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Palladium(II) Complexes with 1,1′−Bis(diphenylphosphino)ferrocenes $[Fe(\eta^5\text{-}C_5R_4PPh_2)_2]^{n+}$ (dppf, R = H, *n* = 0; dppomf, R = Me, *n* = 0; dppomf⁺, R = Me, *n* = 1). Synthesis, Characterization, and Catalytic Activity in Ethene Methoxycarbonylation

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Several palladium(II) complexes with 1,1′-bis(diphenylphosphino)octamethylferrocene (dppomf) and its oxidized form 1,1′-bis(diphenylphosphino)octamethylferrocenium (dppomf⁺) have been synthesized and characterized by spectroscopic and electrochemical methods. For comparative purposes, analogous Pd(II) derivatives with 1,1′-bis(diphenylphosphino)ferrocene (dppf) have been also prepared. Single-crystal X-ray analyses have been carried out for the square-planar mononuclear compounds $[Pd(H_2O)_2(dppf)](OTf)_2$ and $[Pd(H_2O)_2(dppomf)](OTf)_2$ and for the binuclear complex $[Pd(\mu\text{-}OPF_2O)(dppomf^+)]_2(BF_4)_4\cdot6CH_2Cl_2$ in which two $[Pd(dppomf^+)]^{3+}$ moieties are held together by the oxygen atoms of two bridging $PO_2F_2^-$ groups derived from the oxidative degradation of PF_6^- ions. Selected dppf and dppomf Pd(II) complexes have been employed as catalyst precursors for the methoxycarbonylation of ethene (600 psi, 1:1 CO/C_2H_4, 85 °C). It has been found that dppomf generates selective catalysts for the production of methyl propanoate, while dppf leads to a variety of low-molecular-weight oxygenates spanning from methyl propanoate to alternating oligoketones.

Introduction

Since its discovery in the early 1970s,[1] the metallophosphine 1,1′-bis(diphenylphosphino)ferrocene (dppf) has been widely used in organometallic chemistry and homogeneous catalysis.[2,3] Palladium(II) complexes are relatively numerous[4] and have also proved to be effective catalysts in a variety of homogeneous processes.[3] Among the applications of Pd(II)−dppf complexes in catalysis, carbon−carbon and carbon−nitrogen bond-forming reactions are of particular importance. Representative examples include cross-coupling reactions,[5] the Heck reaction,[6] carbonylation of chloroarenes,[7] aryl halide amination,[8] hydroamination of alkynes,[9] and the glyoxylate−ene reaction with chiral controllers.[10]

The wealth of Pd(II) coordination compounds and relative catalytic applications contrasts dramatically

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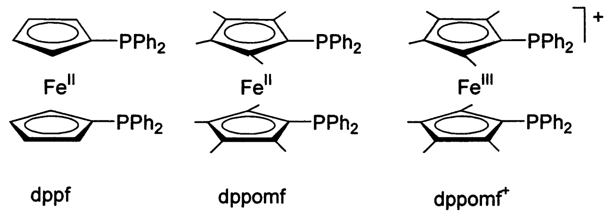
Chart 1



with the absence of reports on Pd(II) complexes containing 1,1′-bis(diphenylphosphino)octamethylferrocene (dppomf) (Chart 1).[11]

We have recently initiated a study of the organometallic chemistry of palladium(II) with dppomf and its oxidized form 1,1′-bis(diphenylphosphino)octamethylferrocenium (dppomf$^+$). In comparison to the dppf analogues, a different behavior is expected for both dppomf and dppomf$^+$ Pd(II) complexes, in particular as regards the influence of the ligands on the catalytic activity, due to the steric and electronic properties of the methyl groups and, in the case of dppomf$^+$, also due to the different iron oxidation state and positive charge of the complexes.

This article describes the preparation and characterization of several mononuclear and binuclear Pd(II) complexes stabilized by either dppomf or dppomf$^+$. For comparative purposes, dppf analogues have been synthesized by known or improved procedures.

Selected dppf and dppomf Pd(II) complexes have been scrutinized for the first time as catalyst precursors for the methoxycarbonylation of ethene, which is an industrially relevant reaction efficiently catalyzed in the homogeneous phase by palladium(II) bis(phosphine) complexes.[12,13] Minor changes in these latter species and/or in the experimental conditions can affect remarkably the selectivity of the alkoxycarbonylation reaction, leading to the formation of a variety of products spanning from alternating polyketones to methyl propanoate.[12−14]

It is shown in this work that dppomf generates selective catalysts for methyl propanoate, while dppf leads to a variety of low-molecular-weight oxygenates spanning from methyl propanoate to alternating oligoketones.

Experimental Section

General Procedures. All experiments were performed under Ar in solvents purified by standard methods. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on Bruker AMX 400 and Varian VXR 400 spectrometers. Chemical shifts are reported in ppm (δ) with reference to either TMS as an internal standard (^{1}H and ^{13}C{^{1}H} NMR spectra) or 85% H_3PO_4 as an external standard (^{31}P{^{1}H} NMR spectra). IR spectra were obtained with a Specord M-82 spectrometer. Microanalyses were performed in the Laboratory of Microanalysis of the A. N. Nesmeyanov Institute of Organoelement Compounds. Conductivities were measured with an ORION Model 990101 conductance cell connected to a Model 101 conductivity meter. The conductivity data[15] were obtained at sample concentrations of ca. 10^{-3} M in nitroethane solutions. The following compounds were synthesized according to published procedures: dppf,[1] $PdCl_2$(dppf) (**1a**),[4a,5a] [Pd(H_2O)$_2$(dppf)](OTf)$_2$ (**2a**),[4c] dppomf,[11] and *cis*-$PdCl_2(PhCN)_2$.[16] Slow diffusion of Et_2O into a saturated CH_2Cl_2 solution of **2a** at room temperature gave crystals suitable for an X-ray analysis. Cyclic voltammetry (CV) data were obtained in CH_2Cl_2 solutions at room temperature under Ar using a PI-50-1 potentiostat. A three-electrode cell was used with an SCE reference electrode, a glassy-carbon working electrode, and a platinum auxiliary electrode. The scan rate was 200 mV s^{-1} in each experiment. The solutions of electroactive substance were 2×10^{-3} M in 0.1 M [Bu_4N]PF_6 as supporting electrolyte. Peak potentials were calibrated against the ferrocene/ferrocenium (+0.46 V) couple by adding ferrocene directly to the solution of the complexes under investigation. Bulk electrolysis experiments were carried out with a P-5827M potentiostat in CH_2Cl_2 solutions with stirring in the presence of 0.1 M [Bu_4N]BF_4. In the electrolysis cell, the cathodic and anodic areas were separated by a G4 frit. The working electrode was a cylindrical glassy-carbon electrode ($S = 35$ cm^2), and the auxiliary electrode was a platinum plate. An aqueous SCE served as reference electrode, in which the KCl phase was separated from the solution by a G4 frit. Carbonylation reactions were performed at constant pressure with a 250 mL stainless steel autoclave, constructed at the ISSECC-CNR (Firenze, Italy), equipped with a magnetic drive stirrer and a Parr 4842 temperature and pressure controller. GC analyses 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. The product composition was determined by using dimethyl oxalate as the internal standard. GC/MS analyses were performed on a Shimadzu QP 5000 apparatus equipped with a column identical with that used for GC analysis.

Synthesis of $PdCl_2$(dppomf) (1b). To a solution of dppomf (1.05 g, 1.58 mmol) in benzene (20 mL) was added a solution of *cis*-$PdCl_2(PhCN)_2$ (0.61 g, 1.58 mmol) in benzene (30 mL). The resulting solution was stirred overnight to give purple crystals of **1b**·C_6H_6, which were filtered off, washed with benzene, and dried under vacuum. Yield: 1.28 g (96%). Anal. Calcd for $C_{48}H_{50}Cl_2FeP_2Pd$: C, 62.60; H, 5.48. Found: C, 62.85; H, 5.59.

Synthesis of [Pd(H_2O)$_2$(dppomf)](OTf)$_2$ (2b). To a solution of **1b** (0.42 g, 0.50 mmol) in CH_2Cl_2 (30 mL) cooled to −78 °C was added AgOTf (0.26 g, 1.02 mmol) with stirring. This mixture was warmed to room temperature and then was stirred overnight. During this time the color slowly changed from violet-blue to green. AgCl was filtered off through Celite, and the filtrate was concentrated to 10 mL and then stored at 0 °C for 30 min. After a small amount of a yellow-green solid was separated by filtration, 15 mL of Et_2O was added to the filtrate. Green prisms were formed on standing overnight at room temperature, which were filtered off, washed with Et_2O and dried under vacuum. Yield: 0.42 g (78%). Suitable crystals for X-ray analysis were obtained by slow diffusion of Et_2O into

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a saturated CH_2Cl_2 solution of **2b** at room temperature. IR (powder sample in KBr pellet): $\nu(OH_2)$ 3440 (br m) cm^{-1}. Anal. Calcd for $C_{44}H_{48}F_6FeO_8P_2PdS_2$: C, 47.73; H, 4.37. Found: C, 47.62; H, 4.39. This complex behaves as a 1:1 electrolyte in nitroethane ($\Lambda_M = 74\ \Omega^{-1}$ cm^2 mol^{-1}),[15] which is consistent with the formula $[Pd(H_2O)(OTf)(dppomf)]OTf$.

Synthesis of $[Pd(H_2O)_2(dppf)](OTs)_2$ (3a). To a solution of **1a** (0.36 g, 0.49 mmol) in CH_2Cl_2 (40 mL) was added AgOTs (0.32 g, 1.05 mmol). This mixture was stirred overnight at room temperature to give a cherry-colored solution, which was filtered through Celite and then concentrated to 10 mL. Benzene (30 mL) was added, and the resulting solution was evaporated to half volume until reddish brown needles precipitated. These were filtered off, washed with benzene and Et_2O, and dried under vacuum. Yield: 0.44 g (85%). IR (powder sample in KBr pellet): $\nu(OH_2)$ 3440 (br m) cm^{-1}. Anal. Calcd for $C_{48}H_{46}FeO_8P_2PdS_2$: C, 55.48; H, 4.46. Found: C, 55.40; H, 4.24. This complex behaves as a 1:1 electrolyte in nitroethane ($\Lambda_M = 30\ \Omega^{-1}$ cm^2 mol^{-1}),[15] which is consistent with the formula $[Pd(H_2O)(OTs)(dppf)]OTs$.

Synthesis of $[Pd(H_2O)_2(dppomf)](OTs)_2$ (3b). To a solution of **1b** (0.41 g, 0.49 mmol) in CH_2Cl_2 (20 mL) was added AgOTs (0.30 g, 1.07 mmol). After it was stirred overnight, this mixture was filtered through Celite and the filtrate was concentrated to 5 mL. The addition of 1 mL of Et_2O caused the precipitation of green crystals. An additional amount of Et_2O (5 mL) was slowly added with stirring to complete the precipitation of the desired product, which was filtered off, washed with Et_2O, and dried under vacuum. Yield: 0.51 g (92%). IR (powder sample in KBr pellet): $\nu(OH_2)$ 3450 (br m) cm^{-1}. Anal. Calcd for $C_{56}H_{62}FeO_8P_2PdS_2$: C, 58.43; H, 5.43. Found: C, 58.22; H, 5.29. This complex behaves as a 1:1 electrolyte in nitroethane ($\Lambda_M = 31\ \Omega^{-1}$ cm^2 mol^{-1}),[15] which is consistent with the formula $[Pd(H_2O)(OTs)(dppomf)]OTs$.

