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Reactions of the Dicarbonyl Complexes $Re_2X_4(dppm)_2(CO)_2$ (X = Cl, Br) and the Mixed Carbonyl-Isocyanide Complexes $Re_2Cl_4(dppm)_2(CO)(CNR)$ (R = *t*-Bu, Xylyl) with Trimethylphosphine and Trialkyl Phosphite Ligands. Structural Characterization of the Complexes $[Re_2Cl_3(\mu\text{-dppm})_2(CO)_2L]PF_6$ (L = PMe_3, $P(OEt)_3$) That Contain an Unsymmetrical Carbonyl Bridge

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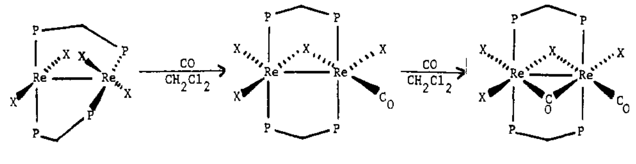
When the complexes $Re_2X_4(\mu\text{-dppm})_2(CO)_2$ (X = Cl, Br) are reacted with PMe_3, $P(OMe)_3$, or $P(OEt)_3$ in CH_2Cl_2 in the presence of $TlPF_6$, the yellow-green diamagnetic dirhenium(II) species $[Re_2X_3(\mu\text{-dppm})_2(CO)_2(PR_3)]PF_6$ are isolated in quite good yield for X = Cl when R = Me, OMe, or OEt and for X = Br when R = Me. In the case of the reaction between $Re_2Cl_4(dppm)_2(CO)_2$ and PMe_3, long reaction times (ca. 72 h) lead to the formation of the paramagnetic complex $Re_2Cl_3(\mu\text{-dppm})_2(CO)_2(PMe_3)$. IR spectroscopy shows the presence of terminal and bridging CO ligands in all these complexes. X-ray crystallography on samples of $[Re_2Cl_3(\mu\text{-dppm})_2(CO)_2(PMe_3)]PF_6$ (**6a**) and $\{Re_2Cl_3(\mu\text{-dppm})_2(CO)_2[P(OEt)_3]\}PF_6$ (**9**) has confirmed this conclusion and shown that the dirhenium cations possess an edge-sharing bioctahedral geometry and contain an unsymmetrical CO ligand bridge. There is an all-cis arrangement of the three chloride ligands on one side of the equatorial plane. The Re–Re distances are 2.593 (1) Å for **6a** and 2.595 (1) and 2.598 (1) Å for the two crystallographically independent molecules of **9**. Therefore, the structures of these cations can be represented as $[Cl(CO)Re(\mu\text{-Cl})(\mu\text{-CO})(\mu\text{-dppm})_2ReCl(PR_3)]^+$ (R = Me, OEt). Crystal data for **6a** at 21 °C are as follows: triclinic space group $P\bar{1}$, $a = 15.479$ (3) Å, $b = 14.944$ (2) Å, $c = 14.485$ (4) Å, $\alpha = 100.22$ (2)°, $\beta = 108.01$ (2)°, $\gamma = 79.41$ (1)°, $V = 3105$ (2) Å^3, and $Z = 2$. The structure was refined to $R = 0.036$ ($R_w = 0.052$) for 5675 data with $I > 3.0\sigma(I)$. Crystal data for **9** at 20 °C are as follows: triclinic space group $P\bar{1}$, $a = 17.973$ (2) Å, $b = 19.068$ (3) Å, $c = 21.557$ (2) Å, $\alpha = 94.32$ (1)°, $\beta = 107.631$ (7)°, $\gamma = 111.56$ (1)°, $V = 6401$ (3) Å^3, and $Z = 4$. The structure was refined to $R = 0.042$ ($R_w = 0.057$) for 11 503 data with $I > 3.0\sigma(I)$. The related reactions of the mixed carbonyl–isocyanide complexes $Re_2Cl_4(\mu\text{-dppm})_2(CO)(CNR)$ (R = *t*-Bu, xylyl) with PMe_3 and $TlPF_6$ occur in an analogous fashion to yield $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(CNR)(PMe_3)]PF_6$. These reactions proceed with retention of the structures of the neutral precursors; viz., when R = *t*-Bu, the structure contains bridging dppm ligands and terminal CO, *t*-BuNC, and chloride ligands, whereas for R = xylyl the structure is that of an edge-sharing bioctahedron with two bridging dppm ligands and a bridging CO and chloride ligand.

Introduction

The dirhenium(II) complexes $Re_2X_4(dppm)_2$ (X = Cl, Br; dppm = $Ph_2PCH_2PPh_2$),[1,2] which possess an electron-rich Re–Re triple bond ($\sigma^2\pi^4\delta^2\delta^{*2}$ ground-state configuration), react with carbon monoxide and organic isocyanide and nitrile ligands in a stepwise fashion with the uptake of up to three of these ligand molecules.[3-5] In some instances, mixed nitrile-isocyanide,[6] carbonyl-nitrile,[7] and carbonyl-isocyanide[5,7-9] complexes have been isolated and, in a few systems, different isomeric forms have been identified.[5,9]

While the reductive coupling of nitrile ligands has been found to occur when organic nitriles are reacted with $Re_2X_4(dppm)_2$ under fairly forcing reaction conditions,[10,11] the same is not true in the case of the analogous reactions with carbon monoxide. The latter proceed in a stepwise fashion (**1** → **2** → **3**), as depicted in Scheme I.[4,8,12] In order to establish how the chemistry of these carbonyl derivatives might be influenced by the presence of additional σ-donors in the coordination environment about the dimetal unit, we are at present investigating how they react with phosphine ligands such as trimethylphosphine. In the present report we describe how $Re_2X_4(dppm)_2(CO)_2$ (**3a**, X = Cl; **3b**, X = Br)[4,12] and the mixed carbonyl-isocyanide complexes of stoichiometry $Re_2Cl_4(dppm)_2(CO)(CNR)$ (**4**, R = *t*-Bu; **5**, R = xylyl)[5] react with PMe_3 and, in the case of **3a**, also with $P(OMe)_3$ and $P(OEt)_3$.

Scheme I



Experimental Section

Starting Materials. The dicarbonyl complexes $Re_2X_4(dppm)_2(CO)_2$ (X = Cl, Br) and the mixed carbonyl-isocyanide complexes $Re_2Cl_4(dppm)_2(CO)(CNR)$, where R = *t*-Bu or xylyl, were prepared from the reactions between $Re_2X_4(dppm)_2$ and the appropriate ligands according to the reported methods.[8,12] Carbon monoxide (99.9%) was purchased from Matheson Gas Products, while the ^{13}C-labeled carbon monoxide (99% enriched) was purchased from Stohler Isotope Chemicals. The tertiary phosphine and phosphite ligands were obtained from Strem Chemicals and Aldrich Chemical Co., respectively. Cobaltocene was obtained from Strem Chemicals while $[(\eta^5\text{-}C_5H_5)_2Fe]PF_6$ was prepared as described in the literature.[13] Solvents used in the preparation of the complexes were of commercial grade and were thoroughly deoxygenated prior to use.

Reaction Procedures. All reactions were performed under an atmosphere of dry dinitrogen.

A. Synthesis of $[Re_2X_3(dppm)_2(CO)_2(PMe_3)]PF_6$ (6a, X = Cl; 6b, X = Br). (i) $[Re_2Cl_3(dppm)_2(CO)_2(PMe_3)]PF_6$ (6a). A mixture of $Re_2Cl_4(dppm)_2(CO)_2$ (0.088 g, 0.066 mmol), $TlPF_6$ (0.023 g, 0.066

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mmol), and ca. 1.2 equiv of PMe_3 (0.008 mL, 0.079 mmol) in dichloromethane (10 mL) was stirred at room temperature for ca. 24 h. The green-yellow precipitate that formed was filtered off, washed with a 10-mL portion of diethyl ether–dichloromethane (10:1), and then extracted with a large volume (250 mL) of dichloromethane. A quantity of white insoluble TlCl remained following this extraction. The green-yellow filtrate was evaporated to dryness to afford the green-yellow title complex; yield 0.061 g (61%). Anal. Calcd for $C_{55}H_{53}Cl_3F_6O_2P_6Re_2$: C, 43.33; H, 3.50. Found: C, 44.62; H, 4.01. The slightly high C and H microanalyses reflect the contamination of this sample by some $Re_2Cl_3(dppm)_2(CO)_2(PMe_3)$ (confirmed by IR spectroscopy).

