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Copolymerization of Carbon Monoxide with Ethene Catalyzed by Palladium(II) Complexes of 1,3-Bis(diphenylphosphino)propane Ligands Bearing Different Substituents on the Carbon Backbone

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ABSTRACT: In this work are described the syntheses of several new dppp-like ligands (dppp =1,3-bis(diphenylphosphino)propane) bearing different substituents on the carbon backbone and of their palladium(II) complexes with acetate or trifluoroacetate coligands (L). The complexes exhibit the general formula $Pd(P-P)(L)_2$ and have been employed as catalyst precursors for the copolymerization of ethene and carbon monoxide in MeOH under experimental conditions that are comparable to those reported in the relevant literature and patents for dppp-based Pd(II) copolymerization catalysts. It has been found that the introduction of alkyl substituents in the 2-position of the carbon backbone of dppp does not significantly improve the performance of the corresponding catalyst precursors (highest productivity value 6.2 kg of copolymer (g of Pd h)$^{-1}$ vs 5.4 kg of copolymer (g of Pd h)$^{-1}$ for $Pd(dppp)(L)_2$). In contrast, the productivity increases remarkably when methyl groups are introduced in both 1-positions of the diphosphine ligand, particularly with *R,S* (*S,R*) stereochemistry as in *meso*-$CH_2(CH_3CHPPh_2)_2$ (productivity of 8.0 kg of copolymer (g of Pd h)$^{-1}$). On the basis of NMR and cyclic voltammetric studies of the catalyst precursors, it is suggested that the increased productivity provided by the C_1-substituted ligands is both electronic and steric in nature. In situ high-pressure NMR experiments in sapphire tubes equipped with Ti alloy valves showed that the only phosphorus-containing species visible on the NMR time scale in effective copolymerization conditions are Pd(II) complexes with the formula $Pd(diphosphine)X_2$ (X = *p*-toluenesulfonate, trifluoroacetate, or MeOH). It has been proposed that these Pd(II) complexes act as a reservoir of $[Pd(diphosphine)]^{2+}$ moieties which may either be delivered into the catalysis cycle by action of various reagents (MeOH, H^+, H_2O, H_2) or be withdrawn after the termination step and watched over deactivation paths.

Introduction

Following the breakthrough of Drent in using palladium(II) diphosphine complexes as catalyst precursors in 1984,[1] the alternating copolymerization of alkenes and carbon monoxide to form polyketone polymers has attracted considerable interest from both academic and industrial sectors over the past decade.[2] The importance of polyketone polymer and the successful research activites in this field are marked with the introduction of Shell's terpolymer Carilon in 1995.[1,3]

For many years, the diphosphine ligand 1,3-bis(diphenylphosphino)propane (dppp) has remained the ligand of choice in the Pd-catalyzed copolymerization (terpolymerization) of carbon monoxide and ethene (ethene/propene) for its high efficiency.[1,2] Efforts to seek catalytic systems with further improvement of activity and prolong the lifetime of precious palladium metal are still of great significance, however. To this purpose several approaches have been developed over recent years.[2] Common strategies involve the design of metal−ligand assemblies containing simultaneously both phosphorus and nitrogen ligands,[4] the replacement of the phenyl substituents on the phosphorus of dppp with other, generally more basic or less sterically demanding, groups,[2] the use of different phase-variation systems,[5] or the copresence in the catalytic mixtures of either Brønsted acids or organic oxidants.[2] Without disregarding any of these protocols, we decided to attempt an alternative route that involves the introduction of substituents on the carbon chain of dppp as they might exert beneficial effects on the productivity and/or the catalyst lifetime while preserving the activity-proven ligand framework.

Herein, we report the synthesis of a variety of dppp-like ligands bearing different substituents on the carbon backbone and the application of their palladium(II) complexes in the copolymerization of ethene and carbon monoxide under different experimental conditions. It has been found that the introduction of certain substituents on the carbon backbone of dppp, in conjuction with 1,4-benzoquinone and/or protic acids with poorly coordinating conjugated bases, can indeed exert beneficial effects on the catalytic activity without affecting the spectacular chemo- and stereoselectivity of the dppp catalysts. High-pressure NMR experiments[6] under catalytic copolymerization conditions and cyclic voltammetric studies were also carried out in the hope of shedding light on both the mechanism of this facile catalytic reaction and the factors that may affect the catalyst stability.

Experimental Section

General Procedure. All reactions and manipulations were carried out under an atmosphere of nitrogen by using Schlenk-type techniques. The starting materials $Pd(dppp)(CO_2CH_3)_2$ (**6a**),[4] $Pd(dppp)(CO_2CF_3)_2$ (**6b**),[4] and η^2-$O(CH_2)_2C(CH_2PPh_2)_2$

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(**5**)[7] were prepared according to literature methods. Diethyl ether and THF were distilled from $LiAlH_4$; DMSO was distilled from CaH_2. Reagent grade MeOH was used in all copolymerization reactions. 1,1,1,3,3,3-Hexafluoropropan-2-ol-d_2 (HFIP-d_2) was purchased from Cambridge Isotope Laboratories, Andover, MA. All the other reagents and solvents were used as purchased from Aldrich, Fluka, or Strem. Copolymerization reactions were performed with a 250 mL stainless steel autoclave, constructed at the ISSECC-CNR (Firenze, Italy), equipped with a magnetic drive stirrer, a Parr 4842 temperature and pressure controller, and a high-pressure injector. The autoclave was connected to a gas reservoir to maintain a constant pressure all over the catalytic reactions. Deuterated solvents for NMR measurements were dried over molecular sieves. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were obtained on a Bruker ACP 200 (200.13, 50.32, and 81.01 MHz, respectively). All chemical shifts are reported in ppm (δ) relative to tetramethylsilane, referenced to the chemical shifts of residual solvent resonances (^1H, ^{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).[8] *Note*: *since high gas pressures are involved, safety precautions must be taken at all stages of studies involving high-pressure NMR tubes.* 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. Molecular weights of selected polyketone materials were measured on a Waters gel permeation chromatograph equipped with a differential refractometer. Either pure HFIP or a mixture of trichlorobenzene/phenol was used as the solvent, and polystyrene standards were used to calibrate the instrument. Limiting viscosity numbers (LVN) were measured in *m*-cresol at 60 °C in a standard capillary viscosity-measuring device. Cyclic voltammetry was performed in a three-electrode cell having a platinum working electrode surrounded by a platinum-spiral counter electrode and the aqueous saturated calomel reference electrode (SCE) mounted with a Luggin capillary. A BAS 100A electrochemical analyzer was used as polarizing unit. Under the present experimental conditions, the one-electrode oxidation of ferrocene occurred at 0.31 V. Controlled potential coulometry was carried out with an Amel 552 potentiostat equipped with an Amel 558 integrator. Anhydrous methyl alcohol (99.8%) (Aldrich) and $LiClO_4$ (Fluka) were used as solvent and supporting electrolyte, respectively.

$(PhCH_2)_2C(CH_2PPh_2)_2$ (1). To a solution of $KPPh_2$, obtained by reacting $KOBu^t$ (6.8 g, 60.8 mmol) with a solution of $HPPh_2$ (11.3 g, 60.8 mmol) in 100 mL of dimethyl sulfoxide at room temperature under an inert atmosphere, was added dropwise 40 mL of a solution of $(PhCH_2)_2C(CH_2Cl)_2$ (6.6 g, 22.5 mmol) in dimethyl sulfoxide. After the resulting orange solution was heated at 100 °C for 5 h, the solution was allowed to stir overnight. The solvent was removed under reduced pressure to give a yellow oily residue. Addition of 10 mL of ethanol and 200 mL of water gave a white solid. The solid was filtered and washed with petroleum ether. Yield: 11.7 g, 88%. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −26.8 (s). ^1H NMR (CD_2Cl_2): δ 2.07 (d, 4H, J(PH) = 3.1 Hz, CH_2P), 2.95 (s, 4H, CH_2Ph), 7.12−7.32 (m, 30H, Ph). Anal. Calcd for $C_{41}H_{38}P_2$: C, 83.10; H, 6.41; P, 10.49. Found: C, 83.12; H, 6.52; P, 10.43.

$(PhCH_2)_2C(CH_2Cl)_2$. To a solution of $(PhCH_2)_2C(CH_2OH)_2$ (14.4 g, 0.06 mol) in 40 mL of anhydrous pyridine at 0 °C was added with stirring under an inert atmosphere 16 mL (26 g, 0.21 mol) of thionyl chloride in ca. 2 h. The resulting mixture was refluxed for 2 h and then stirred at room temperature for 15 h. After cooling to 0 °C, equal volumes of CH_2Cl_2 and water (200 mL each) were added to the reaction mixture. The separated organic layer was washed with an aqueous solution of HCl (pH = 4), an aqueous saturated solution of $NaHCO_3$, and then with distilled water. The solvent of the organic layer, after being dried by anhydrous sodium sulfate, was removed under reduced pressure. To the resulting oily residue was added diethyl ether (30 mL) until an off-white solid precipitated, which was recrystallized from ethanol to give a white crystalline solid. Yield: 10.0 g, 61%. ^1H NMR ($CDCl_3$): δ 2.91 (s, 4H, CH_2Ph), 3.23 (s, 4H, CH_2Cl), 7.5−7.2 (m, 10H, Ph).

$(PhCH_2)_2C(CH_2OH)_2$. A solution of $(PhCH_2)_2C(CO_2Et)_2$ (30 g, 0.09 mol) in diethyl ether (150 mL) was poured by means of a dropping funnel into a suspension of $LiAlH_4$ (10 g, 0.26 mol) in 150 mL of diethyl ether at 0 °C under an inert atmosphere with vigorous stirring. The resulting reaction mixture was then allowed to warm to room temperature, refluxed for 2 h, cooled again to 0 °C, and finally poured slowly into an aqueous solution of HCl (3.4 M) maintained at 0 °C. The mixture was transferred to a separatory funnel. The ether phase was separated, washed several times with distilled water, and then treated with anhydrous sodium sulfate to remove water. Upon removal of the solvent under reduced pressure, $(PhCH_2)_2C(CH_2OH)_2$ was obtained as an off-white solid. Yield: 20.3 g, 90%. ^1H NMR ($CDCl_3$): δ 1.93 (t, 2H, J(HH) = 5.2 Hz, OH), 2.76 (s, 4H, CH_2Ph), 3.57 (d, 4H, J(HH) = 5.2 Hz, CH_2OH), 7.3−7.1 (m, 10H, Ph).