Synthesis of $[Pd(NCMe)_2(dppf)](BF_4)_2$ (4a). $AgBF_4$ (0.33 g, 1.70 mmol) was added to a solution of **1a** (0.57 g, 0.78 mmol) in a mixture of CH_2Cl_2 (40 mL) and MeCN (5 mL) cooled to −78 °C. This mixture was warmed to room temperature slowly, and then it was stirred for 1 h to give a deep violet solution and an off-white precipitate of AgCl. The solution was filtered through Celite, and the solvent was removed in vacuo. The solid residue was dissolved in CH_2Cl_2 (15 mL). To the resulting solution was added dropwise Et_2O (60 mL) until dark violet-blue crystals precipitated, which were filtered off, washed with Et_2O several times, and dried under vacuum. Yield: 0.64 g (90%). IR (Nujol, KBr): $\nu(NCMe)$ 2322 (w), 2292 (w) cm^{-1}; $\nu(BF_4)$ 1054 (s) cm^{-1}. Anal. Calcd for $C_{38}H_{34}B_2F_8FeN_2P_2Pd$: C, 49.80; H, 3.74; N, 3.06. Found: C, 49.70; H, 3.71; N, 2.91. This complex behaves as a 1:2 electrolyte in nitroethane ($\Lambda_M = 139\ \Omega^{-1}$ cm^2 mol^{-1}).[15]

Synthesis of $[Pd(NCMe)_2(dppomf)](BF_4)_2$ (4b). A solution of $AgBF_4$ (0.44 g, 2.26 mmol) in MeCN (10 mL) was added with stirring to a solution of $PdCl_2(MeCN)_2$ (0.29 g, 1.12 mmol) in MeCN (10 mL). After 30 min of stirring, this mixture was filtered through a glass frit and the filtrate was then added dropwise to a solution of dppomf (0.74 g, 1.11 mmol) in CH_2Cl_2 (20 mL) cooled to −40 °C. The resulting mixture was warmed to room temperature and then was stirred overnight. The green slurry obtained was filtered through a glass frit to remove some black product. The solvent was evaporated, and the solid residue was dissolved in CH_2Cl_2 (20 mL). After this solution was filtered through Celite, the filtrate was concentrated to 10 mL. The addition of 10 mL of Et_2O led to the formation of an orange sticky solid that was separated by filtration. Treatment of the mother liquor with 5 mL of Et_2O gave green crystals that were filtered off, washed with Et_2O, and dried under vacuum. Yield: 0.55 g (50%). IR (Nujol, KBr): $\nu(NCMe)$ 2326 (w), 2299 (w) cm^{-1}; $\nu(BF_4)$ 1055 (s) cm^{-1}. Anal. Calcd for $C_{46}H_{50}B_2F_8FeN_2P_2Pd$: C, 53.69; H, 4.90; N, 2.72. Found: C, 53.43; H, 4.82; N, 2.68. This complex behaves as a 1:2 electrolyte in nitroethane ($\Lambda_M = 129\ \Omega^{-1}$ cm^2 mol^{-1}).[15]

Synthesis of $[Pd(PPh_3)(dppf)](BF_4)_2$ (5a).[4i,17] To a solution of **4a** (0.45 g, 0.49 mmol) in CH_2Cl_2 (30 mL) was added triphenylphosphine (0.13 g, 0.50 mmol). This solution was stirred for 1 h until the color became red-brown and then was concentrated to 15 mL. THF (40 mL) was added, and the resulting solution was cooled to 0 °C until dark red needles precipitated, which were filtered off, washed with THF, and dried in vacuo. The mother liquor was evaporated to half its original volume to collect further product. Overall yield: 0.41 g (76%). Anal. Calcd for $C_{52}H_{43}B_2F_8FeP_3Pd$: C, 56.95; H, 3.95. Found: C, 56.75; H, 3.89.

Synthesis of $[Pd(PPh_3)(dppomf)](BF_4)_2$ (5b). To a solution of **4b** (0.44 g, 0.43 mmol) in CH_2Cl_2 (20 mL) was added neat triphenylphosphine (0.12 g, 0.45 mmol). The resulting mixture was stirred for 1 h, during which time the color turned dark blue. Et_2O (20 mL) was added to this solution, which was stored at 0 °C for 15 min to give a greenish blue microcrystalline solid. Further Et_2O (10 mL) was added to favor the precipitation of this product, which was washed with Et_2O and dried under vacuum. Yield: 0.42 g (81%). Anal. Calcd for $C_{60}H_{59}B_2F_8FeP_3Pd$: C, 59.59; H, 4.92. Found: C, 59.20; H, 5.08.

Synthesis of $Pd(OAc)_2(dppf)$ (6a). To a solution of dppf (1.48 g, 2.67 mmol) in benzene (50 mL) was added a solution of $Pd(OAc)_2$ (0.60 g, 2.67 mmol) in benzene (40 mL). The solution was stirred overnight, during which time a yellow precipitate was formed. The solvent was evaporated under reduced pressure to half volume, and the brownish yellow precipitate was filtered off and washed with benzene (2 × 5 mL). This crude product was recrystallized from CH_2Cl_2 (30 mL) and benzene (60 mL). Bright yellow microcrystals were filtered off, washed with benzene, and dried under vacuum. Yield: 1.14 g (55%). IR (CH_2Cl_2): $\nu(OAc)$ 1612, 1590, 1371, 1319 cm^{-1}. Anal. Calcd for $C_{38}H_{34}FeO_4P_2Pd$: C, 58.60; H, 4.40. Found: C, 58.85; H, 4.45. This complex behaves as a nonelectrolyte in nitroethane ($\Lambda_M = 6\ \Omega^{-1}$ cm^2 mol^{-1}).[15]

Reaction of 3a with $Ce(NO_3)_6(NH_4)_2$. To a solution of **3a** (0.20 g, 0.20 mmol) in acetone (20 mL) were added sodium tetrafluoroborate (0.1 g, 0.9 mmol) and cerium(IV) ammonium nitrate (0.10 g, 0.19 mmol). The resulting mixture was stirred at room temperature for 15 min, and then the solvent was removed under reduced pressure. The residue was extracted with CH_2Cl_2 (5 × 10 mL), and the resulting solution was filtered through a glass frit and then concentrated to 5 mL to give red crystals of $Pd(NO_3)_2(dppf)\cdot CH_2Cl_2$ (**7**) that were filtered off, washed with CH_2Cl_2 (5 mL), and dried under vacuum. Yield: 0.12 g (73%). IR (CH_2Cl_2): $\nu(NO_3)$ 1487, 1275 cm^{-1}. Anal. Calcd for $C_{35}H_{30}Cl_2FeN_2O_6P_2Pd$: C, 48.33; H, 3.48; N, 3.22. Found: C, 48.54; H, 3.46; N, 3.22.

Synthesis of $[(dppomf^+)]PF_6$ (8a) and $[(dppomf^+)]BF_4$ (8b). $[FeCp_2]PF_6$ (0.39 g, 1.18 mmol) was added to a solution of dppomf (0.80 g, 1.20 mmol) in CH_2Cl_2 (20 mL). The resulting solution was stirred for 1 h, and then the solvent was evaporated to dryness. The solid residue was filtered off, washed repeatedly with benzene until the filtrate was colorless, and dried under vacuum to give green microcrystals of **8a**. Yield: 0.95 g (99%). Anal. Calcd for $C_{42}H_{44}F_6FeP_3$: C, 62.13; H, 5.47. Found: C, 62.24; H, 5.52. ^1H NMR (CD_3NO_2) for **8a**: δ 15.2 (br s, 8H, *o*-Ph), 9.0 (br s, 8H, *m*-Ph), 7.9 (s, 4H, *p*-Ph), −38.6 (br s, 12H, C_5Me_4), −40.3 (br s, 12H, C_5Me_4). $^{31}P\{^1H\}$ NMR (CD_3NO_2) for **8a**: δ 25.7 (br s, 2P, PPh_2), −143.7 (sept, 1P, $J(PF) = 707$ Hz, PF_6^-).

Complex **8b** was prepared analogously from dppomf (0.49 g, 0.73 mmol) and $[FeCp_2]BF_4$ (0.20 g, 0.73 mmol). Yield: 0.54 g (98%). Anal. Calcd $C_{42}H_{44}BF_4FeP_2$: C, 66.91; H, 5.89. Found: C, 66.81; H, 5.84.

Synthesis of $[PdCl_2(dppomf^+)]PF_6$ (9a) and $[PdCl_2(dppomf^+)]BF_4$ (9b). To a solution of **8a** (0.34 g, 0.40 mmol) in CH_2Cl_2 (20 mL) was added a solution of *cis*-$PdCl_2(PhCN)_2$

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(0.16 g, 0.42 mmol) in CH_2Cl_2 (10 mL). The resulting mixture was stirred overnight until yellowish brown crystals of **9a**·CH_2Cl_2 precipitated. These were filtered off, washed with CH_2Cl_2, and dried under vacuum. Yield: 0.36 g (91%). Anal. Calcd for $C_{43}H_{46}Cl_4F_6FeP_3Pd$: C, 48.10; H, 4.32. Found: C, 48.35; H, 4.29.

Complex **9b** was prepared analogously from **8b** (0.41 g, 0.54 mmol) and *cis*-$PdCl_2(PhCN)_2$ (0.21 g, 0.55 mmol). Yield: 0.40 g (92%). Anal. Calcd for $C_{42}H_{44}BCl_2F_4FeP_2Pd$: C, 54.25; H, 4.77. Found: C, 54.28; H, 4.71.

Synthesis of [Pd(μ-OPF_2O)(dppomf$^+$)]$_2$(OTf)$_4$ (10a) and [Pd(H_2O)$_2$(dppomf$^+$)](OTf)$_2$(BF_4) (11). To a solution of **9a** (0.30 g, 0.30 mmol) in nitromethane (20 mL) was added solid AgOTf (0.16 g, 0.62 mmol). This mixture was stirred overnight at room temperature. After AgCl was filtered off through Celite, the solvent was evaporated under reduced pressure and the solid product was dissolved in CH_2Cl_2 (20 mL) to give a solution which was further filtered through Celite to remove any trace of Ag(I) salts. The filtrate was stored at 0 °C overnight to give yellow-brown crystals of **10a**·CH_2Cl_2, which were filtered off, washed with CH_2Cl_2 and dried in a vacuum. Yield 0.25 g (71%). Anal. Calcd for $C_{89}H_{90}Cl_2F_{16}Fe_2O_{16}P_6Pd_2S_4$: C, 44.01; H, 3.73. Found: C, 43.67; H, 3.99.

The procedure above was used also to prepare **11** from **9b** (0.37 g, 0.40 mmol) and AgOTf (0.21 g, 0.82 mmol). Yield 0.42 g (88%). Λ_M: 107 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for $C_{44}H_{48}BF_{10}FeO_8P_2PdS_2$: C, 44.26; H, 4.05. Found: C, 44.16; H, 4.00.

