Organometallics 1992, *11*, 2212–2220

Fluoride-Induced Reduction of Palladium(II) and Platinum(II) Phosphine Complexes

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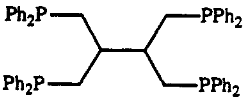
Received March 3, 1992

A novel redox reaction involving fluoride and phosphine complexes of palladium(II) is reported. The scope of this reaction has been investigated using the ligands PPh_3, $Ph_2P(CH_2)_nPPh_2$ (n = 1–4), $Ph_2PCH_2C(CH_3)_2CH_2PPh_2$, Ph_2PCH_3, and $P(CH_2CH_2CN)_3$; several solvents including DMSO, pyridine, acetonitrile, and THF; and either n-$Bu_4NF{\cdot}3H_2O$ or KF/18-crown-6 as the fluoride source. The reduction products are palladium(0) phosphine complexes for which this reaction offers a convenient synthetic route. ^{31}P and ^{19}F NMR spectra permitted identification of the initial oxidation products as difluorophosphoranes (R_3PF_2), which subsequently hydrolyzed, forming phosphine oxides if a hydrated fluoride source is used. Results implicating a fluoride-induced redox reaction in the thermal decomposition of $[(Ph_3P)_3PdCl]BF_4$ to yield $[Pd_3Cl(PPh_2)_2(PPh_3)_3]BF_4$ are also presented. Preliminary results indicate that platinum complexes also undergo this reaction, but nickel complexes yield NiF_2. The X-ray parameters for $Pd(dppp)_2$ (dppp = 1,3-bis(diphenyphosphino)propane) are: monoclinic, space group $C2/c$ (No. 15), a = 18.396 (2) Å, b = 13.290 (1) Å, c = 20.186 (2) Å, β = 109.383 (5)°, and Z = 4.

Introduction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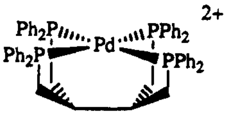
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Recently, we reported[1] the synthesis and some of the coordination chemistry of the new tetratertiary phosphine 1, including unsuccessful attempts to synthesize the monopalladium complex 2. Presumably, the formation of 2 is precluded by steric factors and an unsuitable ligand backbone, incapable of chelating two trans positions. The complexes $[\{Ph_2P(CH_2)_nPPh_2\}_2Pd]^{2+}$ (n = 2–4) are potential models for 2 insofar as they contain four $RPPh_2$ ligands and they possess two six-membered and two seven-membered rings when n = 3 and 4, respectively. Although numerous reports on the chemistry of $[Pd(dppe)_2]^{2+}$ (n = 2) were found,[2] only a brief reference to $[Pd(dppp)_2]Cl_2$ (n = 3) has appeared[3] and $[Pd(dppb)_2]^{2+}$ (n = 4) has not been reported previously. Since we were most interested in the model complexes containing six- and seven-membered chelate rings, we attempted to prepare $[Pd(dppp)_2][BF_4]_2$ by reacting $Pd(BF_4)_2{\cdot}4CH_3CN$ and dppp. As discussed herein, this synthetic approach unexpectedly yielded, as a minor product, the reduced complex $Pd(dppp)_2$ formed via a fluoride-induced redox reaction:

$$3\text{dppp} + \text{Pd}^{2+} + 2\text{F}^- \rightarrow \text{Pd(dppp)}_2 + \text{Ph}_2\text{P(CH}_2)_3\text{PF}_2\text{Ph}_2 \quad (1)$$

Preliminary observations concerning this reaction have been previously communicated.[4] Here we present these and additional results in detail, including the relevance of reaction 1 to the synthesis of the triangular cluster $[Pd_3Cl(PPh_2)_2(PPh_3)_3][BF_4]$ reported by Dixon et al.[5] The molecular structure of $Pd(dppp)_2$ and results concerning attempts to reduce Ni(II) and Pt(II) by this method are also discussed.

Experimental Section

General Procedures. All reactions were performed under an argon atmosphere using standard inert-atmosphere techniques. Tetrahydrofuran, benzene, and diethyl ether were distilled from sodium benzophenone ketyl prior to use. Pyridine, dimethyl sulfoxide, methylene chloride, and acetonitrile were distilled from calcium hydride. The following were prepared as described in the literature: $(Ph_3P)_2PdCl_2$,[6] $(dppp)PdCl_2$,[7] $(dppe)PdCl_2$,[7] $(PhCN)_2PdCl_2$,[8] $[(dppe)_2Pd]Cl_2$,[2a] $[(Ph_3P)_3PdCl]BF_4$,[9] and $Ph_2PCH_2C(CH_3)_2CH_2PPh_2$.[10] $Pd(BF_4)_2{\cdot}4CH_3CN$ was purchased from Strem. All other reagents were purchased from Strem or Aldrich and were used without further purification, except for 18-crown-6, which was purified by a previously reported method[11] and was stored as a THF solution over 4-Å molecular sieves. NMR spectra were recorded on Nicolet NT-300 (^{1}H, ^{13}C), Bruker WM200 (^{13}C, ^{31}P), and Bruker WM300 (^{13}C, ^{19}F, ^{31}P) spectrometers using a deuterated solvent as the internal lock. Chemical shifts are reported relative to TMS (^{1}H, ^{13}C), C_6F_6 (^{19}F), or 85% H_3PO_4 (^{31}P). Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, NY.

Reaction of $(dppp)PdCl_2$ with dppp. A mixture of $(dppp)PdCl_2$ (0.20 g, 0.34 mmol) and dppp (0.14 g, 0.34 mmol) in 5 mL of pyridine and 30 mL of acetonitrile was refluxed for 4 h to yield a yellow solution. The ^{31}P NMR spectrum of this solution showed only broadened resonances for the two starting materials at 11.9 and −16.9 ppm.[2c]

Reaction of dppp with $Pd(BF_4)_2{\cdot}4CH_3CN$. A solution of dppp (0.35 g, 0.86 mmol) in 2 mL of CH_2Cl_2 was added to a yellow solution of $Pd(BF_4)_2{\cdot}4CH_3CN$ (0.19 g, 0.43 mmol) in 20 mL of

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acetonitrile. Within 10 min a cream-colored precipitate began to appear. After the mixture was stirred overnight, the product was isolated by filtration and dried in vacuo providing a 57% yield (0.27 g) based on $[Pd(dppp)_2][BF_4]_2$. The product is poorly soluble in THF, CH_2Cl_2, DMSO, and CH_3CN. ^{31}P NMR (CD_3CN): δ 2.0. CPMAS ^{31}P NMR: δ 1.6. ^1H NMR (CD_3CN): δ 7.45 (m, Ph), 7.28 (m, Ph), 2.55 (m, CH_2), MS (FAB): m/z 930 (M^+). Upon standing overnight, the filtrate yielded yellow crystals of $Pd(dppp)_2$ in approximately 5% yield.

Preparation of $(Ph_2PCH_2C(CH_3)_2CH_2PPh_2)PdCl_2$. A solution of $Ph_2PCH_2(CH_3)_2CH_2PPh_2$ (0.34 g, 0.78 mmol) in 15 mL of benzene was added dropwise to a solution of $(PhCN)_2PdCl_2$ (0.30 g, 0.78 mmol) in 40 mL of benzene. The resulting mixture was stirred overnight. The light tan precipitate was isolated by filtration, rinsed with 10 mL of benzene followed by 10 mL of diethyl ether, and dried in vacuo giving a 95% yield (0.45 g). ^{31}P NMR (DMSO): δ 19.1 (s).

Preparation of $Pd(PPh_3)_4$. Method A. A mixture of $PdCl_2$ (0.11 g, 0.62 mmol) and PPh_3 (0.77 g, 2.9 mmol) was heated to 140 °C in 15 mL of DMSO to give a yellow solution. Heating was discontinued and a solution of n-$Bu_4NF\cdot 3H_2O$ (0.47 g, 1.7 mmol) in 10 mL of DMSO was added to give a dark orange-red solution which rapidly turned bright yellow. The solution was cooled to room temperature with stirring during which time a yellow solid precipitated. Ethanol (20 mL) was added to complete precipitation, and the mixture was stirred for an additional 30 min. The product was isolated by filtration, rinsed with two 10-mL portions of ethanol and one of diethyl ether, and dried in vacuo. Yield: 0.57 g, 80%. Mp: 190–194 °C dec. ^{31}P NMR (CH_2Cl_2): δ 15.5 (br) [lit. δ 15.0 (toluene, 90 °C)].[12] Analysis of the filtrate by ^{31}P NMR spectroscopy revealed the presence of $Ph_3P{=}O$ [δ 29.5 (s)], *trans*-$(Ph_3P)_2Pd(Ph)Cl$ [δ 25.1 (s)], and $[Ph_4P]Cl$ [δ 23.7 (s)], the assignments of which were confirmed by the addition of authentic samples.

