

Mixed Carbonyl–Isocyanide and Carbonyl–Nitrile Complexes  
Derived from the Reactions of the Multiply Bonded  
Dirhenium(II) Complexes  $\text{Re}_2\text{X}_4(\text{dppm})_2(\text{CO})$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ;  
 $\text{dppm} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$ ). The Structural Characterization of  
 $\text{Cl}_2\text{Re}(\mu\text{-Cl})(\mu\text{-dppm})_2\text{ReCl}(\text{CO})$  and  
 $\text{Cl}_2\text{Re}(\mu\text{-Cl})(\mu\text{-CO})(\mu\text{-dppm})_2\text{ReCl}(\text{CNxylyl})$

F. Albert Cotton,\*<sup>1a</sup> Kim R. Dunbar,<sup>1a</sup> Andrew C. Price,<sup>1b</sup> Willi Schwotzer,<sup>1a</sup> and  
Richard A. Walton\*<sup>1b</sup>

Contribution from the Department of Chemistry and Laboratory for Molecular Structure and  
Bonding, Texas A&M University, College Station, Texas 77843, and the Department of  
Chemistry, Purdue University, West Lafayette, Indiana 47907. Received December 31, 1985

**Abstract:** Reactions of the triply bonded dirhenium(II) complexes  $\text{Re}_2\text{X}_4(\text{dppm})_2$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ;  $\text{dppm} = \text{bis}(\text{diphenylphosphino})\text{methane}$ ) with carbon monoxide yield the monocarbonyls  $\text{X}_2\text{Re}(\mu\text{-X})(\mu\text{-dppm})_2\text{ReX}(\text{CO})$ . The chloride derivative  $\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CO})$  (**1**), which has been characterized by X-ray diffraction, cocrystallizes with three independent benzene molecules in the hexagonal space group  $P6_3/m$  (No. 176). The cell dimensions are  $a = 28.469$  (4) Å,  $c = 14.301$  (2) Å,  $V = 10037$  (4) Å<sup>3</sup>, and  $Z = 6$ . The Re–Re bond distance is 2.338 (1) Å and the molecule has a novel A-frame-like structure. The crystal structure was refined to  $R = 0.048$  (unit weights). Reactions of this molecule with 1 equiv of an isocyanide (RNC) generate complexes of stoichiometry  $\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CO})(\text{CNR})$  ( $\text{R} = i\text{-Pr}$ ,  $t\text{-Bu}$ ,  $\text{xylyl}$ , or  $\text{mesityl}$ ) in which the CO ligand is in either a terminal or bridging position, depending on the isocyanide used. The  $\text{xylylNC}$  derivative  $\text{Cl}_2\text{Re}(\mu\text{-Cl})(\mu\text{-CO})(\mu\text{-dppm})_2\text{ReCl}(\text{CNxylyl})$  (**2**) has been characterized by X-ray crystallography. Compound **2** crystallizes in the monoclinic system, space group  $P2_1/n$ , with  $a = 18.211$  (4) Å,  $b = 15.907$  (2) Å,  $c = 20.887$  (6) Å,  $\beta = 93.63$  (3)°,  $V = 6048$  (1) Å<sup>3</sup>, and  $Z = 4$ . The crystal structure was refined to residuals of  $R = 0.0650$ ,  $R_w = 0.0691$ . The Re–Re bond distance is 2.581 (2) Å, and the molecule comprises a pair of distorted, edge-sharing octahedra. The monocarbonyl reacts readily with an excess of nitrile R'CN in the presence of  $\text{TiPF}_6$  to yield the  $\text{PF}_6^-$  salts of stoichiometry  $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CO})(\text{NCR}')_2]\text{PF}_6$  ( $\text{R}' = \text{CH}_3$ ,  $\text{C}_2\text{H}_5$ , or  $\text{C}_6\text{H}_5$ ). The IR and NMR (<sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H}) spectral properties of these particular complexes suggest that there is an *all-cis* arrangement of chloride ligands on one side of the molecule.

Multiply bonded dimetal complexes undergo a variety of interesting reactions with  $\pi$ -acceptor ligands.<sup>2–4</sup> Cleavage reactions with carbon monoxide and isocyanides occur readily for  $\text{Mo}_2^{4+}$  and  $\text{Re}_2^{6+}$  complexes to generate stable mononuclear species.<sup>5–11</sup> We have found that cleavage is prevented if the two metal centers are bridged by a bidentate phosphine such as  $\text{dppm}$  ( $\text{dppm} = \text{bis}(\text{diphenylphosphino})\text{methane}$ ). The triply bonded complex  $\text{Re}_2\text{Cl}_4(\text{dppm})_2$ <sup>12–14</sup> reacts readily with *tert*-butyl isocyanide to yield  $\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CN-}t\text{-Bu})$  and  $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CN-}t\text{-Bu})_2]\text{PF}_6$ .<sup>15,16</sup> Similarly, we have isolated several nitrile-containing salts, viz.,  $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{NCR}')_2]\text{PF}_6$  ( $\text{R}' = \text{CH}_3$ ,  $\text{C}_2\text{H}_5$ ,  $\text{C}_6\text{H}_5$ , or  $4\text{-PhC}_6\text{H}_4$ ).<sup>17,18</sup> A facile reaction occurs between  $\text{Re}_2\text{Cl}_4$ -

$(\text{dppm})_2$  and carbon monoxide to afford a red-brown monocarbonyl,  $\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CO})$ , and a green dicarbonyl,  $\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CO})_2$ .<sup>19</sup> The structure of the dicarbonyl has been determined by X-ray crystallography,<sup>19</sup> and its reactions with isocyanides and nitriles have been investigated in detail.<sup>20</sup>

Herein, we report the X-ray crystal structure of the monocarbonyl and its reactions with isocyanides and nitriles to yield mixed-ligand dirhenium complexes which possess some interesting structural differences.

### Experimental Section

**Starting Materials.** The monocarbonyl complex  $\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CO})$  was prepared as described previously<sup>19</sup> from the reaction of  $\text{Re}_2\text{Cl}_4(\text{dppm})_2$  with carbon monoxide.  $\text{Re}_2\text{Br}_4(\text{dppm})_2$  was prepared from the reaction of  $\text{Re}_2\text{Br}_4(\text{P-}n\text{-Pr}_3)_4$  with an excess of  $\text{dppm}$ .<sup>12</sup> Nitriles and common solvents were obtained from commercial sources and used as received or stored over molecular sieves. Bis(diphenylphosphino)methane (abbreviated  $\text{dppm}$ ) was obtained from Strem Chemicals and used without further purification. Carbon monoxide was purchased from Matheson Gas Products. The isopropyl, *tert*-butyl, and mesityl isocyanide ligands were prepared according to standard literature procedures,<sup>21</sup> and  $\text{xylyl}$  isocyanide was purchased from Fluka Chemicals.

**Reaction Procedures.** All reactions were carried out in a dry atmosphere of dinitrogen, and all solvents were deoxygenated thoroughly with dinitrogen prior to use.

(A) **The Preparation of  $\text{Re}_2\text{Br}_4(\text{dppm})_2(\text{CO})$ .** A quantity of  $\text{Re}_2\text{Br}_4(\text{dppm})_2$  (0.10 g, 0.068 mmol) was dissolved in 10 mL of dry, deoxygenated dichloromethane and placed in a 50-mL Erlenmeyer flask. A slow stream of carbon monoxide was passed through the purple solution at room temperature for ca. 1 min. The resulting amber colored solution

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was treated with 5 mL of hexane and chilled to 0 °C for 10 min. The red crystals were filtered off, washed with diethyl ether, and dried under reduced pressure; yield, 0.082 g (80%). Anal. Calcd for  $C_{51}H_{44}Br_4O_4Re_2$ : C, 41.14; H, 2.98. Found: C, 40.94; H, 3.18.

(B) Reactions of  $Re_2Cl_4(dppm)_2(CO)$  with Isocyanides. (i)  $Re_2Cl_4(dppm)_2(CO)(CNCHMe_2)$ . A stirred solution of  $Re_2Cl_4(dppm)_2(CO)$  (0.10 g, 0.076 mmol) in 10 mL of acetone was treated with 1 equiv of isopropyl isocyanide (7  $\mu$ L, 0.077 mmol). The mixture was stirred for 24 h at room temperature. The resulting pink precipitate was filtered off and washed with 15 mL of diethyl ether. The solid was redissolved in a small volume of dichloromethane, and the solution was then treated with a large excess of diethyl ether and chilled to 0 °C for 30 min. The dark red crystals were filtered off and dried under reduced pressure; yield, 0.082 g (80%). Anal. Calcd for  $C_{55}H_{51}Cl_4NOP_4Re_2$ : C, 47.87; H, 3.72; Cl, 10.28. Found: C, 48.20; H, 3.74; Cl, 10.34.

(ii)  $Re_2Cl_4(dppm)_2(CO)(CNCMe_3)$ . A quantity of  $Re_2Cl_4(dppm)_2(CO)$  (0.20 g, 0.15 mmol) was stirred for 10 min in 15 mL of acetone at room temperature. The addition of a stoichiometric quantity of *tert*-butyl isocyanide (17  $\mu$ L, 0.16 mmol) resulted in the immediate formation of a pink precipitate. The mixture was stirred for 24 h at room temperature. The precipitate was filtered off, washed with 2  $\times$  15 mL portions of diethyl ether, to remove any excess isocyanide, and then redissolved in 5 mL of dichloromethane. This dark red solution was treated with a large excess of diethyl ether and chilled for 2 h at 0 °C to yield dark red crystals which were filtered off and dried under reduced pressure; yield, 0.17 g (80%). Anal. Calcd for  $C_{56}H_{53}Cl_4NOP_4Re_2$ : C, 48.25; H, 3.83. Found: C, 49.08; H, 4.35. The  $^1H$  NMR spectrum of this sample showed the presence of diethyl ether of crystallization, thereby accounting for the slightly high C and H elemental microanalyses.

