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Carbonylation of the Triply Bonded Dirhenium(II) Complexes $Re_2X_4(dppm)_2$ (X = Cl, Br; dppm = $Ph_2PCH_2PPh_2$) To Give $[Re_2X_3(dppm)_2(CO)_3]PF_6$ and $[Re_2X_3(dppm)_2(CO)_2]PF_6$. Structural Characterization of $[(CO)ClRe(\mu\text{-}Cl)(\mu\text{-}CO)(\mu\text{-}dppm)_2ReCl(CO)]PF_6$

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The triply bonded dirhenium(II) complexes $Re_2X_4(\mu\text{-dppm})_2$ (X = Cl, Br; dppm = bis(diphenylphosphino)methane) react with gaseous CO in CH_2Cl_2 to yield sequentially the monocarbonyls $Re_2X_4(dppm)_2(CO)$ and the dicarbonyls $Re_2X_4(dppm)_2(CO)_2$. The synthesis and characterization of $Re_2Br_4(dppm)_2(CO)_2$, which contains one bridging and one terminal CO ligand, are described here for the first time. Dichloromethane solutions of the neutral dicarbonyls react with gaseous CO at room temperature and 1.1–1.2 atm pressure, in the presence of $TlPF_6$, to yield the tricarbonyls $[Re_2X_3(dppm)_2(CO)_3]PF_6$. The chloride derivative $[Re_2Cl_3(dppm)_2(CO)_3]PF_6$ has been structurally characterized by a single-crystal X-ray structure analysis of crystals grown from CH_2Cl_2–hexane. The complex crystallizes in the monoclinic space group *Cc* with cell dimensions $a = 19.292$ (4) Å, $b = 15.450$ (3) Å, $c = 20.237$ (8) Å, $\beta = 99.85$ (3)°, $V = 5943$ (5) Å^3, and $Z = 4$. The structure was refined to $R = 0.066$ ($R_w = 0.091$) for 3537 data with $F^2 > 3.0\sigma(F^2)$. The structure is that of an edge-sharing bioctahedron that can be represented as $[Re_2(\mu\text{-}Cl)(\mu\text{-}CO)(\mu\text{-dppm})_2Cl_2(CO)_2]PF_6$. The $[Re_2Cl_3(CO)_3]$ unit is essentially planar with all three carbonyl ligands in a cis configuration on the same side of the Re_2P_4 plane. This arrangement gives rise to short C···C contacts between the CO groups (~2.38 Å). The Re–Re distance of 2.582 (1) Å is similar to the metal–metal distances in other dirhenium complexes of this type that contain a $Re(\mu\text{-}Cl)(\mu\text{-}CO)Re$ unit. These tricarbonyl complexes can be reduced (by one electron) to their neutral, paramagnetic analogues $Re_2X_3(dppm)_2(CO)_3$, by using acetone solutions of cobaltocene. When an excess of cobaltocene is added to dichloromethane solutions of $Re_2X_3(dppm)_2(CO)_3$, the air-sensitive cobaltocenium salts $[(\eta^5\text{-}C_5H_5)_2Co][Re_2X_3(dppm)_2(CO)_3]$ are formed. $Re_2X_4(\mu\text{-dppm})_2$ and $Re_2X_4(dppm)_2(CO)$ react with gaseous CO, in the presence of $TlPF_6$, to yield $[Re_2X_3(dppm)_2(CO)_2]PF_6$ (X = Cl, Br). These complexes contain terminally bound CO ligands and are believed to have a structure similar to that of their nitrile analogues $[(RCN)_2ClRe(\mu\text{-dppm})_2ReCl_2]PF_6$.

Introduction

The triply bonded dirhenium(II) complex $Re_2Cl_4(\mu\text{-dppm})_2$ (dppm = $Ph_2PCH_2PPh_2$)[1,2] reacts with organic nitriles and isocyanides to coordinate up to three of these ligands and give products in which a metal–metal multiple bond is retained.[3-8] In other instances, complexes that contain mixed nitrile–isocyanide,[7] carbonyl–nitrile,[9] and carbonyl–isocyanide[9-11] ligand sets have been isolated and structurally characterized, including some systems in which structural isomers have been obtained.[11] In the case of the reactions between CO and $Re_2Cl_4(\mu\text{-dppm})_2$, both the multiply bonded A-frame-like 1:1 adduct $Re_2(\mu\text{-}Cl)(\mu\text{-dppm})_2Cl_3(CO)$[10,12] and the edge-sharing bioctahedral 1:2 adduct $Re_2(\mu\text{-}Cl)(\mu\text{-}CO)(\mu\text{-dppm})_2Cl_3(CO)$[12] have been isolated; the analogous bromide complex $Re_2(\mu\text{-}Br)(\mu\text{-dppm})_2Br_3(CO)$ is also known.[10]

While the uptake of more than two molecules of CO by $Re_2X_4(\mu\text{-dppm})_2$ (X = Cl, Br) does not occur directly, we find that in the presence of $TlPF_6$ one of the Re–X bonds is labilized and a third CO ligand becomes bound to the dirhenium unit. This paper describes the synthesis of the tricarbonyl species $[Re_2X_3(dppm)_2(CO)_3]^n$ (n = 1+, 0, 1–) along with the results of a single-crystal X-ray diffraction study of the salt $[Re_2Cl_3(dppm)_2(CO)_3]PF_6$. The salts $[Re_2X_3(dppm)_2(CO)_2]PF_6$ and the bromide derivative $Re_2Br_4(dppm)_2(CO)_2$ are also reported for the first time.

Experimental Section

Starting Materials. The complexes $Re_2X_4(\mu\text{-dppm})_2$ (X = Cl, Br) were prepared by a new improved method.[13] The monocarbonyl complexes of stoichiometry $Re_2X_4(dppm)_2(CO)$ (X = Cl, Br) and the dicarbonyl $Re_2Cl_4(dppm)_2(CO)_2$ were prepared as described previously[10,12] from the reaction of $Re_2X_4(\mu\text{-dppm})_2$ with carbon monoxide. Common solvents were obtained from commercial sources and used as received or stored over molecular sieves. Bis(diphenylphosphino)methane (abbreviated dppm) was obtained either from Strem Chemicals, Inc., or Pressure Chemical Co. Carbon monoxide (99.9%) was purchased from Matheson Gas Products, while cobaltocene and thallium(I) hexafluorophosphate were obtained from Strem Chemicals, Inc. These reagents were used without further purification.

Reaction Procedures. All reactions were performed under a slight pressure of carbon monoxide (~1.2 atm) or under an atmosphere of dry dinitrogen. All solvents were deoxygenated thoroughly with dinitrogen prior to use.

(A) Preparation of $Re_2Br_4(dppm)_2(CO)_2$. A quantity of $Re_2Br_4(dppm)_2$ (0.20 g, 0.14 mmol) was dissolved in 30 mL of dry, deoxygenated dichloromethane in a 50-mL round-bottomed flask. The flask was flushed with carbon monoxide, the gas ports were then closed, and the solution was stirred under an atmosphere of the gas for 24 h at room temperature. The resulting red-brown solution was treated with an excess of hexane to yield a brown precipitate, which was filtered off, washed with 15 mL of diethyl ether, and dried under vacuum; yield 0.19 g (90%). Anal. Calcd for $C_{52}H_{44}Br_4O_2P_4Re_2$: C, 41.18; H, 2.92. Found: C, 41.40; H, 3.32.

This reaction works equally well if the monocarbonyl $Re_2Br_4(dppm)_2(CO)$[10] is used in place of $Re_2Br_4(dppm)_2$.

