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Products of the Redox Reactions of *cis*-$Re_2(O_2CCH_3)_2Cl_4L_2$ (L = H_2O, py) with Bis(dimethylphosphino)methane and the Isolation and Structural Characterization of a Grossly Unsymmetrical Mixed-Valent Dirhenium Complex of Composition $Re_2O_3Cl_2(dmpm)_2$

Irene Ara,[†] Phillip E. Fanwick, and Richard A. Walton*

Department of Chemistry, Purdue University, West Lafayette, Indiana 47907-1393

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The reaction of *cis*-$Re_2(O_2CCH_3)_2Cl_4(H_2O)_2$ with $Me_2PCH_2PMe_2$ (dmpm) in ethanol/toluene at room temperature affords a separable mixture of paramagnetic $Re_2(\mu\text{-}O_2CCH_3)Cl_4(\mu\text{-dmpm})_2$ and diamagnetic $Re_2Cl_4(\mu\text{-dmpm})_3$ and $Re_2O_3Cl_2(dmpm)_2$. The corresponding reactions of *cis*-$Re_2(O_2CC_2H_5)_2Cl_4(H_2O)_2$ and *cis*-$Re_2(O_2CCH_3)_2Br_4(H_2O)_2$ with dmpm give primarily $Re_2(\mu\text{-}O_2CC_2H_5)Cl_4(\mu\text{-dmpm})_2$ and $Re_2(\mu\text{-}O_2CCH_3)Br_4(\mu\text{-dmpm})_2$, respectively, along with small amounts of $Re_2X_4(\mu\text{-dmpm})_3$ (X = Cl, Br). A higher yield (ca. 80%) synthetic route to $Re_2(\mu\text{-}O_2CCH_3)X_4(\mu\text{-dmpm})_2$ (X = Cl, Br), which utilizes *cis*-$Re_2(O_2CCH_3)_2X_4(py)_2$ in place of the aquo adduct, does not involve the formation of other products. The complex $Re_2(O_2CCH_3)Cl_4(dmpm)_2$ reacts with dmpm in hot ethanol/toluene to produce $Re_2Cl_4(\mu\text{-dmpm})_3$. The oxo complex of composition $Re_2O_3Cl_2(dmpm)_2$ is the novel mixed-valent compound $O_3ReReCl_2(dmpm)_2$ whose rhenium centers are formally Re(VI) and Re(II) and which contains a short, unsupported Re–Re bond (2.4705 (5) Å) and a remarkable disparity in the metal coordination numbers (4 and 7). Crystal data at 20 °C: monoclinic space group $P2_1/c$, $a = 15.033$ (2) Å, $b = 18.707$ (2) Å, $c = 14.790$ (2) Å, $\beta = 100.833$ (8)°, $V = 4085$ (2) Å^3, $Z = 8$. The structure was refined to $R = 0.033$ ($R_w = 0.043$) for 4561 data with $I > 3\sigma(I)$. NMR spectral studies indicate that this basic structure is retained in solution.

