

Isolation and Structural Characterization of Mixed Carbonyl–Bis(dimethylphosphino)methane Complexes of Dirhenium(II)

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The triply bonded dirhenium(II) complex $\text{Re}_2\text{Cl}_4(\mu\text{-dmpm})_3$ ($\text{dmpm} = \text{Me}_2\text{PCH}_2\text{PMe}_2$) reacts with CO and xylNC in deoxygenated acetone in the presence of TlPF₆ to form the salts $[\text{Re}_2\text{Cl}_3(\text{L})(\mu\text{-dmpm})_3]\text{PF}_6$ ($\text{L} = \text{CO}, \text{xylNC}$) in which one of the equatorial chloride ligands has been displaced by a π -acceptor ligand L. A crystal structure determination of the carbonyl complex shows that a very short Re–Re bond distance is still present (2.3565(7) Å), in accord with the retention of a $\text{Re}\equiv\text{Re}$ bond. The dicarbonyl complexes $[\text{Re}_2\text{X}_2(\text{CO})_2(\text{dmpm})_3](\text{H}_2\text{PO}_4)_2$ are produced upon the reaction of $[\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)\text{X}_2(\mu\text{-dmpm})_3]\text{PF}_6$ ($\text{X} = \text{Cl}, \text{Br}$) with CO in deoxygenated acetone/HPF₆(aq) mixtures. These compounds have a structure in which two of the bridging dmpm ligands have switched to a chelating mode and the two halide ligands are now bridging the two metal centers, i.e. $[\text{Re}_2(\mu\text{-X})_2(\mu\text{-dmpm})(\text{CO})_2(\text{dmpm})_2](\text{H}_2\text{PO}_4)_2$. A crystal structure determination of the chloro complex has revealed that the Re–Re distance is quite long (2.918(2) Å); this distance is consistent with the presence of a Re–Re single bond. Crystal data for $[\text{Re}_2\text{Cl}_3(\text{CO})(\text{dmpm})_3]\text{PF}_6$ (+20 °C): orthorhombic space group $P2_12_12_1$ (No. 19), $a = 12.270(2)$ Å, $b = 15.389(2)$ Å, $c = 17.147(2)$ Å, $V = 3237(1)$ Å³, $Z = 4$. The structure was refined to $R = 0.023$ ($R_w = 0.027$) for 2091 data with $I > 3.0\sigma(I)$. Crystal data for $[\text{Re}_2\text{Cl}_2(\text{CO})_2(\text{dmpm})_3](\text{H}_2\text{PO}_4)_2$ (+20 °C): orthorhombic space group $P2_12_12_1$ (No. 18), $a = 12.576(1)$ Å, $b = 14.374(2)$ Å, $c = 10.872(2)$ Å, $V = 1965.3(8)$ Å³, $Z = 2$. The structure was refined to $R = 0.052$ ($R_w = 0.064$) for 1232 data with $I > 3.0\sigma(I)$.

Introduction

A rich and varied carbonyl chemistry has been developed over the last few years from the reactions of the triply-bonded dirhenium(II) complexes $\text{Re}_2\text{X}_4(\mu\text{-dppm})_2$ ($\text{X} = \text{Cl}, \text{Br}$; $\text{dppm} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$) with carbon monoxide,^{1–5} including, most recently, several novel species that are formed from the reactions of the resulting carbonyl complexes with alkynes.^{6,7} To develop this chemistry further, we had hoped to study the reactions of CO with the analogous complexes $\text{Re}_2\text{X}_4(\mu\text{-dmpm})_2$ ($\text{dmpm} = \text{Me}_2\text{PCH}_2\text{PMe}_2$), but our attempts to prepare the latter starting materials have so far been unsuccessful.^{8,9} Instead, the much more stable $(\text{dmpm})_3$ complexes $\text{Re}_2\text{X}_4(\mu\text{-dmpm})_3$ are always isolated.^{8,9} Accordingly, we decided instead to investigate the carbonylation of $\text{Re}_2\text{Cl}_4(\mu\text{-dmpm})_3$ as well as the related behavior of other closely allied dmpm-containing dirhenium(II) complexes, namely, $[\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)\text{X}_2(\mu\text{-dmpm})_3]\text{PF}_6$ ($\text{X} = \text{Cl}, \text{Br}$).¹⁰ Some aspects of the analogous reactions of these complexes with xyllyl isocyanide have also been studied. Details of this work are described in the present report.¹¹

Experimental Section

Starting Materials and Reaction Procedures. The dirhenium complexes $\text{Re}_2\text{Cl}_4(\text{dmpm})_3$ ^{8,9} and $[\text{Re}_2(\text{O}_2\text{CCH}_3)\text{X}_2(\text{dmpm})_3]\text{PF}_6$ ($\text{X} = \text{Cl}, \text{Br}$)¹⁰ were prepared as described in the literature. Carbon monoxide was

obtained from Matheson Gas Products while 2,6-dimethylphenyl isocyanide (xyllyl isocyanide, xylNC) was purchased from Fluka Chemical Co. Solvents and other reagents were obtained from commercial sources and were used as received. Syntheses were performed under an atmosphere of dry nitrogen, and solvents were deoxygenated prior to use.

A. Reactions of $\text{Re}_2\text{Cl}_4(\text{dmpm})_3$ with Carbon Monoxide and Xyllyl Isocyanide. (i) **Synthesis of $[\text{Re}_2\text{Cl}_3(\text{CO})(\text{dmpm})_3]\text{PF}_6$.** A quantity of $\text{Re}_2\text{Cl}_4(\text{dmpm})_3$ (0.060 g, 0.065 mmol) was dissolved in 15 mL of acetone and the solution treated with 0.027 g (0.065 mmol) of TlPF₆. Carbon monoxide was slowly bubbled through the reaction mixture for 30 min and the mixture then stirred under a CO atmosphere for a further 2 h. The reaction mixture was filtered to remove the precipitate of TlCl and the filtrate evaporated to dryness. The green residue was triturated with ethanol and the product filtered off and washed with diethyl ether; yield 0.052 g (75%). Anal. Calcd for $\text{C}_{16}\text{H}_{12}\text{Cl}_3\text{F}_6\text{OP}_7\text{Re}_2$: C, 18.13; H, 3.96. Found: C, 18.10; H, 4.13.

