hexane afforded the unreacted starting material when X = Cl. For X = Br, CF_3CO_2, or NO_3, a mixture of the starting material and the cationic hydride complex *trans*-$[PtH(CO)\{P(t\text{-}Bu)_3\}_2]X$ was obtained upon evaporation of the solvent as shown by the infrared and ^1H and $^{31}P\{^1H\}$ NMR spectral measurements. (b) CO was passed through a stirred suspension of **1a** (0.5 mmol) and LiX (X = BF_4, PF_6) in a mixture (15 mL) of acetone/dichloromethane (2:1). After 4 h, the volatiles were removed and the residue was extracted with dichloromethane (5 mL). The resulting solution was diluted with pentane and then cooled to give colorless plates of *trans*-$[PtH(CO)\{P(t\text{-}Bu)_3\}_2]X$; the infrared ^1H and $^{31}P\{^1H\}$ NMR spectral data were identical with those for authentic samples.[35]

Reaction of *trans*-$PtH_2[P(t\text{-}Bu)_3]_2$ with CO. A colorless solution of *trans*-$PtH_2[P(t\text{-}Bu)_3]_2$ (0.4 mmol) in pentane (40 mL) became orange upon bubbling with CO for ca. 1 h. Bubbling of CO was continued until all the solvent evaporated to give a dark orange solid which was washed twice with 10 mL of hexane and then recrystallized from a mixture of hexane and benzene: mol wt calcd 1265, found 1237; IR (Nujol mull) 2200–1700 cm^{-1} region: 1785 (vs), 1730 (vs) cm^{-1}. Anal. Calcd for $C_{39}H_{81}P_3O_3Pt_3$: C, 36.7; H, 6.41. Found: C, 37.01; H, 6.31.

Reaction of *trans*-$PtH_2[P(t\text{-}Bu)_3]_2$ with *t*-BuNC. A solution of the isocyanide (1.1 mmol) in pentane (5 mL) was added dropwise to that of the dihydride (0.5 mmol) in the same solvent (10 mL). An orange-red solid gradually separated which was filtered, washed with pentane, and dried. It was characterized to be $Pt_3(\mu\text{-}CN\text{-}t\text{-}Bu)_3(CN\text{-}t\text{-}Bu)_3$: yield 90%; IR (Nujol mull) 2200–1700 cm^{-1} region: 2142 (vs), 2092 (sh), 1728 (s, sh), and 1704 (vs) cm^{-1}. Anal. Calcd for $C_3OH_{54}N_6Pt_3$: C, 33.25; H, 4.98. Found: C, 33.40; H, 4.85.

Reactions of the Hydrides with Strong Bases. (a) To a solution of *trans*-$PtHX[P(t\text{-}Bu)_3]_2$ (X = Cl, Br) (50 mg) in benzene (4 mL) was added a drop of the saturated solution of KOH in ethanol. The $^{31}P\{^1H\}$ NMR spectra of the solutions, after 1 h, showed the presence of $Pt[P(t\text{-}Bu)_3]_2$ as the only phosphorus-containing species. Removal of the volatiles in vacuo and recrystallization of the resulting solid gave $Pt[P(t\text{-}Bu)_3]_2$ in 90% yield. Neither *trans*-$PtHCN[P(t\text{-}Bu)_3]_2$ nor *trans*-$PtH_2[P(t\text{-}Bu)_3]_2$ reacted with KOH/EtOH under similar conditions. (b) *trans*-$PtHCl[P(t\text{-}Bu)_3]_2$ (0.5 mmol) in benzene (5 mL) was added to a solution of NaOMe (0.5 mmol) in methanol (10 mL). The reaction mixture was stirred for 5 h. The volatiles were removed in vacuo, and the residue was extracted with pentane (25 mL). Removal of the pentane gave colorless $Pt[P(t\text{-}Bu)_3]_2$ in 95% yield.

Reactions of *trans*-$PtH_2[P(t\text{-}Bu)_3]_2$ with ROH (R = C_6Cl_5, C_6H_5, C_2H_5). To a solution of the dihydride in benzene was added a slight excess of the phenol. Immediate evolution of dihydrogen occurred in the case of C_6Cl_5OH; the reaction with C_6H_5OH was complete in about 3 h. In both cases, the $^{31}P\{^1H\}$ NMR spectrum of the resulting solution showed the presence of $Pt[P(t\text{-}Bu)_3]_2$ as the only phosphorus-containing species. About 70% *trans*-$PtH_2[P(t\text{-}Bu)_3]_2$ was converted into $Pt[P(t\text{-}Bu)_3]_2$ when its solution in ethanol was kept at room temperature for about 3 weeks.

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Registry No. **1a**, 67901-03-3; **1b**, 67871-27-6; **1c**, 67950-30-5; **1d**, 67871-28-7; **1e**, 81476-54-2; **1f**, 81476-55-3; **2**, 67870-05-7; **3a**, 63230-78-4; **3b**, 67870-02-4; **3c**, 67870-03-5; **3d**, 67870-04-6; **3e**, 81476-56-4; **4a**, 69393-57-3; **4b**, 81476-57-5; **4c**, 79138-87-7; **5a**, 81476-58-6; **5b**, 81476-59-7; **5d**, 81476-60-0; **5e**, 81476-61-1; **6**, 79136-89-9; 1, 55664-26-1; $Pt[P(t\text{-}Bu)_3]_2$, 60648-70-6.