Introduction

The reactions of the quadruply bonded dirhenium(III) carboxylate complexes of the types $Re_2(O_2CR)_4X_2$ and *cis*-$Re_2(O_2CR)_2X_4L_2$ (X = Cl, Br; L = H_2O, 4-methylpyridine, DMF, DMSO) with $Ph_2PCH_2PPh_2$ (dppm) or $Ph_2PNHPPh_2$ (dppa) afford the dirhenium(III,II) and dirhenium(II,II) complexes $Re_2(\mu\text{-}O_2CR)X_4(\mu\text{-LL})_2$, *cis-* or *trans*-$[Re_2(\mu\text{-}O_2CR)_2X_2(\mu\text{-LL})_2]^+$, *cis-* or *trans*-$Re_2(\mu\text{-}O_2CR)_2X_2(\mu\text{-LL})_2$, and $Re_2X_4(\mu\text{-LL})_2$ (LL = dppm, dppa) depending upon the choice of reaction conditions and the ligand LL.[1,2] In contrast, the reactions of *cis*-$Re_2(O_2CR)_2X_4L_2$ (L = H_2O, py) with PMe_3, PMe_2Ph, and $PMePh_2$ in ethanol give the dirhenium(II) complexes $Re_2Cl_4(PR_3)_4$, while *cis*-$Re_2(O_2CR)_2X_4L_2$ complexes (X = Cl, Br; L = H_2O, DMF, DMSO) react with PPh_3 under these same conditions in R′OH (R′ = Me, Et, *n*-Pr, *i*-Pr) to give the mixed-valent dirhenium(IV,II) complexes $(R'O)_2X_2ReReX_2(PPh_3)_2$.[3] In a subsequent study, we showed[4] that the ligand $Me_2PCH_2PMe_2$ (dmpm) reacts with $Re_2(O_2CR)_4X_2$ to afford the dirhenium(II,II) complexes $[Re_2(\mu\text{-}O_2CR)X_2(\mu\text{-dmpm})_3]X$ via the intermediacy of the paramagnetic dirhenium(III,II) species *trans*-$[Re_2(O_2CR)_2X_2(dmpm)_2]^+$. We now describe the reactions of the complexes *cis*-$Re_2(O_2CR)_2X_4L_2$ (R = CH_3, C_2H_5; X = Cl, Br; L = H_2O, py) with dmpm which not only show characteristics of the aforementioned systems, namely, reduction to dirhenium(III,II) and dirhenium(II,II), but also provide a route to an unusual product in which formally Re(VI) and Re(II) centers are united by a short, unsupported Re–Re bond. A report describing some of these results in preliminary form has been published previously.[5]

Experimental Section

Starting Materials. The compounds *cis*-$Re_2(O_2CR)_2X_4L_2$ (R = CH_3, C_2H_5; X = Cl, Br; L = H_2O, py) were synthesized as described in the literature.[3] The $Me_2PCH_2PMe_2$ (dmpm) ligand was purchased from Quantum Design, Inc. It was used as a solution in toluene (1.3 M). Solvents used in the preparation and workup of the complexes were of commercial grade and were thoroughly deoxygenated prior to use.

Reaction Procedures. All reactions were performed under an atmosphere of dry nitrogen by using standard procedures.

A. Reactions of *cis*-$Re_2(O_2CR)_2X_4(H_2O)_2$ with dmpm. (i) R = CH_3, X = Cl. A quantity of *cis*-$Re_2(O_2CCH_3)_2Cl_4(H_2O)_2$ (0.20 g, 0.299 mmol) in 15 mL of ethanol was mixed with 0.48 mL of a dmpm/toluene solution (1.3 M, 0.62 mmol) and the mixture stirred at room temperature for 15 min. A brown insoluble product was filtered off, washed with ethanol and diethyl ether, and recrystallized from CH_2Cl_2/hexane; yield 0.09 g (36%). Anal. Calcd for $C_{12}H_{31}Cl_4O_2P_4Re_2$ (i.e. $Re_2(O_2CCH_3)Cl_4(dmpm)_2$): C, 17.04; H, 3.67; Cl, 16.78. Found: C, 16.76; H, 3.65; Cl, 16.56.

The reaction filtrate was evaporated to dryness, and the sticky solid residue triturated with a small volume of acetone to yield an orange-red solid whose properties accorded with it being a mixture. This solid was dissolved in dichloromethane, and two products were separated by column chromatography on a silica gel column (230–400 mesh, column length 10 cm, column diameter 1.5 cm) with CH_2Cl_2/acetone (ca. 1:3 by volume) as eluent. A red-pink band eluted first, followed by a yellow-orange band. The pale red solution was evaporated to dryness to afford a small quantity of $Re_2Cl_4(\mu\text{-dmpm})_3$; yield 0.5 g (18%). This product was identified from a comparison of its spectroscopic and electrochemical properties with the literature data for this complex.[6,7] The orange solution was evaporated to give a crop of red-orange microcrystals of $Re_2O_3Cl_2(dmpm)_2$; yield 0.03 g (13%). Anal. Calcd for $C_{10}H_{28}Cl_2O_3P_4Re_2$: C, 15.73; H, 3.70. Found: C, 15.43; H, 3.88. The identity of this complex was established by a single-crystal X-ray structure determination.