When an additional equivalent of TlPF₆ was used in the aforementioned reaction, a similar reaction procedure and workup led to the isolation of a brown solid. IR spectroscopy and cyclic voltammetric measurements showed the product to be a mixture of carbonyl-containing products, of which $[\text{Re}_2\text{Cl}_3(\text{CO})(\text{dmpm})_3]\text{PF}_6$ was the major component ($\nu(\text{CO}) = 1978 \text{ cm}^{-1}$); minor products were $[\text{Re}_2\text{Cl}_2(\text{CO})_2(\text{dmpm})_3](\text{PF}_6)_2$ ($\nu(\text{CO}) = 1880 \text{ cm}^{-1}$) as well as unidentified species with $\nu(\text{CO})$ bands at 1908 and 1820 cm^{-1} .

(ii) **Synthesis of $[\text{Re}_2\text{Cl}_3(\text{CNxyl})(\text{dmpm})_3]\text{PF}_6$.** A mixture of $\text{Re}_2\text{Cl}_4(\text{dmpm})_3$ (0.050 g, 0.052 mmol), xyllyl isocyanide (0.007 g, 0.052 mmol), and TlPF₆ (0.019 g, 0.052 mmol) in 10 mL of acetone was stirred at room temperature for 3 h and then filtered. The filtrate was evaporated to dryness and treated with ethanol, and the green solid was filtered off and dried; yield 0.043 g (68%). Anal. Calcd for $\text{C}_{24}\text{H}_{51}\text{Cl}_3\text{F}_6\text{NP}_7\text{Re}_2$: C, 24.78; H, 4.38; N, 1.20. Found: C, 23.97; H, 4.55; N, 1.24.

B. Reactions of $[\text{Re}_2(\text{O}_2\text{CCH}_3)\text{X}_2(\text{dmpm})_3]\text{PF}_6$ ($\text{X} = \text{Cl}$ or Br) with Carbon Monoxide and Xyllyl Isocyanide. (i) **Synthesis of $[\text{Re}_2\text{Cl}_2(\text{CO})_2(\text{dmpm})_3](\text{H}_2\text{PO}_4)_2$.** A solution of $[\text{Re}_2(\text{O}_2\text{CCH}_3)\text{Cl}_2(\text{dmpm})_3]\text{PF}_6$ (0.050 g, 0.053 mmol) in deoxygenated acetone (15 mL) was saturated with CO gas for 5 min, and a small quantity of HPF₆(aq) (0.025 mL) was added. The passage of CO(g) was continued for a further 1 h, during which time the color of the solution changed from green to pale yellow-green. The reaction mixture was stirred for 18 h under a static atmosphere of CO and then evaporated to dryness. The purple residue was washed with ethanol and diethyl ether and then dissolved in a minimum volume of acetone and the solution layered with hexane. A crop of crystals was isolated after several days and dried; yield 0.025 g (49%). This product

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Table I. Crystallographic Data for $[\text{Re}_2\text{Cl}_3(\text{CO})(\text{dmpm})_3]\text{PF}_6$ (**1**) and $[\text{Re}_2\text{Cl}_2(\text{CO})_2(\text{dmpm})_3](\text{H}_2\text{PO}_4)_2$

	1	2
chem formula	$\text{Re}_2\text{Cl}_3\text{P}_7\text{F}_6\text{OC}_{16}\text{H}_{42}$	$\text{Re}_2\text{Cl}_3\text{P}_8\text{O}_{10}\text{C}_{17}\text{H}_{42}$
fw	1060.08	1097.62
space group	$P2_12_12_1$ (No. 19)	$P2_12_12_1$ (No. 18)
a, Å	12.270(2)	12.576(1)
b, Å	15.389(2)	14.374(2)
c, Å	17.147(2)	10.872(2)
V, Å ³	3237(1)	1965.3(8)
Z	4	2
T, °C	20	20
λ, Å (Mo Kα)	0.710 73	0.710 73
ρ _{calc} , g cm ⁻³	2.175	1.855
μ(Mo Kα), cm ⁻¹	82.12	67.35
transm coeff	1.00–0.79	1.00–0.32
R ^a	0.023	0.052
R _w ^b	0.027	0.064

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

was identified as being of composition $[\text{Re}_2\text{Cl}_2(\text{CO})_2(\text{dmpm})_3](\text{H}_2\text{PO}_4)_2$ by a single-crystal X-ray structure determination.

Anion-exchange reactions to obtain the salts $[\text{Re}_2\text{Cl}_2(\text{CO})_2(\text{dmpm})_3](\text{PF}_6)_2$ and $[\text{Re}_2\text{Cl}_2(\text{CO})_2(\text{dmpm})_3](\text{ClO}_4)_2$ were carried out by the use of metathesis reactions between $[\text{Re}_2\text{Cl}_2(\text{CO})_2(\text{dmpm})_3](\text{H}_2\text{PO}_4)_2$ and KPF_6 and NaClO_4 , respectively, in acetone. The purple crystalline products were characterized on the basis of their spectroscopic and conductivity properties.

(ii) **Synthesis of $[\text{Re}_2\text{Br}_2(\text{CO})_2(\text{dmpm})_3](\text{H}_2\text{PO}_4)_2$.** The reaction between $[\text{Re}_2(\text{O}_2\text{CCH}_3)\text{Br}_2(\text{dmpm})_3]\text{PF}_6$ (0.040 g, 0.046 mmol) and $\text{CO}(\text{g})$ in acetone was carried out by use of a procedure similar to that described in section B(i) to give purple crystals of the title complex; yield 0.015 g (37%). Anal. Calcd for $\text{C}_{17}\text{H}_{46}\text{Br}_2\text{O}_{10}\text{P}_8\text{Re}_2$: C, 17.14; H, 3.38. Found: C, 17.89; H, 3.75.

(iii) **Synthesis of $[\text{Re}_2\text{Cl}_3(\text{CNxyl})(\text{dmpm})_3]\text{H}_2\text{PO}_4$.** The reaction between $[\text{Re}_2(\text{O}_2\text{CCH}_3)\text{Cl}_2(\text{dmpm})_3]\text{PF}_6$ (0.070 g, 0.066 mmol), xylol isocyanide (0.017 g, 0.133 mmol), and $\text{HPF}_6(\text{aq})$ (0.023 mL) in 10 mL of acetone was carried out for 18 h at room temperature; during this period the color of the reaction solution changed from green to yellow-green. The reaction mixture was then evaporated to dryness and the residue treated with diethyl ether to give an oily solid. This was dissolved in acetone and the extract layered with hexane. After a few days, a crop of green crystals was harvested; yield 0.03 g. Anal. Calcd for $\text{C}_{24}\text{H}_{53}\text{Cl}_3\text{NO}_7\text{P}_7\text{Re}_2$: C, 25.85; H, 4.80; N, 1.26. Found: C, 25.19; H, 4.64; N, 1.32.

