$ (see below) and then to higher homologues $[Pd(CH_2CH_2C(O)\text{-chain})(dppp)]^+$, where "chain" is the propagating copolymer (trace b). By ^1H NMR integration on a spectrum acquired after 10 min, the average repeating units of the chain have been estimated to be 11.[2,4,8,15−17] ^1H NMR spectroscopy was also useful to confirm the formation of the β-chelates, as all the methyl Pd(II) precursors and the β-chelates are featured by a fortuitous coincidence of the $^{31}P\{^1H\}$ chemical shifts, with different J(PP) values, however.

The β-chelates were the only phosphorus-containing compounds visible on the NMR time scale up to 40 °C. A new resonance (singlet at δ 15.3) appeared only at 50 °C in fact (trace c, recorded after 15 min at 50 °C). An independent study showed this new signal to be due to the μ-hydroxo complex $[Pd(\mu\text{-}OH)(dppp)]_2(PF_6)_2$ (**13**) apparently formed by chain transfer with adventitious water (see below).[18a,b] Increasing the temperature to 70 °C accelerated the formation of this complex, which was the only species visible on the NMR time scale after 10 min (trace d). With time, however, the μ-hydroxo complex decomposed to give the bis-chelate complex $[Pd(dppp)_2](PF_6)_2$ (**16**) (singlet at δ −0.9, trace e) and palladium metal.[4,19,20] After 1 h at 70 °C, the bis-chelate was the largely predominant species. This complex was stable at room temperature (trace f) even after depressurizing the tube. Besides polyketone, some black palladium metal was recovered in the tube.

The copolymerization reactions catalyzed by **5PF$_6$** and **6PF$_6$** (Figure 4) gave a NMR picture qualitatively similar to that of **4PF$_6$**; yet an important difference was noticed in the higher stability to carbonylation of the *rac*-bdpp μ-hydroxo complex $[Pd(\mu\text{-}OH)(rac\text{-bdpp})]^{2+}$.

The $^{31}P\{^1H\}$ NMR spectrum at room temperature under nitrogen of **6PF$_6$** (AM pattern with δ 40.8 and 8.0, J(PP) = 52.7 Hz) is shown in trace a. Pressurizing the tube to 40 bar with a 1:1 mixture of carbon monoxide/ethene at room temperature transformed the methyl precursor into the β-chelate complexes $[Pd(CH_2CH_2C(O)\text{-chain})(rac\text{-bdpp})]^+$ (AM pattern, δ 39.6, 8.3 and J(PP) = 54.5 Hz, number of average repeating units after 10 min = 7) and also gave the μ-hydroxo complex $[Pd(\mu\text{-}OH)(rac\text{-bdpp})]_2(PF_6)_2$ (***cis***-/***trans***-**15**) as mixture of *cis* and *trans* stereoisomers (broad resonance at δ 27.5 due to overlapping of two singlets, see below) (trace b).[4]

(14) (a) Bianchini, C.; Herrera, V.; Jiménez, M. V.; Meli, A.; Sánchez-Delgado, R. A.; Vizza, F. *J. Am. Chem. Soc.* **1995**, *117*, 8567. (b) Bianchini, C.; Fabbri, D.; Gladiali, S.; Meli, A.; Pohl, W.; Vizza, F. *Organometallics* **1996**, *15*, 4604. (c) Bianchini, C.; Jiménez, M. V.; Meli, A.; Moneti, S.; Patinec, V.; Vizza, F. *Organometallics* **1997**, *16*, 5696. (d) Bianchini, C.; Meli, A.; Patinec, V.; Sernau, V.; Vizza, F. *J. Am. Chem. Soc.* **1997**, *119*, 4945. (e) Bianchini, C.; Meli, A.; Moneti, S.; Oberhauser, W.; Vizza, F.; Herrera, V.; Fuentes, A.; Sánchez-Delgado, R. A. *J. Am. Chem. Soc.* **1999**, *121*, 7071. (f) Bianchini, C.; Lee, H. M.; Meli, A.; Vizza, F. *Organometallics* **2000**, *19*, 849.

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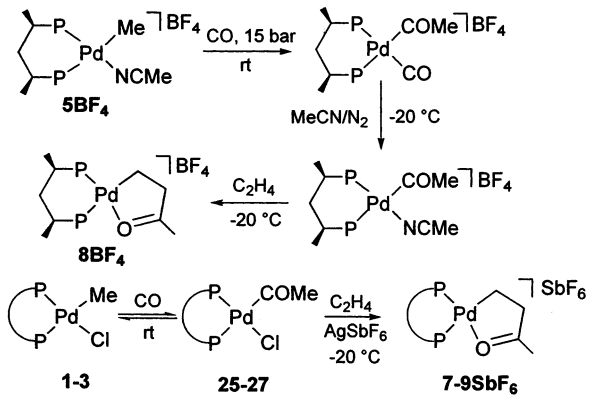
(19) Bianchini, C.; Mantovani, G.; Meli, A.; Oberhauser, W.; Brüggeller, P.; Stampfl, T. *J. Chem. Soc., Dalton Trans.* **2001**, 690.