Synthesis of [Pd(μ-OPF_2O)(dppomf$^+$)]$_2$(BF_4)$_4$ (10b). To a solution of **9a** (0.56 g, 0.56 mmol) in MeCN (20 mL) cooled to −78 °C was added $AgBF_4$ (0.23 g, 1.18 mmol). This mixture was warmed to room temperature, and the solvent was removed under reduced pressure. The residue was dissolved in CH_3NO_2 (20 mL) to give a slurry that was filtered through a short Celite column. The filtrate was evaporated under reduced pressure to obtain a solid residue that was dissolved in CH_2Cl_2 (20 mL). This solution was rapidly passed through Celite. Yellow-brown crystals of **10b** began almost immediately to form from the filtrate. When the precipitation was complete, the product was filtered off, washed with CH_2Cl_2, and dried under vacuum. Yield: 0.39 g (67%). Crystals of **10b**·$6CH_2Cl_2$ suitable for an X-ray structure analysis were obtained by slow crystallization from diluted CH_2Cl_2 solutions of **10b** at room temperature. Anal. Calcd for $C_{90}H_{100}B_4Cl_{12}F_{20}Fe_2O_4P_6Pd_2$: C, 41.50; H, 3.87. Found: C, 41.32; H, 3.79.

Reaction of dppomf with 1 Equiv of AgOTf. To a yellow solution of dppomf (0.24 g, 0.36 mmol) in CH_2Cl_2 (20 mL) cooled to −78 °C was added AgOTf (0.09 g, 0.35 mmol). A green solution was obtained. This mixture was stirred for 2 days at room temperature to give a yellow solution. The solvent was evaporated, and the residue was dissolved in benzene (50 mL). The resulting solution was filtered with a glass frit to remove some green crystals. The filtrate was concentrated to 5 mL to obtain a yellow-orange solid product. This was filtered off, washed with benzene (5 mL), and dried in vacuo to give Ag(OTf)(dppomf) (**12**). Yield: 0.25 g (75%). Anal. Calcd for $C_{43}H_{44}FeF_3O_3P_2Ag$: C, 54.13; H, 4.61. Found: C, 54.01; H, 4.57. This complex behaves as a nonelectrolyte in nitroethane ($\Lambda_M = 8$ Ω^{-1} cm^2 mol^{-1}). ^{1}H NMR ($CDCl_3$): δ 1.33 (br s, 12H), 1.62 (br s, 12H), 7.35 (br s, 12H, *p*-Ph + *m*-Ph), 7.60 (br s, 8H, *o*-Ph). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −4.3 (d, $J(^{107}AgP)$ = 458 Hz, $J(^{109}AgP)$ = 526 Hz).[18]

Reaction of dppomf with 2 Equiv of $AgBF_4$. To a solution of dppomf (0.78 g, 1.17 mmol) in CH_2Cl_2 (20 mL) was added $AgBF_4$ (0.47 g, 2.41 mmol), and the mixture was stirred overnight to give a green solution that separated a green precipitate. The slurry was filtered through a glass frit, and the solid product was washed with CH_2Cl_2 (4 × 10 mL). The filtrate was concentrated to 10 mL, and the microcrystalline product obtained was filtered off, washed with CH_2Cl_2 (5 mL), and dried under reduced pressure to give [Ag (dppomf)](BF_4)$_2$ (**13**). Yield: 0.78 g (70%). Anal. Calcd for $C_{42}H_{44}B_2FeF_8P_2Ag$: C, 53.23; H, 4.64. Found: C, 53.00; H, 4.50. This complex behaves as a 1:2 electrolyte in nitroethane (Λ_M = 141 Ω^{-1} cm^2 mol^{-1}).[15] ^{1}H NMR (CD_3NO_2): δ −46.3 (br s, 12H), −34.5 (br s, 12H), 8.4 (s, 4H, *p*-Ph), 9.6 (br s, 16H, *o*-Ph + *m*-Ph). ^{31}P{^{1}H} NMR (CD_3NO_2): δ −65.2 (br d, $\omega_{1/2}$ = 100 Hz, J(AgP) = 472 Hz).

Electrochemical Oxidation of 1a. The oxidation of **1a** (0.20 g, 0.027 mmol) was carried out at a glassy-carbon electrode (+0.7 V) in CH_2Cl_2 (25 mL) (0.1 M [Bu_4N]BF_4). The initial current was 60 mA. After consumption of one electron (Q_{exptl} = 27.3 C, Q_{theor} = 26.4 C) the current decreased to 5 mA. A greenish blue microcrystalline product precipitated on the glassy-carbon electrode.

Electrochemical Oxidation of 2a. The oxidation of **2a** (0.10 g, 0.010 mmol) was carried out at a glassy-carbon electrode (+1.0 V) in CH_2Cl_2 (25 mL) (0.1 M [Bu_4N]BF_4). The initial current was 18 mA. After consumption of one electron (Q_{exptl} = 10.8 C, Q_{theor} = 9.8 C) the current decreased to 4 mA. The color of the solution changed from violet to dark green.

Electrochemical Oxidation of 3a. The oxidation of **3a** (0.20 g, 0.020 mmol) was carried out at a glassy-carbon electrode (+0.9 V) in CH_2Cl_2 (25 mL) (0.1 M [Bu_4N]BF_4). The initial current was 55 mA. After consumption of one electron (Q_{exptl} = 21.0 C, Q_{theor} = 19.2 C) the current decreased to 8 mA. The color of the solution changed from violet to dark green.

Catalytic Carbonylation of Ethene in Methanol. Typically, MeOH (100 mL) was introduced by suction into a 250 mL autoclave, previously evacuated by a vacuum pump, containing 0.01 mmol of catalyst precursor along with the desired amounts of 1,4-benzoquinone (BQ) and/or *p*-toluenesulfonic acid (TsOH). The autoclave was then pressurized with 1:1 CO/C_2H_4 (600 psi) at room temperature and heated to 85 °C. As soon as the reaction mixture in the autoclave reached the desired temperature, stirring (1400 rpm) was applied for the desired time (1−3 h). A constant pressure was maintained all over the experiments by a continuous feeding of the same mixture of CO/C_2H_4 from a gas reservoir. The reaction was stopped by cooling the autoclave to room temperature by means of an ice−acetone bath. After the unreacted gases were released, the insoluble ethene/CO copolymer, if any, was filtered off, washed with cold MeOH, and dried overnight under reduced pressure at 70 °C. The filtrate was analyzed by GC using dimethyl oxalate as the internal standard.

Characterization of the Copolymer. 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.[12,13] In particular, the ^{1}H and ^{13}C{^{1}H} NMR spectra of the samples show the contemporaneous presence of both ketonic and ester end groups. Anal. Calcd for $(COCH_2CH_2)_n$: C, 64.27; H, 7.19. Found: C, 64.21; H, 7.16. 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}. ^{1}H 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{^{1}H} 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 ($COCH_2CH_3$).

X-ray Data Collection and Structure Determination of 2a,b and 10b·$6CH_2Cl_2$. Single crystals were analyzed with a Bruker Smart 1000 CCD diffractometer. X-ray diffraction data were collected at 110 K. A set of 994 reflections for **2a** and **10b** and a set of 100 reflections for **2b** with 4° ≤ θ ≤ 25° were used to determine the lattice constants. Atomic scattering with anomalous dispersion corrections were taken from ref 19. All structures were solved by direct methods and refined by

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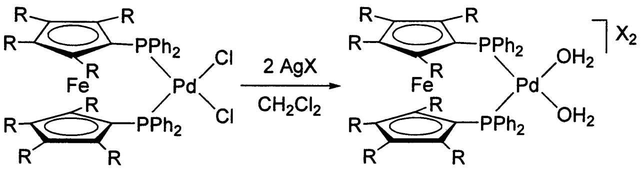
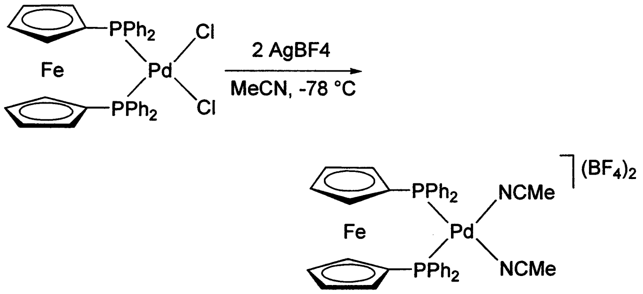
Scheme 1



1a,b

2a, R = H, X = OTf; **2b**, R = Me, X = OTf
3a, R = H, X = OTs; **3b**, R = Me, X = OTs

Scheme 2



4a

full-matrix least squares against F^2 using the SHELXTL-97 package. The data were corrected for Lorentz−polarization effects. All of the non-hydrogen atoms were found through a series of F_o Fourier maps and refined initially with isotropic thermal parameters and finally with anisotropic thermal parameters. The hydrogen atoms of the phenyl groups were introduced at calculated positions and refined by applying the riding model. The hydrogen atoms of the water molecules and the methyl groups were located from a Fourier density synthesis and refined afterwards by applying a riding model.

Results and Discussion

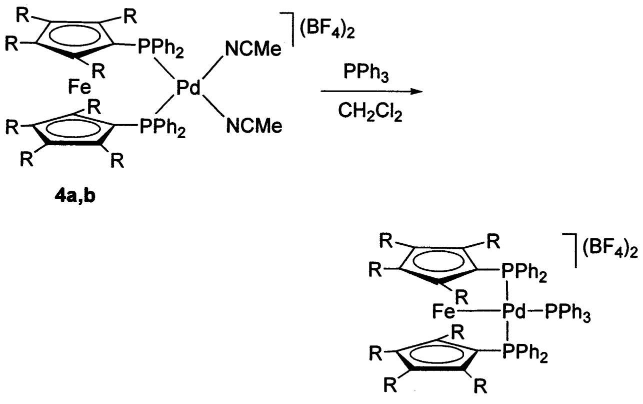
Synthesis of Palladium(II) Complexes with dppf and dppomf. Common synthetic methods developed to prepare Pd^{II}−dppf complexes can be successfully applied to obtain the dppomf analogues. Therefore, the straightforward reaction of *cis*-$PdCl_2(PhCN)_2$ with dppomf in benzene gave the dichloride complex $PdCl_2$(dppomf) (**1b**), analogous to $PdCl_2$(dppf)[4a,5a] (**1a**).

$[Pd(H_2O)_2(dppomf)](OTf)_2$ (**2b**) was prepared using a procedure previously designed for $[Pd(H_2O)_2(dppf)](OTf)_2$ (**2a**): i.e., treatment of **1b** with a chloride scavenger in a noncoordinating solvent (Scheme 1).[4c] The tosylate complexes **3a**,**b** were synthesized analogously.

$[Pd(NCMe)_2(dppf)](BF_4)_2$ (**4a**) was straightforwardly prepared in MeCN solution using a Ag(I) salt as chloride scavenger (Scheme 2). This procedure could not be used to prepare the dppomf derivative $[Pd(NCMe)_2(dppomf)](BF_4)_2$ (**4b**) because of the formation of paramagnetic byproducts, most likely containing "Pd(dppomf$^+$)" species, that were difficult to separate from the desired product. However, **4b** was successfully obtained in pure form by an alternative procedure involving stoichiometric addition of dppomf to a MeCN solution of $[Pd(MeCN)_4](BF_4)_2$ generated in situ by treatment of $PdCl_2(MeCN)_2$ with $AgBF_4$.