Method B. A solution of $PdCl_2$ (0.10 g, 0.56 mmol) and PPh_3 (0.74 g, 2.82 mmol) in 15 mL of DMSO was heated to 140 °C. Anhydrous KF (0.080 g, 1.4 mmol) was added, and the resulting yellow solution was heated at 120 °C for 10 min to dissolve most of the remaining undissolved KF. The solution was cooled to room temperature, yielding a precipitate identified as $Pd(PPh_3)_4$. The product was isolated by filtration, washed with diethyl ether, and dried in vacuo, providing a 54% yield (0.35 g). The ^{31}P NMR spectrum of the filtrate revealed the presence of $Ph_3P{=}O$, $[Ph_4P]Cl$, PPh_3, and a much larger quantity of *trans*-$(Ph_3P)_2Pd(Ph)Cl$ than was observed using method A. Clear crystals of *trans*-$(Ph_3P)_2Pd(Ph)Cl$ were obtained from the filtrate upon standing several days. Mp: 210 °C. ^{31}P NMR (CH_2Cl_2): δ 24.4 (s). ^1H NMR ($CDCl_3$): δ 7.6–7.2 (m, PPh_3), 6.71 (d, $^3J_{HH}$ = 7 Hz, 2 H, ortho Ph), 6.35 (t, $^3J_{HH}$ = 7 Hz, 1 H, para Ph), 6.22 (t, $^3J_{HH}$ = 7 Hz, 2 H, meta Ph).

Preparation of $Pd_2(dppm)_3$. $PdCl_2$ (0.10 g, 0.56 mmol), dppm (0.65 g, 1.7 mmol), and n-$Bu_4NF\cdot 3H_2O$ (0.47 g, 1.5 mmol) were reacted using method A given above to yield an orange-red solid. Yield: 0.33 g, 86%. Mp: 195–215 °C dec. ^{31}P NMR (C_6H_6): δ 14.4 (s).[13] Analysis of the filtrate by ^{31}P NMR spectroscopy revealed the presence of the following: $Ph_2PCH_2P(O)Ph_2$ δ 28.8 (d, $^2J_{PP}$ = 50.5 Hz, $P(O)Ph_2$), –27.0 (d, $^2J_{PP}$ = 50.5 Hz, PPh_2);[14] dppm δ –22.3 (s); $Ph_2PCH_2PF_2Ph_2$ δ –23.9 (dt, $^2J_{PP}$ = 63.9 Hz, $^3J_{PF}$ = 22.5 Hz, PPh_2), –41.9 (td, $^1J_{PF}$ = 643 Hz, $^2J_{PP}$ = 63.9 Hz, PF_2Ph_2).[15] ^{19}F NMR: δ 136.1 (ddt, $^1J_{PF}$ = 644 Hz, $^3J_{PF}$ = 22 Hz, $^3J_{HF}$ = 15 Hz, $Ph_2PCH_2PF_2Ph_2$).

Preparation of $Pd(dppe)_2$. $PdCl_2$ (0.10 g, 0.56 mmol), dppe (0.67 g, 1.7 mmol), and n-$Bu_4NF\cdot 3H_2O$ (0.47 g, 1.5 mmol) were reacted using method A given above to yield the title product. Yield: 0.51 g, 91%. ^{31}P NMR (CH_2Cl_2): δ 30.6. Analysis of the filtrate by ^{31}P NMR spectroscopy revealed the presence of the following: $[Pd(dppe)_2]^{2+}$ δ 58.0 (s);[2c] $Ph_2P(O)CH_2CH_2PPh_2$ δ 32.4 (d, $^3J_{PP}$ = 47.3 Hz, $P(O)Ph_2$), –12.4 (d, $^3J_{PP}$ = 47.3 Hz, PPh_2);[16] $Ph_2PCH_2CH_2PF_2Ph_2$ δ –12.4 (m, PPh_2), –40.5 (td, $^1J_{PF}$ = 644 Hz, $^3J_{PF}$ = 69 Hz, PF_2Ph_2).[15]

Alternatively, $(dppe)PdCl_2$ (0.15 g, 2.6 mmol), dppe (0.21 g, 5.2 mmol), anhydrous KF (0.10 g, 1.7 mmol), and 18-crown-6 (0.10 g) were suspended in a solution of 10 mL of pyridine and 5 mL of THF. This mixture was heated at 100 °C for 2 h. A ^{31}P NMR spectrum of this reaction solution showed only the presence of $Pd(dppe)_2$, $Ph_2PCH_2CH_2P(O)Ph_2$, $Ph_2PCH_2CH_2PF_2Ph_2$, and a trace of unreacted dppe. The difluorophosphorane product accounted for approximately 65% of the total oxidation products.

Preparation of $Pd(dppp)_2$. $PdCl_2$ (0.10 g, 0.56 mmol), dppp (0.70 g, 1.7 mmol), and n-$Bu_4NF\cdot 3H_2O$ (0.47 g, 1.5 mmol) were reacted using method A given above to yield 0.48 g (91%) of the yellow product. ^{31}P NMR (THF): δ 4.2 (s). ^{13}C NMR (CD_2Cl_2): δ 143.0 (m, ipso Ph), 132.8 (m, ortho Ph), 127.8 (bs, meta Ph), 127.6 (s, para Ph), 31.9 (m, CH_2PPh_2), 19.0 (bs, $CH_2CH_2CH_2$). Analysis of the filtrate by ^{31}P NMR spectroscopy revealed the presence of the following: $Ph_2P(O)CH_2CH_2CH_2PPh_2$ δ 31.0 (s, $P(O)Ph_2$), –17.2 (s, PPh_2); $Ph_2PCH_2CH_2CH_2PF_2Ph_2$ δ –17.3 (s, PPh_2), –42.4 (t, $^1J_{PF}$ = 644 Hz, PF_2Ph_2).[15] ^{19}F NMR: δ 125.8 (d, $^1J_{PF}$ = 643 Hz).

Preparation of $Pd\{Ph_2PCH_2C(CH_3)_2CH_2PPh_2\}_2$. $PdCl_2$, (0.10 g, 0.56 mmol), $Ph_2PCH_2C(CH_3)_2CH_2PPh_2$ (0.75 g, 1.7 mmol), and n-$Bu_4NF\cdot 3H_2O$ (0.47 g, 1.5 mmol) were reacted using method A above to yield 0.51 g (91%) of the yellow product. An analytical sample was obtained by recrystallization from 2:1 THF:EtOH. ^{31}P NMR (CH_2Cl_2): δ 1.2 (s). ^{13}C NMR (CD_2Cl_2): δ 144.6 (apparent pentet, separation 6 Hz, ipso Ph), 132.8 (m, ortho Ph), 127.8 (s, meta Ph), 127.4 (s, para Ph), 41.9 (m, CH_2), 36.0 (m, CC_4), 34.6 (m, CH_3). Anal. Calcd for $C_{58}H_{30}P_4Pd\cdot 2CH_3CH_2OH$: C, 68.98; H, 6.72; Pd, 9.86. Found: C, 68.95; H, 6.43; Pd, 9.65. Analysis of the filtrate by ^{31}P NMR spectroscopy revealed the presence of the following: $Ph_2P(O)CH_2C(CH_3)_2CH_2PPh_2$ δ 26.1 (s, $P(O)Ph_2$), 23.3 (s, PPh_2).

Alternatively, $\{Ph_2PCH_2C(CH_3)_2CH_2PPh_2\}PdCl_2$ (0.20 g, 0.32 mmol), $Ph_2PCH_2C(CH_3)_2CH_2PPh_2$ (0.19 g, 0.65 mmol), anhydrous KF (0.12 g, 2.1 mmol), and 18-crown-6 (0.10 g) were suspended in a mixture of 10 mL of pyridine and 5 mL of THF. The mixture was refluxed for 2 h to yield a bright yellow solution containing some undissolved KF. The ^{31}P NMR spectrum of this solution revealed the presence of $Pd\{Ph_2PCH_2C(CH_3)_2CH_2PPh_2\}_2$, $Ph_2PCH_2C(CH_3)_2CH_2P(O)Ph_2$, a trace of $Ph_2P(O)CH_2C(CH_3)_2CH_2P(O)Ph_2$, and unreacted ligand. A singlet at –23.6 ppm (PPh_2) and triplet at –44.4 ppm with $^1J_{PF}$ = 658 Hz (PF_2Ph_2) indicate the presence of the difluorophosphorane $Ph_2PCH_2C(CH_3)_2CH_2PF_2Ph_2$ which accounted for approximately 75% of the oxidation products. Addition of 20 mL of ethanol to this solution resulted in the precipitation of $Pd\{Ph_2PCH_2C(CH_3)_2CH_2PPh_2\}_2$ which was isolated by filtration, washed twice with 5 mL of water followed by 10 mL of ethanol, and dried in vacuo. Yield: 0.23 g, 75%.