(20) Luo, H.-K.; Kou, Y.; Wang, X.-W.; Li, D.-G. *J. Mol. Catal.* **2000**, *151*, 91.

Scheme 2



The appearance of the β-chelates at room temperature coincided with the formation of the copolymer product. As the temperature was increased to 50 °C, the intensity of the β-chelate signal decreased remarkably with concomitant increase of the concentration of the μ-hydroxo complexes (trace c). The latter species were apparently stable even at 70 °C (trace d). Only after 30 min at 70 °C did the formation of the bis-chelate complexes *cis*/*trans*-[Pd(*rac*-bdpp)$_2$](PF$_6$)$_2$ (***cis***-/***trans***-**18**) become appreciable (singlet at δ 17.5; the other singlet is not observable due to the high noise/signal ratio) and was accompanied by the formation of palladium metal. After 1 h at 70 °C, both the bis-chelate and μ-hydroxo complexes were present in comparable amounts (trace e), showing that the *rac*-bdpp catalytic system diverges significantly from the dppp-based system for the stability of the μ-hydroxo complexes under copolymerization conditions.

Independent NMR experiments with isolated [Pd(μ-OH)(P−P)]$_2$(PF$_6$)$_2$ (**13**−**15**) showed these complexes to decompose in CH_2Cl_2 to [Pd(P−P)$_2$](PF$_6$)$_2$ (**16**−**18**) and palladium metal when treated with 40 bar CO/ethene at 70 °C (see below).

Synthesis and Reactivity of Palladium(II) Compounds Relevant to Propagation and Chain Transfer and their Use in HPNMR Catalytic Experiments. Several model compounds with relevance to intermediate species in CO/ethene copolymerization were synthesized in an attempt to rationalize the catalytic performance of the dppp, *meso*-bdpp, and *rac*-bdpp catalysts in CH_2Cl_2 as well as to elucidate the results of in situ HPNMR studies.

Scheme 2 shows the two routes employed to isolate the β-chelates [Pd(CH_2CH_2C(O)Me)(P−P)]$^+$ as either BF_4^- or SbF_6^- salts (P−P = dppp, **7**; *meso*-bdpp, **8**; *rac*-bdpp, **9**). The procedure involving the removal of chloride from Pd(acyl)(chloride) compounds by $AgSbF_6$ has been developed by Brookhart and co-workers[8] to synthesize [Pd(CH_2CH_2C(O)Me)(dppp)]SbF_6 (**7SbF$_6$**), while the method involving Pd(acyl)(MeCN) intermediates to synthesize **8BF$_4$** was designed by us to prepare the β-chelates [Pd(CH_2CH_2C(O)Me)(P−P)]BF_4 (P−P = *meso*-dppb, *rac*-dppb).[4]

The bis-chloride complexes $PdCl_2$(P−P) (P−P = dppp, **10**; *meso*-bdpp, **11**; *rac*-bdpp, **12**) were conveniently prepared by the plain reaction of $PdCl_2(COD)$[6a] with the appropriate chelating diphosphine.[9,21a] Then, the desired μ-hydroxo complexes [Pd(μ-OH)(P−P)]$_2$(PF$_6$)$_2$ (P−P = dppp, **13**; *meso*-bdpp, **14**; *rac*-bdpp, **15**) were obtained as off-white crystals by treatment of the bis-chlorides in CH_2Cl_2 with $AgPF_6$, followed by reaction with an aqueous solution of KOBu^t.[18] In turn, the bis-chelates [Pd(P−P)$_2$](PF$_6$)$_2$ (P−P = dppp, **16**; *meso*-bdpp, **17**; *rac*-bdpp, **18**) were prepared by reacting the bis-chlorides **10**−**12** with 2 equiv of $AgPF_6$ in a CH_2Cl_2/MeCN mixture, followed by addition of 1 equiv of the appropriate diphosphine.[4,19,20] As previously observed for analogous *meso*- and *rac*-dppb compounds,[4] both the μ-hydroxo and bis-chelate Pd(II) complexes with *meso*- and *rac*-bdpp were formed as a mixture of stereoisomers differing from each other by the orientation of the methyl substituents in the ligand backbone (Scheme 3).