Addition of Carbon Monoxide and Methyl Isocyanide to Methylpalladium A-Frame Complexes and Some Reactions of the Product Acyl Complexes

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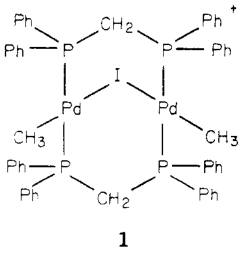
Addition of carbon monoxide to $[Pd_2(dpm)_2(\mu\text{-}X)(CH_3)_2]X$ (X = I^-, Br^-; dpm = $Ph_2PCH_2PPh_2$) produces the A-frame acyls $[Pd_2(dpm)_2(\mu\text{-}X)(COCH_3)_2]X$ which have been isolated as crystalline solids and characterized by ^1H and ^{31}P NMR spectroscopy and infrared spectroscopy. Reaction of $[Pd_2(dpm)_2(\mu\text{-}I)(COCH_3)_2]X$ with dioxygen yields acetic anhydride and $Pd_2(dpm)_2I_2$. With iodine, bromine, and diphenyl disulfide, the binuclear acyl complex yields acetyl iodide, acetyl bromine, and (*S*)-phenyl thioacetate, respectively, as the organic products. Addition of carbon monoxide to $[Pd_2(dpm)_2(\mu\text{-}I)(CH_3)I]BF_4$ yields brown, crystalline $[Pd_2(dpm)_2(\mu\text{-}I)(COCH_3)I][BF_4]$ which appears to retain the weak metal–metal bond found in $[Pd_2(dpm)_2(\mu\text{-}I)(CH_3)I][BF_4]$. Methyl isocyanide reacts with $[Pd_2(dpm)_2(\mu\text{-}I)(CH_3)I][BF_4]$ to form $[Pd_2(dpm)_2(\mu\text{-}CH_3C{=}NCH_3)(CNCH_3)_2]^{3+}$, a complex with a bridging iminoacyl ligand, which has been isolated as a hexafluorophosphate salt.

Introduction

Recently the binuclear palladium methyl complexes $[Pd_2(dpm)_2(\mu\text{-}X)(CH_3)_2]^+$ (X = I, Br) **1** and $[Pd_2(dpm)_2(\mu\text{-}I)CH_3I]^+$ **2** (dpm is bis(diphenylphosphino)methane) have become available.[1] The dimethyl complex **1** is prepared from $Pd_2(dpm)_3$ and alkyl halides, while **2** is obtained upon protonation of $Pd_2(dpm)_2(\mu\text{-}CH_2)I_2$. While these two cations are valence isoelectronic, **2**, which has been structurally characterized by X-ray crystallography, possesses an unusual metal–metal separation of 3.0 Å and appears to have a greater degree of metal–metal bonding than **1**.[2]



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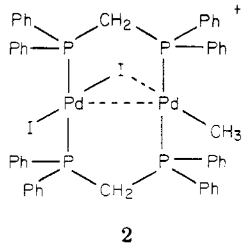

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As part of our program of study of binuclear complexes,[3,4] we have undertaken an examination of the reactivity of these two complexes. Carbonylation of metal alkyls can produce either η- or η^2-acyl complexes.[5-9] These can, in turn, lead to the formation of ketones[10,11] or α-diketones. Because of the known propensity of dpm-bridged complexes to facilitate the formation of novel metal–metal interactions and unusual bridging ligands, we undertook an examination of the addition of carbon monoxide and isocyanides to 1 and 2.

Experimental Section

Preparation of Compounds. $[Pd_2(dpm)_2(\mu\text{-}X)(CH_3)_2]X$,[1] $[Pd_2(dpm)_2(\mu\text{-}I)(CH_3)I]BF_4$,[1] and methyl isocyanide[13] were prepared by established procedures. Dichloromethane was dried by distillation from phosphorus pentoxide and was stored over no. 3 molecular sieves. Other reagents were obtained from commercial sources and were used without further purification. All compounds were prepared under an atmosphere of purified dinitrogen in carefully degassed solvents. The crystalline acetyl complexes can be handled in air for short periods but were always stored under vacuum. Their solutions were always handled under air-free conditions.

$[Pd_2(dpm)_2(\mu\text{-}I)(COCH_3)_2]I$. A solution 200 mg (0.158 mmol) of $[Pd_2(dpm)_2(\mu\text{-}I)(CH_3)_2]I$ in 6 mL of dichloromethane was purged with carbon monoxide and pressurized to 45 psig. The constantly stirred solution was kept under carbon monoxide at this pressure for 3 days during which the yellow color of the solution turned orange. After the carbon monoxide pressure was released, the solution was filtered. Ethyl ether was added to the filtrate to precipitate the product as yellow crystals. The product was collected by filtration and washed with ether. Purification was achieved by recrystallization from dichloromethane/ethyl ether; yield 171 mg, 82%. Anal. Calcd for $C_{54}H_{50}I_2O_2P_4Pd_2$: C, 49.08, H, 3.81. Found: C, 49.16; H, 3.99.

$[Pd_2(dpm)_2(\mu\text{-}I)(COCH_3)_2][PF_6]$. A solution of 170 mg (1.0 mmol) of ammonium hexafluorophosphate in 3 mL of methanol was added to a solution of 200 mg (0.15 mmol) of $[Pd_2(dpm)_2(\mu\text{-}I)(COCH_3)_2]I$ in 10 mL of methanol. The solution was evaporated to dryness on a rotary evaporator. The residue was extracted with 8 mL of dichloromethane. After filtration of the solution, ethyl ether was added slowly to precipitate the product as orange crystals. Further purification was accomplished by recrystallization from dichloromethane/ethyl ether; yield 154 mg, 76%. Anal. Calcd for $C_{54}H_{50}F_6IO_2P_5Pd_2$: C, 48.42; H, 3.76; I, 9.47. Found: C, 48.39; H, 3.86; I, 9.50.

$[Pd_2(dpm)_2(\mu\text{-}Br)(COCH_3)_2][PF_6]$. A dichloromethane solution of 200 mg of $[Pd_2(dpm)_2(\mu\text{-}Br)(CH_3)_2]Br$ in 6 mL of dichloromethane was purged with carbon monoxide and pressurized to 45 psig. The solution was stirred for 5 days under 45 psig of carbon monoxide. The solution was then filtered, and $[Pd_2(dpm)_2(\mu\text{-}Br)(COCH_3)_2]Br$ was isolated as a pale yellow solid by the addition of ethyl ether in 81% yield. The identity of this intermediate was established spectroscopically. A solution of 139 mg (0.86 mmol) of ammonium hexafluorophosphate in 2 mL of methanol was added to a solution of (150 mg, 0.12 mmol) of $[Pd_2(dpm)_2(\mu\text{-}Br)(COCH_3)_2]Br$ in 5 mL of methanol. The yellow crystals which formed slowly were collected by filtration, washed with methanol, and recrystallized from dichloromethane/ethyl ether: 140 mg, 89%. Anal. Calcd for $C_{54}H_{50}BrF_6O_2P_5Pd_2$: C, 50.18; H, 3.90; Br, 6.18. Found: C, 50.10; H, 3.93; Br, 6.14.