The analogous reaction between $Re_2Cl_4(dppm)_2(^{13}CO)_2$, PMe_3, and $TlPF_6$ was used to prepare the labeled complex $[Re_2Cl_3(dppm)_2(^{13}CO)_2(PMe_3)]PF_6$; yield 45%.

(ii) $[Re_2Br_3(dppm)_2(CO)_2(PMe_3)]PF_6$ (6b). The procedure for the preparation of this complex from $Re_2Br_4(dppm)_2(CO)_2$ is analogous to that described in section A(i). It was obtained as a yellow powder; yield 34%. Anal. Calcd for $C_{55}H_{53}Br_3F_6O_2P_6Re_2$: C, 39.84; H, 3.22. Found: C, 39.32; H, 3.13.

B. Synthesis of $Re_2Cl_3(dppm)_2(CO)_2(PMe_3)$ (7). A mixture of $Re_2Cl_4(dppm)_2(CO)_2$ (0.204 g, 0.152 mmol), $TlPF_6$ (0.053 g, 0.152 mmol), and 2 equiv of PMe_3 (0.031 mL, 0.304 mmol) in dichloromethane (10 mL) was stirred at room temperature for at least 72 h. The color of the reaction mixture changed from green to blue. The resulting blue reaction mixture was filtered to remove the white precipitate of TlCl. The product was obtained in crystalline form by the slow diffusion of hexane vapor into the dichloromethane solution of the complex over a 2-week period. The blue crystals were washed with a 10-mL portion of methanol and then with 5 mL of hexane and finally dried in vacuum; yield 0.17 g (81%). Anal. Calcd for $C_{55}H_{53}Cl_3O_2P_5Re_2$: C, 47.88; H, 3.87. Found: C, 47.25; H, 4.03.

A sample of $Re_2Cl_3(dppm)_2(^{13}CO)_2(PMe_3)$ was prepared with the use of this same procedure through the reaction of $Re_2Cl_4(dppm)_2(^{13}CO)_2$ with PMe_3 and $TlPF_6$; yield 40%.

C. Synthesis of $\{Re_2Cl_3(dppm)_2(CO)_2[P(OMe)_3]\}PF_6$ (8). A mixture of $Re_2Cl_4(dppm)_2(CO)_2$ (0.056 g, 0.042 mmol), $TlPF_6$ (0.0145 g, 0.042 mmol), and 2 equiv of $P(OMe)_3$ (0.01 mL, 0.084 mmol) in dichloromethane (10 mL) was stirred at room temperature for 48 h. A workup procedure similar to that described in section A(i) gave the title complex as a green-yellow powder; yield 0.065 g (44%). Anal. Calcd for $C_{55}H_{53}Cl_3F_6O_5P_6Re_2$: C, 42.01; H, 3.40. Found: C, 42.57; H, 3.70.

D. Synthesis of $\{Re_2Cl_3(dppm)_2(CO)_2[P(OEt)_3]\}PF_6$ (9). A mixture of $Re_2Cl_4(dppm)_2(CO)_2$ (0.047 g, 0.035 mmol), $TlPF_6$ (0.012 g, 0.035 mmol), and 2 equiv of $P(OEt)_3$ (0.012 mL, 0.070 mmol) in dichloromethane (10 mL) was stirred at room temperature for 48 h. The product was soluble in the reaction medium thereby allowing for its easy separation from the insoluble TlCl. It was purified by the use of a crystallization procedure similar to that described in section B(i). The green crystals were washed with a 10-mL portion of hexane–dichloromethane (10:1); yield 0.045 g (80%). Anal. Calcd for $C_{58}H_{59}Cl_3F_6O_5P_6Re_2$: C, 43.14; H, 3.68. Found: C, 43.09; H, 3.76.

E. Synthesis of $[Re_2Cl_3(dppm)_2(CO)(CNR)(PMe_3)]PF_6$ (10, R = *t*-Bu; 11, R = Xylyl). (i) $[Re_2Cl_3(dppm)_2(CO)(CN\text{-}t\text{-}Bu)(PMe_3)]PF_6$ (10). A mixture of $Re_2Cl_4(dppm)_2(CO)(CN\text{-}t\text{-}Bu)$ (0.048 g, 0.034 mmol), $TlPF_6$ (0.012 g, 0.034 mmol), and 2 equiv of PMe_3 (0.0070 mL, 0.068 mmol) was stirred in dichloromethane (10 mL) at room temperature for 3 days. The resulting dark green reaction mixture was filtered to remove the white precipitated TlCl, and the filtrate was evaporated to dryness. The residue was redissolved in a small volume of dichloromethane, the mixture was filtered, and to the filtrate was added an excess of diethyl ether to yield a green precipitate. This was filtered off and dried in vacuum. The complex was recrystallized from dichloromethane–diethyl ether at 0 °C to afford green microcrystals; yield 0.012 g (23%). Anal. Calcd for $C_{59}H_{62}Cl_3F_6NOP_6Re_2$: C, 44.86; H, 3.96. Found: C, 44.02; H, 4.17.

(ii) $[Re_2Cl_3(dppm)_2(CO)(CNxyl)(PMe_3)]PF_6$ (11; xyl = Xylyl). A mixture of $Re_2Cl_4(dppm)_2(CO)(CNxyl)$ (0.030 g, 0.021 mmol), $TlPF_6$ (0.007 g, 0.021 mmol), and 1 equiv of PMe_3 (0.002 mL, 0.021 mmol) was stirred in dichloromethane (10 mL) at room temperature for 3 days. Workup as in section E(i) afforded this complex as green microcrystals; yield 0.014 g (42%). Anal. Calcd for $C_{63}H_{62}Cl_3F_6NOP_6Re_2$: C, 46.49; H, 3.84. Found: C, 46.40; H, 4.03.

F. Redox Chemistry of $[Re_2Cl_3(dppm)_2(CO)_2(PMe_3)]^{n+}$ (n = 0, 1). (i) Reduction of $[Re_2Cl_3(dppm)_2(CO)_2(PMe_3)]PF_6$ with $(\eta^5\text{-}C_5H_5)_2Co$. The reduction of $[Re_2Cl_3(dppm)_2(CO)_2(PMe_3)]PF_6$ was achieved chemically upon reacting a mixture of this complex (0.047 g, 0.031 mmol) and 1 equiv of cobaltocene (0.006 g, 0.031 mmol) in 10 mL of acetone. The reaction mixture was stirred at room temperature for 6 h, and the insoluble product was filtered off and washed with acetone to remove any unreacted cobaltocene as well as the $[(\eta^5\text{-}C_5H_5)_2Co]PF_6$ reaction byproduct. The remaining solid was finally washed with diethyl ether and recrystallized from dichloromethane–hexane at 0 °C to yield blue $Re_2Cl_3(dppm)_2(CO)_2(PMe_3)$; yield 0.029 g (68%). The identity of the product was shown by its spectroscopic and electrochemical properties.