Preparation of $Pd(dppb)_2$. $PdCl_2$ (0.10 g, 0.56 mmol), dppb (0.72 g, 1.7 mmol), and n-$Bu_4NF\cdot 3H_2O$ (0.47 g, 1.5 mmol) were reacted using method A to yield 0.35 g (65%) of the yellow product. ^{31}P NMR (CH_2Cl_2): δ 12 (br). Analysis of the filtrate by ^{31}P NMR spectroscopy revealed the presence of the following: $Ph_2P(O)(CH_2)_4PPh_2$ δ 33.7 (s, $P(O)Ph_2$), –15.6 (s, PPh_2); $Ph_2PF_2(CH_2)_4PPh_2$ δ –15.6 (s, PPh_2), –40.8 (t, $^1J_{PF}$ = 639 Hz, PF_2Ph_2).[15]

Preparation of $Pd(PPh_2Me)_4$. $PdCl_2$ (0.10 g, 0.56 mmol), Ph_2PMe (0.57 g, 2.8 mmol), and n-$Bu_4NF\cdot 3H_2O$ (0.47 g, 1.5 mmol) were reacted using method A; however no precipitate formed upon cooling. The ^{31}P NMR spectrum of this solution showed a singlet at 28.7 ppm for $Ph_2P(O)Me$, unidentified resonances at 62.1 and 49.9 ppm, and a large broad resonance centered at –10.4 ppm, assigned to the presence of $Pd(PPh_2Me)_x$ and free Ph_2PMe. Addition of 100 mL of methanol followed by cooling overnight yielded yellow crystals of $Pd(PPh_2Me)_4$. ^{31}P NMR (THF): δ –4.2 (s).

Preparation of $Pd\{P(CH_2CH_2CN)_3\}_x$. $PdCl_2$ (0.10 g, 0.56 mmol), $P(CH_2CH_2CN)_3$ (0.55 g, 2.8 mmol), and n-$Bu_4NF\cdot 3H_2O$ (0.47 g, 1.5 mmol) were reacted using the general procedure given in method A to yield a yellow solution. The ^{31}P NMR spectrum

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of this solution showed a sharp singlet at 44.7 ppm assigned to $(NCCH_2CH_2)_3P{=}O$ and broadened singlets at 9.7 and −23.9 ppm assigned to $Pd\{P(CH_2CH_2CN)_3\}_x$ and an uncoordinated ligand, respectively. The palladium(0) complex was not isolated. Reaction of $PdCl_2$ and $P(CH_2CH_2CN)_3$ under these conditions without the addition of fluoride yields a product, presumably $\{(NCCH_2CH_2)_3P\}_2PdCl_2$, which exhibits a sharp singlet at 16.2 ppm. Phosphine oxide was not produced in the absence of fluoride.

Reaction of PPh_3 with $PdCl_2$ in DMSO. A mixture of $PdCl_2$ (0.10 g, 0.56 mmol), PPh_3 (0.74 g, 2.8 mmol), and water (0.50 g, 27 mmol) in 15 mL of DMSO was heated to 140 °C to give a yellow-orange solution. Upon cooling to room temperature, $(Ph_3P)_2PdCl_2$ precipitated as a poorly soluble yellow solid. The solid was isolated by filtration, washed with diethyl ether, and dried in vacuo. Yield: 0.35 g, 90%. A ^{31}P NMR spectrum of the filtrate showed only the presence of unreacted Ph_3P.

Reaction of dppe with $PdCl_2$ in DMSO. A mixture of $PdCl_2$ (0.10 g, 0.56 mmol) and dppe (0.67 g, 1.7 mmol) in 20 mL of DMSO was heated to 140 °C to give a white mixture. This mixture was cooled to room temperature and stirred for 3 h. $[Pd(dppe)_2]Cl_2$, 0.53 g, 96%, was isolated by filtration, washed with 15 mL of diethyl ether, and dried in vacuo. ^{31}P NMR (CH_3CN): δ 58.1 (s).

Competition Experiment between PPh_3 and dppe. A mixture of $PdCl_2$ (0.10 g, 0.56 mmol), dppe (0.67 g, 1.7 mmol), and PPh_3 (0.75 g, 2.9 mmol) in 15 mL of DMSO was heated to 130 °C. A solution of n-$Bu_4NF{\cdot}3H_2O$ (0.47 g, 1.5 mmol) in 5 mL of DMSO was added to give a yellow solution. After cooling to room temperature, 15 mL of ethanol was added to complete the precipitation. $Pd(dppe)_2$ (0.37 g, 73%) was isolated by filtration, washed with ethanol, and dried in vacuo. A ^{31}P NMR spectrum of the supernatant before the addition of ethanol indicated the presence of $Pd(dppe)_2$, $Ph_2P(O)CH_2CH_2PPh_2$, $Ph_2PCH_2CH_2PF_2Ph_2$, and PPh_3. There was no evidence for the formation of $Ph_3P{=}O$ or Ph_3PF_2.

Reaction of $(dppp)NiBr_2$ with n-$Bu_4NF{\cdot}3H_2O$. A mixture of $NiBr_2{\cdot}$glyme (0.15 g, 0.49 mmol) and dppp (0.60 g, 1.5 mmol) in 15 mL of acetonitrile was heated to 80 °C to give a red-violet solution containing $(dppp)NiBr_2$. Addition of a solution of n-$Bu_4NF{\cdot}3H_2O$ (0.38 g, 1.2 mmol) in 5 mL of acetonitrile resulted in the immediate formation of a yellow solution. Heat was removed, and upon cooling, a small quantity of yellow solid precipitated.

Preparation of $Pt(dppe)_2$. A mixture of $PtCl_2$ (0.15 g, 0.56 mmol) and dppe (0.67 g, 1.7 mmol) in 15 mL of DMSO was heated to 130 °C to yield a milky white mixture, presumably due to the formation of $[Pt(dppe)_2]Cl_2$. A solution of n-$Bu_4NF{\cdot}3H_2O$ (0.47 g, 1.5 mmol) in 5 mL of DMSO was added to this hot mixture to form a bright yellow solution which still contained some white precipitate. The heat was removed and this mixture was stirred for 2 h. A ^{31}P NMR spectrum of the supernatant exhibited resonances of approximately equal intensity at 49.1 ppm with $^1J_{Pt-P}$ = 2338 Hz and 30.3 ppm with $^1J_{Pt-P}$ = 3733 Hz assigned to $[Pt(dppe)_2]Cl_2$[17] and $Pt(dppe)_2$, respectively. A large quantity of unreacted dppe as well as a small quantity of $Ph_2PCH_2CH_2P(O)Ph_2$ were also identified. Numerous smaller unidentified resonances were also present between 55 and 42 ppm.

Preparation of $Pt(PPh_3)_4$. PPh_3 (0.32 g, 1.2 mmol) and $(Ph_3P)_2PtCl_2$ (0.48 g, 0.61 mmol) were suspended in 5 mL of THF. To this mixture was added n-$Bu_4NF{\cdot}3H_2O$ (0.48 g, 1.5 mmol) in 5 mL of THF to yield a yellow solution in which some unreacted $(Ph_3P)_2PtCl_2$ remained. This mixture was stirred for 30 min. The ^{31}P NMR spectrum of the supernatant showed the presence of $Ph_3P{=}O$ and a broad resonance at 45 ppm for $Pt(PPh_3)_x$. Two 2-mL aliquots of this supernatant were removed and reacted with methyl iodide in the first case and dppe in the second. The ^{31}P NMR spectrum of the methyl iodide reaction sample exhibited resonances at 28.3 ($^1J_{Pt-P}$ = 3077 Hz), 25.4, and 22.8 ppm assigned to *trans*-$(Ph_3P)_2Pt(Me)I$, $Ph_3P{=}O$, and $[Ph_3PMe]I$, respectively. The ^{31}P NMR spectrum of the dppe reaction solution exhibited resonances at 30.9 ($^1J_{Pt-P}$ = 3731 Hz), 25.3, −4.8, and −12.2 ppm assigned to $Pt(dppe)_2$, $Ph_3P{=}O$, Ph_3P, and dppe, respectively.[18]

Reduction of $[(Ph_3P)_3PdCl]BF_4$. To a suspension of $[(Ph_3P)_3PdCl]BF_4$ (0.20 g, 0.19 mmol) in 10 mL of THF was added a solution of n-$Bu_4NF{\cdot}3H_2O$ (0.16 g, 0.49 mmol) in 5 mL of THF to yield a bright yellow solution within 15 s. The ^{31}P NMR spectrum of this solution exhibited a singlet at 24.5 ppm assigned to $Ph_3P{=}O$ and a broadened singlet at 22.5 ppm assigned to $Pd(PPh_3)_2$. Three aliquots of 2 mL each were removed and treated with PPh_3, maleic anhydride, and iodobenzene, respectively. The PPh_3 reaction sample exhibited a broad resonance which shifted upfield with increasing concentration of PPh_3, as expected for the palladium(0) complex $Pd(PPh_3)_x$.[12] The ^{31}P NMR spectrum of the maleic anhydride reaction sample exhibited a sharp singlet at 27.5 ppm assigned to $(Ph_3P)_2Pd(C_4H_2O_3)$, and the iodobenzene reaction sample exhibited a sharp singlet at 24.5 ppm assigned to *trans*-$(Ph_3P)_2Pd(Ph)I$.[19]

Alternatively, $[(Ph_3P)_3PdCl]BF_4$ (0.285 g, 0.281 mmol) and KF (0.090 g, 1.6 mmol) were suspended in 5 mL of THF. A solution of 18-crown-6 in THF (5.5 mL, 0.20 M) was added, and the mixture was stirred for 1 h to give a yellow solution which contained some unreacted starting material. This mixture was heated at 60 °C for 15 min to further the reaction. The ^{31}P NMR spectrum of the resulting solution exhibited singlets at 24.2 and 21.7 ppm and a triplet at −56.2 ppm ($^1J_{PF}$ = 669 Hz) assigned to $Ph_3P{=}O$, $Pd(PPh_3)_2$, and Ph_3PF_2,[20] respectively.