The known complex $[Pd(PPh_3)(dppf)](BF_4)_2$ (**5a**)[4i,17] and the novel dppomf derivative $[Pd(PPh_3)(dppomf)](BF_4)_2$ (**5b**), both containing an Fe−Pd bond, were conveniently prepared by reaction of the bis-MeCN precursors with PPh_3 in CH_2Cl_2 (Scheme 3).

Scheme 3



5a, R = H; **5b**, R = Me

The synthesis[20] of $[Pd(OAc)_2\{Fe(\eta^5\text{-}C_5R_4PPh_2)_2\}]$ (**6a**, R = H; **6b**, R = Me) by treatment of dichloride precursors with $Pd(OAc)_2$ in benzene was unexpectedly complicated by the formation of many different products, especially in the case of the permethylated complex **6b**. The dppf derivative **6a** is appreciably more stable than the dppomf analogue and could be isolated, although in moderate yield (55%). As was reported by Amatore and co-workers for $Pd(PPh_3)_2(OAc)_2$,[21] the degradation of the acetate compounds might be due to intramolecular nucleophilic attack of the acetate on the phosphine donor, followed by phosphine oxide formation.

All the complexes obtained were unambiguously characterized by elemental analysis and NMR spectroscopy (Tables 1 and 2). Moreover, the molecular structures of complexes **2a**,**b** were determined by single-crystal X-ray diffractometry (see below).

As a general trend, the chemical shifts of the chemically equivalent $-PPh_2$ groups reflect the charge of the complex: the ^{31}P resonances of the neutral dppf derivatives fall in the range 30−38 ppm, while the dicationic complexes exhibit singlets at lower field between 43 and 48 ppm. The dppomf complexes behave similarly (Table 1). It may be worth commenting that the ^{31}P resonances of the dppomf complexes are shifted to low field by 18−26 ppm as compared to the dppf analogues. This effect has been previously observed for Pd(II) complexes containing 1,3-diphenylphosphino-like ligands and has been attributed to the influence exerted by methyl groups on the s orbital electron density of α-phosphorus atoms.[22] Besides the dppomf phosphorus atoms, **5b** contains a PPh_3 ligand, and therefore the $^{31}P\{^1H\}$ NMR spectrum contains a doublet (2P) and a triplet (1P). The chemical shift of the ferrocenyl phosphorus nuclei is remarkably high field shifted (−22.8 ppm), which is in line with the presence of an Fe−Pd bond.[4i,17]

Typical of all $^{13}C\{^1H\}$ NMR spectra, signals are multiplets corresponding to second-order ABX spin

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Table 1. Selected ^{1}H and ^{31}P{^{1}H} NMR Spectral Data for Pd(II) Complexes with the Diphosphines dppf, dppomf, and dppomf$^+$ [a]

	^{1}H NMR chem shift (multiplicity, J)			^{31}P{^{1}H} NMR chem shift (multiplicity, J)
complex	C$_5$R$_4$	PPh$_2$	Pd−X	
2a	4.60 (s, 4H) 4.61 (s, 4H)	7.78 (dd, 8H, J = 13.2, 7.6, *o*-Ph) 7.49 (dd, 8H, J = 7.6, 7.2, *m*-Ph) 7.63 (t, 4H, J = 7.2, *p*-Ph)		48.1 (s)
3a[b]	4.40 (s, 4H) 4.57 (s, 4H)	7.92 (dd, 8H, J = 12.4, 7.6, *o*-Ph) 7.41 (dd, 8H, J = 8.0, 7.2, *m*-Ph) 7.53 (t, 4H, J = 7.2, *p*-Ph)		44.9 (s)
4a	4.56 (s, 4H) 4.66 (s, 4H)	7.77 (dd, 8H, J = 13.2, 7.6, *o*-Ph) 7.51 (dd, 8H, J = 7.6, 7.2, *m*-Ph) 7.61 (t, 4H, J = 7.2, *p*-Ph)	1.85 (s, 6H, MeCN)	43.4 (s)
5a	4.34 (s, 4H) 5.61 (s, 4H)	7.2−7.5 (m, 35H)	*c*	−15.9 (d, 2P, J = 14.6, PPh$_2$) 37.0 (t, 1P, J = 14.6, PPh$_3$)
6a	4.39 (s, 4H) 4.42 (s, 4H)	7.93 (dd, 8H, J = 12.4, 7.6, *o*-Ph) 7.40 (ddd, 8H, J = 8.0, 7.2, 2.0, *m*-Ph) 7.78 (dt, 4H, J = 7.2, 2.0, *p*-Ph)	1.39 (br s, 6H, AcO)	30.4 (s)
7[d]	4.40 (s, 4H) 4.51 (s, 4H)	7.77 (dd, 8H, J = 12.4, 7.6, *o*-Ph) 7.48 (dd, 8H, J = 7.6, 7.2, *m*-Ph) 7.59 (t, 4H, J = 7.2, *p*-Ph)		38.2 (s)
1b	1.21 (s, 12H) 1.51 (s, 12H)	8.27 (br dd, 8H, *o*-Ph) 7.42 (br dd, 8H, *m*-Ph) 7.40 (br t, 4H, *p*-Ph)		50.6 (s)
2b[e]	1.45 (s, 12H) 1.56 (s, 12H)	8.13 (br dd, 8H, *o*-Ph) 7.62 (br dd, 8H, *m*-Ph) 7.64 (br t, 4H, *p*-Ph)		69.1 (s)
3b[f]	1.42 (s, 12H) 1.55 (s, 12H)	8.20 (br dd, 8H, *o*-Ph) 7.56 (br dd, 8H, *m*-Ph) 7.52 (br t, 4H, *p*-Ph)		63.0 (s)
4b	1.41 (s, 12H) 1.55 (s, 12H)	8.17 (br dd, 8H, *o*-Ph) 7.61 (br dd, 8H, *m*-Ph) 7.64 (br t, 4H, *p*-Ph)	1.96 (s, 6H, MeCN)	69.3 (s)
5b	0.88 (s, 12H) 1.72 (s, 12H)	7.2 −7.5 (m, 35H)	*c*	−22.8 (d, 2P, J = 20.3, PPh$_2$) 19.9 (t, 1P, J = 20.3, PPh$_3$)
9a,**b**[g]	−16.6 (br s, 12H) −38.1 (br s, 12H)	13.8 (br s, 8H, *o*-Ph) 9.3 (br s, 8H, *m*-Ph) 8.3 (s, 4H, *p*-Ph)		−82.4 (br s, 2P, PPh$_2$) −143.5 (sept, 1P, J = 707, PF$_6^-$)[h]
10a[g]	−10.9 (br s, 12H) −39.4 (br s, 12H)	12.0 (br s, 8H, *o*-Ph) 8.7 (br s, 8H, *m*-Ph) 7.9 (s, 4H, *p*-Ph)		−145.5 (br s, 2P, PPh$_2$) −26.9 (br t, 1P, J = 965, PO$_2$F$_2^-$)
10b[g]	−10.8 (br s, 12H) −40.2 (br s, 12H)	11.8 (br s, 8H, *o*-Ph) 8.7 (br s, 8H, *m*-Ph) 7.9 (s, 4H, *p*-Ph)		−148.8 (br s, 2P, PPh$_2$) −32.4 (br t, 1P, J = 967, PO$_2$F$_2^-$)
11[g]	−10.9 (br s, 12H) −40.0 (br s, 12H)	12.2 (br s, 8H, *o*-Ph) 8.9 (br s, 8H, *m*-Ph) 8.1 (s, 4H, *p*-Ph)		−148.6 (s)

[a] All spectra were recorded at room temperature in CDCl$_3$ solutions unless otherwise stated. Chemical shifts are reported in ppm (δ) relative to TMS, referenced to the chemical shifts of residual solvent resonances (^{1}H NMR) or 85% H$_3$PO$_4$ (^{31}P{^{1}H} NMR, downfield values are assumed as positive). Key: s, singlet; d, doublet; t, triplet; sept, septuplet; m, multiplet; br, broad. Coupling constants (J) are in hertz. [b] OTs resonances: 2.24 (s, 6H, Me), 7.37 (d, 4H, J = 8.0), 6.81 (d, 4H, J = 8.0). [c] The hydrogen resonances of PPh$_3$ are masked by those of PPh$_2$. [d] CH$_2$Cl$_2$ singlet at 5.31. [e] In CD$_2$Cl$_2$. [f] OTs resonances: 2.26 (s, 6H, Me), 7.68 (br s, 4H), 6.99 (br s, 4H). [g] In CD$_3$NO$_2$. [h] PF$_6$ signal for **9a**.

systems due to the Cp carbon atoms and to the ipso, ortho, and meta phenyl carbon atoms (Table 2).[11a,23]

Cyclic Voltammetry Study of 1a,b−5a,b and 6a. The electrochemistry of Pd(II) complexes with dppf has been scarcely investigated,[4d] while no report concerning dppomf compounds is available in the relevant literature. Therefore, we have examined the cyclic voltammetry behavior of various dppf and dppomf Pd(II) complexes in CH$_2$Cl$_2$ solution. The results obtained are reported in Table 3.

All the Pd(II) complexes showed an irreversible two-electron reduction centered at the palladium metal.[4d,22a,24−27] As expected, the neutral complexes **1a**,**b** and **6a** were reduced at significantly less positive potentials than those of the dicationic complexes **2a**,**b**−**4a**,**b**. The reduction potentials of the latter complexes were close to each other and did not show any dependence on either the nature of the coligand/counterion or the presence of methyl groups in the ferrocenyl moiety. Unlike **1a**,**b**−**4a**,**b**, the complexes **5a**,**b** underwent two chemically and electrochemically reversible one-electron-reduction steps to form Pd(0) complexes. These were quite stable in solution under Ar but