Unambiguous characterization of all new complexes was achieved by multinuclear NMR spectroscopy as well as comparisons with literature data on structurally related compounds.[4,7−9,15−21]

Palladium β-chelate complexes have several important roles in Pd(II)-assisted CO/ethene copolymerizations in either solutions or slurries of aprotic solvents. Indeed, besides controlling the perfect alternating insertion of the two comonomers,[2] they have been shown to be crucial compounds in the chain transfer by protonolysis.[15] Scheme 4 shows the role played by β-chelates in this chain-transfer process and indirectly in the formation of two resting states of palladium(II) during the copolymerization, namely, the μ-hydroxo binuclear complexes [Pd(μ-OH)(P−P)]$_2^{2+}$ and the mononuclear bis-chelates [Pd(P−P)$_2$]$^{2+}$.[4,15] In situ NMR experiments proved the present β-chelates **7**−**9** to undergo the reaction sequence illustrated in Scheme 4 upon heating in either freshly distilled or "wet" CD_2Cl_2. The experiments were carried out in high-pressure sapphire tubes in order to study the further reactivity of the chain-transfer μ-hydroxo products with CO/ethene.

A 10 mm sapphire HPNMR tube was therefore charged with a solution of a β-chelate complex in CD_2Cl_2 under nitrogen. The $^{31}P\{^1H\}$ NMR spectra recorded at room temperature showed in all cases the exclusive presence of the β-chelates. With time the β-chelates disappeared with formation of several palladium products including the bis-chelates, the μ-hydroxo complexes, and traces of palladium metal. After 15 h, GC/MS analysis of the solution showed the presence of a ca. 4:1 mixture of methyl vinyl ketone and methyl ethyl ketone. The formation of the latter product was ascribed to traces of water in the solvent.[4,15] Increasing the temperature to 70 °C had the effect of only accelerating this degradation process.

When 20 μL of H_2O was syringed under nitrogen into the CD_2Cl_2 solutions of the β-chelates, $^{31}P\{^1H\}$ NMR spectra showed the selective formation of the binuclear μ-OH species [Pd(μ-OH)(P−P)]$_2^{2+}$ in ca. 4 h at room temperature and in ca. 10 min at 70 °C.

NMR tubes containing these solutions of μ-hydroxo complexes were pressurized with ethene to 20 bar at room temperature. No reaction was observed at 70 °C. Then, the tubes were pressurized with 20 bar CO at

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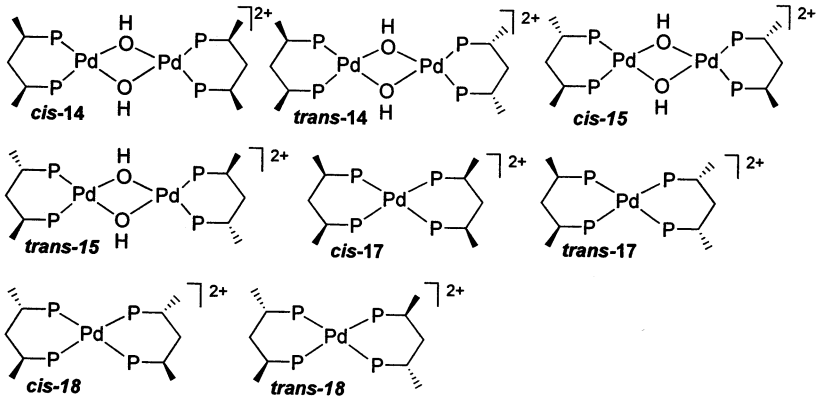
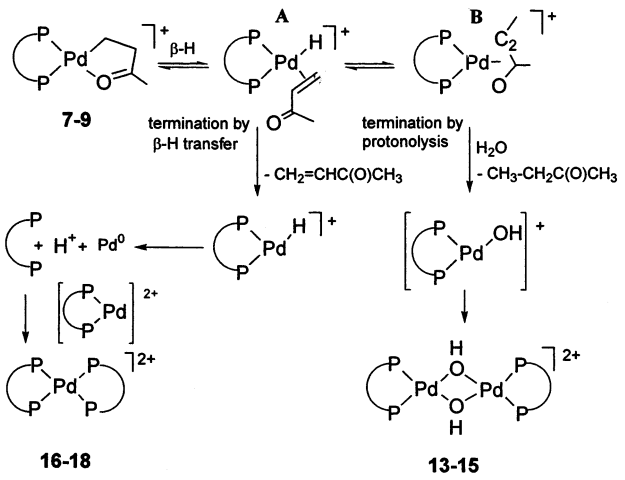
Scheme 3



Scheme 4



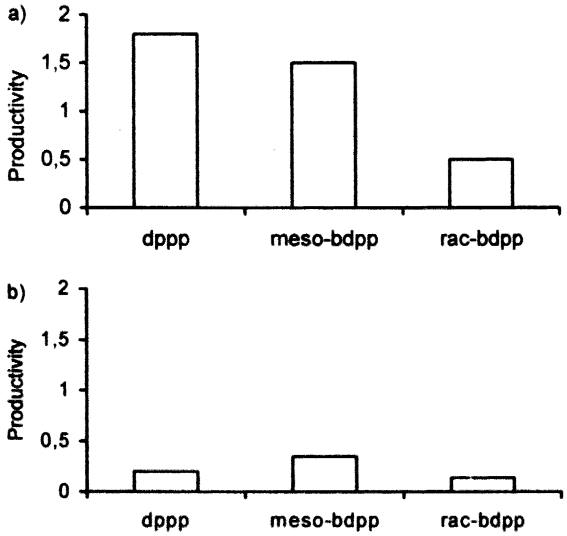


Figure 5. Productivity expressed as kg of polyketone (g of Pd)$^{-1}$ vs chelating diphosphine ligand for the series of precursors (a) $[Pd(\mu\text{-}OH)(P{-}P)]_2(PF_6)_2$; (b) $[Pd(P{-}P)_2](PF_6)_2$ (P−P = dppp, *meso*-bdpp, *rac*-bdpp). Reaction conditions: solvent, CH_2Cl_2; time, 30 min.