Table I. Crystallographic Data for $[Re_2Cl_3(dppm)_2(CO)_2(PMe_3)]PF_6$ (**6a**) and $\{Re_2Cl_3(dppm)_2(CO)_2[P(OEt)_3]\}PF_6$ (**9**)

	6a	**9**
chem formula	$Re_2Cl_3P_6F_6O_2C_{55}H_{53}$	$Re_2Cl_3P_6F_6O_5C_{58}H_{59}$
a, Å	15.479 (3)	17.973 (2)
b, Å	14.944 (2)	19.068 (3)
c, Å	14.485 (4)	21.557 (2)
α, deg	100.22 (2)	94.32 (1)
β, deg	108.01 (2)	107.631 (7)
γ, deg	79.41 (1)	111.56 (1)
V, Å^3	3105 (2)	6401 (3)
Z	2	4
fw	1524.63	1614.71
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
T, °C	21	20
λ(Mo Kα), Å	0.71073	0.71073
ρ_{calcd}, g cm^{-3}	1.630	1.675
μ(Mo Kα), cm^{-1}	42.84	41.65
transm coeff	1.000–0.747	1.000–0.778
R^a	0.036	0.042
$R_w{}^b$	0.052	0.057

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

(ii) Oxidation of $Re_2Cl_3(dppm)_2(CO)_2(PMe_3)$ with $[(\eta^5\text{-}C_5H_5)_2Fe]PF_6$. A mixture of $Re_2Cl_3(dppm)_2(CO)_2(PMe_3)$ (0.011 g, 0.008 mmol) and $[(\eta^5\text{-}C_5H_5)_2Fe]PF_6$ (0.0026 g, 0.008 mmol) in dichloromethane (7 mL) was stirred at room temperature for 24 h. The reaction mixture changed from blue to yellow. The solution was evaporated and the yellow residue washed with a 5-mL portion of diethyl ether; yield 0.011 g (95%). This product was shown to be $[Re_2Cl_3(dppm)_2(CO)_2(PMe_3)]PF_6$ on the basis of its spectroscopic and electrochemical properties.

Preparation of Single Crystals for Structure Determinations. Crystals of $[Re_2Cl_3(dppm)_2(CO)_2(PMe_3)]PF_6$ (**6a**) and $\{Re_2Cl_3(dppm)_2(CO)_2[P(OEt)_3]\}PF_6$ (**9**) were grown by the slow diffusion of hexane and cyclohexane vapor, respectively, into dichloromethane solutions of these complexes in a closed system. Suitable platelike crystals were isolated after ca. 2 weeks.

X-ray Crystallography. The structures of **6a** and **9** were determined by application of standard procedures. The basic crystallographic parameters are listed in Table I. The cell constants are based on 25 reflections with $18.8 < \theta < 21.4°$ for **6a** and $20.0 < \theta < 22.0°$ for **9**. Three standard reflections were measured after every 5000 s of beam time during data collection. There was no systematic variations in intensity for either of the crystals. Calculations were performed on a MicroVAX computer using the Enraf-Nonius structure determination package.

Both crystals belong to the triclinic space group $P\bar{1}$ with Z = 2 and 4 for **6a** and **9**, respectively. Accordingly, **9** contains two crystallographically independent molecules in the unit cell. Both structures were solved by the use of the Patterson heavy-atom method, which revealed the positions of the Re atoms. The remaining atoms were located in succeeding difference Fourier syntheses. Lorentz and polarization corrections were applied to the data. In both instances an empirical absorption correction was applied,[14] the linear absorption coefficients being 42.84 cm^{-1} (for **6a**) and 41.65 cm^{-1} (for **9**). No corrections for extinction were applied. The structures were refined in full-matrix least squares where the function minimized was $\sum w(|F_o| - |F_c|)^2$, where w is the weighting factor defined as $w = 1/\sigma^2(F_o)$. For **6a**, the positions for the hydrogen atoms were calculated by assuming idealized geometry and a C–H bond distance of 0.95 Å. For the methyl groups of the PMe_3 ligand, one hydrogen was located in a difference Fourier map, its position idealized, and the remaining positions were calculated. We assumed that the value of B(H), i.e. the isotopic equivalent thermal parameter for the hydrogen atoms, was equal to $1.3[B_{eqv}(C)]$ at the time of the inclusion of this parameter in the refinement procedure. While these hydrogen atoms were used in the calculation of F_o, they were not included in the least-squares refinement. For complex **9**, hydrogens were not included. All non-hydrogen atoms of complex **6a** were refined anisotropically, while for **9** all atoms except the phenyl ring carbon atoms were refined aniso-

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Table II. Positional Parameters and Equivalent Isotropic Displacement Parameters (Å^2) for Non-Phenyl Atoms and Non-Hexafluorophosphate Atoms of **6a** and Their Estimated Standard Deviations[a]

atom	*x*	*y*	*z*	*B*
Re(1)	0.22760 (3)	0.73383 (3)	0.07046 (3)	2.34 (1)
Re(2)	0.29317 (3)	0.86327 (3)	0.02686 (3)	2.28 (1)
Cl(1)	0.2525 (2)	0.5836 (2)	0.1216 (2)	3.54 (7)
Cl(2)	0.4268 (2)	0.9110 (2)	0.0083 (2)	3.65 (7)
Cl(3)	0.3911 (2)	0.7214 (2)	0.0847 (2)	2.62 (6)
P(11)	0.1874 (2)	0.6490 (2)	−0.0963 (2)	2.80 (7)
P(12)	0.2498 (2)	0.7938 (2)	0.2456 (2)	3.03 (7)
P(21)	0.2783 (2)	0.7892 (2)	−0.1447 (2)	2.64 (7)
P(22)	0.3457 (2)	0.9334 (2)	0.2010 (2)	2.72 (7)
P(23)	0.2089 (2)	1.0097 (2)	−0.0279 (3)	3.49 (8)
O(11)	0.0260 (6)	0.7497 (6)	0.0579 (7)	4.7 (2)
O(21)	0.0896 (6)	0.9066 (6)	0.0153 (8)	5.7 (3)
C(1)	0.1789 (7)	0.7279 (8)	−0.1831 (8)	2.9 (3)
C(2)	0.2632 (8)	0.9159 (8)	0.2622 (8)	3.1 (3)
C(10)	0.1012 (7)	0.7444 (7)	0.0613 (8)	2.7 (3)
C(20)	0.1661 (8)	0.8680 (9)	0.0282 (9)	3.4 (3)
C(2311)	0.109 (1)	1.003 (1)	−0.134 (1)	5.4 (4)
C(2321)	0.159 (1)	1.090 (1)	0.057 (1)	4.9 (4)
C(2331)	0.274 (1)	1.081 (1)	−0.060 (1)	6.7 (5)

[a] *B* values for anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$. Data for the phenyl group atoms and the atoms of the PF_6^- anion are available as supplementary material.

Scheme II

$$Re_2X_4(dppm)_2(CO)_2 + PR_3 + TlPF_6 \xrightarrow{CH_2Cl_2} [Re_2X_3(dppm)_2(CO)_2(PR_3)]PF_6 \quad (1)$$

X = Cl 3a

X = Br 3b

X = Cl, R = Me 6a

X = Br, R = Me 6b

X = Cl, R = OMe 8

X = Cl, R = OEt 9

$$\underset{\mathbf{6a}}{[Re_2Cl_3(dppm)_2(CO)_2(PMe_3)]PF_6} \underset{[(\eta^5\text{-}C_5H_5)_2Fe]PF_6/CH_2Cl_2}{\overset{(\eta^5\text{-}C_5H_5)_2Co/acetone}{\rightleftarrows}} \underset{\mathbf{7}}{Re_2Cl_3(dppm)_2(CO)_2(PMe_3)} \quad (2)$$

$$Re_2Cl_4(dppm)_2(CO)(CNR) + PMe_3 + TlPF_6 \xrightarrow{CH_2Cl_2} [Re_2Cl_3(dppm)(CO)(CNR)(PMe_3)]PF_6 \quad (3)$$