(iii)  $Re_2Cl_4(dppm)_2(CO)(CNxylyl)$ . A solution containing  $Re_2Cl_4(dppm)_2(CO)$  (0.20 g, 0.14 mmol) and *xylyl*NC (0.020 g, 0.15 mmol) in 15 mL of acetone was stirred at room temperature for 24 h. The resulting green precipitate was filtered off and washed with 2  $\times$  15 mL portions of diethyl ether. Recrystallization from dichloromethane–hexanes yielded yellow-green crystals which were filtered off and dried under reduced pressure; yield, 0.17 g (80%). Anal. Calcd for  $C_{60}H_{53}Cl_4NOP_4Re_2$ : C, 49.97; H, 3.70; Cl, 9.83. Found: C, 49.18; H, 3.94; Cl, 10.26.

(iv)  $Re_2Cl_4(dppm)_2(CO)(CNmesityl)$ . A suspension of  $Re_2Cl_4(dppm)_2(CO)$  (0.10 g, 0.076 mmol) in 8 mL of acetone was stirred at room temperature for 5 min. This was then treated with a solution containing *mesityl*NC (0.011 g, 0.076 mmol) in 2 mL of acetone. The mixture was stirred for 24 h at room temperature, and the resulting green precipitate was filtered off and washed with 15 mL of diethyl ether. Recrystallization from benzene–hexanes yielded a light-green solid which after filtering and drying gave a powder; yield, 0.051 g (50%). Anal. Calcd for  $C_{61}H_{53}Cl_4NOP_4Re_2$ : C, 50.31; H, 3.81; Cl, 9.74. Found: C, 50.55; H, 4.30; Cl, 10.06.

(C) Reactions of  $Re_2Cl_4(dppm)_2(CO)$  with Nitriles. (i)  $[Re_2Cl_3(dppm)_2(CO)(NCC_2H_5)_2]PF_6$ . A solution containing  $Re_2Cl_4(dppm)_2(CO)$  (0.10 g, 0.076 mmol) and  $TiPF_6$  (0.028 g, 0.080 mmol) in 10 mL of acetone–acetonitrile (1:1) was stirred at room temperature for 24 h. The resulting green-brown solution was filtered to remove the precipitated  $TiCl$ , and the filtrate was evaporated to dryness. The residue was extracted with dichloromethane to give a green solution and a small amount of unreacted  $TiPF_6$  which was filtered off. Diethyl ether was added to the filtrate to initiate precipitation, and the yellow-green solid was filtered off and recrystallized from acetone–hexane mixtures; yield, 0.085 g (75%). Anal. Calcd for  $C_{55}H_{50}Cl_3F_6N_2OP_5Re_2$ : C, 43.96; H, 3.35; Cl, 7.08. Found: C, 43.96; H, 3.77; Cl, 7.80.

(ii)  $[Re_2Cl_3(dppm)_2(CO)(NCC_2H_5)_2]PF_6$ . A solution containing  $Re_2Cl_4(dppm)_2(CO)$  (0.10 g, 0.076 mmol) and  $TiPF_6$  (0.028 g, 0.080 mmol) in 10 mL of acetone–propionitrile (1:1) was stirred at room temperature for 24 h. The product, a green solid, was worked up in exactly the same manner as that described in section Ci; yield, 0.080 g (70%). Anal. Calcd for  $C_{57}H_{54}Cl_3F_6N_2OP_5Re_2$ : C, 44.73; H, 3.56. Found: C, 44.01; H, 4.15.

(iii)  $[Re_2Cl_3(dppm)_2(CO)(NCC_2H_5)_2]PF_6$ . A mixture of  $Re_2Cl_4(dppm)_2(CO)$  (0.10 g, 0.076 mmol) and  $TiPF_6$  (0.028 g, 0.080 mmol) in acetone (8 mL) and benzonitrile (2 mL) was allowed to react for 10 h at room temperature. The yellow-green solution was then filtered to remove insoluble  $TiCl$ , and the filtrate was reduced in volume under a stream of gaseous nitrogen. When the acetone solvent was evaporated, the product began to oil, so an excess of diethyl ether was added which resulted in the precipitation of a dark-green solid. This was filtered off and redissolved in a small volume of dichloromethane to remove any  $TiPF_6$  or  $TiCl$  impurities. Treatment of the filtrate with diethyl ether produced a green solid; yield, 0.065 g (50%). Anal. Calcd for  $C_{66}H_{56}Cl_3F_6N_2OP_5Re_2$ : C, 43.31; H, 3.30. Found: C, 46.60; H, 3.73.

Table I. Crystal Data for  $Re_2Cl_4(dppm)_2(CO) \cdot 3C_6H_6$  (1) and  $Re_2Cl_4(dppm)_2(CO)(CNxylyl) \cdot CH_3OH$  (2)

formula	$Re_2Cl_4P_4OC_51H_{44}$ (1)	$Re_2Cl_4P_4O_2N_1C_{61}H_{57}$ (2)
formula weight	1545.4	1474.25
space group	$P6_3/m$	$P2_1/n$
systematic absences	000: $l = 2n + 1$	$h0l, h + 1 = 2n, 0k0,$ $k = 2n$
<i>a</i> , Å	28.469 (4)	18.211 (4)
<i>b</i> , Å		15.907 (2)
<i>c</i> , Å	14.301 (2)	20.887 (6)
$\alpha$ , deg		90
$\beta$ , deg		93.63 (3)
$\gamma$ , deg		90
<i>V</i> , Å <sup>3</sup>	10037 (4)	6048 (1)
<i>Z</i>	6	4
<i>d</i> <sub>calcd</sub> , g/cm <sup>3</sup>	1.534	1.619
crystal size, mm	0.40 $\times$ 0.20 $\times$ 0.20	0.30 $\times$ 0.30 $\times$ 0.06
$\mu$ (Mo K $\alpha$ ), cm <sup>-1</sup>	35.6	43.773
data collection instrument	Enraf-Nonius CAD4	
radiation (monochromated in incident beam)	Mo K $\alpha$ ( $\lambda_\alpha = 0.71073$ Å)	Mo K $\alpha$ ( $\lambda_\alpha = 0.71073$ Å)
orientation reflcns, no. range (2 $\theta$ )	25, $13 \leq 2\theta \leq 29^\circ$	25, $12 \leq 2\theta \leq 25^\circ$
temp, °C	ambient	25 $\pm$ 1 °C
scan method	$\omega$ -2 $\theta$	$\omega$ -scan
data col. range, 2 $\theta$ , deg	$4 \leq 2\theta \leq 50^\circ$	$4 \leq 2\theta \leq 45^\circ$
no. of unique data, total with $F_o^2 > 3\sigma(F_o^2)$	1716	2787
no. of parameters refined	247	446
trans. factors, max, min (exptl)	98%, 59%	99%, 59%
<i>R</i> <sup>a</sup>	0.048 (unit weights)	0.065
<i>R</i> <sub>w</sub> <sup>b</sup>		0.069
quality-of-fit indicator <sup>c</sup>	1.55	1.368
largest shift/esd, final cycle	0.03	0.58
largest peak, e/Å <sup>3</sup>	0.73	1.48

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

Evidence for the formulation of this complex as a monosolvate with  $CH_2Cl_2$  was provided by  $^1H$  NMR spectroscopy.

**Preparation of Single Crystals of  $Re_2Cl_4(dppm)_2(CO)$  and  $Re_2Cl_4(dppm)_2(CO)(CNxylyl)$ .** Crystals of  $Re_2Cl_4(dppm)_2(CO)$  were obtained from a variety of solvent systems. Slow diffusion of hexane into  $CH_2Cl_2$  solutions yielded bundles of fine needles. From toluene solution, crystals of attractive appearance were obtained which not only were poor diffractors of X-rays but also, without exception, twinned (rotational twinning in a monoclinic system). The crystals which were employed for diffraction work grew from a  $CH_2Cl_2/C_6H_6$  solution on the inside of an NMR tube. Difficulties in growing X-ray quality crystals of *dppm* containing dimetallic complexes were encountered before.<sup>14</sup> Additionally, in this case, we are aware, from IR data (see below), that there is a solvent-dependent equilibrium of isomers present in solution.

Suitable single crystals of  $Re_2Cl_4(dppm)_2(CO)(CNxylyl)$  were grown by dissolving approximately 0.01 g of this compound in 1 mL of dichloromethane contained in a small sample vial. About 2 mL of methanol was carefully layered on top of this solution, and the vial was then capped. Very slow evaporation was allowed to take place, through a small hole in the cap, for a 2-week period until yellow-green crystals formed on the side and at the bottom of the vial.