room temperature. Only when the temperature was increased to 70 °C did the μ-hydroxo compounds start to transform into the corresponding bis-chelate complexes. Notably, the dppp and *meso*-bdpp μ-hydroxo complexes converted almost completely to the bis-chelates in ca. 1 h at 70 °C, while ca. 50% conversion was observed for the *rac* complex. At this point the temperature was decreased to 20 °C, and the tubes were removed from the spectrometer. The formation of polyketone as a fluffy solid had occurred, while GC/MS analysis of the filtrate revealed the presence of methyl ethyl ketone.

Alternating Copolymerization of Ethene and Carbon Monoxide Catalyzed by $[Pd(\mu\text{-}OH)(P{-}P)]_2(PF_6)_2$ and $[Pd(P{-}P)_2](PF_6)_2$ Precursors in CH_2Cl_2. It has been recently shown that Pd(II) μ-hydroxo precursors with dppe and *meso*/*rac*-dppb ligands catalyze the CO/ethene copolymerization in CH_2Cl_2.[4] Our first evidence that also the μ-hydroxo complexes with dppp, *meso*-bdpp, and *rac*-bdpp do not represent a dead end to copolymerization was actually provided by the HPNMR experiments described above. Confirmatory evidence was obtained from the results of batch reactions in which **13**−**15** were used as precursors (Figure 5a). Interestingly, the productivity was found to decrease in the ligand order dppp (1.8 kg of polyketone (g of Pd)$^{-1}$) > *meso*-bdpp (1.5) ≫ *rac*-bdpp (0.5), which resembles the order of stability of the μ-hydroxo complexes in catalytic conditions (see Figures 3 and 4 and relative comments).

The next step was to look at the bis-chelates **16**−**18** as potential catalyst precursors for the CO/ethylene copolymerization in CH_2Cl_2. Indeed, we were aware of a previous report showing that $[Pd(dppp)_2](TFA)_2$ (TFA = trifluoroacetate) was active in MeOH.[22] Therefore, batch reactions were performed with the bis-chelates **16**−**18**. Polyketone was obtained in all cases, albeit in low yield, as the *meso* derivative gave 350 g of polyketone (g of Pd)$^{-1}$, while the *rac* complex was the least efficient with 140 g (g of Pd)$^{-1}$ (Figure 5b).

The mechanism through which Pd(II) μ-hydroxo resting states can re-enter the copolymerization catalytic cycle has already been discussed.[2,4] Active Pd−H moieties have been proposed to form by the stepwise process shown in Scheme 5a, which involves the cleavage of the binuclear structure by CO, followed by CO insertion to give Pd−COOH, and finally by CO_2 elimination.

In contrast, there is no mechanism that may allow the bis-chelates to generate catalytically active Pd(II) in copolymerization reactions performed in anhydrous CH_2Cl_2. Some water is needed to convert the bis-chelates to Pd−COOH via either Pd−OH or Pd−CO in

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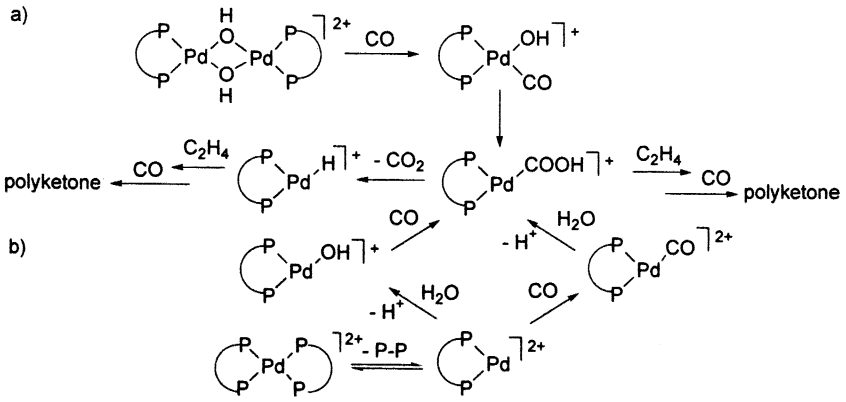
Scheme 5



fact (Scheme 5b). Therefore, the catalytic activity of the bis-chelates under the conditions of Figure 5b confirms once more that the presence of water in batch copolymerization reactions is virtually unavoidable (traces of water may be delivered by the two gases or may be present on the reactor walls or in the solvent).