(ii) R = CH_3, X = Br. A mixture of *cis*-$Re_2(O_2CCH_3)_2Br_4(H_2O)_2$ (0.30 g, 0.355 mmol) and 0.55 mL of a dmpm/toluene solution (1.3 M, 0.71 mmol) in 20 mL of ethanol was stirred at room temperature for 15 min. The brown insoluble product was filtered off and recrystallized from CH_2Cl_2/diethyl ether; yield 0.13 g (35%). Anal. Calcd for $C_{14}H_{36}Br_4O_{2.5}P_4Re_2$ (i.e. $Re_2(O_2CCH_3)Br_4(dmpm)_2\cdot0.5(C_2H_5)_2O$): C, 15.71;

[†] Permanent address: Departmento De Quimica Inorganica, Universidad De Zaragoza, 50009 Zaragoza, Spain.

(1) Cutler, A. R.; Derringer, D. R.; Fanwick, P. E.; Walton, R. A. *J. Am. Chem. Soc.* **1988,** *110,* 5024.

(2) Derringer, D. R.; Fanwick, P. E.; Moran, J.; Walton, R. A. *Inorg. Chem.* **1989,** *28,* 1384.

(3) Chakravarty, A. R.; Cotton, F. A.; Cutler, A. R.; Walton, R. A. *Inorg. Chem.* **1986,** *25,* 3619.

(4) Ara, I.; Fanwick, P. E.; Walton, R. A. *Inorg. Chem.* **1991,** *30,* 1227.

(5) Ara, I.; Fanwick, P. E.; Walton, R. A. *J. Am. Chem. Soc.* **1991,** *113,* 1429.

(6) Anderson, L. B.; Cotton, F. A.; Falvello, L. R.; Harwood, W. S.; Lewis, D.; Walton, R. A. *Inorg. Chem.* **1986,** *25,* 3637.

(7) Ara, I.; Walton, R. A. *Inorg. Chim. Acta* **1992,** *198–200,* 787.

0020-1669/92/1331-3211$03.00/0

Table I. Crystallographic Data for $Re_2O_3Cl_2(dmpm)_2$

chem formula	$Re_2Cl_2P_4O_3C_{10}H_{28}$	Z	8
fw	763.53	T, °C	20
space group	$P2_1/c$ (No. 14)	λ (Mo Kα), Å	0.710 73
a, Å	15.033 (2)	ρ_{calcd}, g cm^{-3}	2.483
b, Å	18.707 (2)	μ(Mo Kα), cm^{-1}	125.85
c, Å	14.790 (2)	transm coeff	1.00–0.60
β, deg	100.833 (8)	R^a	0.033
V, $Å^3$	4085 (2)	$R_w{}^b$	0.043

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

Table II. Positional Parameters and Equivalent Isotropic Displacement Parameters ($Å^2$) for the Non-Hydrogen Atoms of $Re_2O_3Cl_2(dmpm)_2$ and Their Estimated Standard Deviations[a]