(B) Reactions of $Re_2X_4(dppm)_2(CO)_2$ with CO and $TlPF_6$. (i) $[Re_2Cl_3(dppm)_2(CO)_3]PF_6$. A solution that contained $Re_2Cl_4(dppm)_2(CO)_2$ (0.20 g, 0.15 mmol) and 2 equiv of $TlPF_6$ (0.11 g, 0.31 mmol) in dichloromethane (35 mL) was stirred under an atmosphere of carbon monoxide at room temperature for 24 h. The brown reaction mixture was filtered to remove the precipitated TlCl and the excess of $TlPF_6$. The filtrate was treated with sufficient diethyl ether to yield a brown precipitate. This was filtered off, recrystallized from dichloromethane–diethyl ether at 0 °C, and then refiltered and dried under reduced pressure; yield 0.14 g (65%). Anal. Calcd for $C_{53}H_{44}Cl_3F_6O_3P_5Re_2$: C, 43.11; H, 3.00. Found: C, 43.43; H, 3.28.

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(ii) $[Re_2Br_3(dppm)_2(CO)_3]PF_6$. This bromide derivative of the tricarbonyl was prepared by the use of a procedure similar to that described in section **B**(i); yield 50%. Anal. Calcd for $C_{53}H_{44}Br_3F_6O_3P_5Re_2$: C, 39.54; H, 2.75. Found: C, 39.07; H, 2.93.

(C) Reduction of $[Re_2X_3(dppm)_2(CO)_3]PF_6$ with Cobaltocene. (i) $Re_2Cl_3(dppm)_2(CO)_3$. The reduction of $[Re_2Cl_3(dppm)_2(CO)_3]PF_6$ was achieved chemically by dissolving a quantity of this complex (0.10 g, 0.068 mmol) in 10 mL of acetone and then adding an acetone solution (2 mL) that contained 1 equiv of cobaltocene (0.013 g, 0.069 mmol). A dark blue solid precipitated from the reaction mixture upon stirring the solution at room temperature for 4 h. This 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, and the solid was finally washed with diethyl ether. Recrystallization of the crude product from dichloromethane–hexane at 0 °C yielded a blue solid; yield 0.080 g (90%). Anal. Calcd for $C_{53}H_{44}Cl_3O_3P_4Re_2$: C, 47.81; H, 3.33. Found: C, 47.54; H, 3.60.

(ii) $Re_2Br_3(dppm)_2(CO)_3$. The reduction of the bromide derivative to yield this neutral, turquoise-colored species was achieved by the use of a method similar to that described in section C(i); yield 80%. Anal. Calcd for $C_{53}H_{44}Br_3O_3P_4Re_2$: C, 43.45; H, 3.03. Found: C, 43.71; H, 3.25.

(iii) $[(\eta^5\text{-}C_5H_5)_2Co][Re_2Cl_3(dppm)_2(CO)_3]$. Further reduction of the neutral tricarbonyl (whose preparation is described in section C(i)) was accomplished by stirring a mixture of $Re_2Cl_3(dppm)_2(CO)_3$ (0.080 g, 0.060 mmol) with an excess of cobaltocene (0.10 g, 0.53 mmol) in 10 mL of dichloromethane for 48 h at room temperature. The resulting yellow-brown precipitate was filtered off under vacuum and washed with 5 mL of acetone to remove the unreacted cobaltocene. The solid, which is highly air-sensitive, was dried under reduced pressure; yield 0.075 g (80%). Attempts to recrystallize the complex failed because it was immediately oxidized back to the neutral species $Re_2Cl_3(dppm)_2(CO)_3$ when dissolved in dry, deoxygenated dichloromethane. The identity of this product was based upon its spectroscopic and electrochemical properties.

(iv) $[(\eta^5\text{-}C_5H_5)_2Co][Re_2Br_3(dppm)_2(CO)_3]$. This salt was prepared in exactly the same manner as that described in section C(iii); yield 66%. This complex is very air-sensitive, and satisfactory microanalytical data were not obtained.

(D) Reactions of $Re_2X_4(dppm)_2$ and $Re_2X_4(dppm)_2(CO)$ with CO and $TlPF_6$. (i) $[Re_2Cl_3(dppm)_2(CO)_2]PF_6$. A mixture of $Re_2Cl_4(dppm)_2$ (0.10 g, 0.078 mmol), 1 equiv of $TlPF_6$ (0.027 g, 0.078 mmol), and dichloromethane (10 mL) was stirred under an atmosphere of carbon monoxide for 15 min at room temperature. A white precipitate of TlCl was removed by filtration, and the green filtrate was treated with an excess of diethyl ether to precipitate a green product. This was filtered off and redissolved in a small volume of dichloromethane, and diethyl ether was added slowly to the solution until green crystals formed. These were filtered off and dried under reduced pressure; yield 0.075 g (65%). Anal. Calcd for $C_{52}H_{44}Cl_3F_6O_2P_5Re_2$: C, 43.12; H, 3.06. Found: C, 42.32; H, 2.93.

An alternative procedure utilized the monocarbonyl complex $Re_2Cl_4(dppm)_2(CO)$ in place of $Re_2Cl_4(dppm)_2$; yield 38%.

(ii) $[Re_2Br_3(dppm)_2(CO)_2]PF_6$. The bromide derivative was prepared in a fashion analogous to that described for its chloride derivative. The use of $Re_2Br_4(dppm)_2$ gave the title complex in 60% yield. Anal. Calcd for $C_{52}H_{44}Br_3F_6O_2P_5Re_2$: C, 39.48; H, 2.80. Found: C, 38.21; H, 2.61.

When $Re_2Br_4(dppm)_2(CO)$ was used as the starting material, $[Re_2Br_3(dppm)_2(CO)_2]PF_6$ was isolated in 40% yield.

Preparation of Single Crystals of $[Re_2Cl_3(dppm)_2(CO)_3]PF_6$. Suitable single crystals of $[Re_2Cl_3(dppm)_2(CO)_3]PF_6$ were grown by dissolving approximately 0.01 g of this compound in 0.2 mL of dichloromethane in an NMR tube. About 1 mL of hexane was carefully layered on top of this solution, and the tube was then capped. After a period of 24 h red-brown crystals had formed on the walls of the tube.

X-ray Crystallographic Procedures. The structure of the complex of stoichiometry $[Re_2Cl_3(dppm)_2(CO)_3]PF_6$ was determined by application of general procedures that are described more fully elswhere.[14] A single crystal of dimensions 0.68 × 0.35 × 0.26 mm was mounted on a glass fiber with epoxy resin. The crystal was indexed, and data were collected on an Enraf-Nonius CAD-4 diffractometer equipped with a graphite monochromator and a standard-focus molybdenum X-ray tube. Crystal data and information relating to data collection and structure refinement are listed in Table I. The cell parameters are based on 25 reflections with $13.9 < \theta < 19.4°$. Three standard reflections were measured every 5000 s of beam exposure during data collection and displayed no systematic variation in intensity.

Table I. Crystallographic Data and Data Collection Parameters for $[Re_2Cl_3(dppm)_2(CO)_3]PF_6$[a]

formula	$Re_2Cl_3P_5F_6O_3C_{53}H_{44}$
fw	1476.56
space gp	*Cc*
a, Å	19.292 (4)
b, Å	15.450 (3)
c, Å	20.237 (8)
β, deg	99.85 (3)
V, Å^3	5943 (5)
Z	4
d_{calcd}, g cm^{-3}	1.650
cryst dimens, mm	0.68 × 0.35 × 0.26
temp, °C	22.0
radiation (λ, Å)	Mo Kα (0.71073)
monochromator	graphite
linear abs coeff, cm^{-1}	44.51
abs cor applied	empirical[b]
diffractometer	Enraf-Nonius CAD4
scan method	θ–2θ
h, k, l limits	−20 to +20, 0 to 16, 0 to 21
2θ range, deg	4.00–45.00
scan width, deg	$0.85 + 0.35 \tan \theta$
takeoff angle, deg	4.90
programs used	Enraf-Nonius SDP
F_{000}	2864.0
p factor used in weighting	0.070
no. of unique data	4045
no. of data with $I > 3.0\sigma(I)$	3537
no. of variables	392
largest shift/esd in final cycle	0.22
R[c]	0.066
R_w[d]	0.091
goodness of fit[e]	1.791

[a] Numbers in parentheses following certain data are estimated standard deviations occurring in the least significant digit. [b] Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A: Found Crystallogr.* **1983**, *A39*, 158. [c] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [d] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(F_o)$. [e] Goodness of fit $= [\sum w(|F_o| - |F_c|)^2/(N_{observns} - N_{params})]^{1/2}$.