Alternating Copolymerization of Ethene and Carbon Monoxide Catalyzed by [Pd(μ-OH)(P−P)]$_2$-(PF$_6$)$_2$ and [Pd(P−P)$_2$](PF$_6$)$_2$ Precursors in MeOH. The presence of some water is not a problem at all in copolymerization reactions catalyzed by Pd(II)-diphosphine systems in MeOH, as these reactions are commonly carried out in the presence of a strong protic acid such as TsOH that converts eventual Pd−OH to Pd−OTs.[2] The initiation proceeds via Pd−OMe and Pd−H species.[2] As in CH_2Cl_2, however, catalyst deactivation is rather fast in MeOH due to the inherent propensity of [PdH(P−P)]$^+$ species to form Pd^0, H$^+$, and free P−P ligand.[2] The latter can form bis-chelates [Pd(P−P)$_2$]$^{2+}$ by reaction with monochelate [Pd(P−P)]$^{2+}$ moieties.[2,4,19−21] In light of the results reported in Figure 5b, we decided to carry out CO/ethene copolymerization reactions in MeOH in the presence of the bis-chelates **16**−**18**. The results of this study are reported in Figure 6a, while Figure 6b reports productivity data obtained with Pd(OTs)$_2$((P−P) precursors in MeOH under comparable experimental conditions.[3b] It turned out that the productivity decreases in the ligand order *meso*-bdpp > *rac*-bdpp ≫ dppp.

Generation and Migratory Insertion Barriers of [Pd(Me)(CO)(P−P)]BF$_4$. Migratory insertion barriers relative to reactions that occur during the propagation of the alternating copolymerization catalyzed by the Pd(II) methyl complexes **4**−**6BF$_4$** were estimated by NMR spectroscopy for various model intermediates.[4]

The methyl carbonyl complexes [Pd(Me)(CO)(P−P)]-BF$_4$ (P−P = dppp, **19**; *meso*-bdpp, **20**; *rac*-bdpp, **21**) were generated in HPNMR tubes by pressurizing CD_2Cl_2 solutions of the corresponding methyl acetonitrile compounds (**4**−**6BF$_4$**) with CO (15 bar) at −117 °C. The quantitative formation of the methyl carbonyl complexes occurred already at −80 °C. Upon slow heating of the NMR probe-head, the methyl carbonyl complexes transformed selectively into the corresponding carbonyl acyl derivatives [Pd(COMe)(CO)(P−P)]BF$_4$ (P−P = dppp, **22**; *meso*-bdpp, **23**; *rac*-bdpp, **24**) (Scheme 6).

This transformation started to occur at −70 °C for **19** and at −80 °C for **20** and **21**. Both the methyl carbonyl and acyl carbonyl compounds were straightforwardly

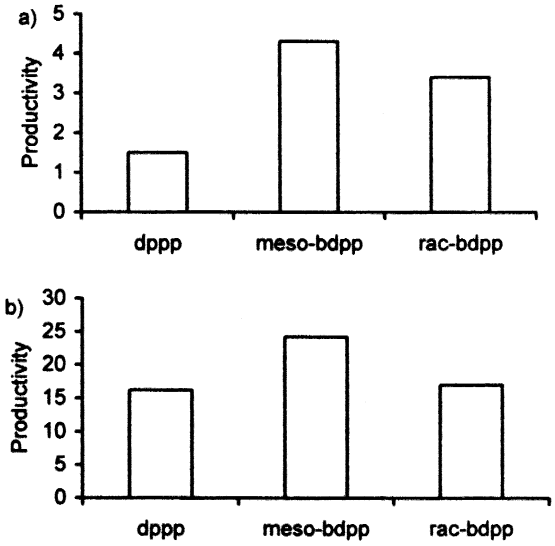
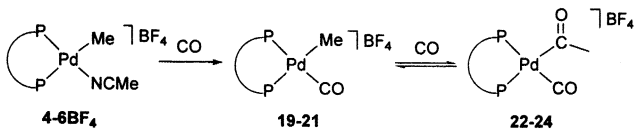


Figure 6. Productivities expressed as kg of polyketone (g of Pd)$^{-1}$ for the copolymerization reactions (precursor, 0.01 mmol; MeOH; 100 mL; BQ, 80 equiv; *p*-TsOH, 20 equiv) with (a) [Pd(P−P)$_2$](PF$_6$)$_2$ (time, 30 min); (b) Pd(TFA)$_2$(P−P) (time, 3 h).