Reaction of $[(Ph_3P)_3PdCl]BF_4$ with KHF_2. A mixture of $[(Ph_3P)_3PdCl]BF_4$ (0.30 g, 0.29 mmol), KHF_2 (0.54 g, 0.69 mmol), and 18-crown-6 (5.5 mL, 0.20 M) in 15 mL of THF was stirred at room temperature to yield a light tan colored suspension. A ^{31}P NMR spectrum of the supernatant exhibited a singlet at 24.2 ppm and a broad resonance at 16.2 ppm assigned to $Ph_3P{=}O$ and $Pd(PPh_3)_x$, respectively. A small triplet assigned to Ph_3PF_2 was present at −56.0 ppm. There were additional unassigned resonances at 29.1 and 24.7 ppm. Prolonged stirring resulted in a deep brown decomposition mixture. Analogous results were obtained when (dimethylamino)pyridine (DMAP) was added in an effort to complex the HF present.

Synthesis of $[Pd_3Cl(PPh_2)_2(PPh_3)_3][BF_4]$. As described by Dixon et al.,[5] $[(Ph_3P)_3PdCl]BF_4$ (0.500 g, mmol) was suspended in 10 mL of THF in a thick-walled Pyrex tube equipped with a small stirring bar and the tube was then sealed in vacuo. This tube was then placed in an oil bath and heated at 125 °C for 5 days to yield a deep red solution which contained a yellow precipitate. After the reaction mixture was allowed to cool several hours at room temperature, the reaction tube was opened under nitrogen and the mixture was filtered. The pale yellow solid obtained was identified as $(Ph_3P)_2PdCl_2$. A ^{31}P NMR spectrum of the filtrate exhibited resonances consistent with the presence of $[Pd_3Cl(PPh_2)_2(PPh_3)_3][BF_4]$, $[Ph_4P]^+$, and $Ph_3P{=}O$, as described by Dixon, as well as a broad resonance at 6 ppm. The resonance at 6 ppm was identified as $Pd(PPh_3)_x$ by the addition of iodobenzene to yield PPh_3 (−4.7 ppm) and *trans*-$(Ph_3P)_2Pd(Ph)I$ (25.2 ppm). No Ph_3PF_2 was observed in the filtrate. The filtrate was cooled overnight in the freezer to yield a small quantity of red-orange crystals of $[Pd_3Cl(PPh_2)_2(PPh_3)_3][BF_4]$.

Preparation of $[(Ph_3P)_3PdCl][OSO_2CF_3]$. As described for the synthesis of $[(Ph_3P)_3PdCl]BF_4$,[9] $(Ph_3P)_2PdCl_2$ (0.500 g, 0.712 mmol) and $AgOSO_2CF_3$ (0.183 g, 0.712 mmol) were stirred in 50 mL of nitromethane for 2 h. The AgCl which precipitated was removed by filtration through Celite. The yellow filtrate was added to diethyl ether to precipitate a pale yellow solid, presumably $[(Ph_3P)_4Pd_2(\mu\text{-}Cl)_2][OSO_2CF_3]_2$. A ^{31}P NMR spectrum of a CH_3NO_2 solution of this solid exhibits a singlet at 23.9 ppm as the major resonance and two much smaller, slightly broadened resonances at 35 and 34.5 ppm.

This yellow solid was redissolved in 25 mL of nitromethane and Ph_3P (0.500 g, 1.91 mmol) was added. The volume of the resulting yellow solution was reduced to 10 mL in vacuo and the pale yellow solid was isolated by filtration. Yield: 0.54 g, 77%. ^{31}P NMR (CH_3NO_2): δ 34.2 (t, $^2J_{PP}$ = 16 Hz), 30.8 (d, $^2J_{PP}$ = 16 Hz).

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Table I. Crystallographic Data for Pd(dppp)$_2$

formula	$PdP_4C_{54}H_{52}$
fw	931.31
space group	$C2/c$ (No. 15)
a, Å	18.396 (2)
b, Å	13.290 (1)
c, Å	20.186 (2)
β, deg	109.383 (5)
V, Å^3	4655 (1)
Z	4
d_{calc}, g/cm^3	1.329
cryst size, mm	0.35 × 0.30 × 0.48
μ(Mo Kα), cm^{-1}	5.621
data colln instrument	Enraf-Nonius CAD4
radiation (monochromated in incident beam)	Mo Kα (λ = 0.71073 Å)
no. of orientation reflns; 2θ range, deg	25; 20.5–35.3
temp, °C	22 ± 1
scan method	θ–2θ
data colln range (2θ), deg	4–55
total no. of unique data	5337
no. of data with $F_o^2 > 3\sigma(F_o^2)$	4431
no. of params refined	268
R^a	0.0225
$R_w{}^b$	0.0341
quality-of-fit indicator^c	1.11
largest shift/esd, final cycle	0.01
largest peak, e/Å^3	0.162

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. ^{c} Quality-of-fit $= [\sum w(|F_o| - |F_c|)^2/(N_{obs} - N_{parameters})]^{1/2}$.

Attempted Synthesis of [$Pd_3Cl(PPh_2)_2(PPh_3)_3$][OSO_2CF_3]. As described for the cluster synthesis above, [$(Ph_3P)_3PdCl$][OSO_2CF_3] (0.450 g, 0.418 mmol) in 10 mL of THF was sealed in a thick-walled Pyrex tube and heated at 125 °C for 7 days. The mixture remained yellow throughout this period and the supernatant became only lightly brown in color. The reaction mixture was filtered to yield 0.33 g (97%) of a pale yellow solid which was rinsed with 10 mL of THF and dried in vacuo. This solid was identified as [$(Ph_3P)_2Pd(\mu$-$Cl)]_2[OSO_2CF_3]_2$ by a sharp singlet at 23.1 ppm and two smaller broadened resonances at 34.8 and 33.0 ppm in the ^{31}P NMR spectrum of a CH_2Cl_2/CH_3CN solution of this compound. Addition of PPh_3 to this solution yielded a clean conversion to [$(Ph_3P)_3PdCl$][OSO_2CF_3]. The ^{31}P NMR spectrum of the reaction filtrate exhibited resonances for [$(Ph_3P)_3PdCl$][OSO_2CF_3], PPh_3, and a trace of $Ph_3P{=}O$ and small unidentified resonances at 25.0 and 24.3 ppm.

Crystal and Molecular Structure of Pd(dppp)$_2$. A yellow crystal of the title compound was mounted on a glass fiber in a random orientation. The cell constants were determined from a list of reflections found by an automated search routine. Pertinent data collection and reduction information are given in Table I.

A total of 10317 reflections were collected in the $\pm h,+k,\pm l$ hemisphere, of which 5337 were unique and not systematically absent. The agreement factor for the averaging of 8526 observed reflections was 1.6% based on intensity and 1.2% based on F_o. The intensities of three standards, checked hourly over the course of the data collection, indicated only random variations within the errors of the measurement. Lorentz and polarization corrections were applied and an absorption correction based on a series of ψ-scans was made.

Table II. Selected Bond Distances (Å) and Angles (deg) in Pd(dppp)$_2$

	Distances		
Pd–P(1)	2.3299 (4)	Pd–P(2)	2.3314 (4)
	Angles		
P(1)–Pd–P(1)′	121.54 (2)	P(1)–Pd–P(2)′	116.69 (1)
P(1)–Pd–P(2)	97.60 (1)	P(2)–Pd–P(2)′	106.92 (2)

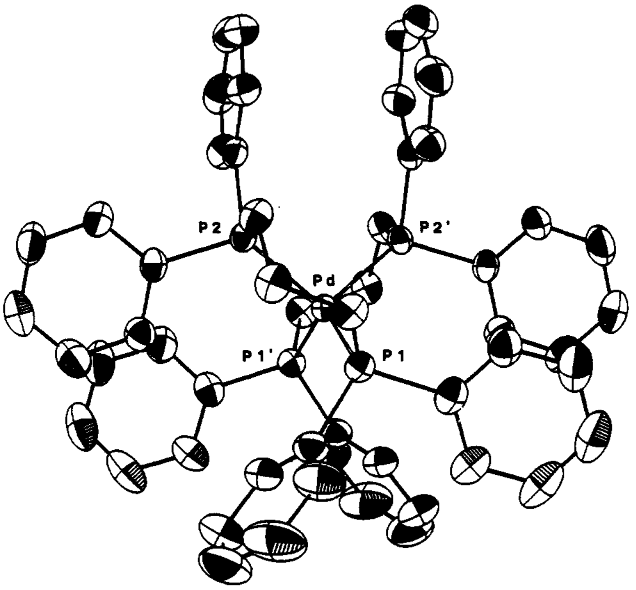

Figure 1. ORTEP drawing of Pd(dppp)$_2$. Thermal ellipsoids are drawn at the 50% probability level.