Calculations were performed on a PDP11/34 computer using the Enraf-Nonius structure determination package. The atoms were located and refined from an initial Patterson map. The crystal was found to belong to the monoclinic space group Cc, which is enantiomorphic. An empirical absorption correction was applied.[15] The linear absorption coefficient was 44.51 cm^{-1}. No correction for extinction was applied. The least-squares program minimized the function $\sum w(|F_o| - |F_c|)^2$, where w is a weighting factor defined as $w = 1/\sigma^2(F_o)$. All atoms except the phenyl and carbonyl carbons were refined anisotropically, and corrections for anomalous scattering were applied.[16] Hydrogens were not included in the least-squares refinement. The final residuals for the two enantiomorphs were as follows: $R = 0.066$, $R_w = 0.091$, goodness of fit = 1.791; $R = 0.079$, $R_w = 0.097$, goodness of fit = 1.887. Refinement was completed on the enantimorph that had the lower R factor. No molecules of lattice solvent were found, and the final difference Fourier map displayed no peaks of chemical significance.

Further details concerning the data set, the structure solution, and the structure refinement may be obtained from P.E.F. Figure 1 shows the structure of the cation with the phenyl rings omitted for clarity. Note that the flattening of the thermal ellipsoid associated with atom O21 of one of the terminal CO groups may reflect some inadequacies in the absorption correction, the data, or the model used. We chose not to refine this atom isotropically since this only serves to camouflage the problem. Table II lists the atomic positional parameters and their errors, while Tables III and IV list important intramolecular bond distances and angles. Tables listing thermal parameters (Table S1) and bond distances and bond angles associated with the phenyl rings and PF_6^- anion (Tables S2 and S3, respectively) are available as supplementary material, as well as a figure (Figure S1) showing the full atomic numbering scheme. The large thermal parameters associated with the PF_6^- anion may be due to an unresolved disorder problem and/or to a small partial occupancy by

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

atom	*x*	*y*	*z*	*B*, Å^2	atom	*x*	*y*	*z*	*B*, Å^2
Re(1)	0	0.27241 (6)	0	3.18 (2)	C(211)	0.147 (1)	0.000 (2)	−0.046 (1)	3.8 (5)*
Re(2)	0.12188 (6)	0.20054 (7)	0.03277 (7)	3.27 (2)	C(212)	0.221 (2)	−0.007 (2)	−0.037 (2)	4.7 (6)*
Cl(1)	−0.0704 (4)	0.3825 (5)	−0.0619 (4)	4.7 (2)	C(213)	0.253 (2)	−0.092 (2)	−0.018 (2)	6.0 (8)*
Cl(2)	0.1045 (4)	0.3269 (4)	−0.0440 (4)	4.2 (1)	C(214)	0.215 (3)	−0.152 (3)	−0.006 (3)	8 (1)*
Cl(3)	0.2462 (4)	0.1981 (7)	0.0300 (5)	5.9 (2)	C(215)	0.141 (2)	−0.156 (3)	−0.019 (2)	8 (1)*
P(1)	−0.0392 (4)	0.1780 (5)	−0.0977 (4)	3.9 (2)	C(216)	0.109 (2)	−0.077 (3)	−0.036 (2)	6.4 (8)*
P(2)	0.1088 (4)	0.1034 (5)	−0.0657 (4)	4.1 (2)	C(221)	0.136 (1)	0.141 (2)	−0.143 (1)	4.1 (5)*
P(3)	0.0215 (4)	0.3798 (5)	0.0911 (4)	3.9 (1)	C(222)	0.187 (2)	0.202 (2)	−0.145 (2)	5.5 (7)*
P(4)	0.1573 (4)	0.2860 (5)	0.1365 (4)	3.7 (1)	C(223)	0.206 (2)	0.226 (3)	−0.206 (2)	6.4 (8)*
P(5)	0.9503 (9)	0.158 (1)	0.307 (1)	11.7 (4)	C(224)	0.185 (2)	0.180 (3)	−0.260 (2)	7.0 (9)*
F(1)	0.945 (3)	0.138 (2)	0.378 (3)	18 (2)	C(225)	0.132 (2)	0.118 (2)	−0.264 (2)	6.2 (8)*
F(2)	0.925 (3)	0.066 (3)	0.287 (7)	47 (7)	C(226)	0.108 (2)	0.093 (3)	−0.205 (2)	6.8 (9)*
F(3)	0.973 (3)	0.175 (4)	0.236 (3)	29 (2)	C(311)	0.063 (2)	0.485 (2)	0.080 (2)	4.3 (6)*
F(4)	1.020 (3)	0.107 (4)	0.320 (3)	21 (2)	C(312)	0.067 (2)	0.516 (3)	0.019 (2)	6.0 (8)*
F(5)	0.975 (6)	0.252 (4)	0.319 (3)	38 (4)	C(313)	0.102 (3)	0.597 (3)	0.010 (2)	8 (1)*
F(6)	0.877 (3)	0.170 (4)	0.272 (6)	29 (4)	C(314)	0.132 (3)	0.643 (4)	0.074 (3)	9 (1)*
O(11)	−0.131 (1)	0.207 (2)	0.053 (1)	6.6 (6)	C(315)	0.129 (3)	0.608 (3)	0.135 (3)	8 (1)*
O(21)	0.148 (1)	0.036 (1)	0.116 (1)	5.7 (4)	C(316)	0.091 (2)	0.533 (2)	0.141 (2)	5.5 (7)*
O(31)	0.002 (1)	0.110 (1)	0.087 (1)	6.9 (6)	C(321)	−0.059 (1)	0.412 (2)	0.124 (1)	3.1 (4)*
C(1)	0.013 (2)	0.082 (2)	−0.089 (1)	4.1 (6)	C(322)	−0.085 (2)	0.359 (3)	0.167 (2)	6.1 (8)*
C(2)	0.060 (1)	0.330 (2)	0.162 (2)	4.2 (6)	C(323)	−0.149 (2)	0.380 (3)	0.189 (2)	6.9 (9)*
C(11)	−0.082 (1)	0.233 (2)	0.036 (1)	3.7 (5)*	C(324)	−0.182 (2)	0.456 (3)	0.169 (2)	6.6 (9)*
C(21)	0.140 (1)	0.091 (1)	0.087 (1)	1.5 (3)*	C(325)	−0.151 (2)	0.512 (2)	0.126 (2)	5.9 (8)*
C(31)	0.030 (1)	0.164 (1)	0.063 (1)	1.7 (3)*	C(326)	−0.095 (1)	0.486 (2)	0.103 (1)	3.7 (5)*
C(111)	−0.035 (1)	0.215 (2)	−0.183 (1)	3.4 (5)*	C(411)	0.197 (2)	0.216 (2)	0.205 (2)	4.2 (6)*
C(112)	−0.007 (2)	0.294 (3)	−0.197 (2)	6.4 (9)*	C(412)	0.156 (2)	0.174 (2)	0.248 (2)	5.1 (6)*
C(113)	−0.006 (2)	0.317 (2)	−0.264 (2)	6.2 (8)*	C(413)	0.190 (2)	0.118 (2)	0.296 (2)	6.1 (8)*
C(114)	−0.040 (3)	0.259 (3)	−0.317 (3)	8 (1)*	C(414)	0.259 (2)	0.103 (3)	0.301 (2)	7.1 (9)*
C(115)	−0.068 (2)	0.183 (3)	−0.303 (2)	7.2 (9)*	C(415)	0.300 (2)	0.145 (2)	0.259 (2)	5.8 (8)*
C(116)	−0.069 (2)	0.159 (2)	−0.235 (2)	5.2 (6)*	C(416)	0.270 (2)	0.200 (2)	0.210 (2)	4.8 (6)*
C(121)	−0.130 (2)	0.136 (2)	−0.102 (2)	5.0 (6)*	C(421)	0.218 (2)	0.378 (2)	0.140 (2)	4.5 (6)*
C(122)	−0.185 (2)	0.191 (2)	−0.111 (2)	5.5 (7)*	C(422)	0.241 (2)	0.414 (2)	0.203 (2)	4.7 (6)*
C(123)	−0.252 (2)	0.160 (2)	−0.117 (2)	4.7 (6)*	C(423)	0.284 (2)	0.489 (2)	0.210 (2)	4.8 (6)*
C(124)	−0.270 (2)	0.073 (3)	−0.114 (2)	6.8 (9)*	C(424)	0.304 (2)	0.522 (2)	0.152 (2)	5.9 (7)*
C(125)	−0.211 (2)	0.019 (3)	−0.098 (2)	6.5 (8)*	C(425)	0.285 (2)	0.483 (2)	0.090 (2)	5.3 (7)*
C(126)	−0.144 (2)	0.051 (2)	−0.097 (2)	5.5 (7)*	C(426)	0.239 (2)	0.416 (2)	0.087 (2)	4.9 (6)*