A metathesis reaction between $[\text{Re}_2\text{Cl}_3(\text{CNxyl})(\text{dmpm})_3]\text{H}_2\text{PO}_4$ and KPF_6 in acetone led to the crystallization of a quantity of $[\text{Re}_2\text{Cl}_3(\text{CNxyl})(\text{dmpm})_3]\text{PF}_6$. This product was identified on the basis of a comparison of its spectroscopic and electrochemical properties to those of a sample of this complex prepared as described in procedure A(ii).

Preparation of Single Crystals for X-ray Structure Analysis. Crystals of $[\text{Re}_2\text{Cl}_3(\text{CO})(\text{dmpm})_3]\text{PF}_6$ (**1**) were grown by the slow diffusion of hexane into an acetone solution of this complex, while suitable crystals of composition $[\text{Re}_2\text{Cl}_2(\text{CO})_2(\text{dmpm})_3](\text{H}_2\text{PO}_4)_2$ (**2**) were obtained directly from the reaction medium as described in synthetic procedure B(i).

X-ray Structure Analyses. The structures of **1** and **2** were determined by the application of standard procedures. The basic crystallographic parameters for these complexes are listed in Table I. The cell constants are based on 25 reflections with $17 < \theta < 21^\circ$ for **1** and $15 < \theta < 20^\circ$ for **2**. Three standard reflections were measured after every 5000 s of beam exposure during data collection, but we observed no systematic variations in decay of these standards. Lorentz and polarization corrections were applied to the data sets. An empirical absorption correction was applied,¹² the linear absorption coefficients being 82.12 cm⁻¹ for **1** and 67.35 cm⁻¹ for **2**. No corrections were made for extinction. Calculations were performed on a microVAX II computer using the Enraf-Nonius structure determination package.

The structures of **1** and **2** were solved by the Enraf-Nonius structure solution procedure MolEN. Hydrogen atoms of the dmpm ligands were introduced at calculated positions (C–H = 0.95 Å, B = 1.3B_C), not refined but constrained to ride on their C atoms. All non-hydrogen atoms of **1**

Table II. Positional Parameters and Equivalent Isotropic Displacement Parameters (Å²) for the Non-Hydrogen Atoms of **1**^a

atom	x	y	z	B
Re(1)	0.80465(4)	0.17088(3)	0.16599(3)	1.312(8)
Re(2)	0.67160(4)	0.06985(3)	0.20599(3)	1.369(8)
Cl(11)	0.9369(3)	0.2999(2)	0.1565(2)	2.84(7)
Cl(12)	0.8605(3)	0.1462(2)	0.0327(2)	2.66(7)
Cl(21)	0.5395(3)	-0.0564(2)	0.2280(2)	3.22(7)
P(11)	0.9602(2)	0.0759(2)	0.1925(2)	2.00(6)
P(12)	0.8068(3)	0.2334(2)	0.2958(2)	1.84(6)
P(13)	0.6751(3)	0.2747(2)	0.1061(2)	2.42(7)
P(21)	0.7939(3)	-0.0339(2)	0.2710(2)	2.11(6)
P(22)	0.6083(2)	0.1309(2)	0.3325(2)	1.90(6)
P(23)	0.5165(3)	0.1315(3)	0.1364(2)	2.78(8)
O(2)	0.7206(8)	-0.0327(6)	0.0554(5)	3.6(2)
C(2)	0.709(1)	0.0088(8)	0.1111(7)	2.1(3)
C(B1)	0.932(1)	0.0066(9)	0.2770(7)	2.5(3)
C(B2)	0.7338(9)	0.1745(9)	0.3732(7)	2.2(2)
C(B3)	0.533(1)	0.2497(9)	0.1287(9)	3.5(3)
C(111)	0.997(1)	-0.0018(8)	0.1164(8)	2.8(3)
C(112)	1.092(1)	0.1234(9)	0.2115(9)	3.0(3)
C(121)	0.936(1)	0.2435(9)	0.3465(8)	3.3(3)
C(122)	0.757(1)	0.3441(8)	0.3070(8)	2.8(3)
C(131)	0.678(1)	0.3904(9)	0.127(1)	4.8(4)
C(132)	0.675(2)	0.282(1)	0.0005(8)	5.4(4)
C(211)	0.772(1)	-0.0737(9)	0.3684(8)	3.8(3)
C(212)	0.802(1)	-0.1366(9)	0.2200(8)	3.4(3)
C(221)	0.553(1)	0.0598(9)	0.4068(8)	2.7(3)
C(222)	0.511(1)	0.2193(8)	0.3397(9)	2.9(3)
C(231)	0.381(1)	0.118(1)	0.176(1)	5.0(4)
C(232)	0.503(1)	0.094(1)	0.042(1)	5.4(4)
P(100)	0.7924(3)	0.6238(3)	0.0529(2)	3.06(8)
F(1)	0.6914(8)	0.6740(7)	0.0139(5)	6.7(2)
F(2)	0.821(1)	0.7061(7)	0.1007(8)	9.9(4)
F(3)	0.7152(9)	0.5943(8)	0.1207(7)	8.3(3)
F(4)	0.762(1)	0.5409(8)	0.0041(7)	8.1(3)
F(5)	0.8662(9)	0.6551(9)	-0.0149(7)	8.4(3)
F(6)	0.8894(8)	0.5732(7)	0.0894(6)	6.2(3)

^a Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos \gamma)\beta(1,2) + ac(\cos \beta)\beta(1,3) + bc(\cos \alpha)\beta(2,3)]$.

and **2** were refined with anisotropic thermal parameters. Corrections for anomalous scattering were applied to these atoms.¹³ The final residuals for **1** were $R = 0.023$ ($R_w = 0.027$) and $\text{GOF} = 0.728$; for the other enantiomorph $R = 0.043$ ($R_w = 0.054$) and $\text{GOF} = 1.424$. In the case of **2**, $R = 0.052$ ($R_w = 0.064$) and $\text{GOF} = 1.817$; for the other enantiomorph $R = 0.062$ ($R_w = 0.077$) and $\text{GOF} = 2.153$.

Positional parameters and their errors for the non-hydrogen atoms of compounds **1** and **2** are listed in Tables II and III. Important intramolecular bond distances and angles are given in Tables IV and V. Full details of the crystal data, data collection parameters, and all structural parameters are available as supplementary material.