R = *t*-Bu 4

R = xylyl 5

R = *t*-Bu 10

R = xylyl 11

Table III. Positional Parameters and Equivalent Isotropic Displacement Parameters (Å^2) for Non-Phenyl Atoms and Non-Hexafluorophosphate Atoms of **9** and Their Estimated Standard Deviations[a]

	x	*y*	*z*	*B*
Re(11)	0.16973 (3)	0.02919 (2)	0.19530 (2)	2.18 (1)
Re(12)	0.21819 (3)	0.00380 (3)	0.31448 (2)	2.37 (1)
Cl(11)	0.0531 (2)	−0.0021 (2)	0.0914 (1)	3.25 (8)
Cl(12)	0.1846 (2)	−0.0615 (2)	0.4005 (1)	3.58 (8)
Cl(13)	0.0672 (2)	−0.0615 (2)	0.2389 (1)	2.69 (7)
P(111)	0.1840 (2)	−0.0843 (2)	0.1434 (1)	2.55 (7)
P(112)	0.1292 (2)	0.1334 (2)	0.2308 (2)	2.59 (7)
P(113)	0.2558 (2)	0.1138 (2)	0.1455 (2)	2.86 (8)
P(121)	0.2604 (2)	−0.1003 (2)	0.2851 (2)	2.73 (7)
P(122)	0.1929 (2)	0.1066 (2)	0.3695 (2)	2.94 (8)
O(12)	0.4036 (5)	0.0853 (5)	0.4099 (4)	4.4 (3)
O(13)	0.3619 (5)	0.1173 (6)	0.2765 (4)	4.9 (3)
O(1131)	0.3245 (5)	0.0867 (5)	0.1375 (4)	4.2 (2)
O(1132)	0.3018 (5)	0.1980 (4)	0.1880 (4)	3.7 (2)
O(1133)	0.2121 (6)	0.1318 (6)	0.0763 (4)	5.2 (3)
C(12)	0.3341 (7)	0.0556 (7)	0.3749 (6)	3.3 (3)
C(13)	0.2890 (7)	0.0750 (7)	0.2641 (6)	3.5 (3)
C(11311)	0.397 (1)	0.127 (1)	0.1151 (9)	6.8 (4)*
C(11312)	0.472 (1)	0.170 (1)	0.177 (1)	8.5 (5)*
C(11321)	0.3382 (9)	0.2692 (8)	0.1637 (7)	5.1 (3)*
C(11322)	0.400 (1)	0.3313 (9)	0.2250 (8)	6.5 (4)*
C(11331)	0.190 (1)	0.0900 (9)	0.0101 (8)	6.1 (4)*
C(11332)	0.202 (1)	0.146 (1)	−0.035 (1)	8.1 (5)*
Re(21)	0.78286 (3)	0.46372 (2)	0.32127 (2)	2.19 (1)
Re(22)	0.71302 (3)	0.46721 (3)	0.19759 (2)	2.40 (1)
Cl(21)	0.9128 (2)	0.5117 (2)	0.4176 (1)	3.36 (8)
Cl(22)	0.7308 (2)	0.5216 (2)	0.1027 (1)	3.58 (8)
Cl(23)	0.8673 (2)	0.5425 (2)	0.2595 (1)	2.64 (7)
P(211)	0.7654 (2)	0.5789 (2)	0.3650 (1)	2.67 (7)
P(212)	0.8282 (2)	0.3609 (2)	0.2907 (1)	2.54 (7)
P(213)	0.7135 (2)	0.3971 (2)	0.3911 (2)	3.18 (8)
P(221)	0.6707 (2)	0.5731 (2)	0.2218 (2)	2.97 (8)
P(222)	0.7355 (2)	0.3590 (2)	0.1468 (2)	2.94 (8)
O(22)	0.5225 (5)	0.3711 (5)	0.1206 (5)	5.0 (3)
O(23)	0.5954 (5)	0.3492 (5)	0.2546 (4)	4.9 (3)
O(2131)	0.6340 (5)	0.4154 (5)	0.3892 (4)	4.2 (2)
O(2132)	0.6825 (5)	0.3076 (5)	0.3763 (5)	5.4 (3)
O(2133)	0.7657 (6)	0.4224 (6)	0.4677 (5)	5.4 (3)
C(22)	0.5931 (7)	0.4071 (7)	0.1478 (6)	3.3 (3)
C(23)	0.6626 (7)	0.3994 (7)	0.2619 (6)	3.1 (3)
C(21311)	0.596 (1)	0.4012 (9)	0.4415 (8)	6.0 (4)*
C(21312)	0.506 (1)	0.398 (1)	0.410 (1)	8.5 (5)*
C(21321)	0.601 (1)	0.247 (1)	0.352 (1)	8.1 (5)*
C(21322)	0.590 (1)	0.182 (1)	0.385 (1)	10.0 (7)*
C(21331)	0.823 (1)	0.396 (1)	0.511 (1)	9.8 (6)*
C(21332)	0.784 (1)	0.349 (1)	0.549 (1)	11.2 (7)*
C(B11)	0.2753 (7)	−0.0931 (6)	0.2045 (6)	2.9 (2)*
C(B12)	0.2003 (7)	0.1802 (6)	0.3174 (6)	3.1 (2)*
C(B21)	0.6651 (7)	0.5776 (6)	0.3062 (6)	2.9 (2)*
C(B22)	0.7478 (7)	0.2999 (6)	0.2103 (6)	3.0 (2)*

[a] *B* values for anisotropically refined atoms are given in the form of isotropic equivalent thermal parameter defined as: $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$. Values marked with an asterisk are for isotropically refined atoms. Data for the phenyl group atoms and the atoms of the PF_6^- anion are available as supplementary material.

tropically; corrections for anomalous scattering were applied to all atoms so refined.[15]

Positional parameters and their errors for the non phenyl group atoms of the dirhenium cations of **6a** and **9** are listed in Tables II and III. Important intramolecular bond distances and angles for these two structures are in Tables IV and V. Tables giving full details of the crystal data and data collection parameters for **6a** and **9** (Tables S1 and S2), the non-hydrogen positional parameters for **6a** and **9** (Tables S3 and S4), the positional parameters for the hydrogen atoms of **6a** (Table S5), the thermal parameters for **6a** and **9** (Tables S6 and S7), and complete bond distances (Tables S8 and S9) and bond angles (Tables S10 and S11) are available as supplementary material, as well as figures (Figures S1 and S2) showing the full atomic numbering schemes for the dirhenium cations in the two crystallographically independent molecules of **9**.

Physical Measurements. Infrared spectra were recorded as Nujol mulls between KBr plates on an IBM Instruments IR/32 Fourier transform spectrometer or a Perkin-Elmer Model 1420 spectrophotometer. Electrochemical measurements were carried out on dichloromethane solutions that contained 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte. $E_{1/2}$ values, determined as $(E_{p,a} + E_{p,c})/2$, were referenced to the silver/silver chloride (Ag/AgCl) electrode at room temperature and are uncorrected for junction potentials. Under our experimental conditions $E_{1/2} = +0.47$ V vs Ag/AgCl for the ferrocenium/ferrocene couple. Voltammetric experiments were performed with a Bioanalytical Systems Inc. Model CV-1A instrument in conjunction with a Hewlett-Packard Model 7035 B x-y recorder. Conductivity measurements were performed on 1×10^{-3} M acetone or DMF solutions of the complexes on an Industrial Instruments Inc. Model RC-16B2 conductivity bridge. $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian XL-200 spectrometer operated at 80.98 MHz with the use of an internal deuterium lock and 85% H_3PO_4 as an external standard. ^1H NMR spectra were obtained on a Varian XL-200 spectrometer. Resonances were referenced internally to the residual protons in the incompletely deuteriated solvent.

Analytical Procedures. Elemental microanalyses were performed by Dr. H. D. Lee of the Purdue University Microanalytical Laboratory.

Results

The transformations observed in this study are summarized in Scheme II. Electrochemical and spectroscopic properties of the

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(15) (a) Cromer, D. T. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.3.1. (b) For the scattering factors used in the structure solution, see: Cromer, D. T.; Waber, J. T. *Ibid.*, Table 2.2B.