[a] 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.

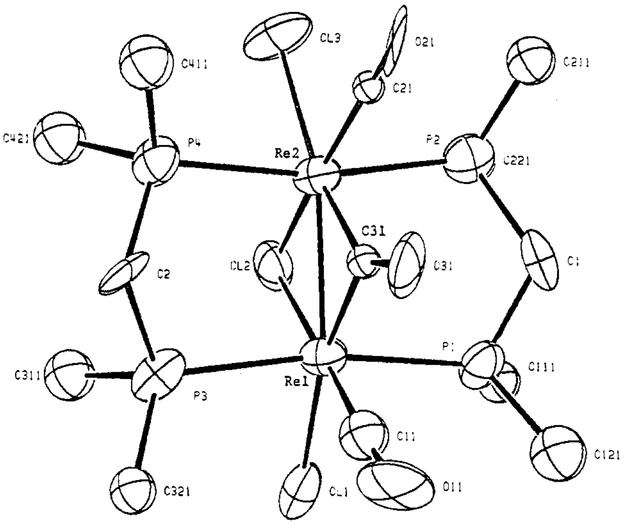

Figure 1. ORTEP view of the $[Re_2Cl_3(dppm)_2(CO)_3]^+$ cation. Thermal ellipsoids are drawn at the 50% probability level. The phenyl groups (on the dppm ligands) have been omitted for clarity.

some other anion (i.e. Cl$^-$). This latter problem could arise if the replacement of Cl$^-$ by PF_6^- is incomplete although we find no independent chemical evidence for this.

Physical Measurements. Infrared spectra were recorded as Nujol mulls or as dichloromethane solutions with an IBM Instruments IR/32 Fourier Transform (4800–400 cm^{-1}) spectrometer. Electronic absorption spectra were recorded on an IBM Instruments 9420 UV-visible, a Hewlett Packard HP8451A, or a Cary 17D spectrophotometer. Electrochemical measurements were carried out by using a Bioanalytical Systems Inc. Model CV-1A instrument on dichloromethane solutions that contained 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as the 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. Conductivity measurements were performed with an Industrial Instruments Inc. Model RC-16B2 conductivity bridge. $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian XL-200 spectrometer operating at 80.98 MHz and using an internal deuterium lock and 85% H_3PO_4 as an external standard. Positive chemical shifts were measured downfield from H_3PO_4. ^1H NMR spectra were also recorded on a Varian XL-200 spectrometer. Resonances were referenced internally to the residual protons in the incompletely deuteriated solvent. Magnetic susceptibility measurements were carried out by the Evans method[17] on dichloro-

Table III. Important Bond Distances (Å) for $[Re_2Cl_3(dppm)_2(CO)_3]PF_6$[a]

Re(1)–Re(2)	2.582 (1)	P(1)–C(111)	1.83 (2)
Re(1)–Cl(1)	2.393 (7)	P(1)–C(121)	1.85 (3)
Re(1)–Cl(2)	2.486 (6)	P(2)–C(1)	1.86 (3)
Re(1)–P(1)	2.469 (7)	P(2)–C(211)	1.77 (2)
Re(1)–P(3)	2.462 (7)	P(2)–C(221)	1.82 (2)
Re(1)–C(11)	1.95 (2)	P(3)–C(2)	1.83 (2)
Re(1)–C(31)	2.13 (2)	P(3)–C(311)	1.85 (2)
Re(2)–Cl(2)	2.481 (7)	P(3)–C(321)	1.86 (2)
Re(2)–Cl(3)	2.406 (6)	P(4)–C(2)	1.79 (2)
Re(2)–P(2)	2.473 (7)	P(4)–C(411)	1.82 (2)
Re(2)–P(4)	2.475 (7)	P(4)–C(421)	1.83 (3)
Re(2)–C(21)	2.02 (2)	O(11)–C(11)	1.13 (3)
Re(2)–C(31)	2.06 (2)	O(21)–C(21)	1.03 (3)
P(1)–C(1)	1.78 (2)	O(31)–C(31)	1.14 (3)

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

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[17] Evans, D. F. *J. Chem. Soc.* **1959**, 2003.

Table IV. Important Bond Angles (deg) for $[Re_2Cl_3(dppm)_2(CO)_3]PF_6$[a]

Re(2)–Re(1)–Cl(1)	148.2 (1)	P(2)–Re(2)–C(21)	84.9 (5)
Re(2)–Re(1)–Cl(2)	58.6 (2)	P(2)–Re(2)–C(31)	95.4 (5)
Re(2)–Re(1)–P(1)	95.3 (2)	P(4)–Re(2)–C(21)	89.5 (5)
Re(2)–Re(1)–P(3)	93.9 (2)	P(4)–Re(2)–C(31)	91.5 (5)
Re(2)–Re(1)–C(11)	121.9 (6)	C(21)–Re(2)–C(31)	71.6 (6)
Re(2)–Re(1)–C(31)	50.7 (4)	Re(1)–Cl(2)–Re(2)	62.6 (2)
Cl(1)–Re(1)–Cl(2)	89.6 (2)	Re(1)–P(1)–C(1)	108.7 (8)
Cl(1)–Re(1)–P(1)	86.1 (2)	Re(1)–P(1)–C(111)	121.1 (7)
Cl(1)–Re(1)–P(3)	85.4 (2)	Re(1)–P(1)–C(121)	113.8 (9)
Cl(1)–Re(1)–C(11)	89.8 (6)	C(1)–P(1)–C(111)	104 (1)
Cl(1)–Re(1)–C(31)	161.1 (4)	C(1)–P(1)–C(121)	103 (1)
Cl(2)–Re(1)–P(1)	94.0 (2)	C(111)–P(1)–C(121)	105 (1)
Cl(2)–Re(1)–P(3)	89.8 (2)	Re(2)–P(2)–C(1)	105.7 (7)
Cl(2)–Re(1)–C(11)	178.3 (7)	Re(2)–P(2)–C(211)	112.5 (8)
Cl(2)–Re(1)–C(31)	109.3 (5)	Re(2)–P(2)–C(221)	119.5 (8)
P(1)–Re(1)–P(3)	170.7 (2)	C(1)–P(2)–C(211)	105 (1)
P(1)–Re(1)–C(11)	87.6 (7)	C(1)–P(2)–C(221)	105 (1)
P(1)–Re(1)–C(31)	91.4 (5)	C(211)–P(2)–C(221)	108 (1)
P(3)–Re(1)–C(11)	88.5 (6)	Re(1)–P(3)–C(2)	107.9 (8)
P(3)–Re(1)–C(31)	95.3 (5)	Re(1)–P(3)–C(311)	121.4 (8)
C(11)–Re(1)–C(31)	71.3 (8)	Re(1)–P(3)–C(321)	113.5 (7)
Re(1)–Re(2)–Cl(2)	58.8 (1)	C(2)–P(3)–C(311)	104 (1)
Re(1)–Re(2)–Cl(3)	150.3 (2)	C(2)–P(3)–C(321)	106 (1)
Re(1)–Re(2)–P(2)	95.2 (2)	C(311)–P(3)–C(321)	103 (1)
Re(1)–Re(2)–P(4)	95.5 (2)	Re(2)–P(4)–C(2)	109.0 (7)
Re(1)–Re(2)–C(21)	124.6 (4)	Re(2)–P(4)–C(411)	110.4 (8)
Re(1)–Re(2)–C(31)	53.1 (4)	Re(2)–P(4)–C(421)	121.7 (9)
Cl(2)–Re(2)–Cl(3)	91.7 (2)	C(2)–P(4)–C(411)	106 (1)
Cl(2)–Re(2)–P(2)	89.4 (2)	C(2)–P(4)–C(421)	104 (1)
Cl(2)–Re(2)–P(4)	95.7 (2)	C(411)–P(4)–C(421)	105 (1)
Cl(2)–Re(2)–C(21)	173.6 (5)	P(1)–C(1)–P(2)	113 (1)
Cl(2)–Re(2)–C(31)	111.9 (5)	P(3)–C(2)–P(4)	111 (1)
Cl(3)–Re(2)–P(2)	86.6 (2)	Re(1)–C(11)–O(11)	175 (2)
Cl(3)–Re(2)–P(4)	83.8 (2)	Re(2)–C(21)–O(21)	177 (2)
Cl(3)–Re(2)–C(21)	85.1 (5)	Re(1)–C(31)–Re(2)	76.2 (6)
Cl(3)–Re(2)–C(31)	156.3 (5)	Re(1)–C(31)–O(31)	137 (2)
P(2)–Re(2)–P(4)	169.3 (2)	Re(2)–C(31)–O(31)	145 (2)