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Table 2. Selected $^{13}C\{^1H\}$ NMR Spectral Data for Pd(II) Complexes with the Diphosphines dppf and dppomf[a]

	chem shift (multiplicity, J)		
complex	C_5R_4	PPh_2	Pd–X
2a[b]	78.44 (t, $J = 5.9$, α-C) 76.27 (t, $J = 4.7$, β-C) 69.45 (m, $\lvert ^1J + ^2J \rvert = 75.4$, ipso-C)	127.85 (m, $\lvert ^1J + ^2J \rvert = 67.6$, ipso-Ph) 134.48 (t, $J = 6.2$, o-Ph) 129.71 (t, $J = 6.1$, m-Ph) 133.57 (s, p-Ph)	
3a	77.61 (t, $J = 5.6$, α-C) 74.88 (t, $J = 4.1$, β-C) 70.65 (m, $\lvert ^1J + ^2J \rvert = 73.2$, ipso-C)	128.31 (m, $\lvert ^1J + ^2J \rvert = 66.1$, ipso-Ph) 134.37 (t, $J = 5.5$, o-Ph) 128.81 (t, $J = 5.7$, m-Ph) 132.25 (s, p-Ph)	
4a	78.35 (t, $J = 6.2$, α-C) 76.13 (t, $J = 4.7$, β-C) 68.25 (m, $\lvert ^1J + ^2J \rvert = 74.8$, ipso-C)	128.10 (m, $\lvert ^1J + ^2J \rvert = 60.4$, ipso-Ph) 133.70 (t, $J = 6.2$, o-Ph) 129.53 (t, $J = 6.1$, m-Ph) 133.20 (s, p-Ph)	1.97 (s, *Me*CN) 122.77 (s, Me*C*N)
6a	76.41 (d, $J = 10.9$, α-C) 73.80 (d, $J = 7.7$, β-C) 76.41 (m, $\lvert ^1J + ^2J \rvert = 60.2$, ipso-C)	130.91 (m, $\lvert ^1J + ^2J \rvert = 55.1$, ipso-Ph) 134.94 (d, $J = 5.9$, o-Ph) 128.82 (d, $J = 5.8$, m-Ph) 131.11 (d, $J = 1.2$, p-Ph)	22.9 (br s, *Me*COO) 177.5 (br s, Me*C*OO)
3b[b]	89.45 (t, $J = 4.8$, α-C) 86.80 (t, $J = 4.0$, β-C) 75.32 (m, $\lvert ^1J + ^2J \rvert = 69.2$, *ipso*-C) 12.50 (s, Me) 8.60 (s, Me)	129.78 (m, $\lvert ^1J + ^2J \rvert = 64.8$, ipso-Ph) 135.08 (t, $J = 6.0$, o-Ph) 129.42 (t, $J = 5.6$, m-Ph) 132.59 (s, p-Ph)	
4b[b]	90.51 (t, $J = 6.2$, α-C) 87.61 (t, $J = 4.7$, β-C) 76.04 (m, $\lvert ^1J + ^2J \rvert = 78.8$, ipso-C) 12.36 (s, Me) 8.43 (s, Me)	~129 (overlapped, ipso-Ph) 134.94 (br s, o-Ph) 129.78 (br s, m-Ph) 133.25 (s, p-Ph)	2.55 (s, *Me*CN) 123.68 (s, Me*C*N)
5b	81.58 (dd, $J = 7.1, 4.6$, α-C) 103.10 (t, $J = 3.5$, β-C) 45.21 (t, $J = 19.8$, ipso-C) 12.53 (s, Me) 9.14 (s, Me)	122.27 (dd, $J = 28.6, 2.8$, ipso-Ph) 135.50 (t, $J = 7.0$, o-Ph) 129.85 (t, $J = 4.5$, m-Ph) 133.45 (s, p-Ph)	129.29 (overlapped, ipso-Ph) 129.68 (d, $J = 12.0$, o-Ph) 133.53 (t, $J = 11.6$, m-Ph) 132.93 (d, $J = 3.2$, p-Ph)

[a] All spectra were recorded at room temperature in $CDCl_3$ solutions unless otherwise stated. Chemical shifts are reported in ppm (δ) relative to TMS, referenced to the chemical shifts of residual solvent resonances. Key: s, singlet; d, doublet; t, triplet; br, broad. Coupling constants (J) are in Hertz. [b] In CD_2Cl_2.

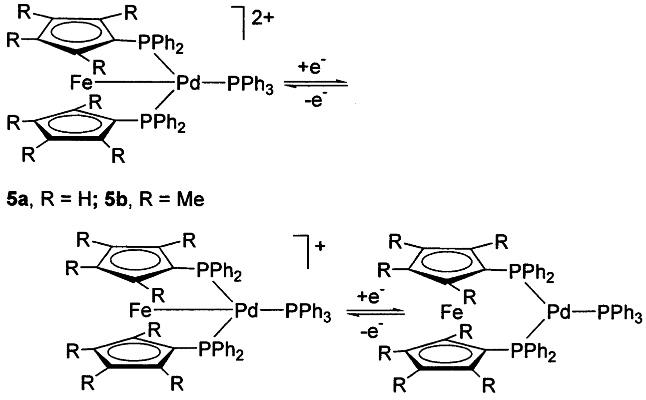
Table 3. Cyclic Voltammetry Data for dppf, dppomf, and Related Pd(II) Complexes in CH_2Cl_2 Solution[a]

sample	$E_{p,a}$, V	$E_{p,c}$, V	sample	$E_{p,a}$, V	$E_{p,c}$, V
dppf	0.18		dppomf	−0.40	
1a	0.58	−1.59	**1b**	0.07	−1.44
2a	0.82	−0.77	**2b**	0.32	−0.74
3a	0.77	−0.77	**3b**	0.29	−0.77
4a	0.86	−0.74	**4b**	0.36	−0.73
5a	1.09	−0.55, −0.69	**5b**	0.77	−0.64, −0.78
6a	0.56, 0.82	−1.83			

[a] Conditions: 2×10^{-3} M samples; 0.1 M $[Bu_4]NBF_4$; $v = 200$ mV s^{-1}; glassy-carbon working electrode. All potentials are given with reference to the Cp_2Fe^+/Cp_2Fe couple (+0.46 V vs SCE).

decomposed rapidly when exposed to air. For this reason as well as the presence of the supporting electrolyte, all our attempts to isolate the Pd(0) species were unsuccessful. The CV profile and the small difference (140 mV) separating the two reduction waves of **5a**,**b** closely resemble the behavior of several metal complexes that undergo a chemically reversible structural reorganization only in the second electron transfer.[26] For example, $[Fe(\eta^5\text{-}C_5Me_5)(\mu_2\text{-}\eta^{10}\text{-biphenyl})Fe(\eta^5\text{-}C_5Me_5)](PF_6)_2$ was reduced in two electrochemically reversible one-electron steps separated by 130 mV undergoing transformation of the bridging biphenyl ligand to bicyclohexadienylidene upon addition of the second electron.[26c] It is therefore likely, yet quite speculative, that the second reduction of **5a**,**b** leads to the reversible rupture of the Fe–Pd bond, as shown in Scheme 4.

Scheme 4

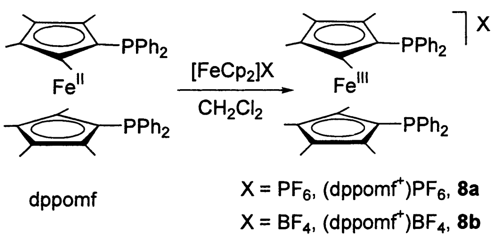


5a, R = H; **5b**, R = Me

Free dppf is known to undergo a quasireversible one-electron oxidation to give the $dppf^+$ cation which is intrinsically unstable and undergoes a fast chemical reaction (EC process).[25] In contrast, the $dppomf^+$ cation is quite stable and can be prepared by bulk electrolysis and characterized by EPR spectroscopy.[24]

Transition-metal complexes with either dppf or dppomf reflect the behavior of the free ligands, as they generally undergo a one-electron oxidation.[4d,24,25] All the Pd(II) complexes described in this work showed a reversible one-electron oxidation of the ferrocenyl fragments with oxidation potentials spanning from 0.07 to 1.09 V. This wide range is apparently occasioned by the dependence of the potential on several factors: the presence of methyl groups in the ferrocenyl moiety, the nature of the counterions and coligands, and the existence of a Fe→Pd bonding interaction. The oxidation potentials of **1b**–**4b** were ca. 0.5 V less positive than

Scheme 5



those of the dppf analogues **1a**–**4a**, which is in line with the more electron-rich character of dppomf vs dppf. The oxidation potentials of the neutral dichloride complexes **1a**,**b** were less positive by ca. 0.25 V than those of the dicationic derivatives **2a**,**b**–**4a**,**b**. The triphenylphosphine complexes **5a**,**b** featured the most positive potentials, irrespective of the ferrocenyl ligand. This result is consistent with a decrease of the electron density on the iron center occasioned by the dative bonding interaction with palladium.[4i,17] It is noteworthy that this donor–acceptor interaction is apparently stronger in the methylated complex **5b** than in the dppf analogue **5a** ($\Delta E = E_{p,a}$(**5b**) $- E_{p,a}$(**4b**) $= 0.41$ V and E_{pa}(**5a**) $- E_{pa}$(**4a**) $= 0.23$ V).

Syntheses of the Ferrocenium Complexes [Pd(dppomf$^+$)(μ-OPF$_2$O)]$_2$X$_4$ (10a,b) and [Pd(dppomf$^+$)(H$_2$O)$_2$](OTf)$_2$(BF$_4$) (11). On the basis of the results of the CV study, several attempts were made to prepare dppomf$^+$ Pd(II) complexes by either macroelectrolysis at controlled potential or appropriate chemical oxidants.

Bulk electrolysis of **1a** in CH_2Cl_2 at +0.7 V resulted in the precipitation of a greenish blue microcrystalline material onto the glassy-carbon electrode after consumption of one electron/molecule. The same product was obtained by oxidation with $NOBF_4$. As previously reported by Corain and co-workers,[4d] the product may have the formula [PdCl$_2$(dppf)]BF$_4$ (on the basis of elemental analysis), but this cannot be proved unequivocally due to the very low solubility in common organic solvents that precluded a thorough spectroscopic analysis.

Bulk electrolysis of **2a** and **3a** was performed under similar conditions at potentials of +1.0 and +0.9 V, respectively. Both experiments gave dark green solutions from which no Pd(II) product could be isolated in a pure form, due to the extreme sensitivity to oxygen as well as the presence of the supporting electrolyte. The oxidation of **2a** and **3a** with $NOBF_4$ was unsuccessful, as no paramagnetic product was obtained. An attempt was then made in acetone with $(NH_4)_2[Ce(NO_3)_6]$ as oxidant, but the reaction gave exclusively Pd(NO$_3$)$_2$(dppf) (**7**), even in the presence of $NaBF_4$.

The best way to prepare dppomf$^+$ Pd(II) complexes was found to involve the use of preformed dppomf$^+$ as either the PF_6^- or BF_4^- salt. For this purpose, ferrocenium as the hexafluorophosphate or tetrafluoroborate salt proved to be an excellent and selective oxidant that allowed for quantitative oxidation of dppomf to dppomf$^+$ (Scheme 5).

All our attempts to oxidize dppomf or Pd^{II}–dppomf complexes with Ag(I) salts were partially successful. In particular, if used stoichiometrically, AgOTf reacted with dppomf, yielding the complex Ag(OTf)(dppomf) (**12**). Only by using an excess of Ag(I) salt was dppomf oxidized to dppomf$^+$ to give the complex [Ag(dppomf$^+$)](BF$_4$)$_2$ (**13**). The direct oxidation of **1b** with Ag(I) salts produced the corresponding ferrocenium derivatives (see below) in very low yield. Moreover, the products were difficult to separate from the nonoxidized complexes.

Using **8a**,**b** in conjunction with *cis*-PdCl$_2$(PhCN)$_2$, [PdCl$_2$(dppomf$^+$)]X (**9a**, X = PF$_6$; **9b**, X = BF$_4$) were finally obtained in good yields and then employed to synthesize other dppomf$^+$ Pd(II) complexes (Scheme 6).

Treatment of **9a** with AgOTf in nitromethane led to the formation of the binuclear complex [Pd(μ-OPF$_2$O)(dppomf$^+$)]$_2$(OTf)$_4$ (**10a**), in which two Pd(II) centers are held together by the oxygen atoms from two bridging $PO_2F_2^-$ groups derived from the oxidative degradation of the PF_6^- ion.[28] Similarly, the reaction of **9a** with 2 equiv of $AgBF_4$ gave the bimetallic analogue **10b**, which was authenticated by a single-crystal X-ray analysis (see below).