Table IV. Important Bond Distances (Å) and Bond Angles (deg) for **6a**[a]

Distances			
Re(1)–Re(2)	2.5927 (8)	P(11)–C(1121)	1.83 (1)
Re(1)–Cl(1)	2.415 (3)	P(12)–C(2)	1.84 (1)
Re(1)–Cl(3)	2.449 (3)	P(12)–C(1211)	1.81 (1)
Re(1)–P(11)	2.471 (3)	P(12)–C(1221)	1.80 (1)
Re(1)–P(12)	2.475 (3)	P(21)–C(1)	1.82 (1)
Re(1)–C(10)	1.90 (1)	P(21)–C(2111)	1.81 (1)
Re(1)–C(20)	2.16 (1)	P(21)–C(2121)	1.84 (1)
Re(2)–Cl(2)	2.412 (4)	P(22)–C(2)	1.84 (1)
Re(2)–Cl(3)	2.482 (3)	P(22)–C(2211)	1.82 (1)
Re(2)–P(21)	2.493 (3)	P(22)–C(2221)	1.85 (1)
Re(2)–P(22)	2.496 (3)	P(23)–C(2311)	1.81 (1)
Re(2)–P(23)	2.458 (3)	P(23)–C(2321)	1.81 (2)
Re(2)–C(20)	1.96 (1)	P(23)–C(2331)	1.80 (2)
P(11)–C(1)	1.83 (1)	O(11)–C(10)	1.14 (1)
P(11)–C(1111)	1.82 (1)	O(21)–C(20)	1.19 (1)
Angles			
Re(2)–Re(1)–Cl(1)	148.95 (8)	P(22)–Re(2)–C(20)	94.1 (3)
Re(2)–Re(1)–Cl(3)	58.90 (7)	P(23)–Re(2)–C(20)	72.8 (4)
Re(2)–Re(1)–P(11)	96.22 (9)	Re(1)–Cl(3)–Re(2)	63.43 (6)
Re(2)–Re(1)–P(12)	96.51 (9)	Re(1)–P(11)–C(1)	108.0 (4)
Re(2)–Re(1)–C(10)	121.1 (4)	Re(1)–P(11)–C(1111)	122.8 (4)
Re(2)–Re(1)–C(20)	47.7 (4)	Re(1)–P(11)–C(1121)	112.4 (4)
Cl(1)–Re(1)–Cl(3)	90.1 (1)	C(1)–P(11)–C(1111)	104.3 (6)
Cl(1)–Re(1)–P(11)	84.1 (1)	C(1)–P(11)–C(1121)	104.9 (5)
Cl(1)–Re(1)–P(12)	85.9 (1)	C(1111)–P(11)–C(1121)	102.9 (6)
Cl(1)–Re(1)–C(10)	89.9 (4)	Re(1)–P(12)–C(2)	108.2 (4)
Cl(1)–Re(1)–C(20)	163.4 (4)	Re(1)–P(12)–C(1211)	113.2 (4)
Cl(3)–Re(1)–P(11)	94.8 (1)	Re(1)–P(12)–C(1221)	122.2 (4)
Cl(3)–Re(1)–P(12)	93.1 (1)	C(2)–P(12)–C(1211)	103.5 (6)
Cl(3)–Re(1)–C(10)	179.1 (3)	C(2)–P(12)–C(1221)	105.7 (5)
Cl(3)–Re(1)–C(20)	106.4 (4)	C(1211)–P(12)–C(1221)	102.2 (6)
P(11)–Re(1)–P(12)	167.2 (1)	Re(2)–P(21)–C(1)	107.5 (4)
P(11)–Re(1)–C(10)	86.0 (3)	Re(2)–P(21)–C(2111)	121.5 (4)
P(11)–Re(1)–C(20)	96.3 (3)	Re(2)–P(21)–C(2121)	119.0 (3)
P(12)–Re(1)–C(10)	86.1 (3)	C(1)–P(21)–C(2111)	104.3 (5)
P(12)–Re(1)–C(20)	91.1 (3)	C(1)–P(21)–C(2121)	104.6 (5)
C(10)–Re(1)–C(20)	73.5 (5)	C(2111)–P(21)–C(2121)	98.0 (6)
Re(1)–Re(2)–Cl(2)	145.92 (7)	Re(2)–P(22)–C(2)	107.3 (3)
Re(1)–Re(2)–Cl(3)	57.66 (8)	Re(2)–P(22)–C(2211)	119.8 (4)
Re(1)–Re(2)–P(21)	93.28 (8)	Re(2)–P(22)–C(2221)	120.2 (4)
Re(1)–Re(2)–P(22)	93.19 (9)	C(2)–P(22)–C(2211)	105.3 (6)
Re(1)–Re(2)–P(23)	127.3 (1)	C(2)–P(22)–C(2221)	103.7 (6)
Re(1)–Re(2)–C(20)	54.6 (4)	C(2211)–P(22)–C(2221)	98.6 (5)
Cl(2)–Re(2)–Cl(3)	88.4 (1)	Re(2)–P(23)–C(2311)	116.7 (5)
Cl(2)–Re(2)–P(21)	82.5 (1)	Re(2)–P(23)–C(2321)	117.7 (5)
Cl(2)–Re(2)–P(22)	85.8 (1)	Re(2)–P(23)–C(2331)	115.7 (5)
Cl(2)–Re(2)–P(23)	86.7 (1)	C(2311)–P(23)–C(2321)	99.8 (6)
Cl(2)–Re(2)–C(20)	159.5 (4)	C(2311)–P(23)–C(2331)	103.0 (8)
Cl(3)–Re(2)–P(21)	88.60 (9)	C(2321)–P(23)–P(2331)	101.4 (8)
Cl(3)–Re(2)–P(22)	85.37 (9)	P(11)–C(1)–P(21)	111.0 (5)
Cl(3)–Re(2)–P(23)	174.9 (1)	P(12)–C(2)–P(22)	110.8 (6)
Cl(3)–Re(2)–C(20)	112.1 (4)	Re(1)–C(10)–O(11)	178 (1)
P(21)–Re(2)–P(22)	167.0 (1)	Re(1)–C(20)–Re(2)	77.8 (4)
P(21)–Re(2)–P(23)	92.1 (1)	Re(1)–C(20)–O(21)	132 (1)
P(21)–Re(2)–C(20)	98.8 (3)	Re(2)–C(20)–O(21)	151 (1)
P(22)–Re(2)–P(23)	92.9 (1)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table V. Important Bond Distances (Å) and Bond Angles (deg) for **9**[a,b]