$(PhCH_2)_2C(CO_2Et)_2$. To a solution of $PhCH_2CH(CO_2Et)_2$ (74.1 g, 0.30 mol) in tetrahydrofuran (THF) (150 mL) at 0 °C under an inert atmosphere (N_2 or Ar) was added portionwise with stirring NaH (60% suspension in mineral oil, 13.6 g, 0.34 mol). After a clear solution was obtained (ca. 1 h), 58.2 g (0.34 mol) of benzyl bromide in 50 mL of THF was added dropwise in 1 h. Afterward, the reaction mixture was allowed to reach room temperature, stirred for ca. 15 h, and then hydrolyzed with an aqueous solution of NH_4Cl (16 g in 200 mL of water) to give two phases. The organic phase was separated and set aside. The aqueous layer was washed three times with ethyl ether. After the washings were poured into the organic phase, the resulting solution was treated with sodium sulfate to remove and pumped to dryness. The oily residue was distilled under reduced pressure to give pure $(PhCH_2)_2C(CO_2Et)_2$. Yield: 91 g, 93%. Bp: 190 °C. ^1H NMR ($CDCl_3$): δ 1.17 (t, 6H, J(HH) = 7.2 Hz, CH_2CH_3), 4.12 (q, 4H, J(HH) = 7.2 Hz, CH_2CH_3), 7.4−7.1 (m, 10H, Ph).

$PhCH_2(CH_3)C(CH_2PPh_2)_2$ (2). The compound was prepared similarly as $(PhCH_2)_2C(CH_2PPh_2)_2$. $HPPh_2$ (10.7 g, 57.5 mmol), $KOBu^t$ (6.5 g, 57.5 mmol), and $(PhCH_2)_2C(CH_2Cl)_2$ (5.0 g, 23.0 mmol) were used. A white solid was obtained. Yield: 10.1 g, 85%. Mp: 87−89 °C. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −25.5 (s). ^1H NMR (CD_2Cl_2): δ 0.91 (s, 3H, CH_3), 2.30 (m, 4H, CH_2Ph), 2.87 (s, 2 H, CH_2P), 7.15−7.37 (m, 25H, Ph). Anal. Calcd for $C_{35}H_{34}P_2$: C, 81.37; H, 6.63; P, 11.99. Found: C, 81.12; H, 6.57; P, 11.44.

$PhCH_2(CH_3)C(CH_2Cl)_2$. The compound was prepared similarly as $(PhCH_2)_2C(CH_2Cl)_2$. $PhCH_2(CH_3)C(CH_2OH)_2$ (15.0 g, 83.3 mmol) and thionyl chloride (29.7 g, 0.25 mol) were used. Upon removal of the solvent, an oily residue remained which was distilled under reduced pressure to give a colorless liquid. Yield: 12.1 g, 67%. Bp: 112−114 °C (0.1 Torr). ^1H NMR ($CDCl_3$): δ 1.05 (s, 3H, CH_3), 2.75 (s, 2H, CH_2Ph), 3.50 (s, 4H, CH_2Cl), 7.28−7.31 (m, 5H, Ph).

$PhCH_2(CH_3)C(CH_2OH)_2$. The compound was prepared similarly as $(PhCH_2)_2C(CH_2OH)_2$. $PhCH_2(CH_3)C(CO_2Et)_2$ (30.0 g, 0.11 mol) and $LiAlH_4$ (10 g, 0.26 mol) were used. A white solid was obtained. Yield: 18.5 g, 91%. ^1H NMR ($CDCl_3$): δ 0.77 (s, 3H, CH_3), 2.56 (br, 2H, OH), 2.72 (s, 2H, CH_2Ph), 3.56 (s, 4H, CH_2OH), 7.21−7.30 (m, 5H, Ph).

$PhCH_2(CH_3)C(CO_2Et)_2$. The compound was prepared similarly as $(PhCH_2)_2C(CO_2Et)_2$. $CH_3CH(CO_2Et)_2$ (40.0 g, 0.23 mol), NaH (60% suspension in mineral oil, 10.0 g, 0.25 mol), and 39.3 g (0.23 mol) of benzyl bromide were used. A colorless liquid was obtained. Yield: 57.7 g, 95%. ^1H NMR ($CDCl_3$): δ 1.26 (t, 6H, J(HH) = 7.2 Hz, CH_2CH_3), 1.35 (s, 3H, CH_3), 3.24 (s, 2H, CH_2Ph), 4.20 (q, 4H, J(HH) = 7.2 Hz, CH_2CH_3), 7.11−7.27 (m, 5H, Ph).

$Et_2C(CH_2PPh_2)_2$ (3). To a solution of potassium diphenylphosphide dioxane adduct (20 g, 0.05 mol) in 50 mL of tetrahydrofuran cooled at 0 °C was added dropwise $Et_2C(CH_2OMs)_2$ (5.8 g, 0.02 mol). The mixture was allowed to stir overnight. The solvent was completely removed under vacuum. Water (100 mL) and ethanol (10 mL) were added. The solvent was then extracted with 2 × 100 mL of diethyl ether. The ethereal solution was then dried by anhydrous $MgSO_4$. Removal of the solvent under reduced pressure gave a yellow oil. Yield: 7.0 g, 75%. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −25.9 (s). ^1H NMR (CD_2Cl_2): δ 0.54 (t, 6H, J(HH) = 7.5 Hz, $2CH_2CH_3$), 1.44 (q, 4H, J(HH) = 7.5 Hz, CH_2CH_3), 2.34 (d, 4H, J(PH) = 3.8 Hz, CH_2P), 7.26−7.53 (m, 20H, Ph). Anal. Calcd for $C_{31}H_{34}P_2$: C, 79.47; H, 7.04; P, 13.22. Found: C, 80.00; H, 7.12; P, 13.40.

$Et_2C(CH_2OMs)_2$. To a solution of $Et_2C(CH_2OH)_2$ (5.0 g, 38.0 mmol) in 20 mL of dry pyridine cooled at 0 °C was added dropwise mesyl chloride (8.9 mL, 114 mmol). The mixture was stirred at room temperature for 2 h. Dichloromethane and water (200 mL each) were added to the reaction mixture. The separated organic layer was washed with an aqueous solution of HCl (pH = 4), an aqueous saturated solution of $NaHCO_3$, and then distilled water. The volume of the organic layer, after dried by anhydrous sodium sulfate, was reduced until a solid began to precipitate. Upon addition of petroleum ether (30 mL) to the resulting suspension, more white solid was precipitated which was recrystallized from dichloromethane/petroleum ether to give a white crystalline solid. Yield: 8.1 g, 74%. ^1H NMR ($CDCl_3$): δ 0.90 (t, 6H, J(HH) = 7.5 Hz, CH_2CH_3), 1.40 (q, 4H, J(HH) = 7.5 Hz, CH_2CH_3), 3.06 (s, 6H, SO_2CH_3), 4.06 (s, 4H, CH_2OS).

$Et_2C(CH_2OH)_2$. To a solution of $LiAlH_4$ (20 g, 0.53 mol) in 150 mL of diethyl ether cooled at 0 °C was added dropwise a solution of dimethyl diethylmalonate (30 g, 0.16 mol). The mixture was then allowed to reach at room temperature and refluxed for 2 h. The mixture was added slowly to an aqueous solution of hydrochloric acid (pH = 1, 150 mL) which was cooled with an ice−water bath. Another 100 mL of diethyl ether was added to the mixture. The organic phase was separated, washed with water, and dried by anhydrous sodium sulfate. Removal of the solvent under reduced pressure gave an colorless liquid. Yield: 10 g, 71%. ^1H NMR ($CDCl_3$): δ 0.83 (t, 6H, J(HH) = 7.5 Hz, CH_3), 1.32 (q, 4H, J(HH) = 7.5 Hz, CH_2CH_3), 2.48 (br, 2H, OH), 3.57 (d, 4H, J(HH) = 3.6 Hz, CH_2OH).

$CH_2(CH_3CHPPh_2)_2$ (4). To 50 mL of tetrahydrofuran solution of lithium diphenylphosphide (8.0 g, 24.8 mmol) cooled at 0 °C was added dropwise 2,4-pentanediol dimesylate (3.1 g, 11.9 mmol). The mixture was allowed to stir overnight. The solvent was completely removed under vacuum. Water (100 mL) and ethanol (10 mL) were added. The solution was then extracted with 2 × 100 mL of diethyl ether. The ethereal layer was separated, washed with diluted hydrochloric acid, an aqueous solution of Na_2CO_3, and water, and then dried by anhydrous $MgSO_4$. The solvent was removed completely under vacuum to give a yellow oil. Recrystallization of the oil with ethanol and petroleum ether gave the pure *meso* compound as a white solid which was filtered and washed with cold petroleum ether. Removal of the solvent of filtrate under reduced pressure gave the racemic mixture as a yellow oil with a purity of 87%. Combined yield: 2.3 g, 44%. *Meso* form (*meso*-**4**): $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −1.1 (s). ^1H NMR ($CDCl_3$): δ 1.03 (dd, 6H, J(PH) = 12.5 Hz, J(HH) = 6.9 Hz, $CHCH_3$), 1.23−1.72 (m, 2H, CH_2), 2.67 (m, 2H, $CHCH_3$), 7.26−7.40 (m, 20H, Ph). Racemic mixture (*rac*-**4**): $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 0.1 (s). ^1H NMR ($CDCl_3$): δ 1.04 (dd, 6H, J(PH) = 15.4 Hz, J(HH) = 6.8 Hz, $CHCH_3$), 1.45 (quintet, 2H, J(PH) = 7.2 Hz, J(HH) = 7.2 Hz, CH_2), 2.55 (septet, 2H, J(PH) = 6.6 Hz, J(HH) = 6.6 Hz, $CHCH_3$), 7.30−7.40 (m, 20H, Ph). Anal. Calcd for $C_{29}H_{24}P_2$: C, 80.17; H, 5.57; P, 14.26. Found: C, 79.82; H, 5.52; P, 13.97.