The systematic absences indicated the space group to be either $C2/c$ (No. 15) or Cc (No. 9), so direct methods were used to give solutions in both choices.[21] Only the centric group ($C2/c$) gave a reasonable solution, and this choice was verified by the final successful refinement of the structure. The positions of all 30 unique non-hydrogen atoms were taken from the direct methods E map. In the final stages of refinement, all non-hydrogen atoms were given anisotropic temperature factors, and all expected hydrogen atoms were placed in calculated positions and used for the calculation of structure factors only. The final cycle of refinement[22] included 268 variable parameters and converged with unweighted and weighted agreement factors of 0.0225 and 0.0341. The standard deviation of an observation of unit weight was 1.11. The largest positive peak in the final difference Fourier had a height of 0.162 e/Å^3. All calculations were performed on a Digital Equipment Corp. MicroVAX II computer using the CAD4/SDP package.[23]

Results and Discussion

As stated in the Introduction, we were initially interested in preparing the cation [$Pd(dppp)_2$]$^{2+}$. Westland[2a] previously reported that the dppe analogue [$Pd(dppe)_2$]Cl_2 is conveniently prepared by reaction of (dppe)$PdCl_2$ and dppe in hot DMF. Gray et al. have noted[3] the formation of [$Pd(dppp)_2$]Cl_2 during the photolysis of $Pd(dppp)_2$ in 5% CH_2Cl_2/THF, but no data were reported to support this assignment. We attempted to prepare this complex by refluxing solutions of (dppp)$PdCl_2$ and dppp in pyridine/acetonitrile. This route, however, does not result in chloride displacement to yield [$Pd(dppp)_2$]Cl_2. The ^{31}P NMR spectrum of this reaction solution exhibited resonances for the two starting materials only, although these resonances were somewhat broadened. A noncoordinating anion was thus employed. Reaction of 2 equiv of dppp with $Pd(BF_4)_2\cdot4CH_3CN$ yields [$Pd(dppp)_2$][BF_4]$_2$ as a creamy white solid which is insoluble in diethyl ether, toluene, and methylene chloride, but is soluble in warm DMSO, DMF, methanol, and acetonitrile.

$$Pd(BF_4)_2\cdot4CH_3CN + 2dppp \rightarrow [Pd(dppp)_2][BF_4]_2 + \text{yellow crystals} \quad (2)$$

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(23) *Enraf-Nonius Structure Determination Package*; Enraf-Nonius: Delft, Holland.

Palladium Reduction Product. The filtrate of reaction 2 deposited yellow crystals upon standing overnight. These crystals were highly soluble in THF and benzene, and the solutions exhibited a single ^{31}P NMR resonance at 4.2 ppm. The presence of at least one dppp ligand was confirmed by ^{1}H NMR spectroscopy. To our surprise, these physical and spectroscopic characteristics matched those for the zerovalent complex $Pd(dppp)_2$. This assignment was confirmed by X-ray crystallography. Selected bond distances and angles are given in Table II. The ORTEP drawing of the molecule is given in Figure 1. The $Pd(dppp)_2$ molecule is centrosymmetric and isomorphous with that recently reported for the platinum analogue $Pt(dppp)_2$.[24] The P—Pd distances of 2.3299 (4) and 2.3314 (4) Å fall in the range 2.27–2.32 Å previously established by the molecular structures of $Pd[P(C{\equiv}CPh)_3]_4$,[25] $Pd(PPh_3)_3$,[26] $Pd(PPhBu_2)_2$,[27] and $Pd(PCy_3)_2$.[28] The longer P—Pd distances[29] of 2.43–2.46 Å for $Pd(PPh_3)_4$ presumably arise from the steric bulk of the four phosphine ligands.

The formation of $Pd(dppp)_2$ as a side product in the reaction of dppp and $Pd(BF_4)_2{\cdot}4CH_3CN$ was quite puzzling since typical routes to zerovalent palladium phosphine complexes involve the reduction of Pd(II) phosphine complexes with $NaBH_4$,[30,31] hydrazine,[32,33] or KOH/phosphine.[34,35] No literature reports were found which explained our result. The only component of this system which we envisioned as potentially noninnocent was tetrafluoroborate, which has previously been shown to be a suitable fluoride source for transition-metal complexes.[36,37] A survey of the literature revealed that the role fluoride might play in the chemistry of palladium(II) phosphine complexes has been scantily investigated.[38] Only three palladium(II) phosphine complexes have been reported to contain a Pd–F bond. Of these, both $[Pd_2(\mu\text{-}F)_2(PPh_3)_4]^{2+}$ and $(Ph_3P)_2Pd(H)(F)$ were characterized by elemental analysis only.[39,40] No spectroscopic data were provided to verify these assignments. Dixon et al. supplied ^{19}F NMR spectroscopic evidence for the formation of $[(Et_3P)_3PdF]BF_4$ via reaction 3, but this complex was evidently not stable enough to allow isolation.[41] Amazingly no further evidence has been presented to substantiate the existence of a stable Pd–F bond in palladium(II) phosphine complexes, even though complexes of the type $(R_3P)_2PdX_2$ have been well studied for X = Cl, Br, and I.

$$[(Et_3P)_3PdCl][BF_4] + AgF \xrightarrow[-AgCl]{acetone} [(Et_3P)_3PdF][BF_4] \qquad (3)$$

Taking into account this lack of a stable Pd–F bond in palladium(II) phosphine complexes, the high P–F bond strength,[42] and the unexpected formation of $Pd(dppp)_2$ in reaction 2, we added fluoride to solutions of palladium(II) phosphine complexes, anticipating that a redox reaction might occur. Addition of 2.5 equiv of $n\text{-}Bu_4NF{\cdot}3H_2O$ to a hot (130 °C) DMSO solution of $PdCl_2$ and 5 equiv of a monodentate or 3 equiv of a bidentate phosphine resulted in an immediate red-orange solution which rapidly turned yellow. Upon cooling, the zerovalent palladium complexes precipitated as yellow solids in yields of 70–90%. This method has been applied to the synthesis of the known complexes $Pd(PPh_3)_4$,[32] $Pd(PPh_2Me)_4$,[43] $Pd_2(dppm)_3$,[33] $Pd(dppe)_2$,[30] $Pd(dppp)_2$,[31,34] and $Pd(dppb)_2$[44] and also the new complex $Pd\{Ph_2PCH_2C(CH_3)_2CH_2PPh_2\}_2$. The conditions employed were based on those described for the synthesis of $Pd(PPh_3)_4$ with the exception that $n\text{-}Bu_4NF{\cdot}3H_2O$ was substituted for hydrazine.[32] The high temperature is required to initially dissolve the $PdCl_2$ and then to keep the resulting palladium(II) complex in solution. DMSO is a convenient solvent since the palladium(0) complexes generally precipitate upon cooling. When $P(CH_2CH_2CN)_3$ was employed in this reaction, reduction of palladium(II) to palladium(0) was signalled by ^{31}P NMR spectroscopy which revealed the presence of phosphine oxide at 44.7 ppm and a broad resonance at 9.7 ppm consistent with a PdL_x species. Complexes of the type PdL_4 are known to exhibit broad resonances in their ^{31}P NMR spectra for monodentate ligands L because of facile ligand dissociation in solution yielding PdL_3 and PdL_4 complexes and free phosphine.[45] The palladium(II) complex $Cl_2Pd\{P(CH_2CH_2CN)_3\}_2$ exhibits a sharp resonance at 16.2 ppm in the presence of excess phosphine. The corresponding palladium(0) complex was not isolated.