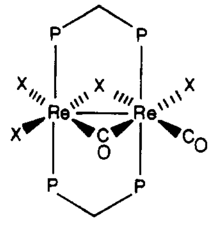
[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

methane solutions of the complexes with the use of a Varian XL-200 spectrometer. X-Band ESR spectra of dichloromethane solutions were recorded at ca. −160 °C with the use of a Varian E-109 spectrometer.

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

Results and Discussion

(a) Preparation and Properties of $Re_2Br_4(dppm)_2(CO)_2$ and $[Re_2X_3(dppm)_2(CO)_2]PF_6$ (X = Cl, Br). The development of a new high-yield synthetic route to the bromide complex $Re_2Br_4(\mu\text{-dppm})_2$[13] has made this an opportune time to study the reactions of this molecule. While the reaction of $Re_2Br_4(\mu\text{-dppm})_2$ with CO in dichloromethane at room temperature gives the monocarbonyl complex $Re_2Br_4(dppm)_2(CO)$ if short reaction times (ca. 1 min) are used,[10] prolonged reaction (24 h) with >1 atm pressure of CO produces the brown dicarbonyl complex $Re_2Br_4(dppm)_2(CO)_2$. Note that the preparation of the analogous chloride complex $Re_2Cl_4(dppm)_2(CO)_2$ requires a much shorter reaction time (ca. 3 h). IR and electronic absorption spectral data and cyclic voltammetric measurements (Table V) have established the close structural similarity of these two dicarbonyls. Also, these two complexes have similar NMR spectral properties. The ^1H NMR spectra (measured in CD_2Cl_2) consist of a complex phenyl region from δ +7.9 to δ +7.0 and an ABX_4 multiplet at δ +4.16 (X = Cl)[12] and δ +4.36 (X = Br) for the methylene protons of the dppm ligands. The $^{31}P\{^1H\}$ NMR spectrum of the bromide derivative is very similar to that of the chloride (at room temperature), namely, a single broad resonance at δ −22.4. While variable-temperature NMR spectral measurements were not performed on $Re_2Br_4(dppm)_2(CO)_2$, it is likely that the molecule is fluxional at room temperature, as has been shown to be the case for the chloride derivative.[12] In all likelihood it has a structure closely akin to $Re_2Cl_4(dppm)_2(CO)_2$, in which there are one bridging and one terminal CO ligand cis to one another,[9,12] viz. structure I.



I (X = Cl, Br)

Several unsuccessful attempts to synthesize the tricarbonyls $[Re_2X_3(dppm)_2(CO)_3]PF_6$ involved the carbonylation of dichloromethane solutions of $Re_2X_4(dppm)_2$ and $Re_2X_4(dppm)_2(CO)$, in the presence of $TlPF_6$, with reaction times of 1 h or more. Workup of these solutions yielded brown solids whose IR spectra showed several ν(CO) modes in the 2100–2600-cm^{-1} region, along with a substantial amount of decomposition. When the reaction time was kept to 15 min, green solutions formed as well as a white precipitate of TlX. Workup of these reaction filtrates yielded green crystalline solids, of formula $[Re_2X_3(dppm)_2(CO)_2]PF_6$.

The IR spectral properties of these complexes (Nujol mulls and dichloromethane solutions) are summarized in Table V. Two terminal ν(CO) modes are present. Cyclic voltammetric measurements show a reversible oxidation at $E_{1/2} \simeq +1.2$ V along with an irreversible reduction at $E_{p,c} \simeq -0.6$ V vs. Ag/AgCl, and associated product waves at −0.02 V (X = Cl) and +0.08 V (X = Br) are also present. Conductivity measurements (in 1×10^{-3} M acetone solutions) confirmed that these products are 1:1 electrolytes ($\Lambda_m \simeq 130\ \Omega^{-1}\ cm^2\ mol^{-1}$). These data lead us to formulate these green products as $[Re_2X_3(dppm)_2(CO)_2]PF_6$.

We have previously synthesized related types of complexes in which there are two isocyanide or nitrile ligands in place of CO. For instance, the bis(isocyanide) complex $[Re_2Cl_3(dppm)_2(CN\text{-}t\text{-}Bu)_2]PF_6$[7] has been isolated in two isomeric forms, one of which most likely resembles structurally the bis(nitrile) complexes

Table V. Spectroscopic and Electrochemical Data for $Re_2X_4(dppm)_2(CO)_2$ and $[Re_2X_3(dppm)_2(CO)_2]PF_6$ (X = Cl, Br)

X		IR spectra[a]		electronic abs spectra	CV half-wave potentials,[c] V			
		$\nu(CO)_t$, cm^{-1}	$\nu(CO)_b$, cm^{-1}	λ_{max}, nm (ϵ)[b]	$E_{1/2}$(ox)(2)	$E_{1/2}$(ox)(1)	$E_{1/2}$(red)(1)	$E_{p,c}$
				$Re_2X_4(dppm)_2(CO)_2$				
Cl[d]	A	1958 vs, 1946 vs	1722 m	1060 (300), 900 sh, 660 (100)[e]	~+1.75	+0.91 (110)	−0.57 (120)	−1.6
	B	1960 vs	1726 m					
Br	A	1962 vs, 1948 vs	1719 m	1100 (230), 650 sh, 472 (12800)		+0.95 (135)	−0.48 (145)	−1.4
	B	1962 vs	1719 m					
				$[Re_2X_3(dppm)_2(CO)_2]PF_6$				
Cl	A	2093 m, 2033 vs		~1050 br sh, 775 (60), ~680 sh, 575 (50), ~390 sh		+1.18 (130)	−0.67[f]	
	B	2097 m, 2041 vs						
Br	A	2089 m, 2029 vs		~1050 br sh, 775 (90), 710 (90), ~590 sh?, ~400 sh		+1.20 (150)	−0.58[f]	
	B	2093 m, 2039 vs						

[a] A = Nujol mull; B = dichloromethane solution. [b] Dichloromethane solution. [c] Cyclic voltammetric (CV) measurements in 0.1 M TBAH–dichloromethane referenced to the Ag/AgCl electrode. Numbers in parentheses are ΔE_p (i.e. $E_{p,a} - E_{p,c}$) values. Sweep rate ν = 200 mV s^{-1}. [d] Data for this complex were taken from ref 12. [e] Additional absorption at 438 nm (ϵ ~6200) observed in the present investigation. [f] $E_{p,c}$ value.