A mononuclear dppomf$^+$ Pd(II) complex was obtained by using **9b** as precursor and AgOTf as halide scavenger. In this way, [Pd(H$_2$O)$_2$(dppomf$^+$)](OTf)$_2$(BF$_4$) (**11**) was isolated in good yield.

Besides elemental analysis, the complexes with dppomf$^+$ were characterized by ^1H and ^{31}P NMR spectroscopy (Table 1). All the signals were quite broad due to the paramagnetic nature of the compounds.

Single-Crystal X-ray Structures of [Pd(OH$_2$)$_2$(dppf)](OTf)$_2$ (2a), [Pd(OH$_2$)$_2$(dppomf)](OTf)$_2$ (2b), and [Pd(μ-OPF$_2$O)(dppomf$^+$)]$_2$(BF$_4$)$_4$ (10b·6CH$_2$Cl$_2$). ORTEP drawings of the complexes **2a**,**b** and **10b**·6CH$_2$Cl$_2$ are reported in Figures 1–3, respectively. Crystallographic data are reported in Table 4. Selected bond distances and angles are listed in Table 5.

In all complexes, the coordination geometry around palladium can be described as a slightly distorted square plane with cis phosphorus atoms. The distances from the centroid of the Cp ring to iron (Cp$_{cent}$–Fe) are 1.639(4) and 1.649(4) Å for **2a** and 1.637(6) Å for **2b** and match well the values reported for PdCl$_2$(dppf).[4a] The distances Cp$_{cent}$–Fe in **10b** are 1.700(4) and 1.704(4) Å and are therefore significantly longer than those in **2a**,**b**, yet they are close to the value 1.710(2) Å reported for $[Fe(C_5Me_5)_2]^+[C_3(CN_5)]^-$.[29]

In all complexes, the Cp rings are planar and tilted toward the palladium atom. The angle between the plane normals related to the Cp rings are 5.3° (**2a**), 2.0° (**2b**), and 6.9° (**10b**). The analogous angle in PdCl$_2$(dppf) is 6.2°.[4a]

The dihedral angle C(1)–Cp$_{cent}$(1)–Cp$_{cent}$(2)–C(2) in **2a** is 30.7° and is close to that reported for [Pt(H$_2$O)$_2$(dppf)](OTf)$_2$ (30.0°)[4c] and larger than that in either **2b** (24.6°) or **10b** (16.2°).

The phosphorus atoms deviate from the plane defined by the Cp rings. In **2a**, the deviation is toward iron by 0.02–0.04 Å, while in **2b** and **10b** the deviation is away from iron by 0.10 and 0.18–0.19 Å, respectively. The distance P–C$_{Cp}$ increases on going from **2a** (1.786(4)–1.794(4) Å) to **2b** (1.796(6)–1.802(6) Å) to **10b** (1.813(6)–1.819(6) Å).

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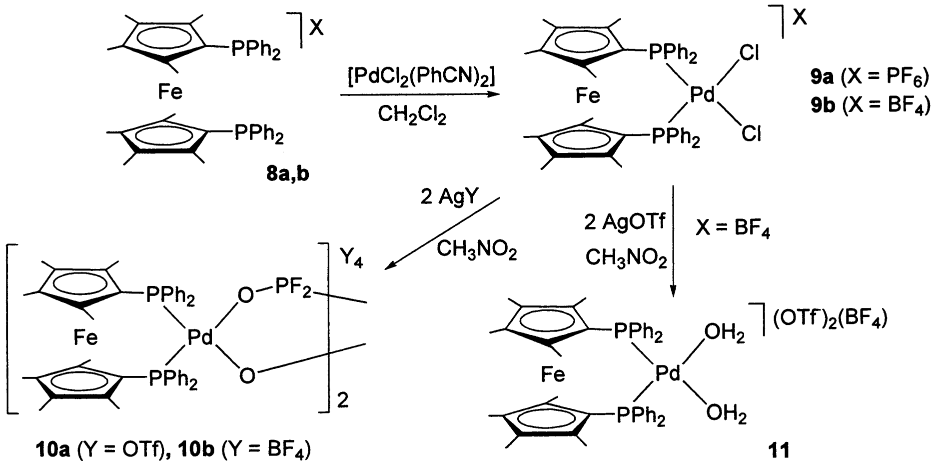
[28] *Phosphorus*, 5th ed.; Corbridge, D. E. C., Ed.; Elsevier Science: Amsterdam, 1995; pp 138–168.

[29] Miller, J. S.; Calabrese, J. C.; Rommelmann, H.; Chittipeddi, S. R.; Zhang, J. H.; Reiff, W. M.; Epstein, A. J. *J. Am. Chem. Soc.* **1987**, *109*, 769.

Scheme 6



8a,b

9a (X = PF_6)
9b (X = BF_4)

10a (Y = OTf), **10b** (Y = BF_4)

11

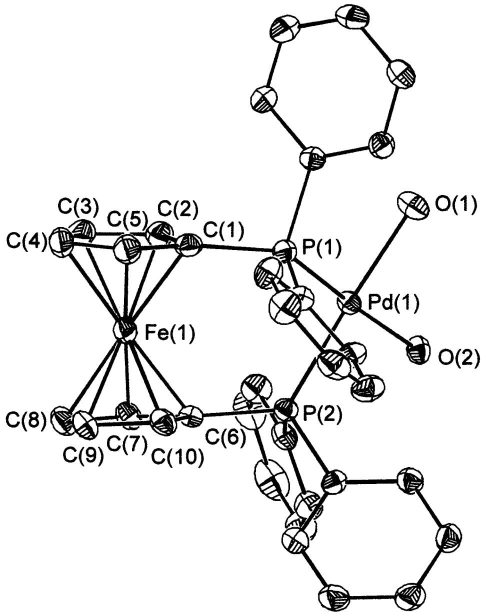


Figure 1. ORTEP drawing of **2a**. Thermal ellipsoids are drawn at the 50% probability level. The OTf^- counteranions have been omitted for clarity.

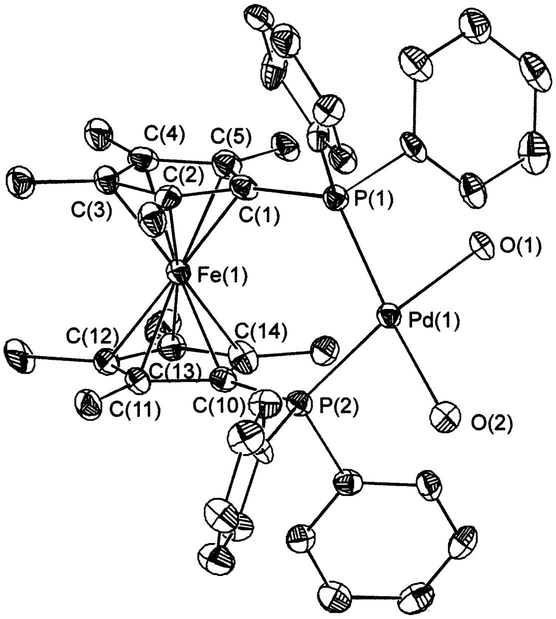


Figure 2. ORTEP drawing of **2b**. Thermal ellipsoids are drawn at the 50% probability level. The OTf^- counteranions have been omitted for clarity.

The Pd–P distances are longer in the dppomf complex **2b** (2.271(2)–2.279(2) Å) than in the dppf analogue **2a** (2.263(1)–2.268(1) Å), probably due to steric effects. The Pd–P bond lengths in **10b** are 2.243(2) and 2.245(2) Å, respectively; these distances are surprisingly short, as the presence of a ferrocenium moiety in **10b** was expected to reduce the σ-donating ability of the phosphorus donors with consequent lengthening of the Pd–P distances. This unexpected shortening of the P–Pd distances may be rationalized in terms of either crystal packing or an increased π-back-bonding Pd–P contribution. The latter hypothesis has been proposed earlier to account for the stability of electrochemically generated $[MCl_2(dppf)]^+$ (M = Pd, Pt).[4d]

The P–Pd–P bond angles in **2a** and in the octamethyl-substituted complexes **2b** and **10b** are remarkably different from each other: this angle in **2a** is 96.38(4)° and is therefore close to the value reported for the cationic square-planar platinum(II) complex $[Pt(OH_2)_2(dppf)](OTf)_2$ (97.37(7)°)[4c] and appreciably smaller than the value observed in the dichloride palladium(II) complex **1a** (98.0(1)°).[4d] The presence of methyl groups in the Cp rings as in **2b** leads to an enlargement of this bond angle to 101.32(5)°. A similar effect has been previously observed for the six-coordinate complexes $M(CO)_4(dppomf)/M(CO)_4(dppf)$ (M = Mo, W).[4a,11a] Interestingly, the oxidation of the ferrocenyl moiety does not

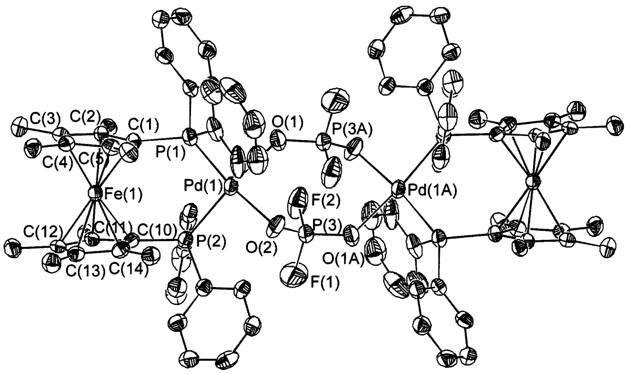


Figure 3. ORTEP drawing of **10b**·$6CH_2Cl_2$. Thermal ellipsoids are drawn at the 50% probability level. The BF_4^- counteranions have been omitted for clarity.