Distances			
Re(11)–Re(12)	2.5952 (7)	P(111)–C(11121)	1.84 (1)
Re(11)–Cl(11)	2.408 (3)	P(112)–C(B12)	1.84 (1)
Re(11)–Cl(13)	2.494 (3)	P(112)–C(11211)	1.85 (1)
Re(11)–P(111)	2.494 (4)	P(112)–C(11221)	1.83 (1)
Re(11)–P(112)	2.497 (4)	P(113)–O(1131)	1.55 (1)
Re(11)–P(113)	2.363 (3)	P(113)–O(1132)	1.564 (8)
Re(11)–C(13)	2.01 (1)	P(113)–O(1133)	1.59 (1)
Re(12)–Cl(12)	2.414 (3)	P(121)–C(B11)	1.84 (1)
Re(12)–Cl(13)	2.471 (2)	P(121)–C(12111)	1.81 (1)
Re(12)–P(121)	2.475 (4)	P(121)–C(12121)	1.83 (1)
Re(12)–P(122)	2.467 (4)	P(122)–C(B12)	1.85 (1)
Re(12)–C(12)	1.91 (1)	P(122)–C(12211)	1.81 (1)
Re(12)–C(13)	2.11 (1)	P(122)–C(12221)	1.81 (1)
P(111)–C(B11)	1.84 (1)	O(12)–C(12)	1.14 (1)
P(111)–C(11111)	1.82 (1)	O(13)–C(13)	1.19 (1)
Angles			
Re(12)–Re(11)–Cl(11)	146.57 (8)	P(122)–Re(12)–C(12)	85.7 (4)
Re(12)–Re(11)–Cl(13)	58.05 (6)	P(122)–Re(12)–C(13)	95.1 (4)
Re(12)–Re(11)–P(111)	93.46 (7)	C(12)–Re(12)–C(13)	72.6 (5)
Re(12)–Re(11)–P(112)	93.45 (8)	Re(11)–P(111)–C(B11)	106.3 (4)
Re(12)–Re(11)–P(113)	127.17 (7)	Re(11)–P(111)–C(11111)	121.7 (4)
Re(12)–Re(11)–C(13)	52.5 (4)	Re(11)–P(111)–C(11121)	119.0 (5)
Cl(11)–Re(11)–Cl(13)	88.54 (9)	C(B11)–P(111)–C(11111)	102.6 (6)
Cl(11)–Re(11)–P(111)	83.3 (1)	C(B11)–P(111)–C(11121)	106.3 (5)
Cl(11)–Re(11)–P(112)	86.5 (1)	C(11111)–P(111)–C(11121)	99.1 (5)
Cl(11)–Re(11)–P(113)	86.2 (1)	Re(11)–P(112)–C(B12)	107.2 (5)
Cl(11)–Re(11)–C(13)	160.8 (4)	Re(11)–P(112)–C(11211)	120.1 (4)
Cl(13)–Re(11)–P(111)	87.9 (1)	Re(11)–P(112)–C(11221)	119.8 (5)
Cl(13)–Re(11)–P(112)	89.1 (1)	C(B12)–P(112)–C(11211)	104.8 (6)
Cl(13)–Re(11)–P(113)	174.71 (9)	C(B12)–P(112)–C(11221)	104.1 (5)
Cl(13)–Re(11)–C(13)	110.6 (4)	C(11211)–P(112)–C(11221)	98.9 (6)
P(111)–Re(11)–P(112)	169.51 (8)	Re(11)–P(113)–O(1131)	110.5 (4)
P(111)–Re(11)–P(113)	92.4 (1)	Re(11)–P(113)–O(1132)	111.3 (4)
P(111)–Re(11)–C(13)	95.2 (4)	Re(11)–P(113)–O(1133)	119.7 (4)
P(112)–Re(11)–P(113)	89.7 (1)	O(1131)–P(113)–O(1132)	108.8 (4)
P(112)–Re(11)–C(13)	95.3 (4)	O(1131)–P(113)–O(1133)	107.3 (6)
P(113)–Re(11)–C(13)	74.7 (4)	O(1132)–P(113)–O(1133)	98.3 (5)
Re(11)–Re((12)–Cl(12)	149.91 (6)	Re(12)–P(121)–C(B11)	107.6 (4)
Re(11)–Re(12)–Cl(13)	58.92 (7)	Re(12)–P(121)–C(12111)	113.7 (4)
Re(11)–Re(12)–P(121)	96.29 (8)	Re(12)–P(121)–C(12121)	121.7 (5)
Re(11)–Re(12)–P(122)	96.27 (8)	C(B11)–P(121)–C(12111)	103.8 (6)
Re(11)–Re(12)–C(12)	122.0 (4)	C(B11)–P(121)–C(12121)	106.0 (5)
Re(11)–Re(12)–C(13)	49.4 (3)	C(12111)–P(121)–C(12121)	102.4 (5)
Cl(12)–Re(12)–Cl(13)	91.00 (9)	Re(12)–P(122)–C(B12)	107.0 (5)
Cl(12)–Re(12)–P(121)	85.9 (1)	Re(12)–P(122)–C(12211)	124.1 (4)
Cl(12)–Re(12)–P(122)	84.5 (1)	Re(12)–P(122)–C(12221)	112.8 (5)
Cl(12)–Re(12)–C(12)	88.1 (4)	C(B12)–P(122)–C(12211)	104.1 (6)
Cl(12)–Re(12)–C(13)	160.6 (3)	C(B12)–P(122)–C(12221)	105.1 (5)
Cl(13)–Re(12)–P(121)	95.98 (9)	C(12211)–P(122)–C(12221)	102.0 (6)
Cl(13)–Re(12)–P(122)	92.7 (1)	Re(12)–C(12)–O(12)	178 (1)
Cl(13)–Re(12)–C(12)	178.3 (5)	Re(11)–C(13)–Re(12)	78.0 (4)
Cl(13)–Re(12)–C(13)	108.3 (3)	Re(11)–C(13)–O(13)	146 (1)
P(121)–Re(12)–P(122)	167.2 (1)	Re(12)–C(13)–O(13)	136.2 (9)
P(121)–Re(12)–C(12)	85.4 (4)	P(111)–C(B11)–P(121)	111.0 (7)
P(121)–Re(12)–C(13)	91.1 (4)	P(112)–C(B12)–P(122)	109.5 (5)

[a] Data are given for one of the crystallographically independent molecules only. The complete listing of bond distances and angles for the other is available as supplementary material. [b] Numbers in parentheses are estimated standard deviations in the least significant digits.

complexes are given in Table VI, and structures have been determined for two of the compounds, $[Re_2Cl_3(dppm)_2(CO)_2(PMe_3)]PF_6$ (**6a**) and $\{Re_2Cl_3(dppm)_2(CO)_2[P(OEt)_3]\}PF_6$ (**9**). The structural data have already been mentioned in the Experimental Section and are discussed below.

Discussion

(a) Reactions of $Re_2X_4(dppm)_2(CO)_2$ (X = Cl, Br) with Trimethylphosphine and Trialkyl Phosphite Ligands. The bis(carbonyl) complexes $Re_2(\mu\text{-}X)(\mu\text{-}CO)(\mu\text{-}dppm)_2X_3(CO)$ (**2a**, X = Cl; **2b**, X = Br) react with PMe_3, $P(OMe)_3$, and $P(OEt)_3$ at room temperature in dichloromethane in the presence of $TlPF_6$ according to eq 1, Scheme II. Reaction times of 24 h or less were used in the case of the PMe_3 derivatives, since longer times caused conversion of the green-yellow salts $[Re_2X_3(dppm)_2(CO)_2(PMe_3)]PF_6$ (**6**) to the blue reduction products $Re_2X_3(dppm)_2(CO)_2(PMe_3)$. In the case of X = Cl, this product (**7**) was isolated in a pure state in high yield by the use of a reaction time of 72 h and characterized spectroscopically and electrochemically. Solutions of the complexes **6** and **8** in acetone had conductivities in accord with their formulation as 1:1 electrolytes,[16] with Λ_m = 107–113 Ω^{-1} cm^2 mol^{-1} for $c_m \simeq 1 \times 10^{-3}$ M, while for a solution of **9** in DMF, Λ_m = 90 Ω^{-1} cm^2 mol^{-1}. In contrast, the reduced complex $Re_2Cl_3(dppm)_2(CO)_2(PMe_3)$ dissolved in DMF to give a solution that had a very low conductivity (Λ_m = 7 Ω^{-1} cm^2 mol^{-1}).

Like those of the complexes $[Re_2X_3(dppm)_2(CO)_2L]PF_6$, where L represents an organic nitrile or isocyanide ligand,[7] solutions of the PMe_3 and trialkylphosphite derivatives in 0.1 M TBAH/CH_2Cl_2 show three electrochemical processes, as measured by the cyclic voltammetric technique (Table VI). One of these corresponds to a one-electron oxidation of the bulk complex; the other two processes are one-electron reductions. The ready accessibility of the first reduction ($E_{1/2} \simeq -0.05$ V) explains why excess of the very basic PMe_3 ligand so easily reduces **6** to **7**. The CV of **7** is the same as that of **6a**, with the exception that the process at $E_{1/2} = -0.08$ V now corresponds to an oxidation of the complex. The potentials for the three electrochemical processes that occur

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(16) Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81.