Physical Measurements. Infrared spectra (4000–200 cm⁻¹) were recorded as Nujol mulls supported on KBr or polyethylene plates with a Perkin-Elmer 1800 FTIR spectrometer. Electrochemical experiments 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 supporting electrolyte. $E_{1/2}$ values, determined as $(E_{p,a} + E_{p,c})/2$, were referenced to the Ag/AgCl electrode at room temperature and are uncorrected for junction potentials. Under our experimental conditions $E_{1/2} = +0.47$ V for the ferrocenium/ferrocene couple, which was used as an internal standard. ¹H NMR spectra were recorded on a GE QE-300 spectrometer. Resonances were referenced internally to the residual protons in the incompletely deuteriated (CD₃)₂CO solvent ($\delta + 2.04$). ³¹P{¹H} NMR spectra were recorded on a Varian XL-200A spectrometer operated at 80.98 MHz with an internal deuterium lock using aqueous 85% H₃PO₄ as an external standard. Conductivity measurements were performed on ca. 10⁻³ M acetone solutions by using an Industrial Instruments Inc. Model RC-16B2 conductivity bridge.

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

(12) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A: Found Crystallogr.* 1983, A39, 158.

Table III. Positional Parameters and Equivalent Isotropic Displacement Parameters (\AA^2) for the Non-Hydrogen Atoms of 2^a

atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
Re	0.98604(7)	0.89925(8)	0.80731(9)	3.43(2)
Cl(B)	0.8704(5)	1.0126(5)	0.7069(6)	4.1(1)
P(1)	0.5694(6)	0.5837(6)	0.9944(6)	4.4(2)
P(2)	1.0796(5)	0.7524(6)	0.7924(7)	4.3(2)
P(3)	0.9389(6)	0.8151(6)	0.6209(7)	4.5(2)
O(1)	0.809(2)	0.809(2)	0.945(2)	6.4(6)
C(1)	0.873(2)	0.849(2)	0.889(2)	4.9(7)
C(11)	0.573(2)	0.681(2)	0.893(3)	5.4(8)
C(12)	0.709(2)	0.549(3)	0.990(3)	6.7(9)
C(1B)	0.5	0.5	0.898(3)	6(1)
C(21)	1.060(3)	0.656(2)	0.896(3)	6.4(9)
C(22)	1.219(2)	0.754(3)	0.764(3)	7(1)
C(2B)	1.018(3)	0.714(2)	0.645(2)	6.3(7)
C(31)	0.976(3)	0.862(2)	0.475(2)	7.1(8)
C(32)	0.804(3)	0.783(3)	0.597(3)	7.0(9)
P(1000)	0.782(2)	0.519(2)	0.614(2)	18.4(6)
O(1001)	0.845(2)	0.549(2)	0.718(2)	9.8(7)
O(1002)	0.680(2)	0.522(3)	0.678(3)	15(1)
O(1003)	0.777(3)	0.430(2)	0.612(6)	35(2)
O(1004)	0.794(5)	0.570(2)	0.528(3)	18(2)

^a Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos \gamma)\beta(1,2) + ac(\cos \beta)\beta(1,3) + bc(\cos \alpha)\beta(2,3)]$.

Table IV. Important Bond Distances (\AA) and Bond Angles (deg) for 1^a

Distances			
Re(1)–Re(2)	2.3565(7)	Re(2)–P(23)	2.439(4)
Re(1)–Cl(11)	2.570(3)	Re(2)–C(2)	1.93(1)
Re(1)–Cl(12)	2.416(3)	O(2)–C(2)	1.16(2)
Re(1)–P(11)	2.446(4)	P(100)–F(1)	1.61(1)
Re(1)–P(12)	2.425(3)	P(100)–F(2)	1.55(1)
Re(1)–P(13)	2.477(4)	P(100)–F(3)	1.57(1)
Re(2)–Cl(21)	2.558(3)	P(100)–F(4)	1.57(1)
Re(2)–P(21)	2.458(3)	P(100)–F(5)	1.55(1)
Re(2)–P(22)	2.488(4)	P(100)–F(6)	1.56(1)
Angles			
Re(2)–Re(1)–Cl(11)	164.97(9)	Cl(21)–Re(2)–C(2)	84.7(4)
Re(2)–Re(1)–Cl(12)	111.60(9)	P(21)–Re(2)–P(22)	92.3(1)
Re(2)–Re(1)–P(11)	95.28(9)	P(21)–Re(2)–P(23)	162.0(1)
Re(2)–Re(1)–P(12)	90.13(8)	P(21)–Re(2)–C(2)	85.4(4)
Re(2)–Re(1)–P(13)	95.84(9)	P(22)–Re(2)–P(23)	92.0(1)
Cl(11)–Re(1)–Cl(12)	83.3(1)	P(22)–Re(2)–C(2)	172.3(4)
Cl(11)–Re(1)–P(11)	88.9(1)	P(23)–Re(2)–C(2)	88.0(4)
Cl(11)–Re(1)–P(12)	75.2(1)	Re(2)–C(2)–O(2)	172(1)
Cl(11)–Re(1)–P(13)	83.2(1)	F(1)–P(100)–F(2)	90.0(7)
Cl(12)–Re(1)–P(11)	82.0(1)	F(1)–P(100)–F(3)	89.0(6)
Cl(12)–Re(1)–P(12)	158.1(1)	F(1)–P(100)–F(4)	89.3(7)
Cl(12)–Re(1)–P(13)	83.7(1)	F(1)–P(100)–F(5)	89.4(6)
P(11)–Re(1)–P(12)	93.3(1)	F(1)–P(100)–F(6)	178.6(7)
P(11)–Re(1)–P(13)	164.4(1)	F(2)–P(100)–F(3)	88.8(9)
P(12)–Re(1)–P(13)	97.5(1)	F(2)–P(100)–F(4)	179.3(8)
Re(1)–Re(2)–Cl(21)	169.41(9)	F(2)–P(100)–F(5)	90.7(9)
Re(1)–Re(2)–P(21)	97.92(9)	F(2)–P(100)–F(6)	91.4(7)
Re(1)–Re(2)–P(22)	102.76(8)	F(3)–P(100)–F(4)	91.0(8)
Re(1)–Re(2)–P(23)	98.1(1)	F(3)–P(100)–F(5)	178.4(7)
Re(1)–Re(2)–C(2)	84.8(4)	F(3)–P(100)–F(6)	91.0(6)
Cl(21)–Re(2)–P(21)	80.0(1)	F(4)–P(100)–F(5)	89.4(8)
Cl(21)–Re(2)–P(22)	87.7(1)	F(4)–P(100)–F(6)	89.3(7)
Cl(21)–Re(2)–P(23)	82.7(1)	F(5)–P(100)–F(6)	90.5(7)