Scheme 6



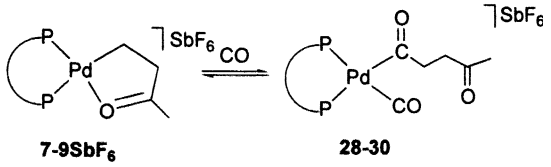
identified by $^{31}P\{^1H\}$ and ^1H NMR spectroscopy (Tables 1 and 2). Comparisons with the spectra of similar or related complexes described in the literature have substantially contributed to validate our structural assignments.[4,7,8,15,17,21]

Kinetics of transformation of the methyl carbonyl complexes into the corresponding acyl carbonyl products were studied by $^{31}P\{^1H\}$ NMR spectroscopy at −60 °C (dppp complex **22**), −70 °C (*meso*-bdpp complex **23**), and −80 °C (*rac*-bdpp complex **24**), where the reactions were sufficiently fast to allow for a reliable determination of the half-life times ($t_{1/2}$). As previously observed by Brookhart and co-workers[8] for [Pd(Me)(CO)(dppp)]BAr′$_4$ and by us for the series [Pd(Me)(CO)(P−P)](PF$_6$) (P−P = dppe, *meso*-dppb, *rac*-dppb),[4] the rate of conversion of the methyl carbonyl complexes is independent of the CO pressure (5−25 bar) and follows first-order kinetics. The observed rate constants are therefore the true rate

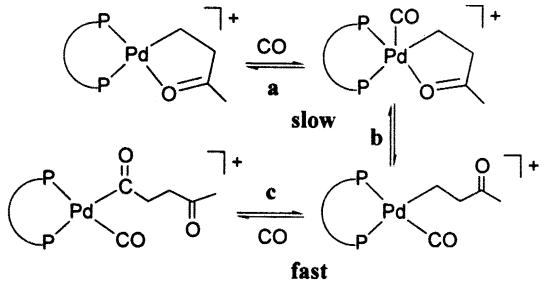
Table 3. Experimental Activation Barriers and Temperatures for Migratory Insertions

	[Pd(Me)(CO)(P−P)]$^+$			[Pd(CH$_2$CH$_2$C(O)Me)(P−P)]$^+$		
P−P	$\Delta G^‡$ (kcal/mol)	$t_{1/2}$ (min)	T (°C)	T (°C)	$t_{1/2}$ (min)	p(CO) (bar)
dppp	15.2(1)	10	−60	−70	84	20
meso-bdpp	14.6(1)	13	−70	−70	200	20
rac-bdpp	14.2(1)	31	−80	−70	13	20

Scheme 7



Scheme 8



constants, and the $\Delta G^‡$ values associated with the migratory insertion of the methyl carbonyl complexes could be straightforwardly calculated from the $t_{1/2}$ values using the equation $\Delta G^‡ = RT(\ln k_r - \ln kT/h)$ with $k_r = \ln 2/t_{1/2}$.[8] The energy barriers were found to increase in the ligand order *rac*-bdpp < *meso*-bdpp < dppp (Table 3). Notably, the activation barriers for insertion calculated in this work nicely fit previous data for [Pd(Me)(CO)(dppp)]BAr′$_4$ (14.8(1) kcal mol^{-1} at −81.7 °C)[8] and [Pd(Me)(CO){(*S*,*S*)-bdpp}]BF$_4$ (14.5 kcal mol^{-1} at −80 °C).[21b]

Generation and Carbonylation of β-Chelates [Pd(CH$_2$CH$_2$C(O)Me)(P−P)]SbF$_6$. The β-chelates [Pd(CH$_2$CH$_2$C(O)Me)(P−P)]SbF$_6$ (**7**−**9SbF$_6$**) were prepared in situ following the procedures described in Scheme 2.[8] HPNMR tubes containing CD_2Cl_2 solutions of these complexes under Ar at room temperature were cooled to ca. −117 °C, pressurized with 20 bar CO, and then inserted into the NMR probe-head precooled at −90 °C. The conversion of the β-chelates to the carbonyl acyl complexes [Pd(CO)(COCH$_2$CH$_2$C(O)Me)(P−P)]SbF$_6$ (P−P = dppp, **28**; *meso*-bdpp, **29**; *rac*-bdpp, **30**) was followed by variable-temperature $^{31}P\{^1H\}$ NMR spectroscopy (Scheme 7). The transformation of all β-chelate complexes occurred already at −80 °C.

Like all the other new products obtained in situ, unambiguous characterization of the carbonyl acyl complexes **28**−**30** was achieved by NMR spectroscopy as well as comparisons with literature data (Tables 1 and 2).[4,8,15,21]