**X-ray Crystallographic Procedures.** The structures of the complexes  $Re_2Cl_4(dppm)_2(CO)$  (1) and  $Re_2Cl_4(dppm)_2(CO)(CNxylyl)$  (2) were determined by application of general procedures which have been fully described elsewhere.<sup>22</sup> The diffraction data for both 1 and 2 were collected on an Enraf-Nonius CAD-4 diffractometer equipped with graphite monochromated Mo K $\alpha$  ( $\alpha = 0.71073$  Å) radiation. The crystal parameters and basic information pertaining to data collection and structure refinement are summarized in Table I. Tables II and III list

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**Table II.** Atomic Positional Parameters and Equivalent Isotropic Displacement Parameters ( $\text{\AA}^2$ ) and Their Estimated Standard Deviations for  $\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CO})$  (1)<sup>a</sup>

atom	x	y	z	B ( $\text{\AA}^2$ )
Re(1)	0.70212 (3)	0.08274 (3)	0.66827 (7)	3.42 (3)
Cl(3)	0.6176 (7)	0.0100 (6)	0.616 (1)	4.6 (3)*
C(1)	0.636 (3)	0.028 (2)	0.666 (5)	7 (1)*
O(1)	0.593 (2)	-0.008 (2)	0.659 (3)	7 (1)*
Cl(1)	0.7883 (3)	0.1516 (3)	0	4.1 (3)
Cl(2)	0.7436 (3)	0.1202 (3)	0.5141 (5)	5.5 (3)
P(1)	0.6640 (3)	0.1419 (3)	0.6462 (5)	4.8 (3)
P(2)	0.7337 (3)	0.0177 (3)	0.6458 (4)	3.5 (2)
C(2)	0.621 (2)	0.134 (1)	0	5 (1)
C(3)	0.713 (1)	-0.026 (1)	0	4 (1)
C(4)	0.6158 (8)	0.1241 (9)	0.552 (1)	6 (1)
C(5)	0.5608 (8)	0.0875 (9)	0.565 (1)	8 (1)
C(6)	0.5249 (8)	0.0734 (9)	0.490 (1)	9 (2)
C(7)	0.5441 (8)	0.0959 (9)	0.402 (1)	11 (2)
C(8)	0.5992 (8)	0.1326 (9)	0.389 (1)	18 (4)
C(9)	0.6351 (8)	0.1467 (9)	0.464 (1)	15 (3)
C(10)	0.7080 (9)	0.2148 (9)	0.630 (2)	7.9 (8)*
C(11)	0.7640 (9)	0.2367 (9)	0.624 (2)	5.3 (6)*
C(12)	0.7976 (9)	0.2921 (9)	0.608 (2)	7.0 (8)*
C(13)	0.7752 (9)	0.3256 (9)	0.598 (2)	15 (2)*
C(14)	0.7192 (9)	0.3037 (9)	0.604 (2)	39 (5)*
C(15)	0.6855 (9)	0.2482 (9)	0.619 (2)	26 (3)*
C(16)	0.8036 (6)	0.0383 (7)	0.631 (1)	3.1 (8)
C(17)	0.8421 (6)	0.0925 (7)	0.615 (1)	5 (1)
C(18)	0.8962 (6)	0.1075 (7)	0.600 (1)	8 (2)
C(19)	0.9117 (6)	0.0681 (7)	0.599 (1)	7 (1)
C(20)	0.8732 (6)	0.0138 (7)	0.615 (1)	7 (2)
C(21)	0.8191 (6)	-0.0011 (7)	0.631 (1)	6 (1)
C(22)	0.7021 (9)	-0.0296 (8)	0.548 (1)	6 (1)
C(23)	0.6638 (9)	-0.0841 (8)	0.562 (1)	9 (2)
C(24)	0.6424 (9)	-0.1191 (8)	0.486 (1)	9 (2)
C(25)	0.6593 (9)	-0.0997 (8)	0.395 (1)	9 (2)
C(26)	0.6977 (9)	-0.0452 (8)	0.381 (1)	12 (2)
C(27)	0.7190 (9)	-0.0101 (8)	0.457 (1)	9 (1)
C(28)	0.860 (2)	0.044 (2)	0	10 (1)*
C(29)	0.853 (1)	0.068 (1)	0.171 (3)	9.0 (9)*
C(30)	0.839 (1)	0.107 (1)	0.166 (2)	7.9 (7)*
C(31)	0.830 (2)	0.125 (2)	0	8 (1)*
C(32)	0.455 (3)	0.244 (3)	0	13 (2)*
C(33)	0.459 (2)	0.223 (2)	0.166 (3)	12 (1)*
C(34)	0.465 (2)	0.176 (2)	0.161 (3)	11 (1)*
C(35)	0.467 (3)	0.154 (3)	0	14 (2)*
C(37)	0.632 (2)	0.032 (2)	0.168 (2)	15 (2)*
C(38)	0.585 (2)	-0.019 (2)	0.167 (1)	18 (2)*
C(39)	0.562 (2)	-0.046 (2)	0	20 (3)*
C(36)	0.662 (2)	0.051 (2)	0	15 (2)*

<sup>a</sup> Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as  $4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos \gamma)\beta_{12} + ac(\cos \beta)\beta_{13} + bc(\cos \alpha)\beta_{23}]$ .

the positional parameters for structures **1** and **2**, respectively. Complete tables of bond distances and angles as well as anisotropic thermal parameters and structure factors are available as supplementary material.

**Re<sub>2</sub>Cl<sub>4</sub>(dppm)<sub>2</sub>(CO)·3C<sub>6</sub>H<sub>6</sub> (1).** Preliminary cell dimensions indicated a trigonal or hexagonal crystal class. The hexagonal symmetry and the Laue class  $6/m$  were determined by comparing the intensities of symmetry-related reflections in a half-shell of  $2^\circ$  (in  $\omega$ ) around  $2\theta = 15^\circ$ . Systematic absences limited the possible space groups to  $P6_3/m$  and  $P6_3$ . A structural model for the dimeric molecule was developed in the centrosymmetric choice starting from the positions of the Re atoms obtained by direct methods (MULTAN).

When the bridging group was identified as Cl (consistent with the IR data), it became apparent that the crystallographically imposed site symmetry ( $m$ ) called for a disorder model with respect to the terminal Cl/CO ligands. Attempts to abandon the crystallographic mirror plane (viz., refinement in  $P6_3$ ) were unproductive with respect to the disorder problem and entailed unreasonably high correlation between most of the formerly symmetry related atoms. We therefore decided to continue refinement in  $P6_3/m$  assuming a 1:1 disorder of a pair of terminal Cl/CO ligands. Although the individual positions of these atoms were apparent from early difference Fourier maps the CO was initially treated as a rigid group. The constraint was later on released.

The disorder is to some extent transmitted to the phenyl rings of the dppm which were refined as rigid groups. Residual peaks in the final

Fourier map were indicative of alternative orientations, but no attempt was made to include them in the model.

**Re<sub>2</sub>Cl<sub>4</sub>(dppm)<sub>2</sub>(CO)(CNxylyl)·CH<sub>3</sub>OH (2).** A thin crystal of **2** (approximate dimensions  $0.30 \times 0.30 \times 0.06$  mm) was mounted on the tip of a glass fiber with epoxy. The unit cell was indexed on 25 reflections in the range  $12^\circ < 2\theta < 25^\circ$ . The compound crystallizes in the monoclinic space group  $P2_1/n$  with four dimeric units contained in one unit cell. The positions of the two Re atoms were obtained from a three-dimensional Patterson map, and the remainder of the structure was solved by using alternating least-squares refinement and difference Fourier maps. In the final cycles, it became evident that a disordered solvent molecule was present, and several attempts to model the disorder were unsuccessful. In the end, the best description of the electron density in this area was a fully occupied molecule of methanol. The last refinement cycle was completed with 446 parameters being refined with 2787 data with  $I$  greater than  $3\sigma$ . The final residuals were  $R = 0.0650$  ( $R_w = 0.0691$ ).

**Physical Measurements.** Infrared spectra were recorded as Nujol mulls between KBr disks or as dichloromethane or toluene solutions with an IBM Instruments IR/32 Fourier Transform ( $4800\text{--}400$   $\text{cm}^{-1}$ ) spectrometer. Electronic absorption spectra were recorded on IBM Instruments 9420 UV-vis and Cary 17 spectrophotometers. Electrochemical measurements were carried out by using a Bioanalytical Systems Inc. Model CV-1A instrument on dichloromethane solutions containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as the supporting electrolyte.  $E_{1/2}$  values, determined as  $(E_{pa} + E_{pc})/2$ , 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.  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra were recorded on a Varian XL-200 spectrometer operated at 80.98 MHz with an internal deuterium lock and 85%  $\text{H}_3\text{PO}_4$  as an external standard.  $^1\text{H}$  NMR spectra were obtained on the same instrument at 200.0 MHz, and the residual protons of dichloromethane- $d_2$  ( $\delta$  5.32 vs.  $\text{Me}_4\text{Si}$ ) were used as a reference. Elemental microanalyses were performed by Dr. H. D. Lee of the Purdue University Microanalytical Laboratory.

## Results and Discussion

**(a) Preparation and Properties of  $\text{Re}_2\text{X}_4(\text{dppm})_2(\text{CO})$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ).** A detailed description of the preparation and characterization of  $\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CO})$  has been presented previously.<sup>19</sup> Good quality single crystals could not be obtained at that time, but since then suitable crystals have been grown and an X-ray determination has revealed an A-frame-like structure:  $\text{Cl}_2\text{Re}(\mu\text{-Cl})(\mu\text{-dppm})_2\text{ReCl}(\text{CO})$  (vide infra). In view of this facile reaction between  $\text{Re}_2\text{Cl}_4(\text{dppm})_2$  and carbon monoxide to give a surprisingly stable monocarbonyl, it was anticipated that an analogous bromide derivative could be synthesized. A solution of  $\text{Re}_2\text{Br}_4(\text{dppm})_2$  in dichloromethane changes, almost instantaneously, from purple to amber upon exposure to carbon monoxide. Red crystals were obtained by treatment with hexane at  $0^\circ\text{C}$ ; this color resembles that of  $\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CO})$ . Because of the tedious synthesis of the  $\text{Re}_2\text{Br}_4(\text{dppm})_2$  starting material which, incidentally, also proceeds in very low yield,<sup>12</sup> further carbonylation reactions (i.e., to give  $\text{Re}_2\text{Br}_4(\text{dppm})_2(\text{CO})_2$ ) have not yet been investigated. IR and electronic absorption spectral data and cyclic voltammetric electrochemical measurements have established the structural similarity of these two complexes (Table IV); IR spectra and CV data for the chloride complex are taken from ref 19. Likewise these two complexes exhibit very similar NMR spectral properties. The  $^1\text{H}$  NMR spectra consist of a complex phenyl region from  $\delta +7.9$  to  $\delta +7.0$  and a pentet for the  $-\text{CH}_2-$  protons of the dppm ligands at  $\delta +5.61$  ( $\text{X} = \text{Cl}$ )<sup>19</sup> and  $\delta +5.71$  ( $\text{X} = \text{Br}$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy (at  $15^\circ\text{C}$  in  $\text{CD}_2\text{Cl}_2$ ) reveals two types of phosphorus nuclei in an AA'BB' pattern.<sup>19,23</sup>