$[Pd_2(dpm)_2(\mu\text{-}I)(COCH_3)I][BF_4]$. A solution of 300 mg (0.224 mmol) of $[Pd_2(dpm)_2(\mu\text{-}I)(CH_3)I][BF_4]$ in 6 mL of dichloromethane was stirred under 45 psig of carbon monoxide for 5 days. After the gas pressure was released, the solution was filtered and 2 mL of ethyl ether was added. Methanol was added dropwise to the cloudy brown solution until the solution became clear. Ether was added dropwise until the solution became cloudy. Then methanol was added to clarify the solution. This procedure was continued until the addition of ether no longer produced cloudiness in the solution. The solution was then stored at −5 °C for several hours. The brown crystals which formed were collected by filtration and washed with ethyl ether. The product (276 mg, 90%) was recrystallized from dichlormethane/ethyl ether. Anal. Calcd for $C_{52}H_{47}BF_4I_2OP_4Pd_2$: C, 45.75; H, 3.47; P, 9.07. Found: C, 45.28; H, 3.53; P, 8.75.

$[Pd_2(dpm)_2(\mu\text{-}CH_3C{=}NCH_3)(CNCH_3)_2][PF_6]_3$. Methyl isocyanide was added dropwise to a suspension of 250 mg (0.187 mmol) of $[Pd_2(dpm)_2(\mu\text{-}I)(CH_3)I][BF_4]$ in 10 mL of methanol until all of the solid had dissolved. The yellow solution was filtered, and a solution of 96 mg (0.60 mmol) of ammonium hexafluorophosphate in 2 mL of methanol was added. The product, which precipitated as pale yellow crystals, was collected by filtration and washed with methanol. Purification was achieved by three recrystallizations from acetone/diethyl ether, which produced white crystals: yield 202 mg, 70%. Anal. Calcd for $C_{57}H_{56}F_{18}N_3P_7Pd_2$: C, 44.04; H, 3.63; N, 2.70. Found: C, 44.27; H, 3.73; N, 2.71.

Decarbonylation of $[Pd_2(dpm)_2(\mu\text{-}I)(COCH_3)_2]I$. A solution of 150 mg (0.113 mmol) of $[Pd_2(dpm)_2(\mu\text{-}I)(COCH_3)_2]I$ in 20 mL of acetonitrile was heated under reflux for 1.5 h. During this period the solution's color changed from yellow to red. Addition of ether to the solution caused a pale yellow crystalline product to form; yield 129 mg, 90%. This was identified as $[Pd_2(dpm)_2(\mu\text{-}I)(CH_3)_2]I$ contaminated by 10% of $Pd_2(dpm)_2I_2$[14] by comparison of the infrared, ^1H and ^{31}P NMR spectra with those of authentic samples.

Reaction of $[Pd_2(dpm)_2(\mu\text{-}I)(COCH_3)_2]I$ with Dioxygen. A solution of 50 mg of $[Pd_2(dpm)_2(\mu\text{-}I)(COCH_3)_2]I$ in 2 mL of dichloromethane-d_2 was kept under 45 psig of dioxygen for 30 h during which the color changed from yellow to brown. Analysis of the solution by ^1H NMR spectroscopy indicated a 90% conversion into $Pd_2(dpm)_2I_2$[14] (4.27 ppm (quintet, $J(PH) = 4$ Hz, dpm methylene protons)) and acetic anhydride (δ 2.19). The presence of acetic anhydride was further confirmed by the infrared spectra shown in Figure 2. The solvent was removed from the reaction mixture by evaporation and the residue subjected to bulb-to-bulb distillation under a closed vacuum. The colorless distillate was identified as acetic anhydride (yield 70%) based on comparison of the ^1H NMR and infrared spectra with those of an authentic specimen.

Reaction of $[Pd_2(dpm)_2(\mu\text{-}I)(COCH_3)_2]I$ with Iodine. A solution of iodine in dichlormethane-d$_2$ was titrated into a solution of 50 mg of $Pd_2(dpm)_2(\mu\text{-}I)(COCH_3)_2]I$ in 2 mL of dichloromethane-d_2. Monitoring the reaction by ^1H NMR spectroscopy indicated the formation of $Pd(dpm)I_2$[14] (dpm methylene protons, 4.55 ppm (t, J(P–H) = 10.4 Hz)) and acetyl iodide (2.97 ppm (s)). No $Pd_2(dpm)_2I_2$ was detected even when substoichiometric amounts of iodine were used. The presence of acetyl iodide was verified through the observation of an infrared absorption at 1795 cm^{-1}. On exposure to air the ^1H NMR resonance at 2.97 ppm disappeared while a new resonance at 2.09 ppm grew. Concomitantly the infrared absorption at 1795 cm^{-1} was replaced by absorptions at 1756 and 1711 cm^{-1}. These changes are due to the conversion of acetyl iodide to acetic acid.

Reaction of $[Pd_2(dpm)_2(\mu\text{-}I)(COCH_3)_2]I$ with Bromine. This reaction was carried out by using the procedure described above for the corresponding reaction with iodine. The formation of $Pd(dpm)Br_2$ was detected by ^1H NMR spectroscopy (dpm methylene, 4.36 ppm (t, J(P–H) = 10.4 Hz)). The formation of

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Table I. Infrared and Conductivity Data for Palladium Complexes

compd	ν(C≡O),[a] cm^{-1}	Λ_M,[b] cm^2 mol^{-1} Ω^{-1}
$[Pd_2(dpm)_2(\mu\text{-}I)(COCH_3)_2]I$	1710	131
$[Pd_2(dpm)_2(\mu\text{-}Br)(COCH_3)_2]Br$	1709	127
$[Pd_2(dpm)_2(\mu\text{-}I)(COCH_3)_2]PF_6$	1713	130
$[Pd_2(dpm)_2(\mu\text{-}Br)(COCH_3)_2]PF_6$	1711	126
$[Pd_2(dpm)_2(\mu\text{-}I)(COCH_3)I]BF_4$	1712	138
$[Pd_2(dpm)_2(\mu\text{-}CH_3CNCH_3)(CNCH_3)_2](PF_6)_3$	2267,[c] 2257,[c] 1590[d]	368

[a] Measured in dichloromethane solution. [b] Measured in acetonitrile solution. [c] ν(C≡N) for terminal isocyanide ligand. [d] ν(C=N) for bridging iminoacyl ligand.