Table 4. Crystal and Structure Refinement Data for 2a,b and 10b·6CH$_2$Cl$_2$

	2a	**2b**	**10b**·6CH$_2$Cl$_2$
empirical formula	$C_{36}H_{32}F_6O_8S_2FeP_2Pd$	$C_{44}H_{48}F_6O_8S_2FeP_2Pd$	$C_{90}H_{100}B_4Cl_{12}F_{20}O_4P_6Fe_2Pd_2$
fw	994.93	1107.13	2604.66
cryst color, shape	red, prism	green, plate	yellow-brown, prism
cryst size, mm	0.35 × 0.30 × 0.15	0.30 × 0.20 × 0.10	0.35 × 0.22 × 0.15
collection temp, K	110	110	110
cryst syst	monoclinic	orthorhombic	monoclinic
space group	$P2_1/n$	$Pca2_1$	$P2_1/n$
unit cell dimens			
a, Å	12.265(2)	20.888(5)	16.616(2)
b, Å	17.796(4)	11.539(3)	18.140(3)
c, Å	17.861(4)	18.889(6)	18.469(3)
β, deg	97.669(4)		111.356(6)
V, Å^3	3863.5(13)	4553(2)	5184.7(15)
Z	4	4	2
F(000)	2000	2256	2620
calcd density, g/cm^3	1.710	1.615	1.668
radiation/wavelength, Å	Mo Kα/0.710 72	Mo Kα/0.710 72	Mo Kα/0.710 72
abs coeff, mm^{-1}	1.112	0.952	1.102
θ range, deg	1.62−29.05	2.16−27.49	1.73−27.52
index ranges	$-16 \leq h \leq 16$ $-24 \leq k \leq 24$ $-24 \leq l \leq 124$	$-26 \leq h \leq 27$ $-14 \leq k \leq 14$ $-24 \leq l \leq 24$	$-21 \leq h \leq 21$ $-23 \leq k \leq 22$ $-23 \leq l \leq 23$
no. of rflns collected	10 280	10 299	11 801
no. of unique rflns	7523 (R(int) = 0.0427)	7954 (R(int) = 0.0882)	6950 (R(int) = 0.0581)
no. of data/restraints/params	7523/0/521	7954/0/587	6950/0/639
refinement method	full-matrix least squares on F^2	full-matrix least squares on F^2	full-matrix least squares on F^2
goodness of fit on F^2	1.093	1.024	1.077
final R1, wR2 indices ($I > 2\sigma(I)$)	0.0550, 0.1197	0.0556, 0.1289	0.0684, 0.1469
R1, wR2 indices (all data)	0.073, 0.1275	0.0738, 0.1389	0.1263, 0.1743
largest diff peak and hole, e/Å^3	1.060 and −0.981	1.504 and −0.528	1.030 and −1.040

affect the P−Pd−P bond angle, which is 101.78(6)° in the dppomf$^+$ complex **10b**.

The O−Pd−O angles in the diaquo complexes **2a**,**b** are comparable to each other (87.56(12) and 87.01(16)°) and somewhat larger than the O−Pt−O angle in the structurally related platinum complex [Pt(OH$_2$)$_2$(dppf)](OTf)$_2$ (86.02(2)°).[4c] The O−Pd−O angle in complex **10b** relative to the bridging PO$_2$F$_2^-$ group is 89.00(20)°.

The iron center in **2a** significantly deviates from the plane P(1)Pd(1)P(2), the dihedral angle between the planes P(1)Fe(1)P(2) and P(1)Pd(1)P(2) being 38.8°. A comparable deviation from planarity was reported for [Pt(OH$_2$)$_2$(dppf)](OTf)$_2$, which shows a dihedral angle P(1)Fe(1)P(2)/P(1)Pt(1)P(2) of 39.1°.[4c] Unlike **2a**, the iron centers in **2b** and **10b** do not appreciably deviate from the plane defined by P(1), Pd(1), and P(2), while the dihedral angles between the planes P(1)Fe(1)P(2) and P(1)Pd(1)P(2) are dramatically smaller than in **2a** (4.6(2) and 0.7(2)°, respectively).

No bonding interaction may be envisaged between the iron and palladium centers in **2a**,**b** and **10b** (distances of 4.192(1), 4.394(1), and 4.437(1) Å, respectively). No abnormal contact was found in **2a**, while the triflate anions in **2b** clearly bring about a hydrogen-bonding interaction with both coordinated water molecules. An agostic contact between a phenyl ortho hydrogen and the palladium atom in both **2b** (C−H···Pd: separation 2.65(2) Å, angle 113.6(4)°) and **10b** (C−H···Pd: separation 2.55(2) Å, angle 118.1(5)°) is suggested by calculations.[30]

To summarize, the molecular structure of the dppf complex **2a** differs from those of the complexes **2b** and **10b** by several parameters: the P−Pd−P bond angle, the dihedral angle between the planes P(1)Fe(1)P(2) and P(1)Pd(1)P(2), the deviation of the phosphorus from the planes of the Cp rings, and the Fe···Pd distance. All these differences cannot be clearly accounted for by crystal packing effects; rather, they appear as a direct consequence of the replacement of the Cp hydrogens by methyl groups. As will be shown in the following section, the presence of either H or Me groups on the Cp rings affects remarkably also the chemistry of the corresponding Pd(II) complexes.

Carbonylation of Ethene in Methanol. The carbonylation of ethene has been investigated in MeOH (methoxycarbonylation) using **3a**,**b** and **5a**,**b** as catalyst precursors. Compounds **3a** and **5a** differ from **3b** and **5b** by the chelating diphosphine ligand (dppf vs dppomf) and from each other by the coligands (weakly bound H$_2$O molecules in **3a**,**b**, strongly bound PPh$_3$ in **5a**,**b**).

No attempt at all has been made to optimize the processes; studies in this direction are in progress together with in situ NMR and IR studies.

A constant 600 psi pressure of 1:1 CO/C$_2$H$_4$ and 85 °C were the experimental parameters chosen to evaluate the catalytic performance of all catalysts. Under these typical conditions,[12,13,22a,31] all the Pd complexes were substantially stable toward decomposition within 1 h of reaction time. For longer times, the formation of some black precipitate of Pd metal was observed in all experiments, yet the systems were still active after 3 h. In some reactions, TsOH was employed as cocatalyst, alone or in conjunction with BQ as organic oxidant.[12,13] The results obtained are reported in Table 6.

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[30] Yao, W.; Eisenstein, O.; Crabtree, R. H. *Inorg. Chim. Acta* **1997**, *254*, 105.

[31] (a) Bianchini, C.; Lee, H. M.; Meli, A.; Oberhauser, W.; Peruzzini, M.; Vizza, F. *Organometallics* **2002**, *21*, 16. (b) Bianchini, C.; Mantovani, G.; Meli, A.; Oberhauser, W.; Brüggeller, P.; Stampfl, T. *J. Chem. Soc., Dalton Trans.* **2001**, 690.

Table 5. Selected Geometrical Parameters for 2a,b and 10b·6CH$_2$Cl$_2$

	2a	**2b**	**10b**·6CH$_2$Cl$_2$
	Bond Lengths (Å)		
Fe(1)−Cp(1)[a]	1.639(4)	1.637(6)	1.704(4)
Fe(1)−Cp(2)[b]	1.649(4)	1.637(6)	1.700(4)
Fe(1)−C_{Cp}	1.994(4)−2.071(4)	2.015(6)−2.077(6)	2.030(6)−2.160(6)
Fe(1)···Pd(1)	4.192(1)	4.394(1)	4.437(1)
Pd(1)−P(1)	2.263(1)	2.279(2)	2.245(2)
Pd(1)−P(2)	2.267(1)	2.271(2)	2.244(2)
Pd(1)−O(1)	2.117(3)	2.117(4)	2.100(5)
Pd(1)−O(2)	2.132(3)	2.169(4)	2.090(5)
P−C_{Cp}	1.786(4)−1.794(4)	1.796(6)−1.802(6)	1.813(6)−1.819(6)
P−C_{Ph}	1.804(3)−1.813(3)	1.821(6)−1.834(6)	1.806(7)−1.818(6)
P(3)−O(1A)			1.473(5)
P(3)−O(2)			1.438(5)
P(3)−F			1.511(5)−1.522(5)
	Bond Angles (deg)		
O(1)−Pd(1)−O(2)	87.56(12)	87.01(16)	89.09(20)
P(1)−Pd(1)−P(2)	96.38(4)	101.32(5)	101.78(6)
P(1)−Pd(1)−O(1)	90.27(9)	85.70(12)	83.57(15)
P(2)−Pd(1)−O(2)	85.98(9)	86.16(12)	85.68(17)
P(1)−Pd(1)−O(2)	175.03(9)	170.70(12)	172.47(17)
P(2)−Pd(1)−O(1)	172.96(9)	172.83(12)	174.53(15)
C_{Cp}−P−Pd(1)	113.1(1)−122.7(1)	124.8(1)	125.3(2)
C_{Ph}−P−Pd(1)	105.3(1)−111.7(1)	102.4(1)−110.8(1)	102.8(3)−111.8(2)
C_{Cp}−P−C_{Ph}	103.0(2)−111.1(2)	98.8(3)−113.4(3)	97.7(3)−108.6(3)
C_{Ph}−P−C_{Ph}	106.0(2)−102.1(2)	105.6(3)−106.2(3)	109.1(3)−111.1(3)
O(2)−P(1)−O(1A)			120.2(3)
F(1)−P(3)−F(2)			99.8(4)
	Dihedral and Pseudotorsion Angles (deg)		
P(1)Cp(1)Cp(2)P(2)	28.7(3)	19.0(2)	12.9(2)
C(1)Cp(1)Cp(2)C(2)	30.7(3)	24.6(2)	16.2(2)
O(1)O(2)Pd(1)/Pd(1)P(1)P(2)	5.1(1)	5.9(1)	1.7(1)
Fe(1)P(1)P(2)/Pd(1)P(1)P(2)	38.8(3)	4.6(2)	0.7(2)
α_{Cp}[c]	−5.3(1)	−2.0(1)	−6.9(1)
Δ_P[d]	0.043(2), 0.021(2)	−0.106(2), −0.102(2)	−0.182(3), −0.186(3)
Δ_{Me}[e]		−0.021(5), −0.044(5)	−0.025(5), −0.041(5)

[a] Cp(1) = center of the C(1)−C(5) Cp ligand. [b] Cp(2) = center of the C(6)−C(10) Cp ligand in **2a** and of C(10)−C(14) in **2b** and **10b**·6CH$_2$Cl$_2$. [c] Dihedral angle between the Cp planes. The negative values correspond to the inclination of the Cp rings toward the Pd atom. [d] Deviations of the P atom from the corresponding Cp ring. The negative value corresponds to the deviation in the opposite direction to the Fe atom. [e] Average value of the deviation of the Me group from the corresponding Cp ring. The negative value corresponds to the deviation in the direction opposite to the Fe atom.

Table 6. Methoxycarbonylation of Ethene Catalyzed by Pd(II) Complexes with dppf and dppomf Ligands[a]

entry no.	precursor	amt of TsOH (equiv)	amt of BQ (equiv)	**alt-E-CO** productivity/ TON[b]	TON[b]			
					A	B	C	D
1	**3a**	0	0	110/214	340	406	5	411
2	**3a**	20	0	580/1069	1378	1780	29	1887
3	**3a**	20	80	940/1785	1085	1274	40	1280
4	**5a**	0	0	0	4	0	0	0
5	**5a**	20	0	470/893	1618	2059	41	4457
6	**5a**	20	80	370/714	799	1008	62	1310
7	**3b**	0	0	0	139	0	0	0
8	**3b**	20	0	0	550	0	0	0
9	**3b**	20	80	0	513	0	0	0
10	**5b**	0	0	0	4	0	0	0
11	**5b**	20	0	0	581	48	0	5
12	**5b**	20	80	0	629	0	0	0

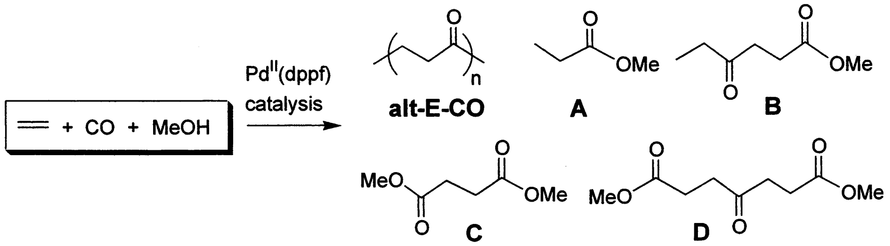
[a] Conditions: catalyst (0.01 mmol); 1:1 CO/C$_2$H$_4$ (600 psi); MeOH (100 mL); 85 °C; 1 h; 1400 rpm. [b] Productivity as grams of product (grams of Pd)$^{-1}$; TON as moles of ethene incorporated (moles of cat)$^{-1}$.