Previous detailed temperature range  $^1\text{H}$ ,  $^{31}\text{P}\{^1\text{H}\}$ , and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectral measurements on the chloride complex (from 25 to  $-50^\circ\text{C}$ ) have established the existence of a fluxional process in solution which we believe interconverts the non-A-frame structure  $\text{Cl}_2\text{Re}(\mu\text{-dppm})_2\text{ReCl}(\text{CO})$  and the A-frame-like species  $\text{Cl}_2\text{Re}(\mu\text{-Cl})(\mu\text{-dppm})_2\text{ReCl}(\text{CO})$ . We suggest that a similar situation will hold in the case of the analogous bromide complex

(23) The spectrum for the bromide complex is actually very close to that of an AA'XX' pattern with  $\delta_A = -30.4$  and  $\delta_X = +0.3$ . For the AA'BB' pattern of  $\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CO})$  we have  $\delta_A = -15.8$  and  $\delta_B = -0.6$ .<sup>19</sup>

**Table III.** Atomic Positional Parameters and Equivalent Isotropic Displacement Parameters ( $\text{\AA}^2$ ) and Their Estimated Standard Deviations for  $\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CO})(\text{CN}_{\text{xylyl}})_2\text{-CH}_3\text{OH}$  (2)<sup>a</sup>

atom	x	y	z	B ( $\text{\AA}^2$ )	atom	x	y	z	B ( $\text{\AA}^2$ )
Re(1)	0.01769 (8)	0.23815 (8)	0.16641 (7)	2.68 (3)	C(26)	0.179 (2)	0.267 (2)	0.042 (2)	7 (1)
Re(2)	0.08563 (8)	0.14167 (9)	0.24993 (7)	3.03 (3)	C(27)	0.231 (2)	0.266 (2)	-0.002 (2)	5.3 (9)*
Cl(1)	-0.0160 (5)	0.2716 (6)	0.0555 (4)	4.0 (2)	C(28)	0.292 (2)	0.318 (3)	-0.000 (2)	7 (1)*
Cl(2)	0.0894 (4)	0.1158 (5)	0.1348 (4)	3.3 (2)	C(29)	0.296 (2)	0.379 (2)	0.051 (2)	5 (1)*
Cl(3)	0.1664 (5)	0.0181 (6)	0.2652 (5)	5.1 (3)	C(30)	0.247 (2)	0.392 (2)	0.105 (2)	7 (1)
Cl(4)	0.0923 (5)	0.1401 (7)	0.3653 (4)	5.2 (2)	C(31)	0.092 (2)	0.447 (2)	0.147 (2)	3.7 (9)
P(1)	-0.1000 (5)	0.1615 (6)	0.1650 (5)	3.5 (2)	C(32)	0.093 (2)	0.497 (2)	0.202 (2)	6 (1)*
P(2)	0.1209 (5)	0.3358 (6)	0.1567 (5)	3.7 (2)	C(33)	0.061 (2)	0.581 (3)	0.190 (2)	7 (1)*
P(3)	-0.0172 (5)	0.0427 (6)	0.2576 (4)	3.1 (2)	C(34)	0.035 (2)	0.606 (3)	0.129 (2)	8 (1)*
P(4)	0.1985 (5)	0.2268 (6)	0.2567 (4)	3.4 (2)	C(35)	0.050 (3)	0.553 (3)	0.073 (2)	9 (1)*
O(1)	0.003 (1)	0.285 (2)	0.307 (1)	6.8 (8)	C(36)	0.069 (2)	0.471 (2)	0.081 (2)	6 (1)
N(1)	-0.069 (1)	0.400 (2)	0.201 (1)	4.4 (7)*	C(37)	-0.028 (2)	-0.049 (2)	0.204 (1)	2.7 (7)*
C(1)	0.025 (2)	0.242 (2)	0.266 (2)	4.6 (8)*	C(38)	-0.094 (2)	-0.090 (2)	0.204 (2)	5 (1)
C(2)	-0.036 (2)	0.340 (2)	0.185 (2)	4.4 (9)*	C(39)	-0.106 (2)	-0.156 (2)	0.161 (2)	6 (1)*
C(3)	-0.110 (2)	0.475 (2)	0.197 (2)	6 (1)*	C(40)	-0.055 (2)	-0.184 (3)	0.118 (2)	7 (1)*
C(4)	-0.151 (2)	0.507 (3)	0.147 (2)	8 (1)	C(41)	0.018 (2)	-0.144 (3)	0.127 (2)	7 (1)*
C(5)	-0.150 (2)	0.458 (3)	0.084 (2)	8 (1)	C(42)	0.033 (2)	-0.075 (2)	0.168 (1)	4.1 (9)
C(6)	-0.188 (2)	0.583 (3)	0.155 (2)	9 (1)	C(43)	-0.037 (2)	-0.002 (2)	0.335 (2)	3.5 (8)*
C(7)	-0.186 (2)	0.618 (3)	0.217 (2)	9 (1)	C(44)	0.014 (2)	-0.069 (2)	0.354 (2)	4.3 (9)
C(8)	-0.145 (2)	0.592 (2)	0.272 (2)	6 (1)*	C(45)	0.005 (2)	-0.105 (3)	0.418 (2)	8 (1)*
C(9)	-0.105 (2)	0.510 (2)	0.264 (2)	7 (1)	C(46)	-0.053 (2)	-0.076 (2)	0.456 (2)	5.0 (9)*
C(10)	-0.065 (3)	0.480 (3)	0.320 (2)	11 (2)	C(47)	-0.095 (2)	-0.008 (2)	0.433 (2)	6 (1)*
C(11)	-0.105 (2)	0.103 (2)	0.243 (2)	4.1 (8)*	C(48)	-0.091 (2)	0.026 (2)	0.372 (2)	6 (1)
C(12)	0.174 (2)	0.336 (2)	0.232 (2)	3.6 (8)*	C(49)	0.243 (2)	0.241 (2)	0.339 (1)	3.5 (7)*
C(13)	-0.180 (2)	0.225 (2)	0.169 (1)	3.3 (8)	C(50)	0.267 (2)	0.164 (3)	0.367 (2)	7 (1)*
C(14)	-0.229 (2)	0.231 (2)	0.111 (2)	6 (1)	C(51)	0.306 (3)	0.180 (3)	0.434 (2)	9 (1)*
C(15)	-0.289 (2)	0.290 (2)	0.118 (2)	7 (1)*	C(52)	0.313 (2)	0.265 (3)	0.453 (2)	7 (1)*
C(16)	-0.302 (2)	0.341 (3)	0.177 (2)	8 (1)*	C(53)	0.288 (3)	0.330 (3)	0.424 (3)	12 (2)*
C(17)	-0.247 (2)	0.337 (2)	0.231 (2)	5.2 (9)*	C(54)	0.249 (2)	0.316 (3)	0.361 (2)	7 (1)*
C(18)	-0.187 (2)	0.277 (2)	0.223 (2)	4.1 (8)*	C(55)	0.276 (2)	0.205 (2)	0.211 (2)	4.7 (9)
C(19)	-0.126 (2)	0.084 (2)	0.103 (1)	2.3 (7)*	C(56)	0.275 (2)	0.136 (2)	0.172 (2)	4.7 (8)*
C(20)	-0.081 (2)	0.065 (2)	0.052 (2)	3.5 (8)*	C(57)	0.338 (3)	0.119 (3)	0.133 (2)	9 (1)*
C(21)	-0.106 (2)	0.009 (2)	0.007 (2)	4.8 (9)*	C(58)	0.399 (3)	0.173 (3)	0.138 (2)	9 (1)*
C(22)	-0.171 (2)	-0.034 (2)	0.006 (2)	5.0 (9)*	C(59)	0.402 (2)	0.235 (3)	0.183 (2)	7 (1)*
C(23)	-0.219 (2)	-0.015 (3)	0.060 (2)	7 (1)*	C(60)	0.339 (2)	0.255 (3)	0.221 (2)	7 (1)
C(24)	-0.198 (2)	0.040 (2)	0.110 (2)	6 (1)	O(2)	0.591	0.104	-0.030	21 (2)*
C(25)	0.186 (2)	0.327 (2)	0.097 (2)	4.2 (9)	C(61)	0.540	0.175	0.000	16 (2)*

<sup>a</sup>Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as  $4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos \gamma)\beta_{12} + ac(\cos \beta)\beta_{13} + bc(\cos \alpha)\beta_{23}]$ .