Table II. ^{1}H and ^{31}P{^{1}H} Nuclear Magnetic Resonance Parameters

	proton resonances[a]				
	dpm methylene				
compd	shift,[b] ppm	J(P-H), Hz	J(H-H), Hz	acetyl,[b] ppm	^{31}P{^{1}H}[a] shift, ppm
$[Pd_2dpm_2(\mu\text{-}I)(COCH_3)_2][I]$	4.14 (4)[c]			1.56 (6)	5.76
$[Pd_2dpm_2(\mu\text{-}Br)(COCH_3)_2][Br]$	3.97 (4)[c]			1.56 (6)	7.60
$[Pd_2dpm_2(\mu\text{-}I)(COCH_3)_2][PF_6]$	3.92 (2), 4.59 (2)	3.9, 5.4	13.5	1.50 (6)	5.40
$[Pd_2dpm_2(\mu\text{-}Br)(COCH_3)_2][PF_6]$	3.56 (2), 4.36 (2)	4.5, 5.5	13.6	1.63 (6)	6.1
$[Pd_2dpm_2(\mu\text{-}I)(COCH_3)I][BF_4]$	4.58 (4)	4.4		1.53 (3)	2.4, 4.3[e]
$[Pd_2dpm_2(\mu\text{-}H_3CC{=}NCH_3)(CNCH_3)_2]_2[PF_6]_3$[d]	3.16 (2), 4.28 (2)	6.0, 3.8	14.1	1.33 (3), 2.12 (3) 3.16 (3), 3.26 (3)	12.6, 16.5[f]

[a] In dichloromethane-d_2 solution unless it is specified. [b] Relative intensity in parentheses. [c] Unresolved broad peaks. [d] In acetonitrile-d_3 solution. [e] AA′BB′ multiplet, J(AA′)-J(BB′) = 31 Hz, J(AB) = J(A′B′) = 22.7 Hz, J(AB′) = J(A′B′) = 20.3 Hz. [f] AA′BB′ multiplet, J(AA′)-J(BB′) = 13.3 Hz, J(AB) = J(A′B′) = 29.1 Hz, J(AB′) = J(A′B) = 8.1 Hz.

acetyl bromide was indicated by the presence of a ^{1}H NMR resonance at 2.81 ppm and infrared absorption at 1798 cm^{-1}. Exposure of the sample to moist air resulted in the conversion of the acetyl bromide to acetic acid.

Reaction of $[Pd_2(dpm)_2(\mu\text{-}I)(COCH_3)_2]I$ with Diphenyl Disulfide. A solution of 8.7 mg (0.040 mmol) of diphenyl disulfide in 0.5 mL of dichloromethane-d_2 was added to a solution of 13 mg (0.01 mmol) of $[Pd_2(dpm)_2(\mu\text{-}I)(COCH_3)_2]I$ in 0.5 mL of dichloromethane-d_2. The solution was sealed in an NMR tube and heated to 40 °C for 7 h. Analysis by ^{1}H NMR spectroscopy revealed complete conversion to $Pd_2(dpm)_2I_2$[14] (dpm methylene, 4.27 ppm (quintet, J(PH) = 4 Hz)) and (*S*)-phenyl thioacetate (methyl, 2.41 ppm (s)). The ^{1}H NMR spectrum clearly indicated that no $Pd_2(dpm)_2(SC_6F_5)_2$ was present. The solution was transferred to a 3 × 30 cm silica gel column, and the products were eluted with dichloromethane. The colored palladium complex adhered to the column. The nearly colorless effluent was collected and evaporated to dryness. The product was examined by NMR spectroscopy, infrared spectroscopy, and gas chromatography and found to contain a 60% yield of (*S*)-phenyl thioacetate.

Spectroscopic Properties. In the product identification in the preceding sections the following spectroscopic features (^{1}H NMR, ν(CO)) in dichloromethane solution were used to identify substances: biacetyl, 2.34 ppm, 1725 cm^{-1}; acetone, 2.7 ppm, 1710 cm^{-1}; acetyl bromide, 2.81 ppm, 1798 cm^{-1}; acetyl iodide 2.97 ppm, 1795 cm^{-1}; acetic anhydride, 2.19 ppm, 1825, 1750 cm^{-1}; acetic acid, 2.08 ppm, 1756, 1711 cm^{-1}; methyl acetate, 3.63, 2.02 ppm, 1738 cm^{-1}; (*S*)-phenyl thioacetate, 2.41 ppm, 1705 cm^{-1}; $Pd(dpm)Cl_2$ methylene protons, 4.28 ppm (t, J(PH) = 10.8 Hz); $Pd(dpm)Br_2$, 4.33 ppm (t, J(PH) = 10.6 Hz); $Pd(dpm)I_2$, 4.55 ppm (t, J(PH) = 10.4 Hz); $Pd_2(dpm)_2Cl_2$, 4.17 ppm (quintet, J(PH) = 4.0 Hz); $Pd_2(dpm)_2Br_2$ 4.22 ppm (q, J(PH) = 4.0 Hz); $Pd_2(dpm)_2I_2$, 4.27 ppm (q, J(PH) = 4.0 Hz); $Pd_2(dpm)_2(SC_6H_5)_2$, 4.09 ppm (q, J(PH) = 3.8 Hz).

Physical Measurements. ^{1}H (5-mm tubes, 200 MHz) and ^{31}P{^{1}H} (12-mm tubes, 81 MHz) were recorded on a Nicolet NT-200 Fourier transform spectrometer. An external 85% phosphoric acid reference was used for ^{31}P NMR spectra and the high-frequency-positive convention, recommended by IUPAC, is used in reporting chemical shifts. Simulations of the entire ^{31}P spectra were performed by using the iterative simulation routine of the Nicolet software on a Model 1180 Nicolet data system. This simulation routine is a modified version of Laocoon III. The fit of the simulation was based on matching the individual peak position and intensities of the observed and the calculated spectra.