Most of these reactions are remarkably clean, as indicated by ^{31}P NMR spectroscopy. The reduction of $PdCl_2$ in the presence of PPh_3, however, leads to the formation of a small quantity of *trans*-$(Ph_3P)_2Pd(Ph)Cl$. When the less soluble KF is utilized as the fluoride source for this reaction, the yield of $Pd(PPh_3)_4$ drops from 80% to 54% as the amount of *trans*-$(Ph_3P)_2Pd(Ph)Cl$ identified in the filtrate increases. Allowing the filtrate to stand at room temperature resulted in the crystallization of *trans*-$(Ph_3P)_2Pd(Ph)Cl$ which was characterized by comparison of its ^{31}P and ^{1}H NMR spectral data to those of an authentic sample.[46,47] A ^{31}P NMR spectrum of the reaction filtrate also indicated the presence of $[Ph_4P]^+$ by comparison to a known sample, as well as other resonances. The decrease in yield using KF and the increase in formation of *trans*-$(Ph_3P)_2Pd(Ph)Cl$ is readily explained by a side reaction between the palladium(II) starting material and the $Pd(PPh_3)_4$ product, as shown in reaction 4. This reaction was reported by Coulson[48] to occur under con-

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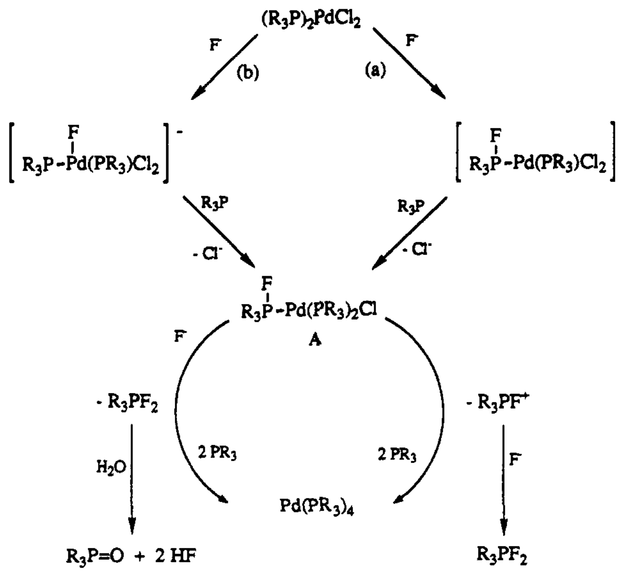
$$6Pd(PPh_3)_4 + 7PdCl_2 \xrightarrow[130\ ^\circ C]{DMSO} 3(Ph_3P)_2PdCl_2 + 4\mathit{trans}\text{-}(Ph_3P)_2Pd(Ph)Cl + 2[Pd_3Cl(PPh_2)_2(PPh_3)_3]Cl \qquad (4)$$

ditions very similar to those employed here, wherein the high temperature is necessary to induce P–C bond cleavage and form the diphenylphosphido bridges of the trinuclear cluster. When the less soluble KF is utilized in our reaction, the starting palladium(II) is consumed at a slower rate than with n-$Bu_4NF{\cdot}3H_2O$, thus allowing this side reaction to become more important.

Phosphorus Oxidation Product. Analysis of the filtrates of these redox reactions by ^{31}P NMR spectroscopy yielded evidence for the formation of phosphine oxides and difluorophosphoranes. For dppm for example, doublets at 28.8 and −27.1 ppm with $^2J_{PP}$ = 50.5 Hz indicate the presence of $Ph_2PCH_2P(O)Ph_2$ by comparison to the known literature values.[14] The presence of the phosphine monoxides, but not the dioxides, was observed in the reactions of all the bidentate ligands employed. The difluorophosphorane products were readily recognizable in the ^{31}P NMR spectra of these filtrates by their large $^1J_{PF}$ values of 639–657 Hz. Again using dppm as an example, $Ph_2PCH_2PF_2Ph_2$ was identified by a doublet of triplets at −23.9 ppm with $^2J_{PP}$ = 63.9 Hz and $^3J_{PF}$ = 22.5 Hz and a triplet of doublets at −41.9 ppm with $^1J_{PF}$ = 643 Hz and $^2J_{PP}$ = 63.9 Hz. The ^{19}F NMR spectra of this filtrate showed a doublet of doublet of triplets at 136.1 ppm with $^1J_{PF}$ = 643 Hz, $^3J_{PF}$ = 22.5 Hz, and $^3J_{HF}$ = 15 Hz. These values are consistent with those previously reported for $Ph_2PCH_2PF_2PPh_2$.[15] In some cases the resonances of the initially formed difluorophosphorane products were of low intensity, presumably due to hydrolysis. Hydrolysis results from water introduced with the hydrated fluoride source, yielding phosphine oxide products. If this redox reaction is carried out using an anhydrous fluoride source, the difluorophosphorane becomes the major oxidation product at the expense of the phosphine oxide product. Addition of water to such a filtrate results in hydrolysis of the difluorophosphorane to give clean conversion to the phosphine oxide. For example, using anhydrous KF as the fluoride source with 18-crown-6 to increase its solubility, the reaction of $\{Ph_2PCH_2C(CH_3)_2CH_2PPh_2\}PdCl_2$ with 2 equiv of $Ph_2PCH_2C(CH_3)_2CH_2PPh_2$ in THF/pyridine at 100 °C yields a yellow solution with some undissolved KF. ^{31}P NMR spectroscopy indicated a clean reaction with only $Pd\{Ph_2PCH_2C(CH_3)_2CH_2PPh_2\}_2$, $Ph_2PCH_2C(CH_3)_2CH_2PF_2Ph_2$, and a trace of $Ph_2PCH_2C(CH_3)_2CH_2P(O)Ph_2$ present. Addition of ethanol resulted in the precipitation of $Pd\{Ph_2PCH_2C(CH_3)_2CH_2PPh_2\}_2$ which was isolated in 75% yield.

Reaction Pathways for the Palladium Reduction. Plausible reaction pathways are illustrated in Scheme I. Nucleophilic attack of fluoride on a coordinated phosphine, path a, or prior coordination of fluoride to palladium followed by a rapid migration to phosphorus, path b, could generate intermediate A. Although we have no direct evidence for the formation of A, Ebsworth et al. have reported[49] the synthesis and molecular structure of $(Et_3P)_2IrCl_2(CO)(PF_4)$ which contains a pentacoordinate phosphorus bound to iridium. This complex reacts with 2 equiv of fluoride to cleave the Ir–P bond generating PF_6^- and presumably $(Et_3P)_2Ir(CO)Cl$. Similarly, A may react with a second equivalent of fluoride, again either by nucleophilic attack on phosphorus or by prior coordination to palladium, followed by fluoride migration to phosphorus, with the transfer of two electrons from phosphorus to palladium to yield a difluorophosphorane and a palladium(0) complex. Alternatively, A may undergo a two-electron transfer to yield a fluorophosphonium cation and the palladium(0) complex. We have no evidence for the formation of a fluorophosphonium cation. The synthesis of the fluorophosphonium cation $[Ph_3PF]^+$ via fluoride abstraction from Ph_3PF_2 has been reported, however.[50] A fluorophosphonium cation produced in our system would rapidly react with fluoride or water to yield a difluorophosphorane or phosphine oxide, respectively.

Scheme I



Previously reported $KOH/EtOH/PPh_3$ reductions proceed by two pathways, the first involving ethanol as the reducing agent to yield acetaldehyde while in the second PPh_3 is the reducing agent resulting in the formation of $Ph_3P{=}O$.[35] Relevant here is the latter pathway, which presumably occurs via prior coordination of OH^- or EtO^- to palladium, followed by elimination of $Ph_3P{=}O$ to form $(Ph_3P)_2Pd(H)Cl$. In the presence of base and PPh_3 the intermediate palladium hydride complex eliminates HCl to yield $(Ph_3P)_4Pd$. This may lend credence in the present case to pathway b involving prior coordination of fluoride to palladium, followed by the elimination of difluorophosphorane.

Although the major pathways utilized in Scheme I are presently uncertain, several conclusions concerning the course of this reaction can be formulated from our results. First, reduction of palladium(II) phosphine complexes under the conditions employed here does not occur in the absence of fluoride. Reactions of $PdCl_2$ and PPh_3 or dppe in the presence of added water, but in the absence of fluoride, yield only $(Ph_3P)_2PdCl_2$ and $[Pd(dppe)_2]Cl_2$, respectively. The necessity of adventitious water has been reported for the reduction of $Pd(acac)_2$ in the presence of excess PPh_3.[51] The successful use of anhydrous fluoride sources in our work seems to rule out the necessity of water in our reaction system, although we always observed some phosphine oxide formation and cannot yet claim to have achieved rigorously anhydrous conditions. The necessity of fluoride has also been demonstrated by the spectroscopic

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identification of difluorophosphorane products. The quantity of the difluorophosphorane product observed in each reaction increases sharply at the expense of the phosphine oxide when anhydrous conditions are approached. Thus, the first oxidation product formed must be the difluorophosphorane, with formation of the phosphine oxide product resulting from hydrolysis. Second, the reducing agent in this redox reaction is a *coordinated* phosphine which provides two electrons to the palladium. The necessity of oxidizing only one coordinated phosphine per palladium explains why only one of the two phosphine groups in 1 equiv of bidentate ligand becomes oxidized to give mono(difluorophosphorane) and phosphine monoxide products when a slight excess of a chelating ligand is used. That the phosphine which becomes oxidized must be coordinated to the palladium was demonstrated with a competition experiment. A heated solution of $PdCl_2$ and 5 equiv of PPh_3 and 3 equiv of dppe in DMSO yielded a white mixture containing $[Pd(dppe)_2]Cl_2$ as expected. Addition of n-$Bu_4NF{\cdot}3H_2O$ resulted in the usual redox reaction with $Pd(dppe)_2$ being the isolated reduction product. Analysis of the filtrate by ^{31}P NMR spectroscopy revealed the oxidation products to be $Ph_2PCH_2CH_2P(O)Ph_2$ and $Ph_2PCH_2CH_2PF_2Ph_2$ only. No $Ph_3P{=}O$ or Ph_3PF_2 was observed, confirming that a coordinated phosphine became oxidized. Third, in some cases where the starting palladium complex is not soluble in the solvent employed, 2.5 equiv of fluoride has not been sufficient to achieve complete conversion to the palladium(0) complex. For example, when a mixture of $(Ph_3P)_2PdCl_2$ or $[Pd(dppe)_2]Cl_2$ suspended in THF was treated with the appropriate phosphine and 2.5 equiv of n-$Bu_4NF{\cdot}3H_2O$ at room temperature, only approximately 50–75% of the starting material reacted. The reaction proceeded to completion, however, when additional fluoride was subsequently added.