**Table IV.** Electrochemical and Spectroscopic Data for  $\text{Re}_2\text{X}_4(\text{dppm})_2(\text{CO})$ 

X	IR spectra $\nu(\text{CO})$ , $\text{cm}^{-1}$	electronic abs spectra $\lambda_{\text{max}}$ , nm ( $\epsilon$ ) <sup>d</sup>	CV half-wave potentials <sup>e</sup>		
			$E_{1/2}(\text{ox})(2)$ , V	$E_{1/2}(\text{ox})(1)$ , V	$E_{1/2}(\text{red})(1)$ , V
Cl	1967 s, 1900 m <sup>a</sup>		~+1.8 <sup>f</sup>	+0.53	~-1.4 <sup>g</sup>
	1967 s, 1898 m <sup>b</sup>	334 (2140), ~446 sh, 740 (100) <sup>b</sup>			
	1973 w m, 1898 s <sup>c</sup>	342 (2140), ~445 sh, 734 (80) <sup>c</sup>			
Br	1970 w, 1917 s, 1900 s <sup>a</sup>		~+1.9 <sup>f</sup>	+0.66	~-1.3 <sup>g</sup>
	1973 m, 1908 s <sup>b</sup>	394 (1860), ~460 sh, 780 (100) <sup>b</sup>			
	1966 w m, 1904 s <sup>c</sup>	394 (2280), ~455 sh, 780 (100) <sup>c</sup>			

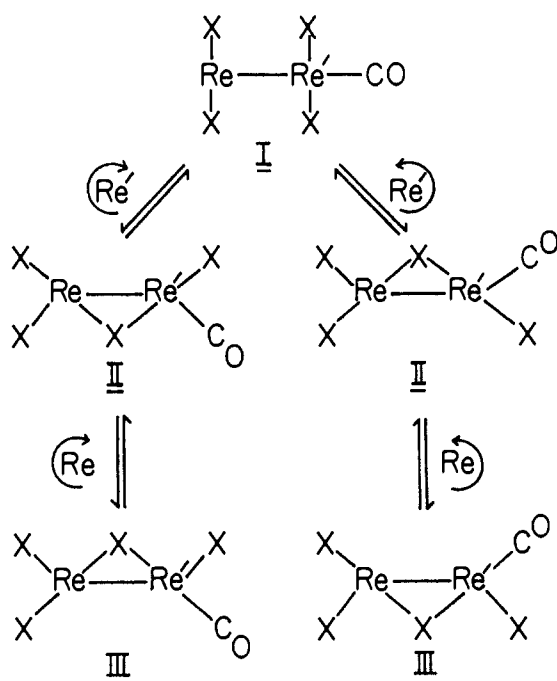
<sup>a</sup>Nujol mull spectrum of crystals isolated directly from the  $\text{CH}_2\text{Cl}_2$  reaction solution. <sup>b</sup>Dichloromethane solution. <sup>c</sup>Toluene solution. <sup>d</sup>Dichloromethane solution  $5 \times 10^{-4}$  M. <sup>e</sup>Electrochemical measurements in 0.1 M TBAH-dichloromethane referenced to  $\text{Ag}/\text{AgCl}$ . <sup>f</sup> $E_{\text{pa}}$ . <sup>g</sup> $E_{\text{pc}}$ .

in view of the striking similarity of its properties to those of its chloride analogue. Such a process is represented in Scheme I (the dppm ligands have been omitted for clarity), where we can envision initial attack of the CO along the Re-Re axis to give I followed by a rotation of the Re-X and Re-CO bonds about the plane perpendicular to the P-Re-P axes in a clockwise or counterclockwise direction to give A-frame-like II and III. This mechanism reflects the fact that NMR measurements have clearly shown<sup>19</sup> that the CO ligand remains bound to only one of the Re atoms throughout the fluxional process.

Confirmation of the existence of I, II, and/or III is provided by IR spectral measurements which convincingly establish the presence of isomers as monitored within the more rapid time scale of this technique (see Table IV and ref 19). The presence of two terminal  $\nu(\text{CO})$  modes in the solution spectra of both complexes indicates the presence of at least two isomers. The band at  $\sim 1900$   $\text{cm}^{-1}$  becomes dominant in benzene and toluene, and it is from a benzene-containing solvent that crystals of  $\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CO})$  were grown for the X-ray structure analysis (see subsection b below). Consequently, we suggest that this band corresponds to

isomer III, but we are uncertain as to which isomer is associated with the higher frequency  $\nu(\text{CO})$  mode at  $\sim 1970$   $\text{cm}^{-1}$ . However, since the cyclic voltammetric properties of these complexes do not provide any evidence for more than one isomer (Table IV), we must conclude that the isomers present must be electronically very similar and, accordingly, we favor for this reason a mixture of II and III.

The cyclic voltammetric data given in Table IV show that corresponding redox processes occur at more positive potentials for the bromide complex. This is in accord with the fact that bromide derivatives of transition-metal complexes are more difficult to oxidize (easier to reduce) than the corresponding chlorides. When this behavior is in turn compared with that for the complex  $\text{Re}_2\text{Cl}_4(\text{dppm})_2$ , which exhibits two reversible one-electron oxidations at  $E_{1/2} = +0.27$  and  $+0.80$  V vs. SCE,<sup>13</sup> it can be seen that the oxidations of the monocarbonyl complexes are shifted to more positive potentials and a one-electron reduction now becomes accessible. This can be attributed to the effect on the metal centers of bonding to a good  $\pi$ -acceptor ligand such as CO which can be expected<sup>11</sup> to lead to an increase in the difficulty

**Scheme I.** A Proposed Mechanism for the Interconversion of Three Possible Isomers (I, II, and III) of  $\text{Re}_2\text{X}_4(\text{dppm})_2(\text{CO})^a$ 

<sup>a</sup>Note that the dppm ligands have been omitted for clarity and lie above and below the  $\text{Re}_2\text{X}_4(\text{CO})$  plane.

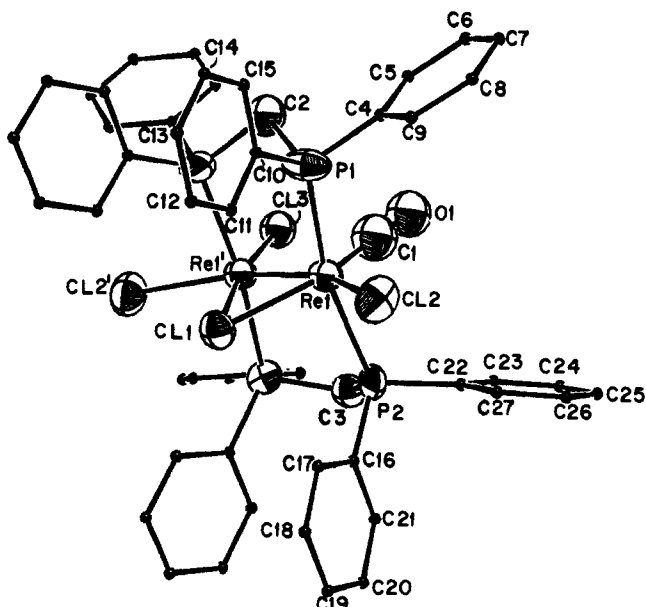
**Table V.** Selected Bond Distances (Å) and Angles (deg) and Their Estimated Standard Deviations for  $\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CO})$ 

Re(1)	Re(1')	2.338 (1)	C(1)	O(1)	1.14 (6)		
Re(1)	Cl(3)	2.377 (13)	P(1)	C(2)	1.87 (3)		
Re(1)	C(1)	1.73 (5)	P(1)	C(4)	1.81 (2)		
Re(1)	Cl(1)	2.533 (6)	P(1)	C(10)	1.82 (2)		
Re(1)	Cl(2)	2.476 (6)	P(2)	C(3)	1.84 (2)		
Re(1)	P(1)	2.438 (9)	P(2)	C(16)	1.79 (2)		
Re(1)	P(2)	2.451 (9)	P(2)	C(22)	1.84 (2)		
Re(1)	Re(1')	Cl(3)	108.3 (3)	C(1)	Re(1)	Cl(1)	154 (2)
Re(1)	Re(1')	C(1)	91 (2)	C(1)	Re(1)	Cl(2)	116 (2)
Re(1)	Re(1')	Cl(1)	62.52 (8)	C(1)	Re(1)	P(1)	88 (3)
Re(1)	Re(1')	Cl(2)	152.9 (1)	C(1)	Re(1)	P(2)	88 (3)
Re(1)	Re(1')	P(1)	97.4 (2)	Cl(1)	Re(1)	Cl(2)	90.5 (2)
Re(1)	Re(1')	P(2)	97.5 (1)	Cl(1)	Re(1)	P(1)	96.8 (3)
Cl(3)	Re(1)	Cl(1)	170.2 (4)	Cl(1)	Re(1)	P(2)	93.8 (3)
Cl(3)	Re(1)	Cl(2)	98.8 (4)	Cl(2)	Re(1)	P(1)	82.4 (3)
Cl(3)	Re(1)	P(1)	87.5 (5)	Cl(2)	Re(1)	P(2)	86.1 (3)
Cl(3)	Re(1)	P(2)	83.9 (5)	P(1)	Re(1)	P(2)	164.4 (2)

of oxidizing such species and an increase in the ease of reduction.

**(b) Crystal Structure of  $\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CO})$ .**  $\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CO})$  (**1**) is a dinuclear molecular complex. The overall arrangement of the  $\text{M}_2\text{L}_9$  core is that of an A frame, viz., a metal–metal bonded dirhenium unit singly bridged by a chlorine atom. The coordination polyhedra of the two rhenium atoms are quite irregular. Perhaps the closest model for a regular polyhedron is that of an octahedron by mutually counting the metals as ligands. The molecule, which is depicted in Figure 1 with the Cl/CO disorder resolved, has a crystallographically imposed mirror plane intersecting the Re–Re vector and containing the bridging chloride. The dirhenium unit, the bridging and terminal chlorides, and the CO are coplanar with deviations from the mean plane of less than 0.1 Å. The Re–P bond vectors are perpendicular ( $90.6^\circ$ ) to this plane. Important bond lengths and angles are listed in Table V.

The A-frame configuration is an unusual one for multiply bonded dimers to form. It has previously been observed as the closely related system  $\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CNR})$ <sup>15,24</sup> and appears to be an important structural type for adducts of  $\pi$ -acceptor ligands.

**Figure 1.** An ORTEP drawing of **1**. The phenyl carbon atoms are represented by arbitrarily small thermal spheres, and the 1:1 disorder between CO and C13 was resolved.

Not only is it formed in almost quantitative yield but, in light of the observed dynamic processes, it also seems to be thermodynamically favored.