Scheme 7 shows the principal reaction products obtained with the dppf precursors **3a** and **5a**: alternating copolymer (**alt-E-CO**) with n = 7, 8 (^{1}H and ^{13}C NMR spectroscopy), methyl propanoate (**A**), methyl 4-oxohexanoate (**B**), dimethyl succinate (**C**), and dimethyl 4-oxoheptanedioate (**D**). Three other oligomeric diesters with higher molecular weight were detected by GC in low amount (overall 20% of **D**).

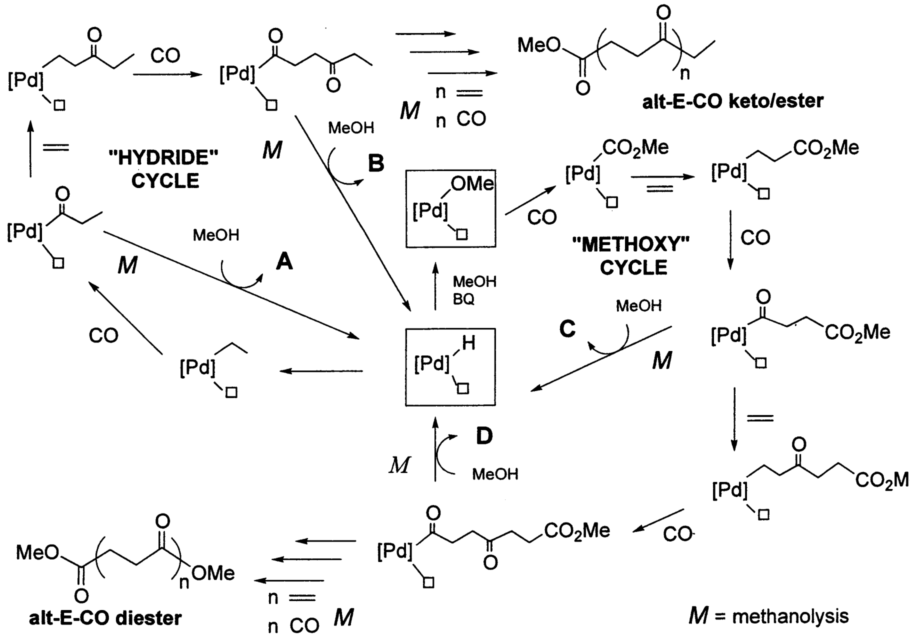
Scheme 8 shows the principal reaction mechanisms reported in the relevant literature for the methoxycarbonylation of ethene, yielding **A**−**D** and **alt-E-CO** products by Pd^{II}−diphosphine catalysis.[12,13,31] The overall mechanism comprises two main cycles catalyzed by hydride and methoxy species, linked to each other by the transformation of Pd−H into Pd−OMe. In principle, there might be other linking reactions, for example the protonolysis of Pd−alkyl to give Pd−OMe, yet the results obtained allow us to rule them out.

The diaquo complex **3a** was active, with no need of added coreagents, but both the selectivity and the overall TON, expressed as moles of ethene consumed per mole of Pd(II) precursor, were low (entry 1). The addition of 20 equiv of TsOH increased the TON values by ca. 5 times without improving the selectivity, however. The coaddition of an organic oxidant in large excess decreased the productivity and slightly favored the production of oligoketones (940 g (g of Pd)$^{-1}$) (entry 3). The absence of dialkyl ketones suggests that the protonolysis of Pd−alkyl is disfavored over CO insertion to give Pd−acyl, while the production of **alt-E-CO** bearing ester and ketone end groups in a ca. 1:1 ratio is consistent with the concomitant occurrence of the “hydride” and “methoxy” cycles (Scheme 8). The relative concentrations of **C** and **D** and the other soluble diesters suggest that the rate of chain transfer by methanolysis prevails over that of propagation, even after the second

Scheme 7



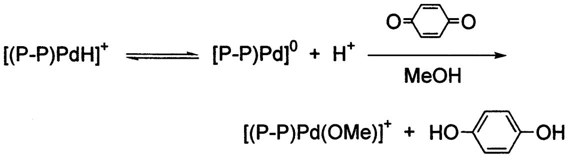
Scheme 8. Principal Reaction Mechanisms for the Methoxycarbonylation of Ethene with Pd(II)−Chelating Diphosphine Precursors Leading to A−D and alt-E-CO Products[a]



[a] [Pd] = [(P−P)Pd]; □ represents either a coligand or a solvent molecule.

insertion of ethene. This confirms that the observed formation of **alt-E-CO** proceeds via two mechanisms.

The promoting effects of TsOH and BQ in olefin carbonylation by Pd(II) catalysis are well-known.[12,13,22a,31] A strong protic acid with a noncoordinating conjugated base is required to remove strongly bound ligands from palladium as well as deliver into the catalysis cycle active Pd(II) that might have been entrapped into less active μ-hydroxo species $[\{Pd(dppf)\}_2(\mu\text{-}OH)_2]^{2+}$, whose formation is unavoidable in reactions carried in reagent grade methanol.[4g,12,13,32,33] The ability of the protic acid to decrease the concentration of binuclear hydroxo species should be particularly important for **3a**, as it contains coordinated water molecules together with tosylate counteranions. The organic oxidant, here BQ, is used in ethene alkoxycarbonylation reactions to oxidize inactive Pd(I) or Pd(0), which may form during the catalysis,[12,13,22a,31,32] to Pd(II) and also transform $(P-P)Pd^{II}-H$ into $(P-P)Pd^{II}-OMe$ (eq 1). In the course of the latter process, protons are consumed. Just this consumption may account for the decreased activity of **3a** in the presence of excess BQ (entry 3), as protons are required to destabilize the μ-OH resting state.



(1)

Unlike the diaquo complex **3a**, the triphenylphosphine complex **5a** was active only in the presence of protic acid, which reflects the good ligating properties of PPh_3 that is most likely removed from the metal as the phosphonium salt to allow for the coordination of the monomers (entries 4 and 5). The use of **5a** in conjunction with 20 equiv of acid gave an overall TON higher than that observed with **3a** under analogous conditions (entry 2 vs entry 5). This surprising effect may be due to the absence of water in the precursor and therefore to a more efficient action of the protic acid.

The major contribution to the TON obtained with **5a**/TsOH was provided by product **D**, which, like **C**, is produced exclusively in the "methoxy cycle". The concomitant addition of BQ and TsOH decreased substantially the overall TON (by ca. 60%), most likely due to consumption of H^+ by BQ and re-formation of PPh_3 in the reaction mixture.

Interestingly, the dppomf precursor **3b** generated a selective catalyst for the production of methyl propanoate (Scheme 9).

Under comparable conditions (entries 7−9), **3b** gave exclusively **A**, the largest TON (550) being obtained in

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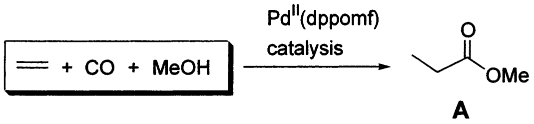
(32) Zuideveld, M. A.; Kamer, P. C. J.; van Leeuwen, P. W. N. M.; Klusener, P. A. A.; Stil, H. A.; Roobeek, C. F. *J. Am. Chem. Soc.* **1998**, *120*, 7977.

(33) Ledford, J.; Shultz, C. S.; Gates, D. P.; White, P. S.; DeSimone, J. M.; Brookhart, M. *Organometallics* **2001**, *20*, 5266.

Scheme 9



the presence of TsOH. As was observed for the dppf precursor, the PPh_3 complex **5b** was inactive in the absence of acid (entry 10), while the best conversion (TON 629) and selectivity (100%) were obtained in the presence of both acid and organic oxidant (entry 12).

The dramatic change in selectivity on going from the dppf precursors to the dppomf analogues is intriguing.

The selectivity in the methoxycarbonylation of ethene by palladium catalysts with phosphine ligands is essentially driven by the nature of the latter.[12−14] At one end, chelating diphosphines, particularly those with PPh_2 end groups and less than four CH_2 spacers, form selective catalysts for the alternating copolymerization leading to polyketones. At the other end, monophosphines give exclusively **A**, irrespective of the phosphorus substituents. In the middle, Pd(II) systems containing chelating diphosphines with more than three carbon spacers or containing alkyl substituents at the phosphorus atoms may appropriately be tuned so as to give various products with low to high chemoselectivity.

The selectivity in **A** obtained with $(L)_2Pd^{II}$ precursors (L = monophosphine) is determined by the occurrence of cis−trans isomerization during the catalysis at the stage in which $Pd-C(O)C_2H_5$ may undergo either methanolysis or ethene insertion.[13] A similar cis−trans isomerization has been also suggested to account for the different selectivity in **A** obtained with 1,2-bis((di-*tert*-butylphosphino)methyl)benzene (99.9%) and 1,2-bis((diphenylphosphino)methyl)benzene (20%).[14] These two chelating ligands differ from each other by the phosphorus substituents but exhibit comparable P−Pd−P bond angles (103.9 and 104.6°).

P−M−P bite angles represent useful parameters to categorize the catalytic activity of metal phosphine complexes.[2b,4f,33] In the present Pd(II) precursors, the dppf and dppomf ligands bear the same aryl substituents, yet they give rise to different bond angles, as determined crystallographically for the derivatives **2a** (96.37(1)°) and **2b** (101.3(1)°). Hence, it is very likely that a substantial contribution to the selectivity exhibited by **3a**,**b** is provided by the respective P−Pd−P bond angles. The bite angles of the archetypal ligand for the selective production of alternating polyketones by Pd(II) catalysis (1,3-bis(diphenylphosphino)propane) generally measure $90 \pm 2°$, whereas those of the ligand 1,4-bis(diphenylphosphino)butane, which gives various esters from methyl propanoate to oligoketones, are in the range 93−97°.[2b,4f,13,14] Therefore, the exclusive formation of methyl propanoate is not unexpected for Pd^{II}−dppomf catalysts, as they show P−Pd−P bond angles as large as 101°.

Conclusions

It has been shown in this article that dppomf and its oxidized form $dppomf^+$ can form stable Pd(II) complexes with primary structures that are similar to those of the parent chelating diphosphine dppf. However, the presence of eight methyl groups in the dppomf induces remarkable changes in the secondary structure of the complexes (P−Pd−P bond angles, dihedral angles between the (P, Fe, P) and (P, Pd, P) planes, deviation of the phosphorus atoms from the planes of the Cp rings). These structural changes and the electronic changes associated with the presence of the methyl groups ultimately contribute to differentiate the chemistry of dppf and dppomf palladium(II) complexes. This effect has been proved in the methoxycarbonylation of ethene, for which dppomf generates selective catalysts for the production of methyl propanoate, while dppf leads to as many as five different products, spanning from methyl propanoate to alternating CO/C_2H_4 copolymer.

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Supporting Information Available: Tables of bond lengths and angles and positional and thermal parameters for compounds **2a**,**b** and **10b**·$6CH_2Cl_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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