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

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

Results

The reactions between acetone solutions of $\text{Re}_2\text{Cl}_4(\mu\text{-dmpm})_3$ and carbon monoxide and xylyl isocyanide in the presence of TIPF_6 proceed quite rapidly and cleanly, with good yield to afford the dirhenium(II) complexes $[\text{Re}_2\text{Cl}_3(\text{L})(\mu\text{-dmpm})_3]\text{PF}_6$, where $\text{L} = \text{CO}$ or xylylNC . In the absence of TIPF_6 , which labilizes one of the Re–Cl bonds, no reaction was observed under otherwise

Table V. Important Bond Distances (\AA) and Bond Angles (deg) for 2^a

Distances			
Re–Re	2.918(2)	Re–C(1)	1.83(3)
Re–Cl(B)	2.442(7)	O(1)–C(1)	1.16(3)
Re–Cl(B)	2.460(7)	P(1000)–O(1001)	1.44(3)
Re–P(1)	2.409(8)	P(1000)–O(1002)	1.46(4)
Re–P(2)	2.422(9)	P(1000)–O(1003)	1.29(5)
Re–P(3)	2.434(8)	P(1000)–O(1004)	1.19(4)
Angles			
Re–Re–Cl(B)	53.8(2)	P(1)–Re–C(1)	86.7(9)
Re–Re–Cl(B)	53.2(2)	P(2)–Re–P(3)	68.2(3)
Re–Re–P(1)	81.2(2)	P(2)–Re–C(1)	94(1)
Re–Re–P(2)	143.8(2)	P(3)–Re–C(1)	91.1(9)
Re–Re–P(3)	121.5(2)	Re–Cl(B)–Re	73.1(2)
Re–Re–C(1)	119(1)	Re–C(1)–O(1)	173(3)
Cl(B)–Re–Cl(B)	84.0(3)	O(1001)–P(1000)–O(1002)	96(2)
Cl(B)–Re–P(1)	126.2(3)	O(1001)–P(1000)–O(1003)	110(4)
Cl(B)–Re–P(2)	147.3(3)	O(1001)–P(1000)–O(1004)	112(3)
Cl(B)–Re–P(3)	79.3(3)	O(1002)–P(1000)–O(1003)	90(4)
Cl(B)–Re–C(1)	91(1)	O(1002)–P(1000)–O(1004)	118(6)
P(1)–Re–P(2)	86.4(3)	O(1003)–P(1000)–O(1004)	127(6)
P(1)–Re–P(3)	154.4(3)		

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

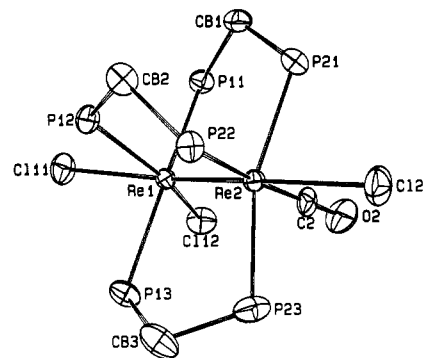


Figure 1. ORTEP representation of the structure of the $[\text{Re}_2\text{Cl}_3(\text{CO})(\text{dmpm})_3]^+$ cation as present in compound **1**. The thermal ellipsoids are drawn at the 50% probability level.

similar conditions. Both complexes behave as 1:1 electrolytes in acetone ($\Lambda_m = 113$ and $117 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ for $\text{L} = \text{CO}$ and xylylNC , respectively), and they possess very similar IR spectra, with $\nu(\text{P}=\text{F})$ for the PF_6^- anion at $836\text{--}840 \text{ cm}^{-1}$, $\nu(\text{CO})$ at 1978 vs cm^{-1} ($\text{L} = \text{CO}$), and $\nu(\text{CN})$ at 2110 vs cm^{-1} ($\text{L} = \text{xylylNC}$). Solutions of these complexes in 0.1 M $\text{TBAH}-\text{CH}_2\text{Cl}_2$ also exhibit very similar cyclic voltammograms, with a reversible one-electron oxidation at $E_{1/2}(\text{ox}) = +1.10 \text{ V vs Ag/AgCl}$ for the compound where $\text{L} = \text{CO}$ and $E_{1/2}(\text{ox}) = +0.93 \text{ V vs Ag/AgCl}$ for $\text{L} = \text{xylylNC}$; for both these processes ΔE_p (i.e. $E_{p,a} - E_{p,c}$) = 90 mV at a sweep rate of 200 mV s^{-1} . Each complex also displays an irreversible reduction in its single-scan cyclic voltammogram with $E_{p,c}$ values of -1.13 and $-1.42 \text{ V vs Ag/AgCl}$ for $\text{L} = \text{CO}$ and xylylNC , respectively, at a sweep rate of 200 mV s^{-1} . This difference of ca. 0.3 V reflects the significantly greater π -acceptor ability of CO compared to xylylNC when bound to the dirhenium core.

The structural identity of the carbonyl complex $[\text{Re}_2\text{Cl}_3(\text{CO})(\mu\text{-dmpm})_3]\text{PF}_6$ was established by single-crystal X-ray crystallography. An ORTEP representation of the structure of the cation is shown in Figure 1. The important details of the crystallographic and structural parameters are given in Tables I, II, and IV.

The ^1H NMR spectrum of the xylyl isocyanide complex $[\text{Re}_2\text{Cl}_3(\text{CNxylyl})(\text{dmpm})_3]\text{PF}_6$ (recorded in $(\text{CD}_3)_2\text{CO}$) accords with a 1:3 ratio of xylylNC to dmpm ligands. The former ligand is characterized by singlets at $\delta +2.81$ (3H) and $\delta +2.79$ (3H) for the methyl groups and a broad singlet at $\delta +7.29$ (3H) for the aryl protons. The presence of two methyl singlets signifies that the xylyl isocyanide ligand is not rotating rapidly on the NMR time scale. The dmpm ligands are most conveniently

characterized through their $-\text{CH}_2-$ resonances since the more complex $-\text{CH}_3$ region ($\delta +2.3$ to $\delta +1.7$) is overlaid by the solvent acetone multiplet at $\delta +2.04$. The $-\text{CH}_2-$ region consists of a triplet at $\delta +4.90$ (2H, $^2J_{\text{P-H}} = 9.7$ Hz), due to the unique dmpm ligand,¹⁴ that overlaps one of the multiplets of an ABX_4 pattern (4H) associated with the methylene protons of the pair of trans dmpm ligands (δ ca. $+5.0$ and ca. $+4.5$). The ^1H NMR spectrum of the less soluble carbonyl complex $[\text{Re}_2\text{Cl}_2(\text{CO})(\text{dmpm})_3]\text{PF}_6$ (recorded in $(\text{CD}_3)_2\text{CO}$) shows a triplet at $\delta +4.56$ (2H) as well as multiplets at δ ca. $+5.0$ and ca. $+4.6$ that are components of an ABX_4 splitting pattern.