A possible explanation for the relative stability as well as the metric properties is obtained from an electron count. A rare gas configuration is reached at each Re center if a triple bond is assumed. The observed Re–Re distance of 2.338 (1) Å is consistent with this model (compare Table X). It also implies the existence of an essentially nonbonding electron pair at each Re center, in agreement with our observation that the acceptor ligands (CO, CNR) are always in terminal rather than bridging position.

**(c) Preparation and Preliminary Characterization of  $\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CO})(\text{CNR})$  ( $\text{R} = \text{CHMe}_2$ ,  $\text{CMe}_3$ , xylyl, or mesityl).** Since the structure determination of the monocarbonyl  $\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CO})$  clearly established its coordinatively unsaturated nature, we suspected that this complex would react readily with other  $\pi$  acceptors to give  $\text{M}_2\text{L}_{10}$  species. As we have demonstrated previously, if carbon monoxide is bubbled through a dichloromethane solution of  $\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CO})$  for a period of 3 h, the corresponding dicarbonyl complex  $\text{Cl}_2\text{Re}(\mu\text{-Cl})(\mu\text{-CO})(\mu\text{-dppm})_2\text{ReCl}(\text{CO})$  is produced in high yield.<sup>19</sup> When an acetone solution of  $\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CO})$  is treated with 1 equiv of an isocyanide, species of the general formula  $\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CO})(\text{CNR})$  are generated quite readily. What is especially interesting about this system is the fact that the CO ligand either remains terminally bound or bridges the two rhenium atoms, depending on the isocyanide used. When isopropyl or *tert*-butyl isocyanide is used, red compounds are isolated. From the IR spectral results (Table VI), it is clear that both  $\pi$ -acceptor ligands (CO and CNR) are terminal. The corresponding reactions with xylyl (2,6-dimethylphenyl) or mesityl (2,4,6-trimethylphenyl) isocyanide yield green complexes which contain a bridging CO ( $\nu(\text{CO})$  at  $\sim 1700 \text{ cm}^{-1}$ ) and a terminal RNC ligand.

The electronic structures of these two types of complexes (terminal CO vs. bridging CO) are quite different, as can be judged from their electrochemical properties (Figure 2). Those complexes with a terminal CO ligand exhibit a reversible one-electron oxidation and an irreversible one-electron reduction (Table VI). In contrast to this we observe two reversible one-electron

(25) (a) Barder, T. J.; Powell, D.; Walton, R. A. *J. Chem. Soc., Chem. Commun.* **1985**, 550. (b) Anderson, L. B.; Barder, T. J.; Cotton, F. A.; Dunbar, K. R.; Falvello, L. R.; Walton, R. A. *Inorg. Chem.*, accepted for publication.

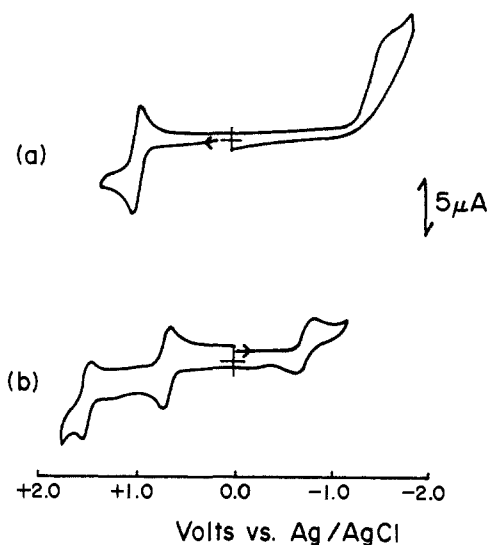
(24) Anderson, L. B.; Barder, T. J.; Esjornson, D.; Walton, R. A.; Bursten, B. *J. Chem. Soc., Dalton Trans.*, submitted for publication.

(26) Anderson, L. B.; Cotton, F. A.; Dunbar, K. R.; Falvello, L. R.; Price, A. C.; Reid, A.; Walton, R. A., manuscript in preparation.

**Table VI.** Electrochemical and Spectroscopic Data for  $\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CO})(\text{CNR})$ 

R	IR spectra (in $\text{cm}^{-1}$ )			electronic abs spectra $\lambda_{\text{max}}$ , nm ( $\epsilon$ ) <sup>c</sup>	CV half-wave potentials <sup>d</sup>		
		$\nu(\text{CN})$	$\nu(\text{CO})_{\text{terminal}}$		$\nu(\text{CO})_{\text{bridging}}$	$E_{1/2}(\text{ox})(2)$ , V	$E_{1/2}(\text{ox})(1)$ , V
CHMe <sub>2</sub>	a	2134 m, 2126 m	1958 s	~512 sh, 745 (100)	+0.99	-1.39 <sup>e</sup>	
	b	2136 s	1958 s				
CMe <sub>3</sub>	a	2118 m	1968 s	~540 sh, 720 (100)	+0.95	-1.20 <sup>e</sup>	
	b	2124 s	1945 s				
xylyl	a	2105 s	1690 m	432 (6040), 776 (210), ~925 sh	~+1.4	+0.60	
	b	2103 s	1690 m				
mesityl	a	2091 s	1703 m	433 (7120), 782 (280), ~925 sh	~+1.4	+0.60	
	b	2095 s	1696 m				

<sup>a</sup> Nujol mull. <sup>b</sup> Dichloromethane solution. <sup>c</sup> Dichloromethane solution ( $5 \times 10^{-4}$  M). <sup>d</sup> Electrochemical measurements in 0.1 M TBAH-dichloromethane referenced to Ag/AgCl. <sup>e</sup>  $E_{\text{pc}}$ .



**Figure 2.** Cyclic voltammograms (scan rate 200 mV/s at a Pt-bead electrode) of  $\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CO})(\text{CNR})$  in 0.1 M TBAH- $\text{CH}_2\text{Cl}_2$  solutions: (a) R = *tert*-butyl, (b) R = xylyl.

oxidations and a reversible one-electron reduction for the complexes with a bridging CO ligand. The green dicarbonyl complex  $\text{Re}_2(\mu\text{-Cl})(\mu\text{-CO})(\mu\text{-dppm})_2\text{Cl}_3(\text{CO})$  shows two reversible one-electron oxidations at  $E_{1/2} = +0.91$  and  $+1.75$  V, a reversible one-electron reduction at  $-0.57$  V, and an irreversible one-electron reduction at  $E_{\text{pc}} = -1.6$  V vs. Ag/AgCl.<sup>19</sup> Hence, a shift to more positive potentials (by 0.2–0.3 V) is observed when two CO groups (one bridging and one terminal) are present rather than one  $\mu\text{-CO}$  and one isocyanide ligand. This reflects (not surprisingly) the superior  $\pi$ -acceptor properties of CO compared to RNC. As we shall discuss later, the close structural similarity of  $\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CO})_2$  and  $\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CO})(\text{CNxylyl})$  has been established by X-ray crystallography.

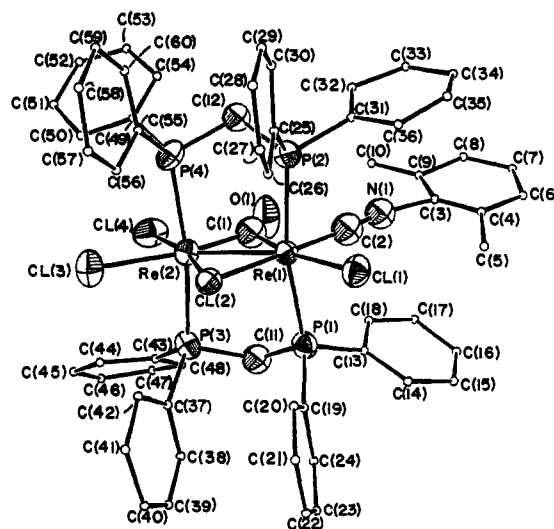
<sup>1</sup>H NMR spectroscopy for all four mixed carbonyl–isocyanide derivatives confirmed the identity and stoichiometry of the products; correct integration of the isocyanide ligand resonances relative to those of the methylene protons of the dppm ligands was observed. The dppm methylene region consists of a second-order AB pattern with superimposed P–H coupling, corresponding to two different environments for the bridgehead protons. In the case of the isopropyl isocyanide derivative, only a single broad peak is observed for the methylene protons. This suggests that a fluxional process may be occurring in solution. These chemical shifts, along with coupling constants, are summarized in Table VII. The <sup>31</sup>P{<sup>1</sup>H} NMR spectra exhibit two complex multiplets in an AA'BB' pattern (Table VII). This result shows that there is an unsymmetric arrangement of the ligands about the Re–Re axis (as confirmed by an X-ray crystallographic study on the xylyl derivative (vide infra)), thereby rendering the two sides of the molecule inequivalent.

(d) **Crystal Structure of  $\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CO})(\text{CNxylyl})$  (2).** The  $\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CO})(\text{CNxylyl})$  complex is a coordinatively saturated molecule possessing the edge-shared bioctahedral geometry.

**Table VII.** NMR Chemical Shift Data for  $\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CO})(\text{CNR})$ <sup>a</sup>

R	<sup>1</sup> H			R <sup>c</sup>	<sup>31</sup> P{ <sup>1</sup> H} <sup>d</sup> $\delta$
	$\delta$	$J(\text{P-H})$ , Hz	$J(\text{H-H})$ , Hz		
CHMe <sub>2</sub>	5.44			4.44 h	-5.73j
				1.10 d	-12.43j
CMe <sub>3</sub>	5.61 <sup>b</sup>	4.6	13.9	1.39 s	-5.80j
	5.44				-12.92j
xylyl	4.11 <sup>b</sup>	4.4	13.2	2.12 s	-12.45j
	4.02				-20.90j
mesityl	4.11 <sup>b</sup>	4.3	13.4	1.43 s	-13.40j
	4.02			2.32 s	-21.13j

<sup>a</sup> Recorded on  $\text{CD}_2\text{Cl}_2$  solutions. <sup>b</sup>  $\nu_A, \nu_B$ ; AB pattern with superimposed P–H coupling. <sup>c</sup> Resonances associated with aliphatic substituents on the RNC ligands; s = singlet, d = doublet, h = heptet. <sup>d</sup> AA'BB' patterns; chemical shifts quoted are of the most intense inner components of each pattern.