atom	x	y	z	B
Re(1)	0.40823 (3)	0.64070 (2)	0.07655 (3)	1.713 (9)
Re(2)	0.25186 (3)	0.63037 (2)	−0.01129 (3)	0.978 (8)
Re(3)	0.22815 (3)	0.01681 (2)	0.01503 (3)	1.544 (9)
Re(4)	0.23094 (3)	0.14114 (2)	−0.03932 (3)	0.947 (8)
Cl(21)	0.0892 (2)	0.6200 (2)	−0.0993 (2)	2.11 (6)
Cl(22)	0.1837 (2)	0.7139 (1)	0.0871 (2)	1.89 (5)
Cl(41)	0.2384 (2)	0.2697 (1)	−0.0958 (2)	2.18 (6)
Cl(42)	0.2215 (2)	0.1120 (1)	−0.2049 (2)	1.52 (5)
P(21)	0.2634 (2)	0.5012 (2)	−0.0332 (2)	1.90 (6)
P(22)	0.2150 (2)	0.5592 (2)	0.1134 (2)	2.34 (6)
P(23)	0.3088 (2)	0.6307 (2)	−0.1566 (2)	1.73 (6)
P(24)	0.2628 (2)	0.7486 (2)	−0.0759 (2)	1.63 (6)
P(41)	0.1273 (2)	0.1814 (2)	0.0610 (2)	2.08 (6)
P(42)	0.0716 (2)	0.1320 (2)	−0.1074 (2)	1.73 (6)
P(43)	0.3858 (2)	0.1248 (2)	−0.0606 (2)	1.72 (6)
P(44)	0.3436 (2)	0.1737 (2)	0.0965 (2)	1.79 (6)
O(11)	0.4054 (5)	0.6988 (5)	0.1658 (5)	2.9 (2)
O(12)	0.4745 (5)	0.6749 (5)	0.0042 (6)	3.3 (2)
O(13)	0.4433 (6)	0.5566 (5)	0.1169 (7)	3.8 (2)
O(31)	0.2111 (7)	−0.0361 (4)	−0.0818 (6)	3.7 (2)
O(32)	0.3314 (6)	−0.0026 (5)	0.0822 (7)	3.6 (2)
O(33)	0.1395 (6)	0.0089 (5)	0.0723 (6)	4.2 (2)
C(211)	0.361 (1)	0.4526 (7)	−0.056 (1)	4.5 (4)
C(212)	0.169 (1)	0.4592 (8)	−0.112 (1)	5.2 (4)
C(221)	0.268 (1)	0.5765 (8)	0.2279 (8)	4.1 (3)
C(222)	0.098 (1)	0.5476 (9)	0.119 (1)	4.9 (4)
C(231)	0.226 (1)	0.6106 (9)	−0.2613 (9)	4.5 (4)
C(232)	0.4123 (8)	0.5904 (8)	−0.1809 (9)	3.4 (3)
C(241)	0.1589 (8)	0.7900 (7)	−0.1342 (9)	2.7 (3)
C(242)	0.3211 (9)	0.8207 (6)	−0.0064 (9)	3.0 (3)
C(411)	0.1088 (9)	0.2771 (7)	0.066 (1)	4.0 (3)
C(412)	0.128 (1)	0.1531 (9)	0.1791 (9)	4.2 (3)
C(421)	0.0245 (8)	0.0510 (7)	−0.1665 (8)	2.5 (3)
C(422)	0.0273 (8)	0.2042 (7)	−0.1844 (9)	2.9 (3)
C(431)	0.4310 (9)	0.1908 (8)	−0.1283 (9)	3.7 (3)
C(432)	0.4252 (8)	0.0417 (7)	−0.1009 (8)	2.7 (3)
C(441)	0.3522 (9)	0.1380 (8)	0.2125 (8)	3.3 (3)
C(442)	0.3674 (9)	0.2667 (8)	0.1174 (9)	3.6 (3)
C(B21)	0.255 (1)	0.4731 (6)	0.0827 (9)	3.4 (3)
C(B22)	0.3288 (8)	0.7247 (7)	−0.1623 (8)	2.7 (3)
C(B41)	0.0244 (7)	0.1448 (7)	−0.0036 (8)	2.3 (3)
C(B42)	0.4446 (7)	0.1383 (7)	0.0583 (8)	2.6 (3)

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

H, 3.49. Found: C, 15.72; H, 3.44. The presence of lattice diethyl ether was confirmed by ^1H NMR spectroscopy of a CD_2Cl_2 solution of this paramagnetic complex.