The $^{31}\text{P}\{\text{H}\}$ NMR spectra of both complexes are very similar, in accord with their possessing similar structures. Each displays a binomial heptet ($\delta -142.8$) for the PF_6^- anion, an AB pattern that appears as two doublets of triplets, and a more complex AA'BB' type of pattern that arises from the four phosphorus atoms of the pair of trans dmpm ligands. For the xylyl isocyanide complex, the pairs of doublets of triplets are centered at $\delta -23.0$ and -23.9 ($J_{\text{P-P}} = 77$ and 22 Hz) and $\delta -36.1$ and -37.1 ($J_{\text{P-P}} = 77$ and 14 Hz), while the AA'BB' multiplets are centered at δ ca. -25 and ca. -27 . The spectrum of the carbonyl complex is very similar although of poorer quality because of the lower solubility of this complex; the AB pattern consists of triplets at $\delta -16.7$ and -17.7 and at $\delta -46.2$ and -47.2 and the AA'BB' pattern consists of multiplets centered at δ ca. -22 and -26.5 .

While preliminary studies indicate that the complex $[\text{Re}_2\text{Cl}_2(\text{CO})(\text{dmpm})_3]\text{PF}_6$ does not react with additional CO in the presence of a further equivalent of TIPF_6 to afford the dicarbonyl complex $[\text{Re}_2\text{Cl}_2(\text{CO})_2(\text{dmpm})_3](\text{PF}_6)_2$ as a major product, small quantities of this compound appear to be formed in this reaction, along with other carbonyl-containing species (on the basis of electrochemical and IR spectroscopic characterization of the resultant product). However, salts of the $[\text{Re}_2\text{Cl}_2(\text{CO})_2(\text{dmpm})_3]^{2+}$ cation are obtained quite readily in moderate yield through the reaction of acetone solutions of the mixed acetate-chloride complex $[\text{Re}_2(\text{O}_2\text{CCH}_3)_2\text{Cl}_2(\text{dmpm})_3]\text{PF}_6$ with CO in the presence of a small quantity of $\text{HPF}_6(\text{aq})$. The product that is isolated from this reaction mixture is the dihydrogenphosphate salt $[\text{Re}_2\text{Cl}_2(\text{CO})_2(\text{dmpm})_3](\text{H}_2\text{PO}_4)_2$. The related reaction of CO with the acetate-bromide complex $[\text{Re}_2(\text{O}_2\text{CCH}_3)_2\text{Br}_2(\text{dmpm})_3]\text{PF}_6$ affords the analogous bromide complex $[\text{Re}_2\text{Br}_2(\text{CO})_2(\text{dmpm})_3](\text{H}_2\text{PO}_4)_2$. The reaction of xylyl isocyanide with a solution of $[\text{Re}_2(\text{O}_2\text{CCH}_3)_2\text{Cl}_2(\text{dmpm})_3]\text{PF}_6$ in acetone that has been acidified with $\text{HPF}_6(\text{aq})$ produces the mono(isocyanide) complex $[\text{Re}_2\text{Cl}_2(\text{CNxylyl})(\text{dmpm})_3]\text{H}_2\text{PO}_4$ rather than $[\text{Re}_2\text{Cl}_2(\text{CNxylyl})_2(\text{dmpm})_3](\text{H}_2\text{PO}_4)_2$. Its IR spectrum ($\nu(\text{CN}) = 2102$ vs cm^{-1} , $\nu(\text{P-O}) = 1056$ vs, br cm^{-1}), electrochemical properties ($E_{1/2}(\text{ox}) = +0.91$ V and $E_{\text{p,c}} = -1.40$ V vs Ag/AgCl in 0.1 M $\text{TBAH}-\text{CH}_2\text{Cl}_2$), and metathesis reaction with KPF_6 to form the previously described salt $[\text{Re}_2\text{Cl}_2(\text{CNxylyl})(\text{dmpm})_3]\text{PF}_6$ support this formulation.

Both dicarbonyl complexes show limited solubility in most nonaqueous solvents, the bromide complex being the least soluble of the two. The cyclic voltammogram of solutions of the chloride complex in 0.1 M $\text{TBAH}-\text{CH}_2\text{Cl}_2$ exhibits a reversible one-electron reduction at $E_{1/2}(\text{red}) = -0.22$ V vs Ag/AgCl ($\Delta E_{\text{p}} = 70$ mV) and an irreversible oxidation at $E_{\text{p,a}} = +1.43$ V vs Ag/AgCl . The IR spectra (Nujol mulls) of the chloride and bromide complexes are essentially identical in the region $2000-600$ cm^{-1} , with a $\nu(\text{CO})$ band at 1056 cm^{-1} (shoulder at 1872 cm^{-1}) and $\nu(\text{P-O})$ of the $[\text{H}_2\text{PO}_4]^{2-}$ anion centered at 1056 s, br cm^{-1} .

The single-crystal X-ray structure determination of the chloride complex confirmed its identity as a dicarbonyl derivative. The structure of the dication is shown in Figure 2. Important details of the crystallographic and structural parameters are given in Tables I, III, and V. While this structure determination confirmed

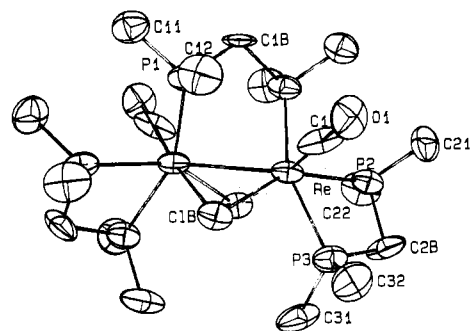


Figure 2. ORTEP representation of the structure of the $[\text{Re}_2\text{Cl}_2(\text{CO})_2(\text{dmpm})_3]^+$ cation as present in compound 2. The thermal ellipsoids are drawn at the 50% probability level.