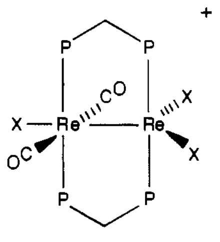
Table VI. Spectroscopic and Electrochemical Data for $[Re_2X_3(dppm)_2(CO)_3]^n$ (X = Cl, Br; n = 1+, 0, 1−)

complex		IR spectra[a]		electronic abs spectra	CV half-wave potentials,[c] V	
		$\nu(CO)_t$, cm^{-1}	$\nu(CO)_b$, cm^{-1}	λ_{max}, nm (ϵ)[b]	$E_{1/2}(1)$	$E_{1/2}(2)$
$[Re_2Cl_3(dppm)_2(CO)_3]PF_6$	A	2047 vs, 2016 vs	1730 vs	920 (160), ~480 sh, 424 (6300), ~320 sh	+0.34 (red)	−0.68 (red)
	B	2047 vs, 2021 vs	1740 m			
$Re_2Cl_3(dppm)_2(CO)_3$	A	1973 vs, 1946 vs	1659 vs	598 (2900), ~390 sh	+0.34 (ox)	−0.68 (red)
	B	1985 vs, 1958 vs	1663 m			
$[(\eta^5\text{-}C_5H_5)_2Co][Re_2Cl_3(dppm)_2(CO)_3]$	A	1912 vs, 1890 vs	1636 m	*d*	+0.33 (ox)	−0.69 (ox)[e]
$[Re_2Br_3(dppm)_2(CO)_3]PF_6$	A	2041 vs, 2018 vs	1736 m	880 sh, ~675 sh, 482 (5100), ~350 sh	+0.38 (red)	−0.62 (red)
	B	2045 vs, 2024 vs	1734 m			
$Re_2Br_3(dppm)_2(CO)_3$	A	1983 vs, 1962 vs	1649 m	622 (3100), ~400 sh	+0.38 (ox)	−0.61 (red)
	B	1985 vs, 1960 vs	1653 m			
$[(\eta^5\text{-}C_5H_5)_2Co][Re_2Br_3(dppm)_2(CO)_3]$	A	1916 vs, 1877 vs	1600 m	*d*	+0.37 (ox)	−0.62 (ox)[e]

[a] A = Nujol mull; B = dichloromethane solution. [b] Dichloromethane solution. [c] Cyclic voltammetric (CV) measurements in 0.1 M TBAH–dichloromethane referenced to the Ag/AgCl electrode. ΔE_p (i.e. $E_{p,a} - E_{p,c}$) values of 105–115 mV characterized each of the couples. Sweep rate v = 200 mV s^{-1}. [d] Spectrum not measured. [e] A reversible process at $E_{1/2}$ = −0.89 V due to the $[(\eta^5\text{-}C_5H_5)_2Co]^+/(\eta^5\text{-}C_5H_5)_2Co$ couple was also observed.

$[Re_2Cl_3(dppm)_2(NCR)_2]PF_6$ (R = Me, Et, or Ph) in which both nitrile ligands are known to coordinate to the same rhenium atom in a disposition trans to one another.[3] The nitrile complexes have electrochemical properties that resemble those of the dicarbonyl derivatives in that they possess an accessibile one-electron oxidation ($E_{1/2} \simeq +0.6$ V) and a one-electron reduction ($E_{1/2} \simeq -1.4$ V). These potentials are consistent with a basic structural resemblance between these two sets of complexes; the electron-withdrawing CO ligands should shift corresponding redox potentials to more positive values since they increase the net positive charge at the dimetal core.

The ^1H NMR spectrum of $[Re_2Cl_3(dppm)_2(CO)_2]PF_6$, measured in CD_2Cl_2, displays a complex phenyl region between δ +7.7 and +7.1 and a pentet centered at δ +5.83 (J(P–H) = 5.2 Hz) for the methylene protons of the dppm ligands. Its $^{31}P\{^1H\}$ NMR spectrum, measured in a 1:1 mixture of CH_2Cl_2–CD_2Cl_2, is a complex AA′BB′ pattern with chemical shifts of δ −6.17 and −13.84 for the most intense inner components of the pattern (δ −5.19 and −14.81 for the most intense outer components). Since these NMR spectral properties resemble those of the bis(isocyanide) (green isomer)[7] and bis(nitrile) salts[3] mentioned earlier, we believe these dicarbonyls may have a similar structure; i.e., the CO ligands are coordinated to the same rhenium atom and are trans to one another:



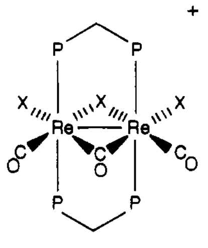
II (X=Cl, Br)

(b) Preparation and Preliminary Characterization of $[Re_2X_3(dppm)_2(CO)_3]PF_6$. Several attempts to prepare these tricarbonyls failed for reasons that are at present not obvious. Substitution of the nitrile ligand in $[Re_2Cl_3(dppm)_2(CO)_2(NCR)]^{n+}$ (R = Me, Et; n = 1, 0) by a CO ligand did not occur, even though substitution does take place with isocyanides.[9,18] Also, the reactions of $Re_2X_4(dppm)_2$ and $Re_2X_4(dppm)_2(CO)$ with CO in the presence of $TlPF_6$ gave the cationic dicarbonyls $[Re_2X_3(dppm)_2(CO)_2]PF_6$ as the only identifiable products (vide supra). Because of the low solubility of the neutral dicarbonyls $Re_2X_4(dppm)_2(CO)_2$ in dichloromethane, it was anticipated that they would not react further with CO, but when a slight excess of $TlPF_6$ was used, and the CO pressure kept at 1.1–1.2 atm for at least 24 h, the tricarbonyls were produced in reasonable yields. No side reactions or secondary products (except TlX) were observed.

From the IR spectral results (Table VI), it is clear that these tricarbonyls contain one bridging and two terminal CO ligands, both in Nujol mulls and in dichloromethane solutions. The electrochemical redox properties, measured in 0.1 M TBAH–CH_2Cl_2, show two reversible reductions at $E_{1/2}$ = +0.34 and −0.68 V (X = Cl) and $E_{1/2}$ = +0.38 and −0.62 V (X = Br). Complexes of this type that contain three π-acceptor ligands usually possess one reversible oxidation in addition to two reversibile reductions. For example, the mixed carbonyl–isocyanide salt $[Re_2Cl_3(dppm)_2(CO)_2(CNxylyl)]PF_6$,[11] which possesses an all-cis arrangement of π-acceptor ligands, has a reversible oxidation at $E_{1/2}$ = +1.74 V as well as reversible reductions at $E_{1/2}$ = +0.08 and −0.90 V. Hence, upon replacement of an isocyanide ligand by CO, a shift to more positive potentials by ~0.3 V is observed. This is reasonable since we would expect three CO ligands to be more effective at stabilizing low oxidation states than only two.

Conductivity measurements, performed on 1 × 10^{-3} M acetone solutions of the tricarbonyls, are in accord with their formulation as 1:1 electrolytes ($\Lambda_m \simeq 120\ \Omega^{-1}$ cm^2 mol^{-1}). The electronic absorption spectra of the two derivatives are also quite similar (Table VI). There is a weak absorption at $\lambda_{max} \simeq 900$ nm along with an intense band at $\lambda_{max} \simeq 450$ nm. The ^1H NMR spectral properties, recorded in acetone-d_6, are consistent with the molecules possessing two dppm ligands. There is a complex phenyl region (δ +8.1 to +7.0) and a broad, unresolved, multiplet centered at δ +4.8 (X = Cl) and δ +4.3 (X = Br) for the bridgehead methylene protons. The $^{31}P\{^1H\}$ NMR spectrum of the chloride derivative (recorded in a 1:1 mixture of CH_2Cl_2 and CD_2Cl_2) revealed a singlet at δ −13.33.