Infrared spectra were recorded from Nujol mulls on a Perkin-Elmer 180 infrared spectrometer. Electrical conductivities were determined by use of an Industrial Instruments conductivity bridge with 10^{-3} M acetonitrile solutions. Electronic spectra were recorded on a Hewlett-Packard spectrometer.

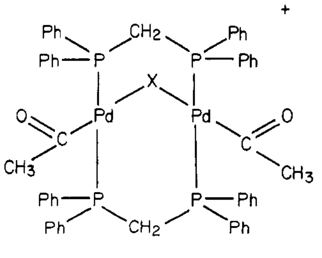
Results and Discussion

Carbonylation of $[Pd_2(dpm)_2(\mu\text{-}X)(CH_3)_2]^+$. Exposure of a dichloromethane solution of $[Pd_2(dpm)_2(\mu\text{-}I)(CH_3)_2]I$ to carbon monoxide at 45 psig for 3 days at 25 °C leads to the isolation of $[Pd_2(dpm)_2(\mu\text{-}I)(COCH_3)_2]I$ as a yellow crystalline solid. The reaction is readily detected by the growth of a carbonyl absorption in the infrared spectrum at ca. 1710 cm^{-1}. Infrared data and conductivity data for the isolated product from this and other reactions are set out in Table I. The salt is soluble in a range of organic solvents including acetone, acetonitrile, methanol, and dichloromethane. In solution it behaves as a 1:1 electrolyte. The yellow solutions are air sensitive and darken upon exposure to dioxygen.

The ^{1}H and ^{31}P{^{1}H} NMR spectra of this and other new compounds are recorded in Table II. Carbonylation results in a downfield shift of the methyl resonance from its position at 0.83 ppm in $[Pd_2(dpm)_2(\mu\text{-}I)(CH_3)_2]I$.[1] Additionally the three-bond phosphorus–proton coupling seen in the methyl complex is absent in the acetyl complex where a smaller four-bond coupling is expected. The methylene resonances of dpm ligands are generally sensitive probes of the geometry of the complexes. In the case of $[Pd_2(dpm)_2(\mu\text{-}I)(COCH_3)_2]I$, only a broad resonance at 4.14 ppm is observed. Evidence to be presented later indicates that the width and the lack of resolution of this resonance results from a rapid halide exchange process.

By monitoring the carbonylation by ^{1}H NMR spectroscopy at low conversions, it has been possible to detect the half-carbonylated species $[Pd_2(dpm)_2(\mu\text{-}I)(COCH_3)(CH_3)]I$. Its ^{1}H NMR spectrum in chloroform-d consists of a methyl resonance at 0.86 ppm (t, J(P–H) = 5.9 Hz, Pd–CH_3), a methyl resonance at 1.55 (s, Pd–$COCH_3$), and a methylene resonance at 4.22 (quintet, J(P–H) = 4 Hz, dpm methylene). The observation of the triplet at 0.86 ppm is particularly significant. In $[Pd_2(dpm)_2(\mu\text{-I})(CH_3)_2]I$ the methyl resonance appears as a quintet with an apparent J(P–H) of 2.8 Hz.[1] The quintet occurs because the coupling among the phosphorus atoms exceeds the proton–phosphorus coupling (i.e., virtual coupling). As a consequence, the observed coupling constant 2.8 Hz is the average of the proton–phosphorus coupling involving the two adjacent phosphorus atoms and the proton–phosphorus coupling involving the two distant phosphorus atoms. The latter coupling constant is expected to be nearly zero. In $[Pd_2(dpm)_2(\mu\text{-I})(COCH_3)(CH_3)]I$ the virtual coupling scheme breaks down since the two phosphorus atoms are chemically inequivalent. Consequently the methyl resonance appears as a triplet, showing coupling only to the two adjacent phosphorus atoms. Moreover the observed coupling constant is twice that seen in $[Pd_2(dpm)_2(\mu\text{-I})(CH_3)_2]I$ because the observed coupling is no longer the average of two coupling constants, one of which is nearly zero. Note also that the proton phosphorus coupling observed for the methyl group in $[Pd_2(dpm)_2(\mu\text{-I})(CH_3)I]BF_4$ is 5.7 Hz.[1] The formation of $[Pd_2(dpm)_2(\mu\text{-I})(COCH_3)(CH_3)]I$ was always accompanied by the formation of $[Pd_2(dpm)_2(\mu\text{-I})(COCH_3)_2]I$, and so separation and isolation of the half carbonylated species was not attempted.

Carbonylation of $[Pd_2(dpm)_2(\mu\text{-Br})(CH_3)_2]Br$ proceeded in a manner similar to that of the iodide analogue. However, the reaction was slower, and 5 days were required to achieve a 81% yield of the product. Under similar conditions, attempts to carbonylate either $[Pd_2(dpm)_2(\mu\text{-I})(CH_3)_2]PF_6$ or $[Pd_2(dpm)_2(\mu\text{-Br})(CH_3)_2]PF_6$ were unsuccessful. Monitoring these reactions by infrared spectroscopy revealed that no acetyl complex had formed after exposure of these complexes to carbon monoxide for 3 days. The failure of this reaction is clearly kinetic rather than thermodynamic, since the salts $[Pd_2(dpm)_2(\mu\text{-X})(COCH_3)_2]PF_6$ are readily prepared by metathesis from the halide salts with ammonium hexafluorophosphate. The products are stable crystalline solids which behave as 1:1 electrolytes. The spectral characteristics are similar to those of the halide salts except for the appearance of the structure sensitive dpm methylene protons in the ^1H NMR spectra. These methylene protons appear as an AB quartet with coupling to four virtually coupled phosphorus atoms in both hexafluorophosphate salts. A representative spectrum is shown in Figure 1, trace A. This pattern is diagnostic of the presence of a A-frame structure for these cations, and consequently the cations are assigned structure 3.[1,14,15] The methylene region of the ^1H NMR spectrum of the hexafluorophosphate salts contrasts with that of the halide salts where only a broad, featureless resonance is seen. The difference is due to a dynamic process involving the counterion. As seen in Figure 1, addition of iodide ion to $[Pd_2(dpm)_2(\mu\text{-I})(COCH_3)_2]PF_6$ causes a loss of structure, broadening, and eventual coalescence of the resonances. This can be explained by an associative process shown in eq 1 in which a face-to-face dimer[16] is formed. Production of this face-to-face dimer renders the two methylene protons of each dpm ligand equivalent. A similar process has also been proposed to account for the behavior of $[Pd_2(dpm)_2(\mu\text{-X})(CH_3)_2]^+$ in solution.[1]