**Figure 3.** An ORTEP diagram showing the molecular structure and atom labeling scheme for  $\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CO})(\text{CNxylyl})\cdot\text{MeOH}$ .

The ORTEP drawing in Figure 3 shows that the arrangement of ligands around the two metal centers is one in which the two  $\pi$ -acceptor ligands, CNxylyl and  $\mu\text{-CO}$ , occupy mutually cis positions in the equatorial plane. A similar structure was found for  $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CO})_2(\text{NCC}_2\text{H}_5)]\text{PF}_6$  in which the two CO ligands are on the same side of the molecule.<sup>20</sup>

The important bond distances and angles for  $\text{Cl}_2\text{Re}(\mu\text{-CO})(\mu\text{-Cl})(\mu\text{-dppm})_2\text{ReCl}(\text{CNxylyl})$  are listed in Table VIII. One aspect of the geometry in the equatorial plane is worth commenting upon. As was noted in earlier crystallographic studies of  $\text{Re}_2\text{Cl}_6(\text{dppm})_2$ <sup>13</sup> and  $\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CO})_2$ ,<sup>19</sup> the angles Re–Re–Cl (terminal) are significantly larger than the Re–Re–C angles for a terminal CO or CNR ligand. In all instances, the  $\pi$ -acceptor ligand is not swept back to the extent that the terminal chlorine ligands are.

Table VIII. Selected Bond Distances (Å) and Angles (deg) and Their Estimated Standard Deviations for  $\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CO})(\text{CNxyllyl})\text{-CH}_3\text{OH}$  (2)

Re(1)	Re(2)	2.581 (2)	Re(2)	C(1)	1.98 (4)		
Re(1)	Cl(1)	2.419 (7)	P(1)	C(11)	1.88 (3)		
Re(1)	Cl(2)	2.458 (7)	P(1)	C(13)	1.79 (3)		
Re(1)	P(1)	2.467 (9)	O(1)	C(1)	1.18 (4)		
Re(1)	C(1)	2.08 (4)	N(1)	C(2)	1.18 (3)		
Re(1)	C(2)	1.94 (4)	N(1)	C(3)	1.41 (4)		
Re(2)	Cl(2)	2.445 (8)	C(3)	C(9)	1.50 (5)		
Re(2)	Cl(3)	2.464 (8)	C(9)	C(10)	1.42 (5)		
Re(2)	Cl(4)	2.406 (8)	C(13)	C(14)	1.46 (4)		
Re(2)	P(3)	2.461 (9)					
Re(2)	Re(1)	Cl(1)	149.4 (2)	Re(1)	Re(2)	P(4)	94.4 (2)
Re(2)	Re(1)	Cl(2)	58.0 (2)	Re(1)	Re(2)	C(1)	52 (1)
Re(2)	Re(1)	C(1)	49 (1)	C(2)	N(1)	C(3)	161 (4)
Re(2)	Re(1)	C(2)	126.0 (9)	Re(1)	C(1)	Re(2)	79 (1)
Re(1)	Re(2)	Cl(2)	58.5 (2)	Re(1)	C(1)	O(1)	137 (3)
Re(1)	Re(2)	Cl(3)	145.0 (2)	Re(2)	C(1)	O(1)	144 (3)
Re(1)	Re(2)	Cl(4)	132.5 (2)	Re(1)	C(2)	N(1)	175 (3)
Re(1)	Re(2)	P(3)	95.1 (2)	P(1)	Re(1)	P(2)	168.9 (3)

The significance of the Re–Re distances in the two compounds whose structures have been presented here, and especially their implications with regard to the metal–metal bonding, can best be determined by comparing them with the results for a series of related dinuclear compounds. This is done in Table X. For compound 1 the oxidation state of the  $\text{Re}_2$  unit is +4 and the formation of a kind of  $d^5\text{-}d^5$  triple bond is consistent with the bond length of 2.338 Å; the same is true for the closely related  $\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CNMe}_3)$  molecule where the Re–Re distance is 2.30 Å.<sup>15,24</sup> The fact that both of these Re–Re distances are somewhat longer than that in  $\text{Re}_2\text{Cl}_4(\text{dppm})_2$  can be attributed to the introduction of a  $\mu\text{-Cl}$  atom which alters the details of the Re–Re bonding. This point is covered in more detail elsewhere.<sup>24</sup>

In compound 2, we believe that the  $\mu\text{-CO}$  group should be treated formally as a divalent bridge thus making the formal oxidation number of the  $\text{Re}_2$  unit +6. We then regard this  $d^4\text{-}d^4$  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  $\text{Re}_2\text{Cl}_6(\text{dppm})_2$ . The  $\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CO})_2$  and  $[\text{Re}_2\text{Cl}_3(\text{dppm})(\text{CO})_2(\text{NCC}_2\text{H}_5)]^+$  species are analogous. In all three cases where the bridging is provided by one  $\mu\text{-Cl}$  and one  $\mu\text{-CO}$  the Re–Re distances are about 0.03 Å shorter than in  $\text{Re}_2\text{Cl}_6(\text{dppm})_2$ . This is not surprising since the smaller size of the carbon atom will obviously tend to have this effect. A further decrease in the bond order to 1.5 (based

on  $\sigma^2\pi^2\delta^2\delta^*2\pi^*$ ) in  $\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CO})_2(\text{CNC}_3\text{H}_7)$  has the expected effect of increasing the Re–Re distance significantly to 2.718 Å.

The data in Table X also imply that for the same electron count the Re–Re distance is not very sensitive to whether the terminal ligands are Cl, CO, RCN, or RNC. The metal–metal bond order itself is the major factor, with the size of the bridging ligands playing a noticeable, but definitely secondary, role.

(e) **Preparation and Preliminary Characterization of  $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CO})(\text{NCR})_2]\text{PF}_6$  ( $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, \text{or } \text{C}_6\text{H}_5$ ).** Recently in our laboratory, we have shown that the green dicarbonyl complex  $\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CO})_2$  reacts readily with nitriles, in the presence of  $\text{TiPF}_6$ , to give the salts  $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CO})_2(\text{NCR})]\text{PF}_6$ .<sup>20</sup> An obvious extension of this work was to establish whether the monocarbonyl complex reacts with nitriles in a related fashion. As was mentioned in a previous paper,<sup>19</sup> the monocarbonyl conducts as a 1:1 electrolyte in acetonitrile ( $\Lambda_m = 130 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$  for  $C_m = 1 \times 10^{-3} \text{ M}$ ), indicating that some sort of reaction has occurred. When the red-brown monocarbonyl is dissolved in a 1:1 mixture of acetone and nitrile RCN, in the presence of 1 equiv of  $\text{TiPF}_6$ , a color change to green occurs within 30 min. Workup of these solutions gives green products of stoichiometry  $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CO})(\text{NCR})_2]\text{PF}_6$  ( $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, \text{or } \text{C}_6\text{H}_5$ ). Conductivity measurements in acetone confirm them to be 1:1 electrolytes and IR spectral results show terminal nitriles and bridging CO ligands (Table IX).

The electrochemical properties of these salts (Table IX) may be contrasted with those of  $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CO})_2(\text{NCR})]\text{PF}_6$ .<sup>20</sup> For the mononitrile complexes, a reversible one-electron oxidation occurs at  $E_{1/2} \approx +1.45 \text{ V}$  and two reversible one-electron reductions at  $E_{1/2} \approx -0.14$  and  $-1.10 \text{ V}$  vs. Ag/AgCl. Similar cyclic voltammograms were obtained for the bis-nitrile species, viz., a reversible one-electron oxidation at  $E_{1/2} \approx +1.03 \text{ V}$  and two reversible one-electron reductions at  $E_{1/2} \approx -0.50$  and  $-1.45 \text{ V}$  vs. Ag/AgCl. This shift to more negative potentials (by  $\sim 0.4 \text{ V}$  for the latter complexes) may be rationalized in terms of replacing a CO group by a better  $\sigma$ -donor nitrile ligand, thereby making the metal centers easier to oxidize but harder to reduce.

The mononitrile compound  $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CO})_2(\text{NCC}_2\text{H}_5)]\text{PF}_6$  has been characterized by X-ray crystallography;<sup>20</sup> the  $\text{C}_2\text{H}_5\text{CN}$ ,  $\mu\text{-CO}$ , and CO ligands lie on the same side of the molecule, in an *all-cis* arrangement. For the bis-nitrile complexes which were isolated in the present work, a fairly symmetrical structure is implied by the spectroscopic properties. The  $^1\text{H}$  NMR spectra (recorded in  $\text{CD}_2\text{Cl}_2$ ) show an unresolved AB pattern for

Table IX. Spectroscopic, Electrochemical, and Conductivity Data for  $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CO})(\text{NCR})_2]\text{PF}_6$ 

R	IR spectra		electronic abs spectra	CV half-wave potentials <sup>d</sup>			molar conductivities, <sup>e</sup> $\text{ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$
	$\nu(\text{CN}), \text{cm}^{-1}$	$\nu(\text{CO}), \text{cm}^{-1}$	$\lambda_{\text{max}}, \text{nm} (\epsilon)^c$	$E_{1/2}(\text{ox})(1), \text{V}$	$E_{1/2}(\text{red})(1), \text{V}$	$E_{1/2}(\text{red})(2), \text{V}$	
$\text{CH}_3$	2292 vw	1678 vs <sup>a</sup> 1676 vs <sup>b</sup>	421 (5080), 874 (170)	+1.03	-0.49	-1.48	114
$\text{C}_2\text{H}_5$	2288 vw	1682 vs <sup>a</sup> 1676 vs <sup>b</sup>	423 (5600), 875 (140)	+1.00	-0.53	-1.49	109
$\text{C}_6\text{H}_5$	2255 vw	1674 vs <sup>a</sup> 1682 vs <sup>b</sup>	426 (6940), 874 (480) 379 (6640)	+1.05	-0.44	-1.37	113

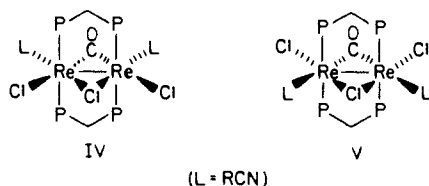
<sup>a</sup> Nujol mull on KBr plates. <sup>b</sup> Dichloromethane solution. <sup>c</sup> Dichloromethane solutions ( $1 \times 10^{-4} \text{ M}$ ). <sup>d</sup> Electrochemical Measurements in 0.1 M TBAH–dichloromethane referenced to Ag/AgCl. <sup>e</sup> Acetone solutions ( $1 \times 10^{-3} \text{ M}$ ).