The aforementioned properties, when taken in conjunction with the IR spectral evidence for a bridging CO ligand, support a structure in which all three CO ligands are located on the same side of the molecule in an all-cis arrangement (III).



III (X=Cl, Br)

(c) X-ray Crystal Structure of $[Re_2Cl_3(dppm)_2(CO)_3]PF_6$. As we expected, the $[Re_2Cl_3(dppm)_2(CO)_3]^+$ cation is a coordinatively saturated molecule possessing the edge-sharing bioctahedral geometry. The ORTEP representation (Figure 1) shows that the arrangement of ligands around the two metal centers is one in which all three CO ligands occupy mutually cis positions in the equatorial plane. The bridgehead methylene carbons C(1) and C(2) are folded over on the side of the molecule that contains the three CO ligands. Related structures have been found for

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(18) Price, A. C.; Walton, R. A., unpublished results.

$[Re_2Cl_3(dppm)_2(CO)_2(NCEt)]PF_6$[9] and $Re_2Cl_3(dppm)_2(CO)_2(CN\text{-}i\text{-}Pr)$.[11]

Important bond distances and angles for this tricarbonyl are listed in Tables III and IV. The Re–Re bond distance of 2.582 (1) Å is indicative of multiple bonding and is very close to that of the dicarbonyl $Re_2Cl_4(dppm)_2(CO)_2$ (2.584 (1) Å),[12] $Re_2Cl_4(dppm)_2(CO)(CNxylyl)$ (2.581 (2) Å),[10] and $[Re_2Cl_3(dppm)_2(CO)_2(NCEt)]PF_6$ (2.586 (1) Å).[9] In all these compounds, the μ-CO group can be treated formally as a divalent bridge, thus making the formal oxidation number of the Re_2 unit +6. In this event, we can regard this d^4–d^4 edge-sharing bioctahedral entity as having a net double bond based on the configuration $\sigma^2\pi^2\delta^{*2}\delta^2$, just as in $Re_2Cl_6(dppm)_2$.[19] However, such a simple analogy takes no account of the presence of π-acceptor CO ligands and a more detailed and quantitative treatment of the bonding will be necessary before further conclusions are justified.

In earlier crystallographic studies on the dicarbonyl $Re_2Cl_4(dppm)_2(CO)_2$ and derivatives thereof,[9,11,12] we noted that the $Re–Re–Cl_t$ angles are significantly larger than the $Re–Re–CO_t$ angle. We can attribute this effect, in part, to the large size of the chlorines relative to that of the carbon atoms; this results in the terminal chloride ligands being pushed away from the bridging chloride ligand (the van der Waals radii for a chlorine atom lies between 1.7 and 1.8 Å and the $Cl_b{\cdots}Cl_t$ distances are ~3.5 Å). This, in turn, causes the terminal CO ligands to be repelled away from the terminal chlorides and gives rise to C–Re–C angles 20° smaller than the Cl–Re–Cl angles. As a consequence, the C···C distances become quite short (2.38 Å) and resemble the short C···C contact found in $Nb(CO)_2(dmpe)_2Cl$, whose tantalum analogue can be induced to undergo a reductive coupling of its carbonyl ligands.[20,21]

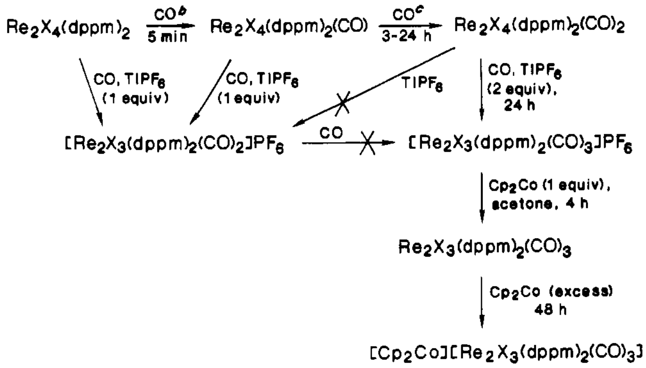
(d) Preparation and Characterization of the Reduced Species $Re_2X_3(dppm)_2(CO)_3$ and $[(\eta^5\text{-}C_5H_5)_2Co][Re_2X_3(dppm)_2(CO)_3]$. As mentioned in section b, the cationic complexes $[Re_2X_3(dppm)_2(CO)_3]PF_6$ exhibit one-electron reductions at $E_{1/2} = +0.34$ V (X = Cl) and +0.38 V (X = Br). The accessibility of these reductions allowed us to use cobaltocene as the reducing agent. This reagent has been used effectively in several recent studies involving other multiply bonded dimetal systems.[9,11,22] Solutions of the cations in acetone react quickly with 1 equiv of cobaltocene to produce stable dark blue (X = Cl) or turquoise-colored (X = Br) solutions. The products were isolated in the form of air stable powders.

X-Band ESR spectra of frozen dichloromethane solutions (−160 °C) confirmed the paramagnetism of these complexes. A complex pattern showing a considerable amount of hyperfine coupling to the phosphorus and rhenium nuclei was observed. The spectra are centered at 2950 G ($g \simeq 2.20$) for the chloride and 2925 G ($g \simeq 2.22$) for the bromide derivative. Magnetic moments of dichloromethane solutions of these neutral species (determined by the Evans method[17]) were found to be 1.5 (±0.1) μ_B.

The electrochemistry of these reduced tricarbonyls (in 0.1 M TBAH–CH_2Cl_2), as determined by cyclic voltammetry, is characterized by two couples. These processes correspond to one oxidation and one reduction, at the same potentials as those found for the parent 1:1 salts (see Table VI). The IR spectra showed essentially the same pattern as that of their respective monocations (Table VI), namely two terminal ν(CO) modes and one bridging ν(CO) mode. These modes were ~70 cm^{-1} lower in energy than those of the monocations.

To see if these neutral tricarbonyls could be reduced any further, an excess of cobaltocene was added to dichloromethane solutions of the complexes $Re_2X_3(dppm)_2(CO)_3$. Within a few hours, brown solids had precipitated from the reaction mixtures. Upon workup, these products were found to be very air-sensitive. Solid samples exposed to the atmosphere for a few minutes turned blue-green (the same color as their neutral precursors), and attempts to recrystallize the materials resulted in oxidation back to the aforementioned neutral species. However, IR spectra of these products (as Nujol mulls) were taken and showed three ν(CO) modes (Table VI). Electrochemical measurements were made on 0.1 M TBAH–CH_2Cl_2 solutions of these complexes. Like their neutral (and cationic) precursors, they possess two reversible processes; both are now oxidations. Also a reversible process was observed at $E_{1/2} = -0.89$ V (corresponding to a reduction) that is due to the $[(\eta^5\text{-}C_5H_5)_2Co]^+/(\eta^5\text{-}C_5H_5)_2Co$ couple. Hence, the properties of these compounds accord with their being the cobaltocenium salts $[(\eta^5\text{-}C_5H_5)_2Co][Re_2X_3(dppm)_2(CO)_3]$, and they are formally derivatives of the Re_2^{2+} core (or Re_2^{4+} if we treat the bridging CO ligand as divalent). This is the first occasion that dirhenium complexes of this type in such a low oxidation state have been isolated.