According to Scheme I, fluoride could theoretically act as a catalyst for this redox reaction since, in the presence of water, the difluorophosphorane product hydrolyzes to give 2 equiv of HF. However, HF is known to react with free fluoride to form HF_2^- and other stable polyhydrogen fluorides.[52] Attempts to reduce palladium(II) phosphine complexes with KHF_2 at room temperature, even in the presence of a base such as (dimethylamino)pyridine, yielded very little reduction and considerable decomposition. Presumably, the incomplete reduction observed in the examples mentioned above arises from the slower rates of the redox reaction due to the insolubility of the starting complex, allowing the HF produced via hydrolysis to scavenge remaining fluoride to form HF_2^-; thus shutting down the reaction.

Except for our preliminary communication[4] of the present work, the fluoride-induced reaction described herein has not been previously reported. The only report of a similar reaction involved the preparation of difluorophosphoranes by reacting phosphines with the strong fluorinating reagent MoF_6.[53] The somewhat related redox reactions involving the formation of platinum(0) phosphine complexes and dichlorotrifluorophosphorane at high temperatures and pressures, as shown in reaction 5, have also been reported.[54]

$$PdCl_2 + 5PF_3 \xrightarrow[100\ °C,\ 22\ h]{200\ atm} Pd(PF_3)_4 + PF_3Cl_2 \qquad (5)$$

The driving force in our redox reaction, in addition to facile accessibility to both the +2 and 0 oxidation states of palladium and the proposed weak affinity of palladium for fluoride,[35] is undoubtedly the formation of two strong P–F bonds in the difluorophosphorane product. Comparison of bond enthalpy terms for P–X bonds for the halogens reveals a decrease down the periodic table.[42] For trivalent phosphorus, PX_3 bond enthalpy values of 490, 319, 264, and 184 kJ/mol have been reported for X = F, Cl, Br, and I, respectively. For pentavalent phosphorus, the bond enthalpy terms for PX_5 are approximately 465 and 257 kJ/mol for X = F and Cl, respectively. This large difference in P–X bond enthalpies for fluorine compared to the other halogens may explain why this redox reaction occurs only for fluoride. The ease of this redox reaction may also rationalize why so little data have been reported for a stable Pd–F bond in palladium(II) phosphine complexes.

Extension of the Redox Reaction to Platinum. In contrast to palladium(II) complexes, the coordination of fluoride to platinum(II) phosphine complexes has been well established. In 1965, McAvoy, Moss, and Sharp reported[55] the preparation of L_2PtF_2 ($L = PPh_3, P(OPh)_3$) by reaction of HF with the appropriate zerovalent platinum complex, as shown in reaction 6. Both of these complexes reportedly react with carbon monoxide to yield $L_2Pt(CO)_2F_2$.

$$PtL_4 + 2HF \xrightarrow[L\ =\ PPh_3,\ P(OPh)_3]{} L_2PtF_2 + H_2 + 2L \qquad (6)$$

In contrast to the results of McAvoy et al., Kemmit, Peacock, and Stocks reported[39] that the product of reaction 6 should actually be formulated as $[(Ph_3P)_3PtF][HF_2^-]$. The results of these early works were based mainly on elemental analysis, and no spectroscopic evidence was offered to verify a Pt–F bond. Since then, the complexes *trans*-$(Et_3P)_2Pt(R)(F)$ (R = Me,[56] Ph[57]), $[L_3PtF]^+$ (L = PEt_3, PPh_3, and $PMePh_2$),[58] and *trans*-$[(Et_3P)_2Pt(L)(F)][ClO_4]$ ($L = PPh_3, P(OPh)_3$)[58] have been prepared as stable solids, fully characterized by ^{19}F, ^{31}P, and ^{13}C NMR spectroscopies as well as by elemental analyses. Additionally, the molecular structures of $[(Et_3P)_3PtF][BF_4]$[59] and *cis*-$(Ph_3P)_2Pt\{CH(CF_3)_2\}(F)$[60] have been determined by X-ray crystallography. The mixed-halogen complexes $(Ph_3P)_2PtX(F)$ (X = Cl, Br)[39] and $(Et_3P)_2PtCl(F)$[61] have also been reported.

Platinum(II) phosphine complexes also undergo a fluoride-induced redox reaction, although not as cleanly as for palladium. Addition of 2.5 equiv of n-$Bu_4NF{\cdot}3H_2O$ to a suspension of $(Ph_3P)_2PtCl_2$ and PPh_3 in THF results in only partial conversion to $Pt(PPh_3)_x$ and $Ph_3P{=}O$. The presence of $Pt(PPh_3)_x$ was confirmed by a broad resonance at 45 ppm in the ^{31}P NMR spectrum of the supernatant. Furthermore, aliquots of this supernatant were treated with methyl iodide and dppe to form *trans*-$(Ph_3P)_2Pt(Me)I$ (28.3 ppm, $^1J_{Pt-P}$ = 3077 Hz) and $Pt(dppe)_2$ (30.9 ppm, $^1J_{Pt-P}$ = 3731 Hz), respectively.[18] Similarly, reaction of $PtCl_2$ and 3 equiv of dppe with 2.5 equiv of n-$Bu_4NF{\cdot}3H_2O$

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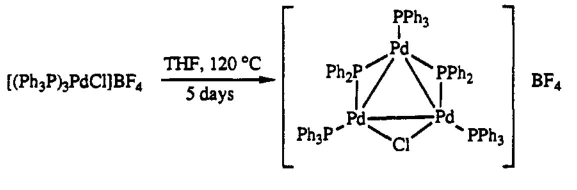
in DMSO yielded only partial conversion to Pt(dppe)$_2$. In addition to numerous unidentified resonances between 55 and 42 ppm, the ^{31}P NMR spectrum of the supernatant revealed the presence of [Pd(dppe)$_2$]Cl$_2$ (49.1 ppm, $^1J_{\mathrm{Pt-P}} = 2338$ Hz),[17] Pt(dppe)$_2$ (30.9 ppm, $^1J_{\mathrm{Pt-P}} = 3733$ Hz), and Ph$_2$PCH$_2$CH$_2$P(O)Ph$_2$. Reactions of platinum(II) and fluoride with additional phosphines have not yet been carried out.

Attempted Extension of the Redox Reaction to Nickel. Nickel(II) phosphine complexes do not participate in our fluoride-assisted redox reaction. Addition of 2.5 equiv of n-Bu$_4$NF·3H$_2$O to a deep red solution of (dppp)NiBr$_2$ in acetonitrile results in the formation of a yellow solution. Cooling to room temperature results in the precipitation of a yellow solid, tentatively identified as NiF$_2$. This result agrees with those previously reported by McAvoy et al. who noted that the reaction of (Pr$_3$P)$_2$NiCl$_2$ with fluoride also yields only NiF$_2$.[55]

BF$_4^-$ as a Fluoride Source. The formation of Pd(dppp)$_2$ as a side product in the reaction of dppp with Pd(BF$_4$)$_2$·4CH$_3$CN suggests that BF$_4^-$ may provide fluoride for the redox reaction. In support of such a proposition, Theopold has recently reported[36] fluoride abstraction from PF$_6^-$ by [Cp*Cr(THF)$_2$Me]$^+$ to yield [Cp*$_4$Cr$_4$(μ-F)$_5$Cl$_2$]PF$_6$, although no change in oxidation state accompanies this reaction. Similarly, Cp$_2$Zr(Me)Cl reacts with AgPF$_6$ to give [Cp$_2$Zr(CH$_3$)(CH$_3$CN)]$^+$ which also rapidly abstracts fluoride from PF$_6^-$ to give Cp$_2$Zr(Me)F.[37] More interesting is the possible contribution of this fluoride-induced redox reaction to the thermal decomposition of [(Ph$_3$P)$_3$PdCl][BF$_4$] to yield the trinuclear cluster [Pd$_3$Cl(PPh$_2$)$_2$(PPh$_3$)$_3$][BF$_4$],[5] as outlined in reaction 7.