Table X. Table of Re–Re Distances for Related Dirhenium Bis(diphenylphosphino)methane Complexes

	Re–Re, Å	formal dinuclear oxidation state	formal bond order	ref
$\text{Re}_2\text{Cl}_4(\text{dppm})_2$	2.234 (3)	4	3	14
$\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CO})$	2.338 (1)	4	3	this work
$\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CNMe}_3)$	2.30 (1)	4	3	15, 24
$\text{Re}_2\text{Cl}_6(\text{dppm})_2$	2.616 (1)	6	2	13
$\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CO})_2$	2.584 (1)	6	2	19
$\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CO})(\text{CNxyllyl})$	2.581 (2)	6	2	this work
$[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CO})_2(\text{NCC}_2\text{H}_5)]\text{PF}_6$	2.586 (1)	6	2	20
$[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CNHMe}_3)(\text{CNMe}_3)]\text{PF}_6$	2.7039 (6)	<i>a</i>	<i>a</i>	25
$\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CO})_2(\text{CNC}_3\text{H}_7)$	2.718 (2)	5	1 <sup>1/2</sup>	26

<sup>a</sup> There are ambiguities in this case that preclude easy assignments. See ref 25 for discussion.

the  $-\text{CH}_2-$  protons of the bridging dppm ligands at  $\delta +4.15$  ( $\pm 0.02$ ), with associated P-H coupling, and only a single resonance for the methyl groups ( $\delta +2.06$ ) of the acetonitrile ligands, and one triplet ( $\delta +0.63$ ) and one quartet ( $\delta +2.31$ ) for the ethyl groups of the propionitrile complex. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra (recorded in  $\text{CD}_2\text{Cl}_2/\text{CH}_2\text{Cl}_2$ ) reveal an apparent singlet for all three bis-nitrile salts ( $\delta -17.9$  to  $-18.6$ ). These data taken in conjunction with IR spectral evidence for a bridging CO ligand support a structure in which the pair of RCN ligands are co-planar with the  $\text{Re}(\mu\text{-CO})\text{Re}$  unit and either both cis or both trans to it (see structures IV and V). The similarity of the electrochemical properties of these complexes to those of the *all-cis* isomers  $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CO})_2(\text{NCR})]\text{PF}_6$  favors structure IV as the most likely possibility of the two.



**(f) Concluding Remarks.** As we have now demonstrated, the triply bonded complexes  $\text{Re}_2\text{X}_4(\text{dppm})_2$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ) have a very rich chemistry. They react readily with CO, without bond cleavage, to give monocarbonyls and, in the case of  $\text{X} = \text{Cl}$ , a dicarbonyl complex.<sup>19</sup> The monocarbonyls are rare examples of multiply bonded A-frame-like molecules. A more detailed appraisal of the electronic structures and metal-metal bond orders of  $\text{Re}_2\text{X}_4(\text{dppm})_2(\text{CO})$  and the related monoisocyanide complexes remains for future consideration.<sup>15,24</sup>

The reactions of the monocarbonyl complex  $\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CO})$  with isocyanide ligands are of special interest since we see here examples of rarely encountered structural isomerization in multiply bonded edge-shared bioctahedral complexes. In the case of the aryl isocyanides *xylyl*NC and *mesityl*NC, we obtained the complexes  $\text{Re}_2(\mu\text{-Cl})(\mu\text{-CO})(\mu\text{-dppm})_2\text{Cl}_3(\text{CNR})$  which bear a very close structural relationship to the related dicarbonyl complex  $\text{Re}_2(\mu\text{-Cl})(\mu\text{-CO})(\mu\text{-dppm})_2\text{Cl}_3(\text{CO})$ . The less effective  $\pi$ -acceptor alkyl isocyanide ligands *i*-PrNC and *t*-BuNC favor the alternative di- $\mu$ -chloro structure  $\text{Re}_2(\mu\text{-Cl})_2(\mu\text{-dppm})_2\text{Cl}_2(\text{CO})(\text{CNR})$ . This structural difference is accompanied by a significant change in the nature of the metal-based HOMO as judged by cyclic voltammetric electrochemical measurements.

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**Registry No. 1,** 96306-83-1; **2,** 102781-91-9;  $\text{Re}_2\text{Br}_4(\text{dppm})_2(\text{CO})$ , 102781-92-0;  $\text{Re}_2\text{Br}_4(\text{dppm})_2$ , 58312-72-4;  $\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CO})(\text{CNCHMe}_3)$ , 102781-93-1;  $\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CO})(\text{CNMe}_3)$ , 102781-94-2;  $\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CO})(\text{CNmesityl})$ , 102781-95-3;  $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CO})(\text{NCC}_2\text{H}_5)_2]\text{PF}_6$ , 102781-97-5;  $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CO})(\text{NCC}_2\text{H}_5)_2]\text{PF}_6$ , 102781-99-7;  $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CO})(\text{NCC}_6\text{H}_5)_2]\text{PF}_6$ , 102782-01-4;  $\text{Re}$ , 7440-15-5.

**Supplementary Material Available:** Tables of anisotropic displacement parameters, full lists of bond lengths and angles, and observed and calculated structure factors for  $\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CO})$  (1) and  $\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CO})(\text{CNxylyl})$  (2) (33 pages). Ordering information is given on any current masthead page.

## The Multiply Bonded Octahalodiosmate(III) Anions. 2.<sup>1</sup> Structure and Bonding

Pradyot A. Agaskar,<sup>2a</sup> F. Albert Cotton,<sup>\*2a</sup> Kim R. Dunbar,<sup>2a</sup> Larry R. Falvello,<sup>2a</sup>  
Stephen M. Tetrick,<sup>2b</sup> and Richard A. Walton<sup>\*2b</sup>

Contribution from the Department of Chemistry and Laboratory for Molecular Structure and Bonding, Texas A&M University, College Station, Texas 77843, and Department of Chemistry, Purdue University, West Lafayette, Indiana 47907. Received January 17, 1986

**Abstract:** The green crystalline compounds  $[(n\text{-Bu})_4\text{N}]_2[\text{Os}_2\text{X}_8]$  ( $\text{X} = \text{Cl}$  (1),  $\text{Br}$  (2)) have been prepared, and their crystal and electronic structures have been studied. The two compounds form isotopic crystals in space group  $P1$ , with the following unit cell dimensions, given first for 1 and then for 2:  $a = 11.797$  (2), 12.143 (3) Å;  $b = 18.650$  (4), 18.687 (6) Å;  $c = 11.506$  (2), 11.764 (3) Å;  $\alpha = 104.73$  (1)°, 103.58 (2)°;  $\beta = 103.06$  (1)°, 105.06 (2)°;  $\gamma = 100.00$  (1)°, 99.81 (2)°;  $V = 2312$  (2), 2428 (1) Å<sup>3</sup>. With  $Z = 2$ , the molecular formula defines the asymmetric unit and no crystallographic symmetry is imposed on the  $\text{Os}_2\text{X}_8^{2-}$  ions. In fact, they come very close to having  $D_{4d}$  symmetry, with the following dimensions for 1 and 2:  $\text{Os}-\text{Os}$ , 2.182 (1), 2.196 (1) Å;  $\text{Os}-\text{X}(\text{av})$ , 2.322 [6], 2.444 [4] Å;  $\angle\text{Os}-\text{Os}-\text{X}$ , 104.2 (3)°, 104.3 (4)°; mean torsion angle, 49.0 [3]°, 46.7 [1]°. The electronic structure of the  $\text{Os}_2\text{Cl}_8^{2-}$  ion in its eclipsed ( $D_{4h}$ ) conformation has been calculated by the SCF- $X\alpha$ -SW method, including relativistic corrections. The results support the shorthand description of the metal-metal bond as a  $d^5-d^5$ ,  $\sigma^2\pi^4\delta^2\delta^*$ , triple bond. The HOMO is the  $2b_{1u}$  ( $\delta^*$ ) orbital, followed closely ( $\sim 0.3$  eV) by the  $2b_{2g}$  ( $\delta$ ) orbital. The  $\text{Os}-\text{Os}$   $\pi$  bonding is concentrated mainly in the  $2e_u$  orbital and the  $\sigma$  bonding almost entirely in the  $2a_{1g}$  orbital. Both of these are very stable, thus accounting for the shortness of the  $\text{Os}-\text{Os}$  bond.

The  $\text{Re}_2\text{Cl}_8^{2-}$  ion is the archetypal species in the field of multiple bonds between metal atoms.<sup>3-5</sup> It owes this distinction not only

to the historical fact that it provided the first recognized example of a quadruple bond<sup>3</sup> but also because the  $\text{M}_2\text{X}_8$  structure is a

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