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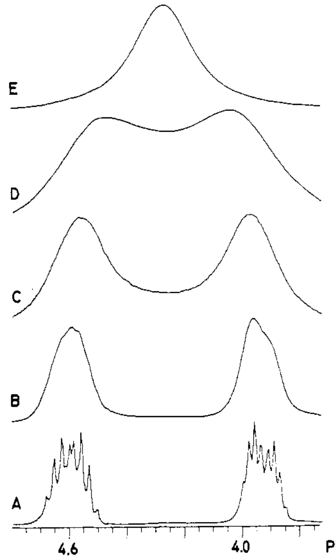
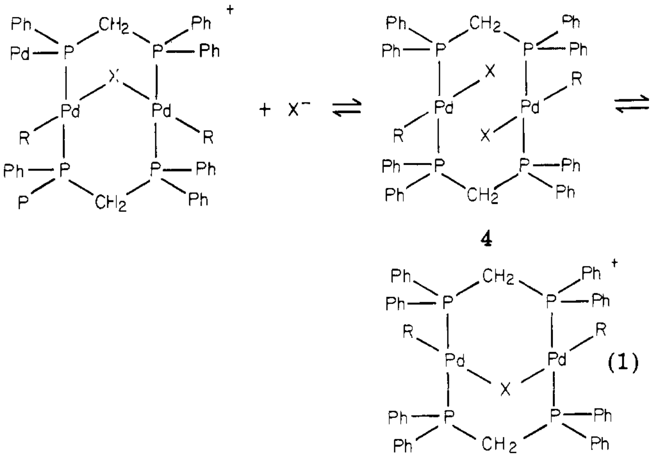


Figure 1. The methylene region of the ^1H NMR spectrum of $[Pd_2(dpm)_2(\mu\text{-I})(COCH_3)_2][PF_6]$ in dichloromethane-d_2 solution in the presence of various quantities of $[Ph_3AsCH_3][I]$. The percentage of iodide ion added to the dinuclear complex is A, 0%; B, 1.3; C, 5; D, 10; E, 100.



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(1)

R = C(=O)CH_3 or CH_3

The mechanism of carbonylation of $[Pd_2(dpm)_2(\mu\text{-X})(CH_3)_2]^+$ clearly involves participation of the counterion since even the crude kinetics observed in our synthetic studies indicate that the rate of carbonylation depends upon the counterion in the order $I^- > Br^- \gg PF_6^-$. One explanation for this trend would involve carbonylation occurring via initial carbon monoxide attack upon the face-to-face dimer 4 (R = CH_3) rather than upon the A-frame 1 itself. Alternatively, of course, the halide could be responsible for promoting carbon monoxide insertion by attacking an as yet undetected carbon monoxide adduct of 1 after it had formed.

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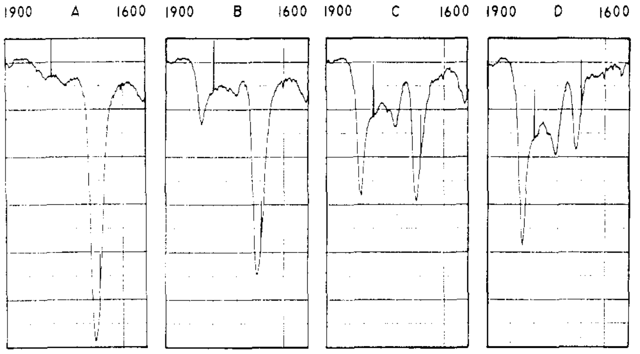


Figure 2. Infrared spectra of a dichloromethane solution of $[Pd_2(dpm)_2(\mu\text{-}I)(COCH_3)_2]I$ after exposure to 45 psig of dioxygen: A, no exposure; B, after 9 h; C, after 18 h; D, after 30 h.

Attempts to add isocyanides to the A-frame methyl complex, 1, led to the formation of complex mixtures which we have as yet not been able to separate.

Reactions of $[Pd_2(dpm)_2(\mu\text{-}I)(COCH_3)_2]^+$. Decarbonylation of $[Pd_2(dpm)_2(\mu\text{-}I)(COCH_3)_2]I$ is readily achieved by heating a solution of the complex in acetonitrile for 1.5 h. Decarbonylation produces $[Pd_2(dpm)_2(\mu\text{-}I)(CH_3)_2]I$ in 80% yield along with about 10% of $Pd_2(dpm)_2I_2$.

Treatment of $[Pd_2(dpm)_2(\mu\text{-}I)(COCH_3)_2]I$ with oxidizing agents results in the smooth loss of the acetyl groups. The reaction with dioxygen has been monitored by both infrared and ^1H NMR spectroscopy. The infrared spectral changes are shown in Figure 2. Under 45 psig of dioxygen in dichloromethane solution, the acetyl absorption at 1710 cm^{-1} decreases in intensity as absorptions due to acetic anhydride at 1750 and 1825 cm^{-1} grow. No other carbonyl-containing species is detected throughout the reaction. The ^1H NMR spectra confirm the formation of acetic anhydride and indicate that the palladium complex formed is $Pd_2(dpm)_2I_2$. Hence, the reaction proceeds as shown in eq 2. Attempts to determine whether the acetic anhydride

$$[Pd_2(dpm)_2(\mu\text{-}I)(COCH_3)_2]I + {}^1/_2O_2 \rightarrow (CH_3CO)_2O + Pd_2(dpm)_2I_2 \quad (2)$$

formation is an intraionic process through isotope-labeled crossover experiments[10] have been thwarted by the rapid exchange of methyl groups between acetic anhydride and acetic anhydride-d_6.