the presence of a phosphate anion in the asymmetric unit, the phosphorus atom and three of the oxygen atoms had large thermal parameters, so we were unable to distinguish a $[\text{H}_2\text{PO}_4]^-$, $[\text{HPO}_4]^{2-}$, or $[\text{PO}_4]^{3-}$ formulation. However, the presence of $[\text{H}_2\text{PO}_4]^{2-}$ is supported by conductivity measurements on an acetone solution of this complex (0.72×10^{-3} M), which showed behavior characteristic of a 1:2 electrolyte¹⁵ with $\Lambda_{\text{m}} = 178$ $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$. Furthermore, metathesis reactions with KPF_6 and NaClO_4 afforded products that we formulate as $[\text{Re}_2\text{Cl}_2(\text{CO})_2(\text{dmpm})_3](\text{PF}_6)_2$ and $[\text{Re}_2\text{Cl}_2(\text{CO})_2(\text{dmpm})_3](\text{ClO}_4)_2$. A solution of the PF_6^- salt in acetone (0.93×10^{-3} M) behaves as a 1:2 electrolyte ($\Lambda_{\text{m}} = 190$ $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$), and both complexes have cyclic voltammograms (in 0.1 M $\text{TBAH}-\text{CH}_2\text{Cl}_2$) that are identical to those of the $[\text{H}_2\text{PO}_4]^{2-}$ salt. Their IR spectra confirm that $[\text{H}_2\text{PO}_4]^{2-}$ has been replaced by PF_6^- ($\nu(\text{P-F}) = 840$ vs cm^{-1}) or ClO_4^- ($\nu(\text{Cl-O}) = 1086$ vs, br cm^{-1}). The $\nu(\text{CO})$ bands of these two complexes occur at 1882 vs cm^{-1} (PF_6^- salt) and at 1868 vs and 1890 m-s cm^{-1} (ClO_4^- salt).

Solutions of salts of the $[\text{Re}_2\text{Cl}_2(\text{CO})_2(\text{dmpm})_3]^{2+}$ cation were sufficiently soluble in $(\text{CD}_3)_2\text{CO}$ to obtain a $^{31}\text{P}\{\text{H}\}$ NMR spectrum. These showed two broad, poorly resolved, multiplets in an intensity ratio of 1:2, an apparent triplet at $\delta -46.3$ (2P), and a complex multiplet centered at δ ca. -62 (4P) which approximates to a AA'BB' pattern. This observation is in accordance with the presence of two types of dmpm ligands as established by the crystal structure determination of $[\text{Re}_2\text{Cl}_2(\text{CO})_2(\text{dmpm})_3](\text{H}_2\text{PO}_4)_2$ (Figure 2). On the basis of a comparison with data for other dirhenium complexes that contain bridging or chelating dmpm ligands,^{8-10,16} we tentatively assign the downfield triplet to the bridging dmpm ligand and the upfield multiplet to the pair of equivalent chelating dmpm ligands. The ^1H NMR spectrum of $[\text{Re}_2\text{Cl}_2(\text{CO})_2(\text{dmpm})_3](\text{H}_2\text{PO}_4)_2$ (recorded in $(\text{CD}_3)_2\text{CO}$) shows a triplet at $\delta +5.4$ (2H) and a broad poorly resolved multiplet spanning the range $\delta +4.6$ to $+4.1$ (4H) for the $-\text{CH}_2-$ protons of the two types of dmpm ligands; a set of overlapping $-\text{CH}_3$ doublets were located between $\delta +2.35$ and $\delta +1.85$.

Discussion

The conversion of $\text{Re}_2\text{Cl}_4(\mu\text{-dmpm})_3$ to the monocarbonyl and mono(isocyanide) complexes $[\text{Re}_2\text{Cl}_2(\text{L})(\mu\text{-dmpm})_3]\text{PF}_6$ (L = CO or xylylNC) requires the labilization of a Re-Cl bond by TIPF_6 and represents the first instances where this coordinatively saturated starting material has been found to react with π -acceptor ligands. The similarity between the spectroscopic and electrochemical properties of the carbonyl and xylyl isocyanide complexes implies that a close structural relationship exists between these compounds. An X-ray crystal structure determination of $[\text{Re}_2\text{Cl}_2(\text{CO})(\mu\text{-dmpm})_3]\text{PF}_6$ (1) established it to be a derivative

(14) The apparent equivalence of the two methylene protons for this ligand suggests that this bridgehead group is involved in a fluxional process.

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

(16) Ara, I.; Fanwick, P. E.; Walton, R. A. *Inorg. Chem.* **1992**, *31*, 3211.

of $\text{Re}_2\text{Cl}_4(\mu\text{-dmpm})_3$, in which one of the equatorial Re–Cl bonds has been replaced by a Re–CO unit.

The structure of the cation of **1** resembles that of the acetato-bridged complex cation $[\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)\text{Cl}_2(\mu\text{-dmpm})_3]^+$, as present in its chloride salt.¹⁰ These two species differ structurally from $\text{Re}_2\text{Cl}_4(\mu\text{-dmpm})_3$ in one important respect: whereas the two equatorial Re–Cl bonds of $\text{Re}_2\text{Cl}_4(\mu\text{-dmpm})_3$ are in an anti disposition to one another,^{8,9} the equatorial CO and Cl ligands of **1** and the oxygen atoms of the acetate ligand of $[\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)\text{Cl}_2(\mu\text{-dmpm})_3]^+$ are in syn arrangements. Consequently, the torsional twist angles (χ) in these two cations are quite small, the average value (χ_{av}) being ca. 12° in the case of $[\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)\text{Cl}_2(\mu\text{-dmpm})_3]^+$ and ca. 13° in $[\text{Re}_2\text{Cl}_3(\text{CO})(\mu\text{-dmpm})_3]^+$; in **1** the individual torsional angles Cl(12)–Re(1)–Re(2)–C(2), P(11)–Re(1)–Re(2)–P(21), P(12)–Re(1)–Re(2)–P(22), and P(13)–Re(1)–Re(2)–P(23) are $11.8(4)$, $12.9(1)$, $13.8(1)$, and $10.2(1)^\circ$, respectively. The Re–Re bond length in **1** ($2.3565(7)$ Å) is a little longer than those in $[\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)\text{Cl}_2(\mu\text{-dmpm})_3]\text{Cl}$ ($2.304(1)$ Å)¹⁰ and $\text{Re}_2\text{Cl}_4(\mu\text{-dmpm})_3$ ($2.309(2)$ and $2.3157(4)$ Å for the orthorhombic and monoclinic crystal forms).⁸ In accord with this result, the Re–Cl_{ax} bond distances in **1** ($2.570(3)$ and $2.558(3)$ Å) are correspondingly shorter than those in $[\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)\text{Cl}_2(\mu\text{-dmpm})_3]\text{Cl}$ ($2.592(5)$ and $2.588(6)$ Å) and $\text{Re}_2\text{Cl}_4(\mu\text{-dmpm})_3$ ($2.652(2)$ and $2.647(2)$ Å in the monoclinic form).⁸ The lengthening of the Re–Re bond in **1** may reflect the effect of the π -acceptor CO ligand in some weakening of the π and δ components of the Re–Re bonding through Re \rightarrow CO(π^*) back-bonding. While the four Re–P bonds of **1** that are trans to another Re–P bond ($2.439(4)$ – $2.477(4)$ Å) are in the usual range,^{8,10} the Re–P bonds associated with the unique dmpm ligand are quite disparate ($2.425(3)$ and $2.488(3)$ Å), reflecting the differing structural trans effects of the Cl[–] and CO ligands.