The racemic mixture was further purified by preparing Ni$\{CH_2(CH_3CHPPh_2)_2\}(NCS)_2$ using a 87:13 mixture of the *rac*-**4** and *meso*-**4**. A mixture of the Ni complex (5 g) in benzene (30 mL) and of KCN (5 g) in 20 mL of water was refluxed for 15 min with stirring. When all the complex dissolved, a clear two-phase system was obtained. The organic phase was separated from the aqueous layer, washed with further water (2 × 20 mL), and then dried over $MgSO_4$. After benzene was removed under reduced pressure, an oily residue was obtained which ^{31}P and ^1H NMR spectroscopy showed to be a 95:5 mixture of the *rac* and *meso* forms of $CH_2(CH_3CHPPh_2)_2$.

$CH_2(CH_3CHOMs)_2$. To a solution of 2,4-pentanediol (10 g, 96 mmol) in dry pyridine (50 mL) cooled at 0 °C was added slowly 18.7 mL of mesyl chloride (240 mmol). The resulting mixture was stirred at room temperature for 2 h. Dichloromethane and water (200 mL each) were added to the reaction mixture. The organic layer was separated, washed with diluted hydrochloric acid, an aqueous solution of Na_2CO_3, and water, and then dried by anhydrous $MgSO_4$. The solvent was removed completely under vacuum to give a colorless liquid. The compound contained a mixture of *rac* and *meso* forms. Yield: 22.5 g, 90%. ^1H NMR ($CDCl_3$): δ 1.47 (d, 6H, J(HH) = 0.6 Hz, $CHCH_3$), 1.78−1.94 (m, 1.43H, *meso*-CHH, *rac*-CH_2), 2.28 (dt, 0.57H, J(HH) = 14.6, 7.3 Hz, *meso*-CHH), 3.02 (s, 3H, OMs), 3.07 (s, 3H, OMs), 4.91 (sept, 2H, J = 6.4 Hz, CHOMs).

$Pd\{(PhCH_2)_2C(CH_2PPh_2)_2\}(CO_2CH_3)_2$ (1a). To 20 mL of methanol solution of Pd(II) acetate (0.17 g, 0.76 mmol) was added a solution of the diphosphine **1** in 20 mL of dichloromethane. The mixture was allowed to stir for 15 min. The volume was reduced to ca. 2 mL under reduced pressure. Then 30 mL of petroleum ether was slowly added to give a pale yellow solid which was filtered on a frit, washed with petroleum ether, and dried by a nitrogen stream. Yield: 0.56 g, 90%. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 15.0 (s). ^1H NMR (CD_2Cl_2): δ 1.50 (s, 6H, CO_2CH_3), 2.30 (d, 4H, J(PH) = 8.9 Hz, CH_2P), 3.14 (s, 4H, CH_2Ph), 7.15−7.47 (m, 20H, Ph).

$Pd\{PhCH_2(CH_3)C(CH_2PPh_2)_2\}(CO_2CH_3)_2$ (2a). The compound was prepared similarly as **1a**. A 0.50 g sample of the diphosphine **2** (0.97 mmol) and 0.20 g of Pd(II) acetate (0.87 mmol) were used. A pale pink solid was obtained. Yield: 0.60 g, 93%. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 16.0 (s). ^1H NMR (CD_2Cl_2): δ 0.68 (s, 3H, CH_3), 1.34 (s, 6H, CO_2CH_3), 2.31 (d, 4H, J(PH) = 9.7 Hz, CH_2P), 2.70 (t, 2H, J(HH) = 2.5 Hz, CH_2Ph), aromatic protons (7.05−7.10 (m, 2H), 7.27−7.57 (m, 19H) 7.97−8.07 (m, 4H)).

$Pd\{CH_2(CH_3CHPPh_2)_2\}(CO_2CH_3)_2$ (4a). The compound was prepared similarly as **2a**. A 0.44 g sample of $CH_2(CH_3CHPPh_2)_2$ (4:1 mixture of *meso*-**4** and *rac*-**4**) (1.0 mmol) and 0.20 g of Pd(II) acetate (0.90 mmol) were used. A pale brown solid was obtained. Yield: 0.54 g, 90%. The compound contained the *meso* and *rac* forms in a 4:1 ratio. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 28.3 (s, *meso*), 23.3 (s, *rac*). ^1H NMR (CD_2Cl_2): δ 1.04 (dd, J(PH) = 14.4 Hz, J(HH) = 7.1 Hz, $CHCH_3$, *meso*), 1.14 (dd, J(PH) = 14.5 Hz, J(HH) = 7.1 Hz, $CHCH_3$, *rac*), 1.30 (br, 6H, $COCH_3$), 1.85−2.22 (m, 2H, CH_2), 2.54 (m, $CHCH_3$, *meso*), 2.70 (m, $CHCH_3$, *rac*), 7.36−7.80 (m, 20H, Ph).

$Pd\{(PhCH_2)_2C(CH_2PPh_2)_2\}(CO_2CF_3)_2$ (1b). To 15 mL of methanol solution of Pd(II) trifluoroacetate (0.17 g, 0.51 mmol) was added a solution of the diphosphine **1** (0.30 g, 0.51 mmol) in 20 mL of dichloromethane. The mixture was allowed to stir for 3 min. The volume was reduced to ca. 2 mL under reduced pressure. Then 30 mL of petroleum ether was slowly added to give a gray solid which was filtered on a frit, washed with petroleum ether, and dried by a nitrogen stream. Yield: 0.43 g, 91%. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 18.6 (s). ^1H NMR (CD_2Cl_2): δ 2.41 (d, 4H, J(PH) = 8.8 Hz, CH_2P), 3.07 (s, 4H, CH_2Ph), 7.20−7.47 (m, 30H, Ph).

$Pd\{PhCH_2(CH_3)C(CH_2PPh_2)_2\}(CO_2CF_3)_2$ (2b). The compound was prepared similarly as **1b**. A 0.40 g sample of the diphosphine **2** (0.78 mmol) and 0.26 g of Pd(II) trifluoroacetate (0.78 mmol) were used. A greenish-yellow solid was obtained. Yield: 0.60 g, 91%. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 19.1 (s). ^1H NMR (CD_2Cl_2): δ 0.79 (s, 3H, CH_3), 2.39 (dd, 4H, J(PH) = 9.0 Hz, J(HH) = 4.0 Hz, CH_2P), 2.75 (t, 2H, J(HH) = 2.6 Hz, CH_2Ph), aromatic protons (7.07−7.12 (m, 2H), 7.41−7.61 (m, 19H), 7.87−7.98 (m, 4H)).

$Pd\{Et_2C(CH_2PPh_2)_2\}(CO_2CF_3)_2$ (3b). The compound was prepared similarly as **1b**. A 0.41 g sample of the diphosphine **3** (0.88 mmol) and 0.20 g of Pd(II) trifluoroacetate (0.60 mmol) were used. A gray solid was obtained. Yield: 0.40 g, 83%. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 19.6 (s). ^1H NMR (CD_2Cl_2): δ 0.51 (t, 6H, J = 7.3 Hz, CH_2CH_3), 1.34 (q, 4H, J = 7.5 Hz, CH_2CH_3), 2.30 (d, 4H, J(PH) = 9.1 Hz, CH_2P), 7.45−7.80 (m, 20H, Ph).

$Pd\{CH_2(CH_3CHPPh_2)_2\}(CO_2CH_3)_2$ (4b). The compound was prepared similarly as **4a**. A 0.44 g sample of $CH_2(CH_3CHPPh_2)_2$ (4:1 mixture of *meso*-**4** and *rac*-**4**) (1.0 mmol) and 0.30 g of Pd(II) trifluoroacetate were used. A pale brown solid was obtained. Yield: 0.60 g, 86%. The compound contained the *meso* and *rac* forms in a 4:1 ratio.

Pd{*rac*-$CH_2(CH_3CHPPh_2)_2$}$(CO_2CF_3)_2$ (*rac*-4b). The compound was prepared similarly as **1b**. A 0.44 g sample of *rac*-$CH_2(CH_3CHPPh_2)_2$ (1.0 mmol) (containing ca. 5% of *meso*-**4**) and 0.30 g of Pd(II) trifluoroacetate (0.90 mmol) were used. A brown solid was obtained. Yield: 0.60 g, 86%. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 25.4 (s). ^1H NMR (CD_2Cl_2): δ 1.27 (dd, 6H, *J*(PH) = 15.4 Hz, *J*(HH) = 7.1 Hz, $CHCH_3$), 2.23 (tt, 2H, *J*(PH) = 19.8 Hz, *J*(HH) = 6.6 Hz, CH_2), 2.78 (m, 2H, $CHCH_3$), 7.36−7.51 (m, 20H, Ph).

Pd{*meso*-($CH_2(CH_3CHPPh_2)_2$}$(CO_2CF_3)_2$ (*meso*-4b). The compound was prepared similarly as *rac*-**4**. A 0.52 g sample of *meso*-**4** (1.2 mmol) and 0.34 g of Pd(II) trifluoroacetate (1.1 mmol) were used. A pale brown solid was obtained. Yield: 0.72 g, 85%. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 30.5 (s). ^1H NMR (CD_2Cl_2): δ 1.09 (dd, 6H, *J*(PH) = 15.6 Hz, *J*(HH) = 7.1 Hz, $CHCH_3$), 1.98−2.40 (m, 2H, CH_2), 2.65 (m, 2H, $CHCH_3$), 7.36−7.54 (m, 20H, Ph).