Table VI. Electrochemical and IR Spectroscopic Properties of $[Re_2X_3(dppm)_2(CO)_2(PR_3)]^{n+}$ (X = Cl, Br; R = Me, OMe, OEt; *n* = 1, 0) and $[Re_2Cl_3(dppm)_2(CO)(CNR)(PMe_3)]PF_6$ (R = *t*-Bu, Xylyl)

complex	IR, cm^{-1} [a] ν(CN)	ν(CO)	CV half-wave potentials, V [b] $E_{1/2}$(ox)	$E_{1/2}$(red)(1)	$E_{1/2}$(red)(2)
$[Re_2Cl_3(dppm)_2(CO)_2(PMe_3)]PF_6$ (**6a**)		2004 s 1692 m-s	+1.56 (130)	−0.08 (100)	−1.10 (100)
$[Re_2Br_3(dppm)_2(CO)_2(PMe_3)]PF_6$ (**6b**)		2006 s 1688 m-s	+1.55 (120)	−0.02 (110)	−1.01 (110)
$Re_2Cl_3(dppm)_2(CO)_2(PMe_3)$ (**7**)		1937 s 1636 m-s	+1.58 (130)	−0.08 (100)[c]	−1.10 (100)
$\{Re_2Cl_3(dppm)_2(CO)_2[P(OMe)_3]\}PF_6$ (**8**)		2004 s 1710 m	+1.60 (140)	−0.07 (100)	−1.10 (160)[d]
$\{Re_2Cl_3(dppm)_2(CO)_2[P(OEt)_3]\}PF_6$ (**9**)		2007 s 1720 m, 1710 sh	+1.61 (130)	−0.07 (130)	−1.05 (130)
$[Re_2Cl_3(dppm)_2(CO)(CN\text{-}t\text{-}Bu)(PMe_3)]PF_6$ (**10**)	2126 s	1952 s	+1.19 (170)	−0.38 (160)	−1.4 (200)[e]
$[Re_2Cl_3(dppm)_2(CO)(CNxyl)(PMe_3)]PF_6$ (**11**)	2137 s	1669 m-s	+0.97 (130)	−0.59 (110)	−1.61 (110)

[a] Recorded as Nujol mulls. Complexes **6** and **8–11** all show a characteristic PF_6^- absorption due to ν(P–F) between 837 and 845 cm^{-1}. [b] Measured on 0.1 TBAH/CH_2Cl_2 solutions and referenced to the Ag/AgCl electrode, with scan rate (*v*) 200 mV s^{-1} at a Pt-bead electrode. Numbers in parentheses are the $E_{p,a} - E_{p,c}$ values. [c] For **7**, this process corresponds to an oxidation. [d] Approximate value, since $i_{p,c} > i_{p,a}$; $E_{p,c} = -1.18$ V and $E_{p,a} = -1.02$ V. [e] Poorly defined process; reduction wave very broad.

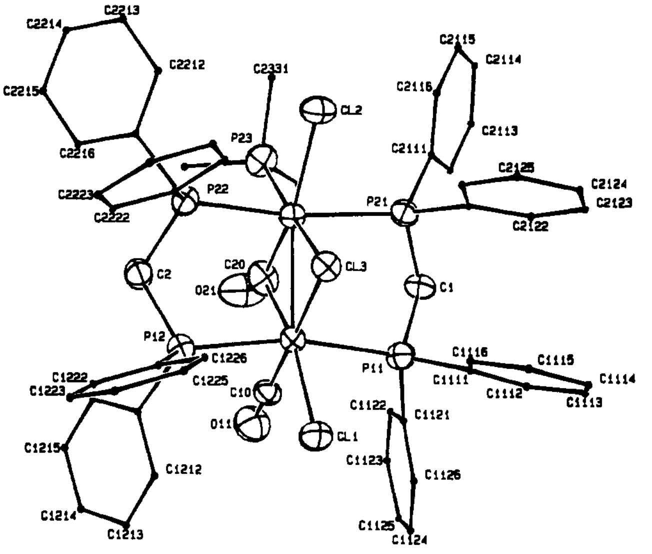

Figure 1. ORTEP representation of the structure of the $[Re_2Cl_3(dppm)_2(CO)_2(PMe_3)]^+$ cation of **6a**, showing the atomic numbering scheme. The thermal ellipsoids are drawn at the 50% probability level except for the carbon atoms of the phenyl rings, which are circles of arbitrary radius.

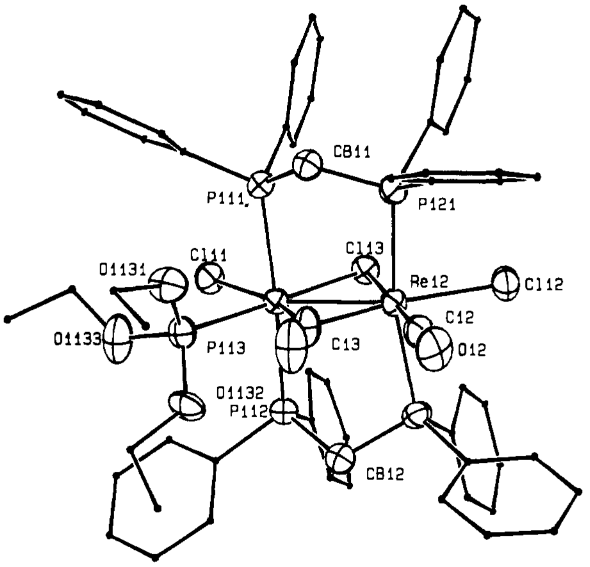

Figure 2. ORTEP representation of the structure of one of the crystallographically independent $\{Re_2Cl_3(dppm)_2(CO)_2[P(OEt)_3]\}^+$ cations of **9**. The thermal ellipsoids are drawn at the 50% probability level except for the carbon atoms of the phenyl rings and $P(OEt)_3$ ligand, which are circles of arbitrary radius. A full atomic numbering scheme is available as supplementary material together with one for the other crystallographically independent cation.

between ca. +1.6 and ca. −1.1 V are very similar to those reported in the case of the related nitrile and isocyanide derivatives.[7]

Whereas the hexafluorophosphate salts **6**, **8**, and **9** are diamagnetic, the blue neutral complex **7** is paramagnetic. The magnetic moment of a dichloromethane solution of this complex (determined by the Evans method[17]) was found to be 2.0 (±0.1) μ_B. It shows an ESR spectrum in dichloromethane (−160 °C) that resembles rather closely the related spectra of $Re_2Cl_3(dppm)_2(CO)_2L$, where L = EtCN, *i*-PrNC, or *t*-BuNC.[7] There is a very complex pattern between 1.5 and 4.5 kG, revealing hyperfine coupling to (presumably) the rhenium, phosphorus, and chloride nuclei. The spectrum is centered at ≃3.0 kG ($g \simeq 2.17$). Its diamagnetic precursor **6a** shows no ESR signal under these same experimental conditions. The close structural similarity between **6a** and **7**, which is shown by the reversibility of the electrochemical couple at $E_{1/2} = -0.08$ V, is further demonstrated by the redox reactions that are represented in eq 2, Scheme II.

The ν(CO) modes in the IR spectra of the complexes **6–9**, which are listed in Table VI, show the presence of both terminal and bridging CO ligands. A comparison between the spectra of **6a** and **7** reveals that the ν(CO) modes of **7** occur at much lower frequencies than those of **6a**, in accord with the more electron-rich character of the dimetal unit in **7** and the associated increase in metal → CO π-back-bonding. In the case of the ^{13}CO-labeled analogues of **6a** and **7**, we observe the following ν(CO) modes, which have shifted in the expected fashion: **6a**(^{13}CO), 1958 s and 1653 m cm^{-1}; **7**(^{13}CO), 1886 s and 1592 m cm^{-1}.