While the monocarbonyl complex $[\text{Re}_2\text{Cl}_3(\text{CO})(\text{dmpm})_3]\text{PF}_6$ does convert to $[\text{Re}_2\text{Cl}_2(\text{CO})_2(\text{dmpm})_3](\text{PF}_6)_2$ upon reaction with additional equivalents of CO and TlPF₆, a more convenient procedure for the synthesis of the dicarbonyl cation involves the reaction of $[\text{Re}_2(\text{O}_2\text{CCH}_3)\text{Cl}_2(\text{dmpm})_3]\text{PF}_6$ with CO in the presence of HPF₆(aq). The latter reagent serves to protonate and labilize the acetate ligand, thereby opening up the two coordination sites for the CO ligands. This procedure also results in the hydrolysis of the PF₆[–] anion and the isolation of the dicarbonyl as the dihydrogenphosphate salt $[\text{Re}_2\text{Cl}_2(\text{CO})_2(\text{dmpm})_3](\text{H}_2\text{PO}_4)_2$ (**2**). The use of the mixed bromide–acetate complex $[\text{Re}_2(\text{O}_2\text{CCH}_3)\text{Br}_2(\text{dmpm})_3]\text{PF}_6$ in place of the analogous chloride results in a similar reaction course to afford $[\text{Re}_2\text{Br}_2(\text{CO})_2(\text{dmpm})_3](\text{H}_2\text{PO}_4)_2$. However, the reaction between $[\text{Re}_2(\text{O}_2\text{CCH}_3)\text{Cl}_2(\text{dmpm})_3]\text{PF}_6$ and xylyl isocyanide in the presence of HPF₆(aq) does not produce the bis(xylyl isocyanide) complex but instead affords the compound $[\text{Re}_2\text{Cl}_3(\text{CNxylyl})(\text{dmpm})_3]\text{H}_2\text{PO}_4$; presumably, the additional chlorine atom in the product must arise from some portion of the dirhenium starting material that has to be sacrificed in the process.

The crystal structure of $[\text{Re}_2\text{Cl}_2(\text{CO})_2(\text{dmpm})_3](\text{H}_2\text{PO}_4)_2$ (**2**) (Figure 2) showed that the dication has a crystallographically imposed 2-fold rotation axis which passes through the –CH₂–

carbon of the $\mu\text{-dmpm}$ ligand and bisects the Re–Re bond. This structure determination shows that the loss of the $\mu\text{-O}_2\text{CCH}_3$ ligand from $[\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)\text{Cl}_2(\mu\text{-dmpm})_3]^+$ and the coordination of two terminally bound CO ligands involve a switch in the binding mode of two of the dmpm ligands from bridging to chelating. The Re–Cl distances are very similar; indeed, they do not differ within 3σ . The three crystallographically independent Re–P distances of **2** span the range $2.409(8)$ – $2.434(8)$ Å; the Re–P bond that is closest to being linear with the Re–Re bond (i.e. Re–P(2)) has a length which is almost the average of the three Re–P bond distances.

The Re–Re bond distance in **2** is unusually long ($2.918(2)$ Å) and is clearly indicative of the absence of a Re–Re multiple bond. Its representation as a single bond accords with the 18-electron rule; we can view this dication as arising formally from the coupling of two mononuclear coordinatively unsaturated 15-electron $\{\text{ReCl}(\text{CO})(\text{P})_3\}^+$ fragments (P represents a phosphine donor) through two Re–Cl–Re bridges and a Re–Re bond. Mononuclear rhenium(II) carbonyls are quite rare, although they have been encountered previously in the case of the six-coordinate species $[\text{ReCl}(\text{CO})(\text{PR}_3)_4]^+$ ¹⁷ and $\text{ReCl}_2(\text{CO})_2(\text{PR}_3)_2$.^{18,19}

In dinuclear metal–metal multiple-bond chemistry the conversion of a $\text{R}_2\text{PCH}_2\text{PR}_2$ ligand from a bridging to a chelating mode is unusual and, indeed, has not previously been encountered in dirhenium chemistry. It is not immediately obvious why the complex dications $[\text{Re}_2\text{X}_2(\text{CO})_2(\text{dmpm})_3]^{2+}$ (X = Cl, Br) assume the structure that they do (Figure 2), rather than the alternative one in which the three dmpm ligands remain bridging and the chloride and carbonyl ligands are terminally bound, i.e. the symmetric structure $[(\text{CO})\text{XRe}(\mu\text{-dmpm})_3\text{ReX}(\text{CO})]^{2+}$. The latter structure could formally be represented as maintaining a Re=Re bond on electron-counting grounds. However, it may well be that the electron-withdrawing capability of the two CO ligands so weakens the Re–Re multiple bonding that the alternative structure $(\text{dmpm})(\text{CO})\text{Re}(\mu\text{-X})_2(\mu\text{-dmpm})\text{Re}(\text{CO})(\text{dmpm})^{2+}$, in which there are two strong, 3-electron $\mu\text{-Cl}$ bridging units as well as a Re–Re single bond, now becomes the favored structure.

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Supplementary Material Available: For compounds **1** and **2**, tables giving full crystal data and data collection parameters (Tables S1 and S7), positional parameters for the non-hydrogen atoms (Tables S2 and S8) and the hydrogen atoms (Tables S3 and S9), thermal parameters (Tables S4 and S10), and complete bond distances (Tables S5 and S11) and bond angles (Tables S6 and S12) (19 pages). Ordering information is given on any current masthead page.

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