Pd{η^2-$O(CH_2)_2C(CH_2PPh_2)_2$}$(CO_2CF_3)_2$ (5b). A mixture of Pd(II) trifluoroacetate (73.1 mg, 0.22 mmol) and η^2-$O(CH_2)_2C(CH_2PPh_2)_2$ (0.10 g, 0.22 mmol) in 10 mL of dichloromethane was stirred at room temperature for 2 h until a clear yellow solution was obtained. The volume was reduced to ca. 2 mL under a strong stream of nitrogen. Then 30 mL of petroleum ether was slowly added to give a yellow solid which was filtered on a frit, washed with petroleum ether, and dried by a nitrogen stream. Yield: 0.15 g, 84%. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 19.7 (s). ^1H NMR (CD_2Cl_2): δ 2.78 (d, 4H, *J*(PH) = 8.1 Hz, CH_2P), 4.01 (s, 4H, CH_2O), 7.40−8.00 (m, 20H, Ph).

Reaction of Pd(dppp)$(CH_3CO_2)_2$ (6a) or Pd(dppp)-$(CF_3CO_2)_2$ (6b) with TsOH. In Situ NMR Experiments. Either **6a** or **6b** was dissolved in MeOH-d_4, and the solution was transferred into a 5 mm NMR tube under nitrogen. $^{31}P\{^1H\}$ NMR spectra showed the exclusive presence of singlets at δ 11.7 and 15.0, respectively. No trace of free acetic acid was detected in the ^1H NMR spectrum of **6a**. A 20-fold excess of TsOH was introduced in each tube. Already at room temperature, free CH_3CO_2H was detected in the solution of **6a** (^1H NMR singlet at δ 1.9), while the ^{31}P NMR singlets disappeared. Formed in their place was a singlet at δ 18.0 that we assign to the bis(*p*-toluenesulfonate) derivative Pd(dppp)-$(TsO)_2$.[9]

Copolymerization of CO and Ethene at Constant Pressure. A 100 mL solution of MeOH containing the required amount of BQ and the required acid was introduced into a mechanically stirred autoclave with an internal volume of 250 mL under nitrogen. A 4 mL portion of the same solvent containing 0.01 mmol of catalyst was introduced into the injector of the autoclave under nitrogen. The autoclave was charged with 300 psi of CO and 300 psi of C_2H_4. After the contents of the autoclave had been brought to 85 °C, the catalyst solution in the injector was introduced into the reaction chamber by a nitrogen pressure of 60 psi higher than the pressure of the reaction vessel. The pressure was then maintained at ca. 700 psi by introducing under pressure a 1:1 carbon monoxide/ethene mixture. The reaction mixture was then stirred (1400 rpm) for the required reaction time. The reaction was stopped by cooling the autoclave to room temperature by means of an ice−water bath. After the unreacted gases were released, the formed insoluble ethene−carbon monoxide copolymer was filtered off, washed with methanol, and dried in a vacuum oven at 70 °C to give a white powder. Anal. Calcd (found) for $(COCH_2CH_2)_n$: C, 64.3 (64.1); H, 7.2 (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). ^1H NMR (HFIP-d_2): δ 3.73 (s, $CH_2CO_2CH_3$), 2.83 (s, CH_2COCH_2), 2.55 (q, *J*(HH) = 7.4 Hz, $COCH_2CH_3$), 1.09 (t, *J*(HH) = 7.4 Hz, $COCH_2CH_3$). $^{13}C\{^1H\}$ NMR (HFIP/$CDCl_3$, 9:1, v:v): δ 217.2 ($COCH_2CH_3$), 213.0 (CH_2COCH_2), 176.6 ($CH_2CO_2CH_3$), 52.6 ($CH_2CO_2CH_3$), 36.1 (CH_2COCH_2), 27.9 ($CH_2CO_2CH_3$), 7.1 ($COCH_2CH_3$).

Characterization of the Copolymer. Irrespective of the catalyst precursor, the copolymer samples isolated were white powders with high melting points (250−258 °C).[1,2,10] These polyketones are insoluble in common organic solvents and dissolve appreciably only in highly polar solvents such as HFIP, *m*-cresol, or trichlorobenzene or in strong protic acids such as trifluoroacetic acid. The elemental analysis values are in agreement with an ethene/CO ratio of 1. Spectroscopically (IR and NMR), the polyketones obtained are identical with those previously isolated in methanol and for which a perfectly alternating structure was assigned.[1,2,10] In particular, the ^1H and $^{13}C\{^1H\}$ NMR spectra of the samples show the contemporaneous presence of both ketonic and ester end groups. The copolymers analyzed present limiting viscosity numbers (LVN, dL g^{-1}) and average molecular weights (M_n, kg mol^{-1}) in the ranges from 0.5 to 0.8 and from 10 to 20, respectively.

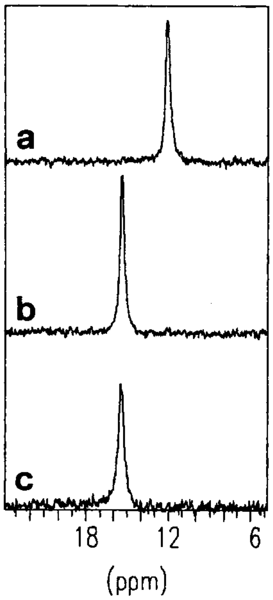
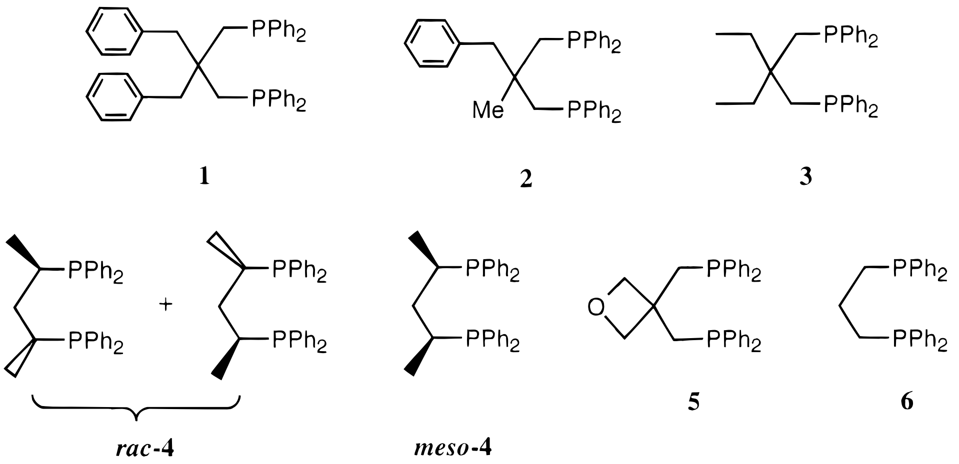


Figure 1. Selected $^{31}P\{^1H\}$ HPNMR spectra, recorded during the copolymerization reaction assisted by **6a** (sapphire tube, MeOH-d_4, 20−85 °C, 81.01 MHz). Spectrum of **6a** at room temperature (a); after addition of TFA (5 equiv) and pressurization with a 1:1 CO/ethene mixture to 600 psi at room temperature (b); after the sapphire tube was heated to 85 °C for 2 h and then cooled to room temperature (c).

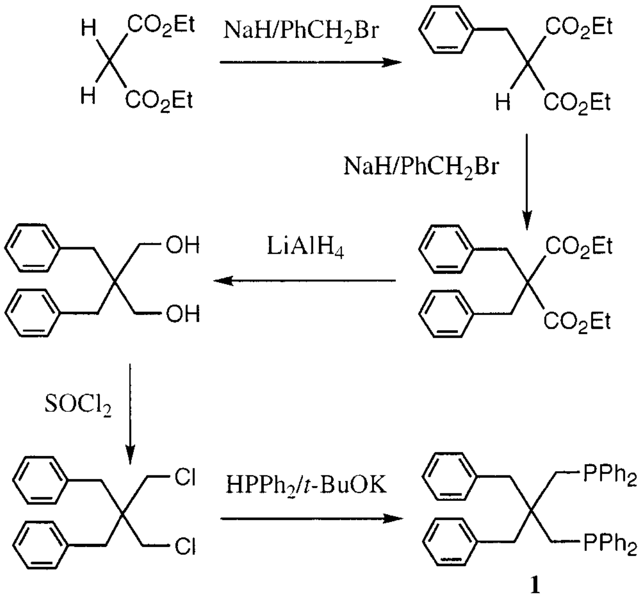
Copolymerization of CO and Ethene. HPNMR Experiments with Pd(dppp)$(CF_3CO_2)_2$ (5b) as Catalyst Precursor. A 10 mm sapphire HPNMR tube was charged with a solution of **6a** (10 mg, 1.35 × 10^{-2} mmol) in MeOH-d_4 (2 mL) under nitrogen and then placed into a NMR probe at 20 °C ($^{31}P\{^1H\}$ NMR singlet at δ 12.1, Figure 1a). Addition of a 5-fold excess of TFA led to the conversion of **6a** into **6b** (downfield shift of the $^{31}P\{^1H\}$ NMR resonance to δ 15.1) and the formation of free acetic acid (^1H NMR singlet at δ 1.89). Pressurizing with an 1:1 mixture of CO and C_2H_4 to 600 psi at room temperature caused no change in both the ^1H and $^{31}P\{^1H\}$ (Figure 1b) NMR spectra. Complex **6b** was the only phosphorus-containing species visible by NMR also during the copolymerization reaction (2 h at 85 °C) though the intensity of its $^{31}P\{^1H\}$ NMR signal slowly decreased with time. The tube was then allowed to cool to room temperature. A comparison between the $^{31}P\{^1H\}$ NMR spectrum of this sample (Figure 1c) and the spectrum acquired at room temperature before the catalytic reaction showed a ca. 15% decrease of **6b** due to tethering of the Pd catalyst to the copolymer accumulated at the liquid−gas interface. The copolymerization reaction was accompanied by the esterification of the free acetic acid with MeOH-d_4 (^1H NMR singlet at δ 1.92 for the methyl ester; GC/MS identification). Once the tube was removed from the probe head, the copolymer appeared as an off-white solid layer over a colorless solution.