Treatment of $[Pd_2(dpm)_2(\mu\text{-}I)(COCH_3)_2]I$ with iodine proceeds by reaction 3. The stoichiometry has been established by titration. The products have been identified by infrared spectroscopy, ^1H NMR spectroscopy and the chemical reactivity of the acetyl iodide (hydrolysis to form acetic acid). The formation of mononuclear $Pd(dpm)I_2$ does not necessarily imply the fragmentation of the dinuclear starting complex before elimination. $Pd_2(dpm)_2I_2$ reacts rapidly with I_2 to yield $Pd_2(dpm)_2I_4$ which then rearranges to form $Pd(dpm)I_2$.[14]

$$[Pd_2(dpm)_2(\mu\text{-}I)(COCH_3)_2]I + 2I_2 \rightarrow 2CH_3COI + 2Pd(dpm)I_2 \quad (3)$$

Similarly bromine (in excess) reacts with $[Pd_2(dpm)_2(\mu\text{-}I)(COCH_3)_2]$ to yield acetyl bromide and $Pd(dpm)Br_2$.

Diphenyl disulfide reacts with $[Pd_2(dpm)_2(\mu\text{-}I)(COCH_3)_2]I$ according to eq 4. The reaction proceeds more slowly than the corresponding reaction with halogens. Formation of (*S*)-phenyl thioacetate has been monitored by both infrared and ^1H NMR spectroscopy. During the reaction there is no evidence for the formation of the alternate product, acetyl iodide.

$$[Pd_2(dpm)_2(\mu\text{-}I)(COCH_3)_2]I + PhSSPh \rightarrow 2PhSC({=}O)CH_3 + Pd_2(dpm)_2I_2 \quad (4)$$

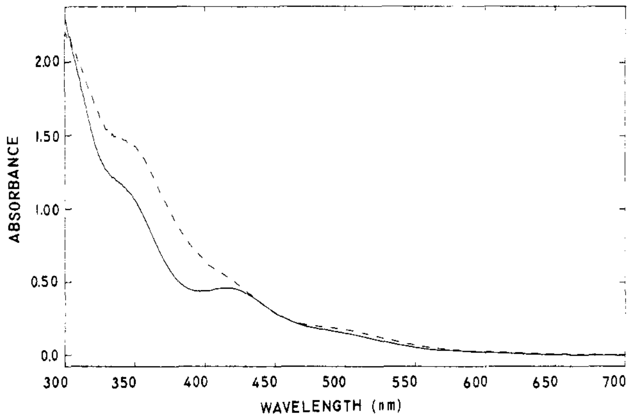
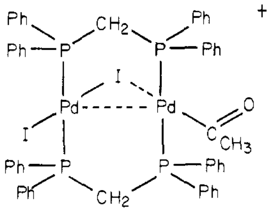


Figure 3. The electronic spectra of A, solid line, $Pd_2(dpm)_2(\mu\text{-}I)(CH_3)I][BF_4]$, and B, broken line, $Pd_2(dpm)_2(\mu\text{-}I)(COCH_3)I][BF_4]$, in dichloromethane solution at 25 °C.

The acetyl elimination reactions appear to conform to the pattern of oxidative addition followed by reductive elimination which has been established for a number of organometallics.[17,18] In the present case, the inability to detect intermediates does not allow us to ascertain whether the initial oxidation produces mixed valence Pd(IV)–Pd(II) species or metal–metal bonded Pd(III) dimers. The lack of coupling of acyl groups to form α-diketones, which have been found to form upon oxidation of at least one *cis*-diacetyl complexes,[19] is not surprising in view of the large geometric separation between the acyl groups in either the A-frame 3 or the face-to-face dimer 4.

Insertion Reactions of $[Pd_2(dpm)_2(\mu\text{-}I)(CH_3)I]^+$. Treatment of a dichloromethane solution of $[Pd_2(dpm)_2(\mu\text{-}I)(CH_3)I]BF_4$ with carbon monoxide at 45 psig for 5 days produces $[Pd_2(dpm)_2(\mu\text{-}I)(COCH_3)I]BF_4$ which has been isolated as dark brown crystals. The product is assigned structure 5 because of the striking similarity of physical properties to those of $[Pd_2(dpm)_2(\mu\text{-}I)(CH_3)I]BF_4$.[1,2] The infrared spectrum indicates that the acetyl group is η^1 and is not significantly perturbed by the presence of the second palladium ion. The ^{31}P NMR spectrum reveals the presence of two dissimilar phosphorus atoms. The spectrum is readily analysed as an AA′BB′ pattern, and the parameters used in the analysis are given in Table II. The electronic spectrum of $[Pd_2(dpm)_2(\mu\text{-}I)(COCH_3)I]BF_4$ is compared with the distinctive spectrum of $[Pd_2(dpm)_2(\mu\text{-}I)(CH_3)I]BF_4$ in Figure 3. The close similarity of these spectra is taken to indicate that a weak metal–metal interaction is present in both complexes. The ^1H NMR spectrum of $[Pd_2(dpm)_2(\mu\text{-}I)(COCH_3)I]BF_4$ shows a symmetrical quintet for the dpm methylene protons at 25 °C. Structure 5 is an A frame, and inequivalent methylene protons are expected. However, rapid rocking of the ligands shown in eq 5 can render the dpm methylene protons



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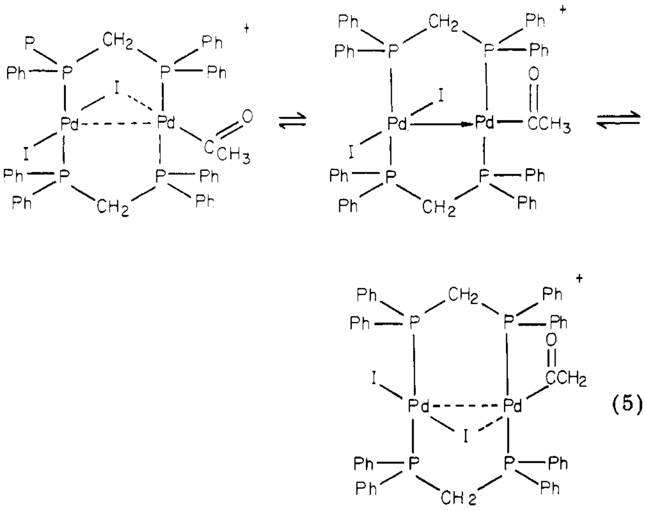
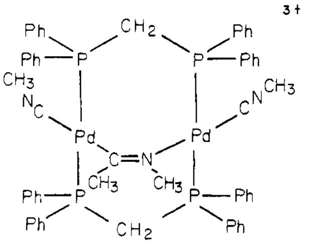
equivalent. A similar process has been proposed to occur in [Pd$_2$(dpm)$_2$(μ-I)(CH$_3$)I]BF$_4$.[1]