The rates of conversion of the β-chelates to carbonyl acyl complexes were evaluated as half-life times obtained from the decay (and increase) of the phosphorus resonances at −70 °C (Table 3). The activation barriers for the processes could not be calculated straightforwardly from the $t_{1/2}$ values, as the reaction rates proved to be dependent on the CO pressure in the range investigated (15−25 bar). The $t_{1/2}$ values decrease in the order *meso*-bdpp > dppp > *rac*-bdpp, yet the difference is not very significant. In line with previous observations,[4] the opening of the metallacycle by CO (steps a, b) is rate limiting in the stepwise process illustrated in Scheme 8 since the following migratory insertion of the alkyl carbonyl complex (step c) is independent of the CO pressure. The opening of the β-chelates by CO is most probably the rate-limiting step of the overall copolymerization reaction in CH_2Cl_2, as previously reported for the reactions catalyzed by [Pd(Me)(MeCN)(P−P)]$^+$ precursors (P−P = dppe, *meso*-dppb, *rac*-dppb).[4] Interestingly, the kinetic and thermodynamic trends reported for the carbonylation of the β-chelates [Pd(CH$_2$CH$_2$C(O)Me)(P−P)]$^+$ containing the latter diphosphine ligands contrast those observed for the present compounds; that is, the opening of the β-chelate by CO was much easier for the *meso*-dppb ($t_{1/2}$ = 97 min at −40 °C) and *rac*-dppb ($t_{1/2}$ = 480 min at −40 °C) derivatives than for the dppe one ($t_{1/2}$ = 15 min at 20 °C). The different behavior of the dppe and dppp systems confirms the importance of the chelating diphosphine structure in determining the intrinsic activity of the corresponding Pd(II) catalysts in the CO/ethene copolymerization.[2,4]

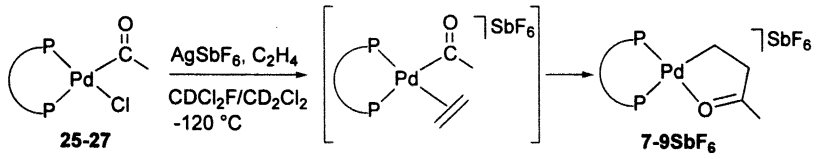
Attempted Determination of the Migratory Insertion Barriers of [Pd(COMe)(C$_2$H$_4$)(P−P)]BF$_4$. In an attempt to determine the activation barriers to the migratory insertion of acyl ethylene intermediates [Pd(COMe)(C$_2$H$_4$)(P−P)]$^+$,[4,8] the chloride ligand was removed from the acyl chloride derivatives **25**−**27** with AgSbF$_6$ in the presence of ethene (15 bar) at −120 °C (Scheme 9). Only the β-chelates were seen already in the first NMR spectrum at −117 °C, which is consistent with an activation barrier lower than 12 kcal mol^{-1} for all reactions. A $\Delta G^‡$ value of 12.3(1) kcal mol^{-1} has been reported by Brookhart and co-workers for [Pd(COMe)(C$_2$H$_4$)(P−P)]SbF$_6$ in an experiment performed at −135 °C.[8]

Discussion

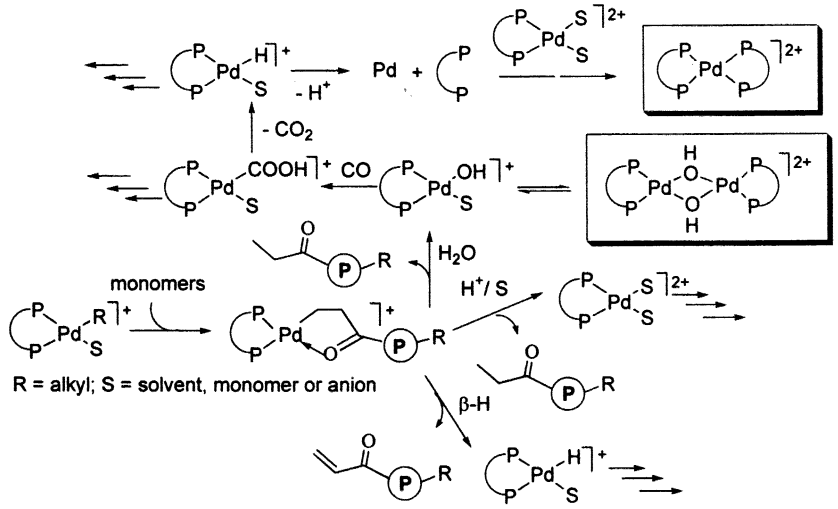
The perfect alternation of the comonomers in the CO/ethene copolymerization by Pd(II)-chelating diphosphine catalysis is thermodynamically and kinetically driven. In particular, misinsertions do not occur, as the migratory insertions of Pd(COR)(CO) and Pd(CH$_2$CH$_2$C(O)R)(C$_2$H$_4$) are thermodynamically and kinetically disfavored, respectively.[2,8,23] This strict control changes neither with the solvent nor with the diphosphine ligand provided the latter is appropriate for CO/ethene copolymerization;[2] yet solvent and ligand are of utmost importance in determining the catalytic productivity as well as many copolymer properties such as the molecular weight, morphology, and nature of the end groups of the polyketone product.[2] Ultimately, the solvent rules

(23) (a) Chen, J.-T.; Sen, A. *J. Am. Chem. Soc.* **1984**, *106*, 1506. (b) Sen, A.; Chen, J.-T.; Vetter, W. M.; Whittle, R. *J. Am. Chem. Soc.* **1987**, *109*, 148.