Replacement of TFA with TsOH (2 equiv) led to the formation of the above-reported bis(*p*-toluenesulfonate) complex Pd(dppp)$(TsO)_2$ which was the only species detected during the course of the polymerization process.

Chart 1



Scheme 1



Identical NMR pictures were observed copolymerization reactions catalyzed by the other carboxylate Pd(II) precursors employed in this work as well as when a 10-fold excess of BQ was added to the reaction mixtures. The acetate complexes were immediately converted to their trifluoroacetate or *p*-toluenesulfonate derivatives, but no other species was visible on the NMR time scale during the catalytic reactions. Interestingly, the transformation of BQ into hydroquinone (^{1}H NMR singlet at δ 6.5 for the phenyl protons) was seen to take place already in the first stages of the reactions.

A truly homogeneous copolymerization reaction was performed in a 9:1 mixture of HFIP-d_2 and MeOH-d_4 starting from **6b**. Again, no other species than the trifluoroacetate Pd complex was visible by $^{31}P\{^1H\}$ NMR resonance during the production of the copolymer (^{1}H NMR singlet at δ 2.8 for the $-(CH_2C{=}O)_n-$ protons).

Results and Discussion

Synthesis of the Ligands. The general protocol for the synthesis of the new ligands (**1**−**3**) described in this work (Chart 1) employed diethyl malonate or its derivatives as starting materials. The substituent was introduced on the carbon backbone by reaction of alkyl halide and diethyl malonate in the presence of sodium hydride. Reduction of the ester with $LiAlH_4$ gave the diol. The diol was converted to either dichloride or dimesylate by reaction with thionyl chloride or mesyl chloride. Subsequent reaction with metal diphenylphosphide gave the desired diphosphine product.

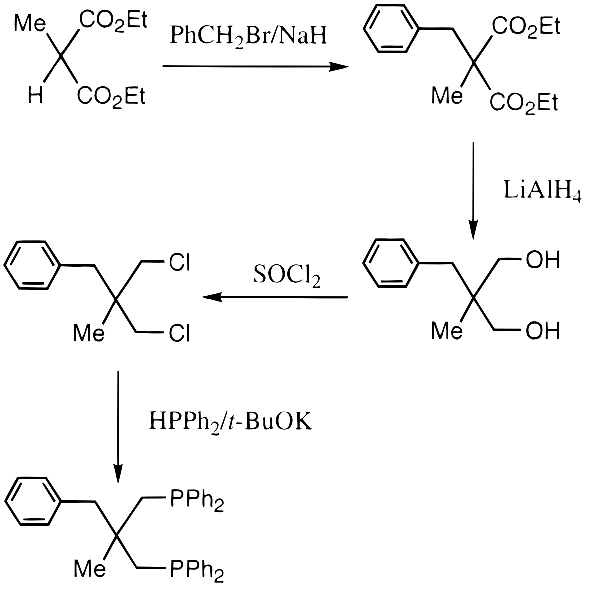
The ligand $(PhCH_2)_2C(CH_2PPh_2)_2$ (**1**) was prepared according to Scheme 1. Reaction of diethyl malonate in tetrahydrofuran (THF) with sodium hydride followed by addition of benzyl bromide gave $PhCH_2CH(CO_2Et)_2$, which was quantitatively converted to $(PhCH_2)_2C(CO_2Et)_2$ by a second treatment with $NaH/PhCH_2Br$. Reduction of the ester with $LiAlH_4$ in diethyl ether gave the diol $(PhCH_2)_2C(CH_2OH)_2$. Reaction of the diol with excess thionyl chloride in pyridine gave the key intermediate chloride $(PhCH_2)_2C(CH_2Cl)_2$. A one pot reaction of the chloride in dimethyl sulfoxide (DMSO) with potassium diphenylphosphide, generated in situ by diphenylphosphine in the presence of potassium *tert*-butoxide, produced the desired ligand **1**. The ligand is an off-white solid which is stable in both the solid state and deaerated solvents. In the $^{31}P\{^1H\}$ NMR spectrum, a singlet at δ −26.8 was observed for the equivalent PPh_2 groups.

A procedure analogous to that employed for **1** was followed in the synthesis of $PhCH_2(CH_3)C(CH_2PPh_2)_2$ (**2**) (Scheme 2). When commercially available $CH_3CH(CO_2Et)_2$ was treated in THF with sodium hydride and then with benzyl bromide, the ester $PhCH_2(CH_3)C(CO_2Et)_2$ was quantitatively obtained. The ester was reduced with $LiAlH_4$ in diethyl ether to give the diol $PhCH_2(CH_3)C(CH_2OH)_2$ which was converted to the dichloride $PhCH_2(CH_3)C(CH_2Cl)_2$ by reaction with thionyl chloride. Subsequent treatment of the dichloride in DMSO with potassium diphenylphosphide produced the ligand **2**. The ligand is a white solid. It is stable in both the solid state and deaerated solvents. In the $^{31}P\{^1H\}$ NMR spectrum, a singlet at δ −25.0 was observed for the equivalent PPh_2 groups.

The ligand $Et_2C(CH_2PPh_2)_2$ (**3**) was synthesized according to Scheme 3. Reduction of the commercially available diester $Et_2C(CO_2CH_3)_2$ with $LiAlH_4$ in diethyl ether produced the diol $Et_2C(CH_2OH)_2$. Treatment of the diol with mesyl chloride produced the mesylate $Et_2C(CH_2OMs)_2$ quantitatively. The ligand **3** was obtained by reaction of the mesylate with $LiPPh_2$ salt in THF. The ligand is a yellow oil which is air-sensitive. Due to its high solubility in common organic solvent, attempts to recrystallize the oil were not successful. In the $^{31}P\{^1H\}$ NMR spectrum, a singlet at δ −25.9 was observed for the equivalent PPh_2 groups.

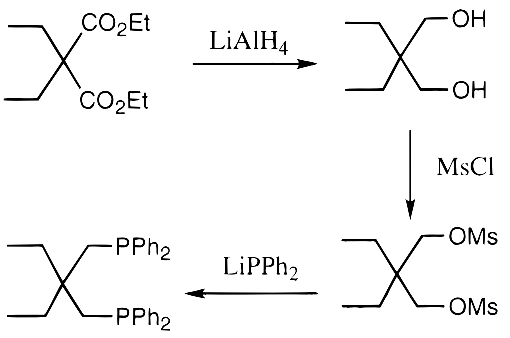
The well-known 2,4-bis(diphenylphosphino)pentane ligand, termed *skewphos* by Bosnich and co-workers[11]

Scheme 2



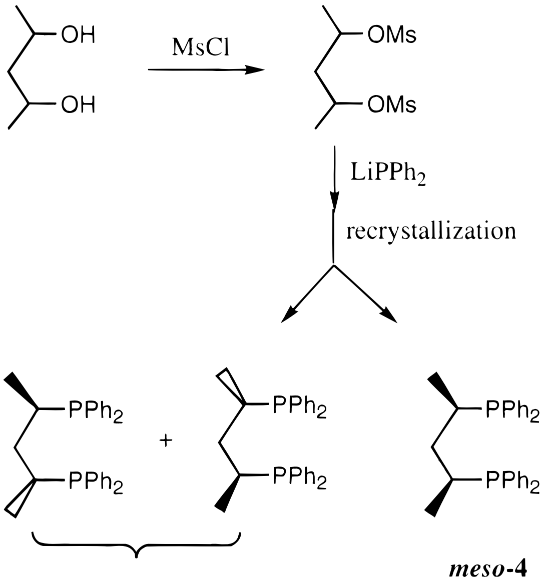
2

Scheme 3



3

Scheme 4



***rac*-4**

***meso*-4**

and BDPP by Bakos and co-workers,[12] has been extensively used in asymmetric catalysis.[11,12] As we were simply interested in 1,3-bis(diphenylphosphino)propanes with substituents on the carbon backbone, the ligand was prepared following a nonasymmetric procedure. However, the *meso* form was separated from the racemic mixture of the enantiomers (2*R*,4*R*) and (2*S*,4*S*) as two diastereoisomers are expected to generate a different spatial arrangement around the metal center and eventually display a different catalytic activity.

A facile method for the preparation of $CH_2(CH_3CHPPh_2)_2$ as a mixture of stereoisomers (**4**) and the separation of *meso*-**4** from the *rac*-**4** has been developed (Scheme 4). Treatment of 2,4-pentanediol with mesyl chloride gave the mesylate $CH_2(CH_3CHOMs)_2$. Subsequent reaction of the mesylate with $LiPPh_2$ salt in THF produced **4** as a mixture of the *meso* and *rac* diastereoisomers. The *meso* form was separated from the racemic mixture as a white solid by recrystallization of the crude oily product with diethyl ether and ethanol. Upon removal of the solvent of the filtrate, *rac*-**4** was obtained with a 87% purity (13% contaminated by the *meso* form). The purity of *rac*-**4** did not appreciably increase on attempts of further recrystallization or column chromatography. However, a sample containing only 5% of the *meso* form was obtained by cyanolysis of the Ni(II) complex $Ni\{CH_2(CH_3CHPPh_2)_2\}(NCS)_2$ obtained from an 87:13 mixture of the *rac* and *meso* forms.

It is worth mentioning that, by preparing the mesylate instead of the tosylate as described in the literature,[11,12] no further purification by preparing the nickel diphosphine complex was needed, and a much higher yield was obtained.

Synthesis and Characterization of Palladium Diphosphine Complexes. A summary of all the palladium complexes described in this report is shown in Chart 2.