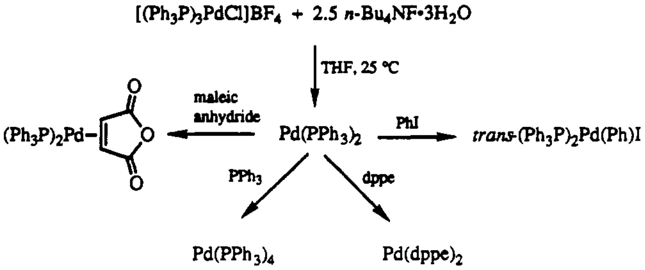
(7)

Such a transformation requires a net two-electron reduction per cluster since the average oxidation state per palladium is $+^4/_3$. The only oxidation product identified in this reaction was Ph$_3$P=O, formed by an unknown mechanism. A referee of the original report suggested[5b] that cluster formation may have proceeded with the concomitant formation of Ph$_3$PCl$_2$ as the oxidation product (reaction 8) which subsequently hydrolyzed with adventitious water to give Ph$_3$P=O. We suggest, however, that thermal decomposition of some of the BF$_4^-$ to yield the fluoride ion occurs under the reaction conditions employed. The thermal decomposition of tetrafluoroborate salts of transition-metal complexes to yield metal fluorides is well-known and has been reviewed.[62] A fluoride-induced redox reaction could then ensue to form Pd(PPh$_3$)$_2$ and Ph$_3$PF$_2$. From the aforementioned work by Coulson,[57] the final step would involve the thermal reaction of Pd(PPh$_3$)$_2$ with a palladium(II) phosphine complex to form the triangular cluster.

$$3[(\mathrm{Ph_3P})_3\mathrm{PdCl}]^+ \rightarrow [\mathrm{Pd_3Cl(PPh_2)_2(PPh_3)_3}]^+ + 2[\mathrm{PPh_4}]^+ + \mathrm{PPh_3} + \mathrm{Ph_3PCl_2} \quad (8)$$

We have briefly reinvestigated this reaction to support our suggestion. To a suspension of [(Ph$_3$P)$_3$PdCl][BF$_4$] in THF at room temperature was added 2.5 equiv of n-Bu$_4$NF·3H$_2$O to yield an immediate yellow solution containing only Ph$_3$P=O and Pd(PPh$_3$)$_2$, as indicated by ^{31}P NMR spectroscopy. Complexation of Pd(PPh$_3$)$_2$ with additional PPh$_3$ or maleic anhydride and reaction with iodobenzene, as shown in Scheme II,[19] confirmed this assignment. This observation supports our proposed route to cluster formation, provided that thermal decomposition of BF$_4^-$ indeed occurs under Dixon's reaction conditions. Following the reported procedure,[5b] we heated [(Ph$_3$P)$_3$PdCl][BF$_4$] at 125 °C in THF for 5 days to yield a small quantity of the triangular cluster. Analysis of the filtrate by ^{31}P NMR spectroscopy confirmed Dixon's reported product distribution, including the presence of Ph$_3$P=O and Pd(PPh$_3$)$_x$. The presence of the palladium(0) complex was confirmed by the addition of iodobenzene, maleic anhydride, and additional PPh$_3$, as described above. However, there was no evidence to suggest the presence of Ph$_3$PF$_2$ which may have been hydrolyzed by adventitious water. In a different approach to the problem, we removed BF$_4^-$ from the starting material and replaced it with the non-fluoride-donating anion $^-$OSO$_2$CF$_3$. Heating [(Ph$_3$P)$_3$PdCl][OSO$_2$CF$_3$] at 125 °C for 7 days resulted in no visually detectable reaction. The yellow solid, isolated in 97% yield from this reaction mixture, was identified as [Pd$_2$(μ-Cl)$_2$(PPh$_3$)$_4$][OSO$_2$CF$_3$] by ^{31}P NMR spectroscopy as well as by its clean conversion to [(Ph$_3$P)$_3$PdCl][OSO$_2$CF$_3$] upon the addition of PPh$_3$ in CH$_3$NO$_2$. A ^{31}P NMR spectrum of the reaction filtrate showed no evidence for the formation of Pd(0) complexes, no evidence for P—C bond cleavage (bridging PPh$_2$ groups usually resonate around 200–270 ppm for palladium complexes),[5] and no formation of Ph$_3$P=O. This result supports our contention that the thermal decomposition of BF$_4^-$ followed by a fluoride-induced redox reaction is required for the formation of [Pd$_3$Cl(PPh$_2$)$_2$(PPh$_3$)$_3$][BF$_4$] from the thermal decomposition of [(Ph$_3$P)$_3$PdCl][BF$_4$].

Scheme II



Conclusions. We have shown that fluoride induces a novel redox reaction among a variety of palladium(II) and to a lesser extent among platinum(II) phosphine complexes to yield zerovalent metal phosphine complexes and difluorophosphoranes. This reaction constitutes a convenient preparation for palladium(0) phosphine complexes. We have also presented evidence that this redox reaction contributes to the formation of [Pd$_3$Cl(PPh$_2$)$_2$(PPh$_3$)$_3$][BF$_4$] from [(Ph$_3$P)$_3$PdCl][BF$_4$], with the fluoride required for the redox reaction arising from thermal decomposition of the tetrafluoroborate anion. Considering the increasing use of BF$_4^-$ in transition-metal chemistry, including its coordination via fluoride bridges to palladium(II) in (Ph$_3$P)$_2$Pd(BF$_4$)$_2$,[63] (dppe)Pd(BF$_4$)$_2$,[63] and {2-(6-chloropyridyl)}Pd(PPh$_3$)(py)(BF$_4$),[64] this fluoride-induced redox reaction may begin to take on increasing significance. The reactivity of fluoride in palladium(II) phosphine complexes, as well as the potential synthesis of compounds containing stable Pd–F bonds, merits further investigation.

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Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Mallinckrodt Chemical Co. for support of this research. We also thank Dr. Lee M. Daniels of the Iowa State Molecular Structure Laboratory for the crystallographic analysis of $Pd(dppp)_2$ by X-ray means.

Supplementary Material Available: Tables of complete bond distances and angles, positional parameters, general displacement parameters, and calculated hydrogen atom positions (7 pages). Ordering information is given on any current masthead page.

OM920119J

Oxidative Cleavage of Tetramethylammonium Pentacarbonyl(1-oxyalkylidene)chromate(0) Complexes: Formation of Carboxylic Acid Derivatives

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Received January 29, 1992

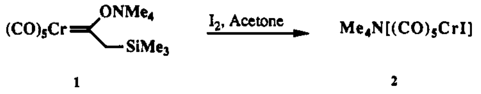
Reaction of tetramethylammonium pentacarbonyl(1-oxyalkylidene)chromate(0) complexes with iodine in the presence of a base and an alcohol afforded carboxylic acid esters in fair to good yield. Substituting an amine or water for the alcohol produced an amide or a carboxylic acid, respectively. The corresponding complexes of molybdenum and tungsten both gave comparable yields of ester product under the same conditions.

Introduction

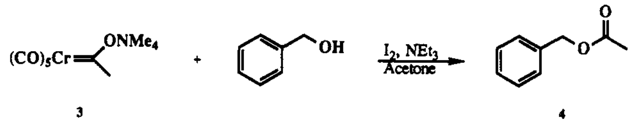
Metal acyl σ-bonds undergo facile cleavage by several reagents to form carboxylic acid derivatives.[1] For example, oxidation of nickel acylates $[RCONi(CO)_3X]$[2] and iron acylates $[RCOFe(CO)_4Na]$[3] with bromine or iodine affords carboxylic acids, esters, or amides, depending on the coreactant present in the reaction mixture. Other metal acylates formed in situ, such as those of palladium,[4] cobalt,[5] and nickel,[6] give esters and amides from alcohols and amines, respectively, without the help of an oxidizing reagent.

To our knowledge, the only example of such a reaction of chromium acylates is that reported by Connor and Jones. The authors isolated tetramethylammonium pentacarbonylchromium(I) iodide (2) in 85% yield as the sole product (Scheme I) upon reaction of tetramethylammonium pentacarbonyl[1-oxy-2-(trimethylsilyl)ethylidene]chromate(0) (1) with iodine in acetone.[7] No reports of organic products isolated from oxidative cleavage of tetramethylammonium pentacarbonyl(1-oxyalkylidene)chromate(0) complexes employing halogens have appeared.

Scheme I



Scheme II



The fate of the carbene ligand from reactions of 1-oxyalkylidene complexes such as 1 is of interest for our understanding and development of novel reactions thereof. As part of a program to develop new synthetic reactions of tetramethylammonium pentacarbonyl(1-oxyalkylidene)chromate(0) complexes,[8] we set out to examine their reactions with iodine or bromine in the presence of a nucleophile. In this paper we report a facile oxidative cleavage of a selected number of tetramethylammonium pentacarbonyl(1-oxyalkylidene)chromate(0) complexes to give carboxylic acid derivatives.

Results and Discussion

Addition of a slight excess of iodine (1.1 equiv) to a solution of tetramethylammonium pentacarbonyl(1-oxyethylidene)chromate(0) (3, 1.0 equiv), triethylamine (1.5 equiv), and benzyl alcohol (1.1 equiv) in acetone followed by stirring for 24 h gave a 58% yield of benzyl acetate (4) (Scheme II) after air oxidation (to remove any arene-bound chromium) and chromatography on a short silica gel column. Benzyl acetate was the only product observed by

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