(5)

Addition of methyl isocyanide, which is also capable of insertion into metal–alkyl bonds,[20] to [Pd$_2$(dpm)$_2$(μ-I)(CH$_3$)I]BF$_4$ results in the formation of a white complex which has been isolated as a hexafluorophosphate salt. The conductivity of this material is consistent with its formulation as a 1:3 electrolyte. Spectroscopic data indicate that it has structure 6 and is the product of isocyanide insertion into the palladium–methyl bond as well as substitution of the isocyanide ligands for the iodide ligands. The terminal isocyanide ligands produce infrared absorptions of 2267 and 2257 cm^{-1}, and the bridging ligand has a characteristic C=N stretch at 1590 cm^{-1}. The ^{31}P{^{1}H} NMR spectrum shown in Figure 4 has been successfully simulated as an AA′BB′ pattern. The simulation is also shown in the figure. Since the coupling constants between the chemically dissimilar phosphorus atoms are all less than 50 Hz, the two different phosphorus atoms do not lie trans to one another and bonded to the same metal. The general pattern of coupling constants is consistent with structure 6 and may be compared to similar complexes.[21] The ^{1}H NMR spectrum reveals the presence of four singlets for the four nonequivalent methyl groups in the molecule. The dpm methylene resonances indicate the presence of an A-frame structure. Finally we note that [Pd$_2$(dpm)$_2$(μ-CH$_3$N=CCH$_3$)(CNCH$_3$)$_2$]$^{3+}$ is isoelectronic with the previously prepared [Pd$_2$(dpm)$_2$(μ-CF$_3$C=CCF$_3$)$_2$(CNCH$_3$)$_2$]$^{2+}$ and both of these are likely to have the long, nonbonded palladium–palladium separation found in Pd$_2$(dpm)$_2$(μ-CF$_3$C=CCF$_3$)Cl$_2$.[22] Other examples of bridging iminoalkyl ligands[23,24] and closely related bridging formimidoyl ligands[25] are known.



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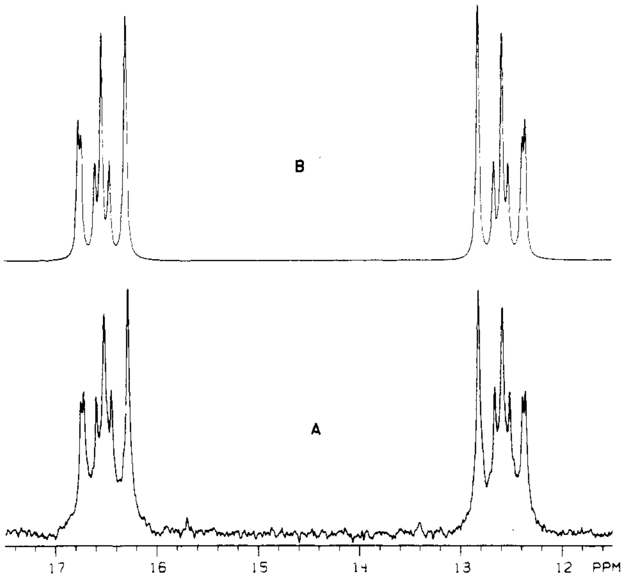

Figure 4. The ^{31}P{^{1}H} NMR spectrum of Pd$_2$(dpm)$_2$(μ-CH$_3$C=NCH$_3$)(CNCH$_3$)$_2$][PF$_6$]$_3$ in dichloromethane solution at 25 °C: A, observed spectrum; B, simulated spectrum using the parameters recorded in Table II.

The formation of 6 does not appear to be general with regard to isocyanide substituent. With *tert*-butyl isocyanide we find that the major product of the reaction is the mononuclear complex (t-BuNC)$_2$Pd(dpm)$_2$$^{2+}$ which contains monodentate dpm ligands.[26]

The palladium-methyl bond in [Pd$_2$(dpm)$_2$(μ-I)(CH$_3$)I]$^+$ resists insertion of either sulfur dioxide or dimethylacetylene dicarboxylate. [Pd$_2$(dpm)$_2$(μ-I)(CH$_3$)I]BF$_4$ dissolves readily in liquid sulfur dioxide. Such a solution has been held sealed at 25 °C. After 2 days, 80% of the unchanged starting complex was recovered from the solution after evaporation of the sulfur dioxide and recrystallization. Similarly when [Pd$_2$(dpm)$_2$(μ-I)(CH$_3$)I]BF$_4$ was allowed to stand for 2 days with a tenfold excess of dimethylacetylene dicarboxylate, only unreacted starting material was recovered in 80% yield.

Acknowledgment. We thank the National Science Foundation (Grant CHE 79 24515) for support and Matthey Bishop for a loan of palladium chloride.

Registry No. [Pd$_2$(dpm)$_2$(μ-I)(COCH$_3$)$_2$]I, 81457-42-3; [Pd$_2$(dpm)$_2$(μ-I)(COCH$_3$)$_2$][PF$_6$], 81457-46-7; [Pd$_2$(dpm)$_2$(μ-Br)(COCH$_3$)$_2$][PF$_6$], 81457-48-9; [Pd$_2$(dpm)$_2$(μ-Br)(COCH$_3$)$_2$]Br, 81457-49-0; [Pd$_2$(dpm)$_2$(μ-I)(COCH$_3$)I][BF$_4$], 81457-51-4; [Pd$_2$(dpm)$_2$(μ-CH$_3$C=NCH$_3$)(CNCH$_3$)$_2$][PF$_6$]$_3$, 81457-53-6; [Pd$_2$(dpm)$_2$(μ-I)(CH$_3$)$_2$]I, 81457-54-7; [Pd$_2$(dpm)$_2$(μ-Br)(CH$_3$)$_2$]Br, 81457-55-8; [Pd$_2$(dpm)$_2$(μ-I)(CH$_3$)I][BF$_4$], 78274-93-8; dioxygen, 7782-44-3; iodine, 7553-56-2; bromine, 7726-95-6; diphenyl disulfide, 882-33-7.

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