Scheme 9



Scheme 10



the kinetics of propagation and the mechanisms of initiation and chain transfer.[2,22,24]

Pd-alkyl complexes, either preformed or generated in situ with alkylating agents,[12b,c] are required to initiate the copolymerization in CH_2Cl_2, whose relevant steps are illustrated in Scheme 10 together with paths leading to the formation of μ-hydroxo and bis-chelate resting states.[2]

Our results confirm the importance of the solvent/ligand assembly in determining the performance of Pd(II)-diphosphine catalysts in CO/ethene copolymerization and also highlight the complexity and variety of the reactions involved in this process.

The first and perhaps most important conclusion that can be reached on the basis of our study is that *the presence and/or stereochemistry of methyl groups in the 1,3-positions of the dppp backbone do not apparently exert a significant influence on the propagation rate of the copolymerization in CH_2Cl_2.* Nevertheless, the ligands dppp and *meso*-bdpp give rise to more productive catalysts than *rac*-bdpp (Figure 1). An explanation for this experimental observable has been provided by in situ NMR experiments under catalytic conditions which have shown that both the rate of formation and stability of the *rac*-bdpp μ-OH complex are appreciably higher than those of the dppp and *meso*-bdpp analogues (Figures 3 and 4). Accordingly, a larger number of palladium active sites would be subtracted to catalyze the reaction assisted by the *rac*-bdpp precursor, which is consistent with the results of the batch copolymerization reactions catalyzed by either [Pd(Me)(MeCN)(P−P)]$^+$ (Figure 1) or isolated [Pd(μ-OH)(P−P)]$_2^{2+}$ (Figure 5a). Since the contribution of the bis-chelates [Pd(P−P)$_2$]$^{2+}$ to the overall productivity is almost negligible and comparable for all precursors within experimental error (Figure 5b), we propose that *both the faster chain-transfer rate by protonolysis with adventitious water and the greater stability of the μ-OH resting state are responsible for the lower activity of the rac-bdpp methyl precursor* ***6PF6*** *in CH_2Cl_2 as compared to* ***4PF6*** *and* ***5PF6***.

No contribution of μ-hydroxo complexes to the productivity of Pd(OTs)$_2$(P−P) precursors in CO/ethene copolymerization in MeOH can be envisaged for the simple reason that these compounds do not form as the reactions are carried out in the presence of a strong protic acid (TsOH).[2,3] On the other hand, all Pd(II)-diphosphine catalysts degrade in MeOH with time to palladium metal and free ligand, following the mechanism detailed in the upper part of Scheme 10, once the organic oxidant and the protic acid are consumed.[2,19,22] Evidence of the formation of Pd(II) bis-chelates upon disappearance of BQ and H^+ in the catalytic mixtures has been provided for ethene and styrene carbonylation in MeOH.[19,22] It is therefore reasonable to conclude that the bis-chelate complexes are likely resting states of copolymerization reactions, able to re-enter the catalysis through the sequence of reactions shown in Scheme 5b using MeOH instead of H_2O.[20] In this eventuality, the amount of polyketone produced by the bis-chelates [Pd(P−P)$_2$]$^{2+}$ (*meso*-bdpp > *rac*-bdpp ≫ dppp) (Figure 6a) might make the difference and hence contribute to determine the overall productivity of the Pd(OTs)$_2$(P−P) precursors (Figure 6b). On the other hand, the overall productivity of CO/olefin copolymerizations is controlled by a complex web of factors, including the fact that the reactions become heterogeneous after the polymer chain is long enough to make the propagating species insoluble in MeOH.[25] Therefore, one may not rule out that other factors, for example the morphology of the pro-

(24) Toniolo, L.; Kulkarni, S. M.; Fatutto, D.; Chaudari, R. V. *Ind. Eng. Chem. Res.* **2001**, *40*, 2037.

(25) Mul, W. P.; Drent, E.; Jansens, P. J.; Kramer, A. H.; Sonnemans, M. H. W. *J. Am. Chem. Soc.* **2001**, *123*, 5350.

duced polymer, contribute to determine the different productivity of the dppp, *meso*-bdpp, and *rac*-bdpp catalysts. In contrast, the intrinsic activity in CH_2Cl_2, being determined at the very early stages of the reaction, allows for more reliable comparisons.

In conclusion, our studies demonstrate that methyl substituents in the 1,3-positions of the dppp backbone do not have any significant influence on the propagation rate of CO/ethene copolymerization in aprotic solvents, yet they may affect the chain-transfer rate by protonolysis with adventitious water. In contrast, these methyl groups might influence the productivity by controlling the stability of μ-OH or bis-chelate resting states under catalytic conditions. This control should be essentially steric in nature and related to the different conformations and rigidity of the Pd(dppp) (fluxional *skew*), Pd(*meso*-bdpp) (*chair*), and Pd(*rac*-bdpp) (rigid δ-*skew*) moieties in solution.[3a,4]

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