Scheme I. Reactions of $Re_2X_4(dppm)_2$ (X = Cl or Br) with Carbon Monoxide[a]



[a] The reaction solvent was CH_2Cl_2 unless otherwise noted. [b] This reaction was reported previously for X = Cl[12] and X = Br.[10] [c] This reaction was reported previously for X = Cl.[12]

(e) Concluding Remarks. In Scheme I, we have summarized the reactions pertaining to the chemistry that has been described herein. The complex $[Re_2X_3(dppm)_2(CO)_2]PF_6$ has no bridging CO ligand and does *not* react with carbon monoxide[23] to give the tricarbonyls. Similarly, the neutral dicarbonyls $Re_2X_4(dppm)_2(CO)_2$ do not react with $TlPF_6$ to give $[Re_2X_3(dppm)_2(CO)_2]PF_6$. In other words, a dicarbonyl complex that has no bridging CO ligand is not converted to one that does, and vice versa. Also, we find that the neutral compounds $Re_2X_3(dppm)_2(CO)_3$ do not react further with carbon monoxide (at least not at pressures of 1.1–1.2 atm) in the presence of $TlPF_6$. Clearly the five-membered $\overline{\mathrm{Re{-}Re{-}P{-}C{-}P}}$ rings enhance the stability of these compounds toward metal–metal bond rupture. Of further interest is our observation that neither $[Re_2Cl_4(dppe)_2]^{n+}$ (dppe = $Ph_2PCH_2CH_2PPh_2$; n = 0, 1)[24] nor $Re_2Cl_4(dppm)(dppe)$[25] reacts readily with CO. This may reflect the greater stability of a *planar* Re_2P_4 unit within two fused five-membered $\overline{\mathrm{Re{-}Re{-}P{-}C{-}P}}$ rings compared to that of the related six membered $\overline{\mathrm{Re{-}Re{-}P{-}C{-}C{-}P}}$ ring system. Such a planarity may be necessary in stabilizing the 1:1 A-frame-like and 1:2 edge-sharing bioctahedral carbonyl adducts $Re_2(\mu\text{-}X)(\mu\text{-}dppm)_2X_3(CO)$ and $Re_2(\mu\text{-}X)(\mu\text{-}CO)(\mu\text{-}dppm)_2X_3(CO)$, where X = Cl or Br.

In spite of the "steric crowding" of the CO ligands in the tricarbonyl complexes $[Re_2X_3(dppm)_2(CO)_3]PF_6$, as reflected by the short C···C contacts in the structurally characterized chloride complex, the reversibility of the electrochemistry of these complexes and the isolation of the related neutral and monoanionic species show that the reductive coupling of the carbonyl ligands

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(23) Neither does $[Re_2Cl_3(dppm)_2(CO)_2]PF_6$ react with xylyl isocyanide or with acetonitrile to give $[Re_2Cl_3(dppm)_2(CO)_2L]PF_6$ (L = RNC, R′CN).

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is not initiated by simple electron transfer in which low-valent dirhenium species are formed. Nonetheless, since we have recently found that nitrile ligands can be reductively coupled at the dirhenium center in $Re_2Cl_4(dppm)_2$,[26] we are currently exploring the possibility that these redox-active dimetal species may induce the reductive coupling of other organic substrates.

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Supplementary Material Available: Listings of anisotropic thermal parameters (Table S1), bond distances (Table S2), and bond angles (Table S3) associated with the phenyl rings and PF_6^- anion and a figure showing the full atomic numbering scheme (Figure S1) (5 pages); a table of observed and calculated structure factors (15 pages). Ordering information is given on any current masthead page.

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Multicomponent Polyanions. 41. Potentiometric and ^{31}P NMR Study of Equilibria in the Molybdophenylphosphonate System in 0.6 M Na(Cl) Medium

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The equilibria in the $H^+-MoO_4^{2-}-C_6H_5PO_3^{2-}$ system have been studied by potentiometry and ^{31}P NMR spectroscopy in 0.6 M Na(Cl) medium at 25 °C. The potentiometric data covered the range $8.2 \gtrsim -\lg [H^+] \gtrsim 1.4$.[1] The NMR spectra were recorded in the range $8.7 \gtrsim -\lg [H^+] \gtrsim 0.0$. The total concentrations of molybdate, B, and phenylphosphonate, C, were varied within the limits $10 \le B/\text{mM} \le 80$ and $5 \le C/\text{mM} \le 40$ with $1 \le B/C \le 16$. The following ternary species, denoted by (p,q,r) according to the general formula $(H^+)_p(MoO_4^{2-})_q(C_6H_5PO_3^{2-})_r$, have been found: (10,5,2), (11,5,2), (11,7,1), (12,7,1), and (12,6,1). Values of the logarithm of the formation constants are as follows: $\lg \beta_{10,5,2} = 68.07 \pm 0.02$, $\lg \beta_{11,5,2} = 69.40 \pm 0.10$, $\lg \beta_{11,7,1} = 71.96 \pm 0.09$, $\lg \beta_{12,7,1} = 75.70 \pm 0.04$, and $\lg \delta_{12,6,1} = 69.04 \pm 0.05$. The structures of the ternary species in solution are discussed.

Introduction

In the field of solution chemistry the importance of studying a given system by more than one method has repeatedly been emphasized in the literature. However, a large number of stability constants have been determined by only one method, partly because it is often difficult to apply two or more methods to the system one is going to investigate. In equilibrium analysis potentiometry is most frequently chosen from several different methods because of its wide range of applicability and high accuracy and precision. Many stability constants have been determined just by measuring the hydrogen ion concentration with a glass electrode.

Although it is a powerful tool for investigating equilibria of simple systems, potentiometry often fails to give an unambiguous speciation for a complicated system like a polyoxometalate system, where several polynuclear species are formed. This is in spite of the fact that high-accuracy data have been collected, a constant medium background has been used, and the total concentrations and the ratios between the components have been extended as much as possible without changing the activity factors. A typical example is the molybdophosphate system, where in a recent reinvestigation by a combined emf-NMR method several new species were found, which could not be established by potentiometry alone.[2]

The equilibria in the title system are expected to be much simpler than in the molybdophosphate system, since one of the reaction sites of the heteroatom group is blocked by the organic group. In the literature only one type of organophosphonate heteropolyanion, $(RPO_3)_2Mo_5O_{15}^{n-}$, with a structure analogous to that of $(HOPO_3)_2Mo_5O_{15}^{4-}$,[3] has been reported.[4,5] As some preliminary experiments at our department showed the existence of two or more heteropoly species in solution, we decided to make a thorough study of the system.

In the present paper we report the result of the equilibrium analysis of the molybdophenylphosphonate system based on both potentiometric and ^{31}P NMR data in 0.6 M Na(Cl) medium. The combined emf-NMR data were evaluated by using a new computer program, LAKE, which was developed in parallel with the current study.

Symbols

The equilibria of the title system can be written in the general form

$$pH^+ + qMoO_4^{2-} + rC_6H_5PO_3^{2-} \rightleftarrows (H^+)_p(MoO_4^{2-})_q(C_6H_5PO_3^{2-})_r$$

The complex on the right-hand side will simply be referred as (p,q,r) and its formation constant as $\beta_{p,q,r}$. In addition the following symbols will be used throughout the text.

H: hydrogen concentration over the chosen zero level; H_2O, MoO_4^{2-} and $C_6H_5PO_3^{2-}$
B: total concentration of MoO_4^{2-}
C: total concentration of $C_6H_5PO_3^{2-}$
h: free concentration of hydrogen ion in M
Z: average number of H^+ bound per MoO_4^{2-} ($Z = (H - h)/B$)
$Z_{B,C}$: average number of H^+ bound per $MoO_4^{2-} + C_6H_5PO_3^{2-}$ ($Z_{B,C} = (H - h)/(B + C)$)

Experimental Section

Chemicals. Phenylphosphonic acid (Aldrich) was dried under vacuum overnight. Sodium chloride (Merck, p.A.) was dried at 180 °C for 8 h.

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(1) Throughout this work, the term "lg" stands for $\log_{10}$, one of three recommendations of the IUPAC Commission on Symbols, Terminology and Units [*Pure Appl. Chem.* **1979**, *51*, 24 (decadic logarithm of a: lg a, $\log_{10} a$, log a)]. The present work performed under constant ionic strength involves calibration of the glass electrode against the concentration of H^+. Thus we use $-\lg [H^+]$ rather than pH to distinguish our scale from the operationally defined NBS scale.

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