The palladium diphosphine acetate complexes **1a**, **2a**, **4a**, and **6a** were prepared by adding a dichloromethane solution containing a slight excess of the diphosphine (P−P) to a methanol solution of palladium acetate (eq 1). Subsequent reduction of the solvent and precipitation with petroleum ether gave the acetate complexes. They are air-stable in the solid state. However, some decomposition to Pd^0 was observed after 2 days in MeOH solution.

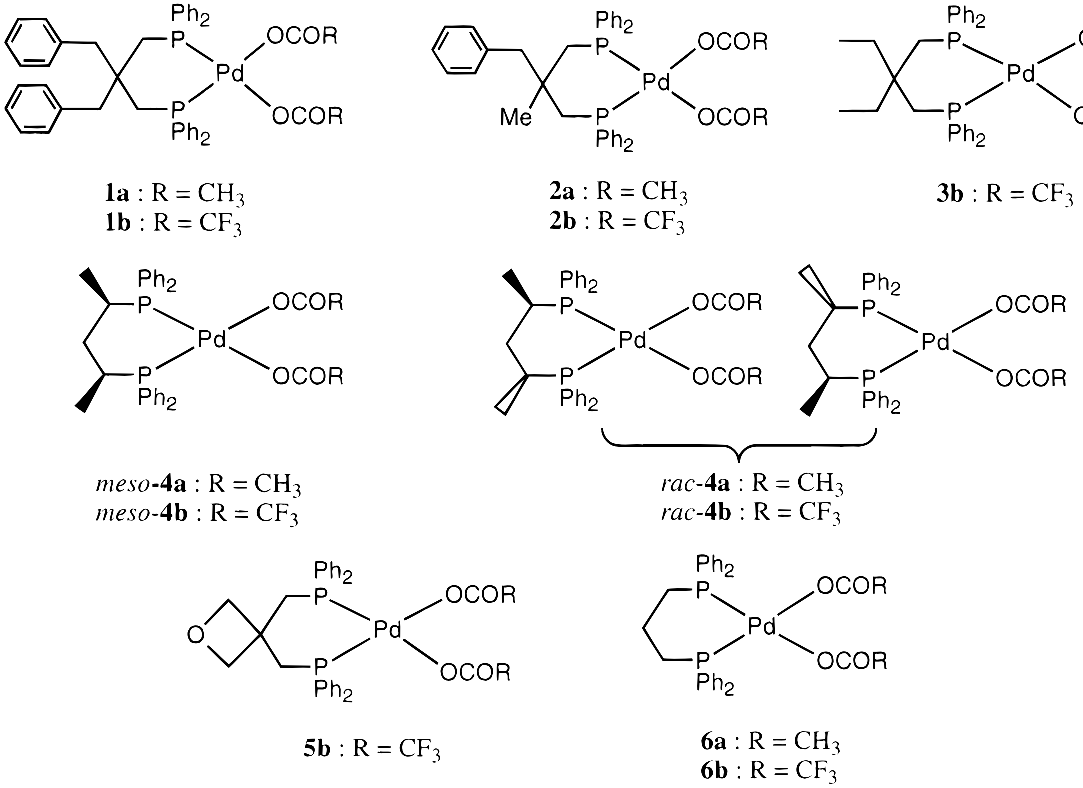
$$Pd(CO_2CH_3)_2 + \underset{\mathbf{1,2,4,6}}{P{-}P} \rightarrow \underset{\mathbf{1,2,4,6}}{Pd(P{-}P)(CO_2CH_3)_2} \quad (1)$$

Palladium diphosphine trifluoroacetate complexes **1b**−**6b** were prepared similarly (eq 2). Since palladium trifluoroacetate is very unstable in methanol, decomposing to Pd^0 within a few minutes, a methanol solution of palladium trifluoroacetate has to be immediately stabilized by a dichloromethane solution of the diphosphine. Upon reduction of the solvent and precipitation with petroleum ether, the trifluoroacetate complexes were obtained. Complexes **1b**−**6b** are air-stable in the solid state. In solution, however, they, except for **5b**, completely decompose to Pd^0 within 6 h.

$$Pd(CO_2CF_3)_2 + \underset{\mathbf{1-6}}{P{-}P} \rightarrow \underset{\mathbf{1b-6b}}{Pd(P{-}P)(CO_2CF_3)_2} \quad (2)$$

The acetate ligands are easily removed from the $[Pd(dppp)]^{2+}$ moiety by reaction with an excess (≥2 equiv) of trifluoroacetic acid (TFA) in MeOH at room temper-

Chart 2



1a : R = CH_3
1b : R = CF_3

2a : R = CH_3
2b : R = CF_3

3b : R = CF_3

meso-**4a** : R = CH_3
meso-**4b** : R = CF_3

rac-**4a** : R = CH_3
rac-**4b** : R = CF_3

5b : R = CF_3

6a : R = CH_3
6b : R = CF_3

Table 1. $^{31}P\{^1H\}$ NMR Chemical Shifts (δ) for Ligands 1−6 and Their Palladium(II) Complexes[a]

free ligand	δ	acetate complex	δ	trifluoroacetate complex	δ
1	−26.8	**1a**	15.0	**1b**	18.6
2	−25.5	**2a**	16.0	**2b**	19.1
3	−25.9			**3b**	19.6
rac-**4**	0.1[b]	*rac*-**4a**	23.3	*rac*-**4b**	25.4
meso-**4**	−1.1[b]	*meso*-**4a**	28.3	*meso*-**4b**	30.5
5	−22.1[b]			**5b**	19.7
6	−17.1	**6a**	10.0	**6b**	12.1

[a] All spectra were recorded at 20 °C in CD_2Cl_2 solutions, unless otherwise stated. [b] In $CDCl_3$.

ature. Once formed, the trifluoroacetate complexes do not regenerate the corresponding acetate derivatives even by treatment with a large excess of acetic acid (20 equiv). The strength of the acid thus prevails over the nucleophilic character of its conjugated base to determine the complex structure. Consistently, *p*-toluenesulfonic acid (TsOH), used in excess, is capable of irreversibly displacing both acetate and trifluoroacetate ligands from **1a**, **2a**, **4a**, **6a**, and **1b**−**6b** with the quantitative formation of the bis(*p*-toluenesulfonate) derivatives Pd(diphosphine)$(TsO)_2$.[9]

A comparison of the $^{31}P\{^1H\}$ NMR data for the acetate complexes, trifluoroacetate complexes, and the free diphosphines is presented in Table 1. In general, the introduction of alkyl groups on the C_2 carbons results in an upfield shift of the phosphorus resonance with respect to the unsubstituted ligand dppp (**6**). This is reasonable as the electron-releasing effect of the substituents renders the phosphorus atoms more electron-rich, and hence an upfield shift of the phosphorus resonance is expected. It is of interest to note, however, that the ligands *meso*- and *rac*-**4** with two methyl substituents on both C_1 carbon atoms exhibit significant downfield chemical shifts compared with other ligands bearing substituents on the C_2 carbon atoms as well as dppp. In this case, the downfield shift is most likely steric in nature as the two methyl substituents may influence the s-orbital electron density of the vicinal phosphorus atoms.[13] The resonances of all complexes are at a lower field with respect to those of the corresponding ligands. In general, the trifluoroacetate complexes have resonances 2−3 ppm downfield with respect to those of their acetate analogues. This can be explained by the fact that the trifluoroacetate ligand exerts a smaller trans influence as compared to that of the acetate ligand.[14]

It is worth noticing that the ^1H NMR spectrum of *meso*-**4b** display resonances due to a single set of CH and CH_3 groups and one diphenylphosphino group, while the central CH_2 group is diastereotopic. The overall pattern of the NMR resonances thus indicates that the complex assumes a time-averaged preferred conformation in which a reflection plane perpendicular to the coordination plane of the metal encompasses the methylene carbon and the Pd atom. The presence of a symmetry plane rules out a skew conformation for the six-membered chelate metallaring, while either boat or chair conformations may equally be plausible, each of which bears equatorial or axial methyl groups.[11,15] Irrespective of the conformation, two phenyl rings are equatorial, while two are axial. By doing so, the steric hindrance at the metal center in *meso*-**4b** would be concentrated below the PPdP plane, leaving a complementary free space for coordination and reactivity. This concept has previously been developed for rationalizing the enantioselectivity of reactions catalyzed by chiral diphosphine ligands.[11,15,16]

The ^1H NMR spectrum of *rac*-**4b** is quite similar to that of *meso*-**4b** except for the presence of a nondiastereotopic CH_2 group. This indicates that the complex in solution adopts a time-preferred conformation in which

Table 2. Copolymerization of Ethene with CO Catalyzed by 6b[a]

run	acid	acid equiv	BQ equiv	other equiv	productivity[b]	productivity/h
1					7.7	2.6
2	TFA	20			12.2	4.1
3			80		12.9	4.3
4	TFA	2	80		12.3	4.1
5	TsOH	2	80		16.2	5.4
6	TFA	20	80		15.5	5.2
7	TsOH	20	80		16.2	5.4
8	TFA	20	160		19.0	6.3
9			80	H_2 40 psi	11.5	3.8
10	TFA	20	80	H_2 40 psi	14.3	4.8
11			80	2 $Cu(CF_3CO_2)_2$	7.0	2.3
12			80	20 $Cu(CF_3CO_2)_2$	5.6	1.9

[a] Catalytic conditions: catalyst, 0.01 mmol; methanol, 100 mL; initial p(CO), 300 psi; initial $p(C_2H_4)$, 300 psi; temperature, 85 °C; time, 3 h. [b] Productivity expressed as kg of copolymer (g of Pd)$^{-1}$.