Of the diamagnetic complexes **6**, **8**, and **9**, only **9** gave good quality ^1H and ^{31}P NMR spectra; the others displayed rather poor solubility in suitable solvents. The ^1H NMR spectrum of **9** was recorded in CD_2Cl_2 and showed a triplet at δ +1.22 and multiplet at δ +3.48 due to the $P(OEt)_3$ ligand, an ABMXX′YY′ pattern centered about δ +4.4 that arises from the bridgehead $-CH_2-$ resonances, and a set of sharp well-resolved phenyl resonances between δ +7.0 and +7.85; these resonances integrated in accord with the presumed stoichiometry of this complex. The $^{31}P\{^1H\}$ NMR spectrum (in CD_2Cl_2) shows a triplet at δ +65.6 (J_{P-P} = 32 Hz) assignable to the phosphite ligand, together with multiplets centered at δ −13.4 and −28.2 that arise from the dppm ligands; the relative intensities of these resonances is 1:2:2.

(b) Crystal Structures of $[Re_2Cl_3(dppm)_2(CO)_2(PR_3)]PF_6$ (R = Me, OEt). The structure of the $[Re_2Cl_3(dppm)_2(CO)_2(PR_3)]^+$ cations (R = Me, OEt) in **6a** and **9** is that of an edge-sharing bioctahedron. An ORTEP representation of the structure of the cation of **6a** is shown in Figure 1. Complex **9** contains two crystallographically independent molecules in the unit cell, the

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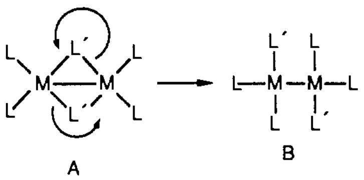
(17) Evans, D. F. *J. Chem. Soc.* **1959**, 2003.

structures of which are, within experimental error, essentially identical; one of them is shown in Figure 2. The important structural parameters for these two structures are listed in Tables IV and V. The structures of both complex cations are in all essential details the same. The Re–Re distances are 2.593 (1) Å for **6a** and 2.595 (1) and 2.598 (1) Å for the crystallographically independent molecules of **9**. These distances, and the other structural features associated with the $[Re_2(\mu\text{-}Cl)Cl_2(\mu\text{-}dppm)_2]$ fragments, are very similar to those reported previously for structurally related complexes such as $[Re_2Cl_3(dppm)_2(CO)_3]PF_6$[4] and $[Re_2Cl_3(dppm)_2(CO)_2(NCEt)]PF_6$.[7]

The structural features of most note concern those that are the consequence of the carbonyl and PMe_3 and $P(OEt)_3$ ligands. The Re–Cl distances involving the bridging chloride ligand are disparate because of the differing structural trans effects of the terminal CO and phosphine or phosphite ligands. For example, in the case of **6a** the distances Re(1)–Cl(3) (trans to CO) and Re(2)–Cl(3) (trans to PMe_3) are 2.449 (3) and 2.482 (3) Å, respectively. Similar bond length differences are seen with the pairs of Re–P(dppm) bonds. The rhenium atom that is coordinated by a PMe_3 or $P(OEt)_3$ ligand is more electron-rich than the other metal center and, consequently, has longer Re–P(dppm) bonds. In the case of **6a** the average distances are as follows: Re(1)–P(dppm) = 2.473 (3) Å and Re(2)–P(dppm) = 2.495 (3) Å. Similar differences are found in the structure of **9**. The final point of note relates to the bridging CO ligand. In both structures, this is found to be bound in an unsymmetrical bridging mode, and the comparable bond distances and angles are essentially the same. Consequently, we need only discuss one of the structures; for convenience this will be **6a**. The shorter Re–C distance is the one that involves the Re atom that has the PMe_3 (or $P(OEt)_3$) ligand coordinated to it; viz., Re(2)–C(20) = 1.96 (1) Å vs Re(1)–C(20) = 2.16(1) Å. Both distances are longer than those involving the terminally bound CO ligands; i.e., Re(1)–C(10) = 1.90 (1) Å in the case of **6a**. The C–O distances also reflect this difference in bonding mode with C(10)–O(11) = 1.14 (1) Å and C(20)–O(21) = 1.19 (1) Å. The angles Re(2)–C(20)–O(21) and Re(1)–C(20)–O(21) at the CO bridge are 151 (1) and 132 (1)°, respectively.

A comparison between the structures of **6a** and **9** and those of $[Re_2Cl_3(dppm)_2(CO)_3]PF_6$[4] and $[Re_2Cl_3(dppm)_2(CO)_2(NCEt)]PF_6$[7] is useful at this point. As expected, the tricarbonyl complex contains an essentially symmetric bridging CO ligand,[4] whereas the propionitrile derivative reveals the beginnings of the distortion that occurs to a much greater extent in **6a** and **9**. In the case of $[Re_2Cl_3(dppm)_2(CO)_2(NCEt)]PF_6$, the Re–C distances involving the bridging CO ligand are 2.13 (2) and 2.00 (2) Å, the shorter of the two involving the Re atom that has the EtCN coordinated to it. The type of "distortion" seen in **6a** and **9** is one that can be considered as representing an intermediate stage in the conversion of an $M_2(\mu\text{-}L')_2L_4$ structure (A) to the open, nonbridged variant B. In this context, we can consider the structurally characterized derivative $[Re_2Cl_3(dppm)_2(CO)(CN\text{-}t\text{-}Bu)_2](PF_6)_{0.5}(OMe)_{0.5}$,[5] i.e. $[Cl_2(CO)Re(\mu\text{-}dppm)_2ReCl(CN\text{-}t\text{-}Bu)_2]^+$, as representing an example of type B. Interestingly, the neutral complex $Re_2Cl_4(dppm)_2(CO)(CN\text{-}t\text{-}Bu)$ (**4**) also possesses the type of open structure represented in B,[5,8] whereas its xylyl isocyanide analogue $Re_2Cl_4(dppm)_2(CO)(CNxyl)$ (**5**) has a structure like A, with bridging Cl and CO ligands.[8] This type of structural change is presumably triggered in some way by the charge disparity that is introduced in this type of unsymmetric dirhenium complex in which the ligands possess disparate donor/acceptor properties. The exact role that interactions between the occupied metal d_π type orbitals and unoccupied $CO(\pi^*)$ orbitals play in this process remains to be established.[18]



(c) Reactions of $Re_2Cl_4(dppm)_2(CO)(CNR)$ (R = *t*-Bu, Xylyl) with Trimethylphosphine. In the context of the preceding discussion, we also studied the reactions of $Re_2Cl_4(dppm)_2(CO)(CNR)$ (**4**, R = *t*-Bu; **5**, R = xylyl) with PMe_3 (eq 3, Scheme II). These reactions proceed in an analogous fashion to those given in eq 1 to afford $[Re_2Cl_3(dppm)(CO)(CNR)(PMe_3)]PF_6$ (**10**, R = *t*-Bu; **11**, R = xylyl). The products preserve the structural characteristics of their precursors **4** and **5**; namely, complex **10** contains terminal CO and isocyanide ligands (on the basis of its IR spectrum; see Table VI), whereas **11** has a bridging CO ligand (ν(CO) at 1669 cm^{-1}) and, presumably, an edge-sharing bioctahedral geometry. In spite of the structural differences that exist between **10** and **11**, both complexes exhibit somewhat similar electrochemical properties (Table VI) with one oxidation and two reduction processes occurring within the potential range +1.2 to −1.7 V vs Ag/AgCl.

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Supplementary Material Available: Tables giving full details of crystal data and data collection parameters of **6a** and **9** (Tables S1 and S2), non-hydrogen positional parameters and their errors of **6a** and **9** (Tables S3 and S4), positional parameters for the hydrogen atoms of **6a** (Table S5), thermal parameters for **6a** and **9** (Tables S6 and S7), and complete bond distances (Tables S8 and S9) and bond angles (Tables S10 and S11) of **6a** and **9** and figures showing the atomic numbering schemes for the dirhenium cations in the two crystallographically independent molecules of **9** (Figures S1 and S2) (48 pages); tables of observed and calculated structure factors of **6a** and **9** (120 pages). Ordering information is given on any current masthead page.

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(18) See, for example: Sargent, A. L.; Hall, M. B. *J. Am. Chem. Soc.* **1989**, *111*, 1563 and references cited therein.