a C_2 axis passes through the Pd atom and the methylene carbon atom. A conformation of this type for six-membered chelate rings is known as "chiral skew", and two possible conformers are possible bearing either pseudoaxial or pseudoequatorial methyl groups.[11,15] On the basis of previous studies of rhodium (*S*,*S*)-bdpp complexes and other related metal complexes with diphosphine ligands,[11,15−17] a δ-skew conformation with equatorial methyl groups might be the preferred one also for *rac*-**4b**. Again, two pairs of pseudoequatorial and pseudoaxial phenyl rings feature either conformation. In this case, however, the crowded space (sterically hindered quadrants) would be diagonally positioned with respect to the PPdP plane so that the free space at the metal center is more dispersed than in *meso*-**4b**.[11,15,16]

Copolymerization of Ethene and CO. Catalytic Reactions. The catalytic activity of dppp-based Pd(II) complexes in the copolymerization of carbon monoxide with ethene in MeOH depends on several chemical and physical factors, some of which have extensively been investigated.[2] From a perusal of the relevant publications and patents, one may roughly conclude that optimal reaction conditions require the copresence in the catalytic mixture of both a strong oxidant with $E°' \geq 0$ (vs SCE) and a protic acid with $pK_a \leq 4$ whose conjugated base must be poorly coordinating toward the $[Pd(dppp)]^{2+}$ moiety. TsOH ($pK_a = -2.7$) or TFA ($pK_a = 0$) and 1,4-benzoquinone (BQ, $E°' = 0.7$) amply fulfill these requirements and indeed constitute the ingredients of most productive catalytic systems.[2] While the oxidant is certainly needed for the regeneration of the catalytically active Pd(II) complex via oxidation of the low-valent Pd(I) or Pd(0) species which may form in the reducing conditions of the copolymerization reaction (vide infra),[18] the protic acid may play different roles in the catalytic cycle depending on both its nature and concentration.[2] A major role of the acid is in the formation of Pd(II) species with coligands (e.g., *p*-toluenesulfonate or trifluoroacetate) which do not prevail over MeOH, CO, or C_2H_4 for coordination. Other relevant roles of the protic acid coreagent will be discussed in forthcoming sections.

To explore the best reaction conditions for the palladium complexes of the new ligands herein described, the palladium dppp complex **6b** was tested for the copolymerization of ethene and carbon monoxide. The results are given in Table 2.

In our hands, 2−20 equiv of TsOH or 20 equiv of TFA and 80 equiv of BQ proved optimal conditions to have productivity values in the upper range of CO/ethene copolymerization reactions catalyzed by **6b** (runs 5−7).[1,2] For this reason, these experimental conditions, which do not refer to an optimized process, were generally used in all the copolymerization reactions reported in this work. It should be noted, however, that doubling the amount of BQ had the beneficial effect of increasing the productivity by 22% (runs 6 and 8), although such a phenomenon is not universal for all the catalyst precursors investigated (see below). In contrast, increasing the amount of acid did not result in an increase of productivity, which eventually decreases for very high concentrations of acids (e.g., 300 equiv). The activity was decreased substantially in the case which was without both acid and BQ (run 1) and to a lesser extent in the runs without either the acid or the oxidant (runs 2 and 3).

In the case of TFA, a slightly excess of acid was also essential for its optimal activity as a decrease in the amount of acid from 20 to 2 equiv resulted in a same degree of decrease in activity as the previous three cases (run 4). An excess of TFA is probably required because, unlike TsOH, it undergoes esterification during the catalysis.

Efforts have been made to increase the activity of **6b** by charging the autoclave with 40 psi of hydrogen in view that the H_2 could speed up the termination step via hydrogenolysis[2] and hence drive the whole catalytic cycle forward. However, only a detrimental effect was observed (runs 9 and 10). It has been reported that the replacement of TsOH with its copper salt may increase the catalytic activity as well as the molecular weight of the copolymer.[1,2] In our hands, however, a decrease in the reaction rate resulted in replacement of TFA with copper(II) trifluoroacetate (runs 11 and 12). In contrast, the substitution of the nonesterifiable acid TsOH for TFA resulted in the expected increase in productivity (compare runs 4 and 5).

On the basis of the reaction conditions explored above, the palladium trifluoraocetate complexes **1b**−**5b** were tested as catalyst precursors. The results are given in Table 3. Selected data of **6b** have been also included in the table for comparative purposes.

Under identical reaction conditions, the activity of these different catalysts in polyketone formation follows the order *meso*-**4b** > **1b** > *rac*-**4b** > **2b** = **6b** > **3b** > **5b**. To our surprise, the commonly used dppp complex was less efficient than three new catalyst precursors. The most active catalytst was indeed that with *meso*-$CH_2(CH_3CHPPh_2)_2$ (runs 12 and 13), but high productivity was also obtained using **4b**, which was a 4:1 mixture of the *meso* and *rac* catalysts (run 10).

It is worth noticing that the activities of catalysts with substituents on the C_2 position of the ligand backbone were similar, within a certain range, to the palladium dppp complex **6b**. The substituents on the C_2 position having no significant effect on the activity of the catalysts may be due to the fact that they are situated away from both the bonding phosphorus atoms and the palladium center. In contrast, the two methyl groups in **4b**, being in proximity of the donor atoms, can influence to a greater extent the electronic and steric properties of the P_2−Pd cavity where the copolymerization takes place.

Table 3. Copolymerization of CO with Ethene Catalyzed by the Trifluoroacetate Palladium Complexes 1b−6b[a]

run	complex	acid	acid equiv	BQ equiv	productivity[b]	productivity/h
1	**1b**	TsOH	2	80	18.6	6.2
2	**1b**	TFA	20	80	17.6	5.9
3	**1b**	TFA	20	160	14.2	4.7
4	**2b**	TsOH	2	80	16.1	5.4
5	**2b**	TFA	20	80	15.5	5.2
6	**2b**	TFA	20	160	15.4	5.1
7	**3b**	TsOH	2	80	13.0	4.3
8	**3b**	TFA	20	80	12.2	4.1
9	**3b**	TFA	20	160	13.9	4.6
10	**4b**[c]	TFA	20	80	22.9	7.6
11	**4b**[c]	TFA	20	160	18.9	6.3
12	*meso*-**4b**	TsOH	2	80	24.0	8.0
13	*meso*-**4b**	TFA	20	80	23.0	7.7
14	*rac*-**4b**	TFA	20	80	16.9	5.6
15	**5b**	TsOH	2	80	12.3	4.1
16	**5b**	TFA	20	80	11.6	3.9
17	**6b**	TsOH	2	80	16.2	5.4
18	**6b**	TFA	20	80	15.5	5.2
19	**6b**	TFA	20	160	19.0	6.3

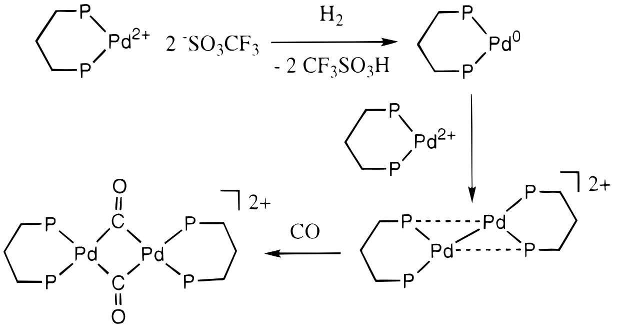
[a] Catalytic conditions: catalyst, 0.01 mmol; methanol, 100 mL; initial p(CO), 300 psi; initial $p(C_2H_4)$, 300 psi; temperature, 85 °C; time, 3 h. [b] Productivity expressed as kg of copolymer (g of Pd)$^{-1}$. [c] *meso*:*rac* = 4:1.

As stated above, doubling the amount of BQ gave different results. While there were beneficial effects on the reaction rates for **3b** and, as stated above, **6b**, negative effects were observed for **1b**, **2b**, and **4b**. The reason for this phenomenon is still unclear.

Copolymerization of Ethene and CO. In Situ HPNMR Studies. The copolymerization of ethene and CO was studied in a HPNMR tube under experimental conditions that were as close as possible to those employed in the batch reactions. The most significant differences were a higher concentration of the catalyst precursor for a better resolution and acquisition of the NMR spectra and, obviously, a much lower stirring rate. However, the amount of the gaseous reagents contained in the headspace of the tubes was large enough to maintain a relatively high concentration of gases in solution during the course of the experiments as evidenced by the constant presence of the ethene resonance in the ^{1}H NMR spectra. Indeed, the mass transfer of gases from the headspace of the 10 mm NMR tubes is generally efficient enough to replenish the solution which is being depleted of the reagents by the catalyst.[6]

When a MeOH-d_4 solution of any Pd(II) complex with either acetate (**1a**, **2a**, **4a**, **6a**) or trifluoroacetate ligands (**1b-6b**) was pressurized in a 10 mm sapphire HPNMR tube with a 1:1 mixture of CO and C_2H_4 to 600 psi in the presence of a 5-fold of TFA, the $^{31}P\{^1H\}$ NMR spectra at room temperature showed the exclusive presence of a singlet at the same chemical shift of the bis(trifluoroacetate) complexes. Upon heating to 85 °C for 2 h, no other species was visible on the NMR time scale. In the meantime, however, the acetic acid released by the acetate derivatives was slowly converted to its methyl ester (^{1}H NMR evidence), and the CO/C_2H_4 copolymer was formed in fairly good yield. After the tube was cooled to room temperature, a significant decrease in the concentration of the diphosphine Pd complexes in the MeOH solution was shown by ^{31}P NMR spectroscopy. The missing Pd was actually tethered to the copolymer accumulated over the liquid surface. A sequence of selected $^{31}P\{^1H\}$ HPNMR spectra, recorded during the copolymerization reaction assisted by **6a**, is reported in Figure 1.

Scheme 5



The substitution of TsOH for TFA gave a quite similar picture. In all the reactions, the resting state of Pd during the catalysis was the bis(p-toluenesulfonate)-palladium complex even in the presence of BQ, which was rapidly reduced to hydroquinone, confirming that a real drawback of the copolymerization reactions is indeed the propensity of the Pd(II) catalyst to reduction.

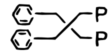
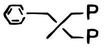
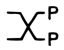
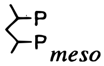
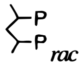
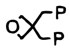
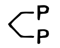
To exclude that Pd species relevant to catalysis are not seen by NMR spectroscopy because of their tethering to the floating copolymer, HPNMR experiments were carried out in a 9:1 mixture of 1,1,1,3,3,3-hexafluoropropan-2-ol-d_2 (HFIP-d_2) and MeOH-d_4 in which the compolymer is fully soluble. Like in MeOH-d_4, no other species than the trifluoroacetate starting complex **6b** was visible in the NMR time scale during the course of this truly homogeneous copolymerization process.

Electrochemical Measurements. All the diphosphine palladium(II) complexes here investigated are inherently unstable in pure methanol. In light of previous studies, their stability is expected to further decrease in the reducing atmosphere of the copolymerization reactions.[2] In particular, it has been shown that the $[Pd(dppp)]^{2+}$ moiety may be readily reduced in MeOH by mild reductants to give catalytically inactive Pd(I) species via Pd(0) intermediates (Scheme 5).[18] In the presence of CO, dimeric μ-COPd(I) complexes have also been detected.

For this reason, it was interesting to study the electrochemistry of the catalyst precursors in methanol so as to see whether the difference in activities, especially in the case of the *meso* and the *rac* forms of **4**, correlates with their propensity to reduction. A summary of the catalytic activities of different complexes together with their reduction potentials $E^{\circ\prime}$ or E_p from a cyclic voltammetric investigation is given in Table 4. As a representative example, Figure 2 illustrates the voltammetric picture exhibited by the palladium complex **1a** in either cyclic or differential pulse voltammetry (DPV).

The complex exhibits two subsequent reduction processes, the first of which only displays characteristics of transient chemical reversibility. The DPV profile shows the second cathodic process to be due to a minor process; i.e., the overall profile features an electron transfer complicated by following chemical reactions yielding further electroreducible byproducts. Consistently, in controlled potential coulometry ($E_w = -1.0$ V), the current suddenly slows down after the consumption of 1 electron/molecule, but it remains slightly higher than the background current up to the overall consumption of about 1.3−1.4 electrons/molecule. In this picture, we assign the reduction pathway to a first Pd(II)/Pd(I) step in which the Pd(I) congener is kinetically labile and degrades to products, some of which display redox

Table 4. Formal Electrode Potentials (V vs SCE) for the First One-Electron Reduction of Diphosphine Pd(II) Complexes in MeOH (0.1 M $LiClO_4$), Corresponding Lifetime, and Catalytic Activity[a]

ligand	complex	productivity/h[b]	$E^{\circ\prime}_{Pd(I)/Pd(II)}$	$t_{1/2}$ (sec)
	**1a**	5.9	-0.67	0.1
	**2a**	5.2	-0.81	0.05
	**3b**	4.1	-0.62[c]	-
	*meso*-**4a**	7.7	-0.77	0.05
	*rac*-**4a**	5.6	-0.71[c]	-
	**5b**	3.9	-0.68	<<0.05
	**6a**	5.2	-0.68[c]	-

[a] Catalytic conditions: catalyst, 0.01 mmol; TFA, 20 equiv; BQ, 80 equiv; methanol, 100 mL; initial p(CO), 300 psi; initial $p(C_2H_4)$, 300 psi; temperature, 85 °C; time, 3 h. [b] Productivity expressed as kg of copolymer (g of Pd)$^{-1}$. [c] Peak potential for irreversible processes.

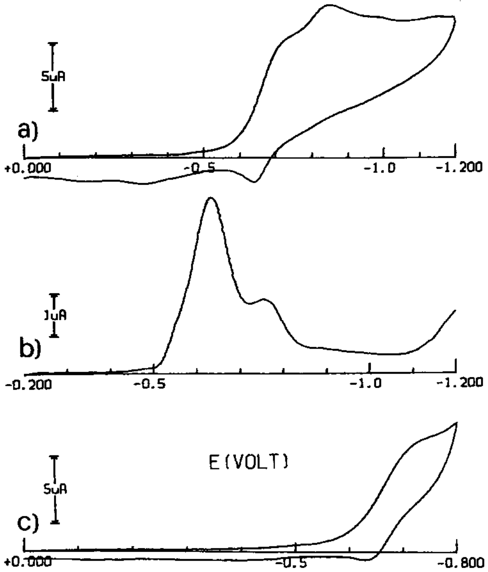


Figure 2. Cyclic voltammetric (a, c) and DPV (b) profiles recorded at a platinum electrode on a MeOH solution containing **1a** (1.2×10^{-3} M) and $LiClO_4$ (0.1 M). Scan rates: (a) 0.2 V s^{-1}; (b) 0.004 V s^{-1}; (c) 0.5 V s^{-1}.

activity. This redox behavior is not unusual for Pd(II) complexes which commonly display the Pd(II)/Pd(I)/Pd(0) sequence with either separated Pd(II)/Pd(I), Pd(I)/Pd(0) sequences or single two-electron steps.[19] In the present case, the further Pd(I)/Pd(0) step would occur beyond the solvent discharge (about −1.3 V).

A qualitatively similar behavior is exhibited also by the complexes **2a** and *meso*-**4a**. In contrast, the first reduction steps of **3b**, *rac*-**4a**, and **6a** display no trace of directly associated reoxidation peaks even at the highest scan rate investigated (5 V s^{-1}). The different electrochemical response of the stereoisomers *meso*-**4a** and *rac*-**4a** is clearly evident from an inspection of Figure 3.

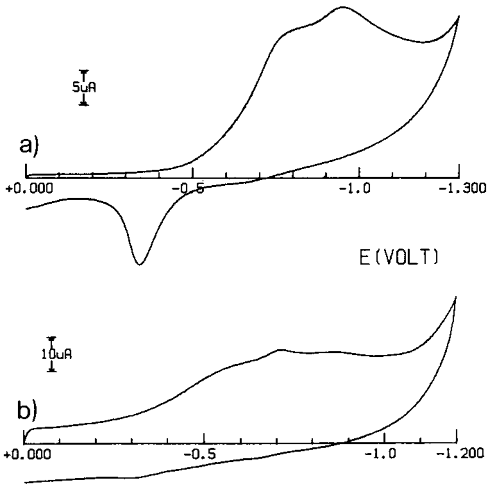


Figure 3. Cyclic voltammetric responses recorded at a platinum electrode on a MeOH solution containing $LiClO_4$ (0.1 M) and *meso*-**4a** (1.6×10^{-3} M) (a) or *rac*-**4a** (1.3×10^{-3} M) (b). Scan rates: 0.2 V s^{-1}.

A rough evaluation of the half-life times of the chemically reversible Pd(I) congeners is given in Table 4.[20] The $t_{1/2}$ values are sufficiently long to allow the reoxidation of Pd(I) to Pd(II) by either H^+ or BQ. From a perusal of Table 4, one may also infer that the proton itself can oxidize the Pd(I) species derived from the reduction of the catalyst precursors. This is most likely one of the reasons why, in the absence of specific organic oxidants, the productivity in copolymer increases with the concentration of the acid (see for example runs 1 and 2 in Table 2).[2] In the case of wet MeOH, the acid may also be needed to convert catalytically inactive μ-OH Pd(II) dimers to active monomers.[21]

Conclusions

Our studies confirm that the activity of CO/C_2H_4 copolymerization catalysts is governed by a complex web of electronic and steric effects.

Under comparable experimental conditions, the introduction of alkyl substituents in the 2-position of the carbon backbone of dppp does not significantly improve the catalytic performance of the dppp-based Pd(II) precursors. Eventually, a decrease may be observed. In contrast, the productivity increases remarkably (even by ca. 50%) when methyl groups are introduced in both 1-positions, particularly with *R,S* (*S,R*) stereochemistry as in *meso*-**4**.

Indeed, both *meso*-**4** and *rac*-**4** exhibit by far the most downfield-shifted ^{31}P NMR resonances in the ligands investigated, suggesting that the Pd centers in the corresponding complexes *meso*-**4b** and *rac*-**4b** are the least electron-rich in the series. Therefore, if the rate-limiting step of the copolymerization reaction is indeed the ethene insertion,[2] then improved activity is expected for the catalysts with less basic metal centers. This effect, however, cannot account, alone, for the remarkable difference in productivity between *meso*-**4b** and *rac*-**4b** (23 vs 17 kg of copolymer/g of Pd) as their ^{31}P NMR resonances differ by 5 ppm only. The different activity of the *meso* and *rac* isomers apparently stems from a subtle balance of steric and electronic effects. Inside the catalysis cycle, an important contribution to the superior activity of the *meso* form may be provided by the less sterically demanding spatial distribution of the phenyl substituents.[11,15−17] Outside the catalysis cyle, it may be relevant the fact that *meso*-**4b**, unlike *rac*-**4b**, exhibits a chemically reversible Pd(II)/Pd(I) reduction step. The lifetime of the reduced species in MeOH ($t_{1/2} = 0.05$ s) is indeed sufficiently long to allow its complete reoxidation to the Pd(II) precursor by the BQ reagent. A minor degradation of the catalyst precursor obviously means a larger number of active centers, particularly in this case where the Pd(diphosphine)X_2 complexes (X = *p*-toluenesulfonate, trifluoroacetate) seem to constitute the resting state of palladium during the catalysis. For all catalyst precursors, Pd(diphosphine)X_2 species, eventually in equilibrium with MeOH, are indeed the only phosphorus-containing complexes visible on the NMR time scale when the copolymer is actually formed: it is thus conceivable that they act as a reservoir of [Pd(diphosphine)]$^{2+}$ moieties which may either be delivered into the catalysis cycle by action of various reagents (MeOH, H^+, H_2O, H_2) or be withdrawn after the termination step and watched over deactivation paths. Within this context, optimal acid coreagents for the CO/C_2H_4 copolymerization should have conjugated bases with low but still effective coordinating capability as is the case of TsOH.

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