The filtrate was evaporated to dryness and a small volume of acetone added. The insoluble product was shown to be $Re_2Br_4(\mu\text{-dmpm})_3$ from its spectroscopic and electrochemical properties;[7] yield 0.04 g (11%). Although other rhenium-containing species were present in the acetone extract, there was no spectroscopic or electrochemical evidence for the presence of $Re_2O_3Br_2(dmpm)_2$, so further workup and separation were not attempted.

(iii) R = C_2H_5, X = Cl. The reaction between *cis*-$Re_2(O_2CC_2H_5)_2Cl_4(H_2O)_2$ (0.104 g, 0.15 mmol) and dmpm/toluene (1.3 M, 0.116 mL, 0.15 mmol) afforded the green-brown insoluble product $Re_2(O_2CC_2H_5)Cl_4(dmpm)_2$ through use of a procedure analogous to that of section A(i); yield 0.05 g (38%). The product was identified as $Re_2(O_2CC_2H_5)Cl_4(dmpm)_2$ on the basis of its spectroscopic and electrochemical properties. While a small additional quantity of $Re_2(O_2CC_2H_5)Cl_4(dmpm)_2$, as well as a trace of $Re_2Cl_4(\mu\text{-dmpm})_3$, was present in the filtrate (as monitored by cyclic voltammetry) there was no evidence for any significant quantities of $Re_2O_3Cl_2(dmpm)_2$ and further workup was not pursued.

B. Reaction of *cis*-$Re_2(O_2CCH_3)_2Cl_4(py)_2$ with dmpm. (i) X = Cl. A quantity of *cis*-$Re_2(O_2CCH_3)_2Cl_4(py)_2$ (0.528 g, 0.668 mmol) was mixed with 1.54 mL of dmpm/toluene (1.3 M, 2.00 mmol) in 10 mL of ethanol and the reaction mixture stirred at room temperature for 60 min. An olive green-brown product formed during this period. The volume of the reaction mixture was then reduced to ca. 2 mL, and the solid was filtered off, washed with diethyl ether, and dried; yield 0.446 g (80%). The product was identified as $Re_2(O_2CCH_3)Cl_4(dmpm)_2$ on the basis of its spectroscopic and electrochemical properties which were identical with those of the complex prepared in section A(i). The same product was obtained in similar yield when THF was used as the reaction solvent.

(ii) X = Br. The conversion of *cis*-$Re_2(O_2CCH_3)_2Br_4(py)_2$ (0.200 g, 0.207 mmol) to $Re_2(O_2CCH_3)Br_4(dmpm)_2$ upon its reaction with 0.38 mL of dmpm/toluene (1.62 M, 0.62 mmol) was accomplished through use of a procedure very similar to that described in section B(i); yield 78%.

C. Reaction of $Re_2(O_2CCH_3)Cl_4(dmpm)_2$ with dmpm. A mixture of $Re_2(O_2CCH_3)Cl_4(dmpm)_2$ (0.06 g, 0.071 mmol) and 0.06 mL of a dmpm/toluene solution (1.3 M, 0.078 mmol) in 10 mL of ethanol was heated for 16 h. The clear orange-pink solution was evaporated to dryness, a small volume of acetone added, and the insoluble product $Re_2Cl_4(\mu\text{-dmpm})_3$ filtered off and washed with diethyl ether; yield 0.03 g (46%).

With reaction conditions similar to those cited above, the bidentate phosphines $Ph_2PCH_2PPh_2$ (dppm) and $Ph_2P(CH_2)_3PPh_2$ (dppp) react with $Re_2(O_2CCH_3)Cl_4(dmpm)_2$ to give the known dirhenium(II) complexes $Re_2Cl_4(dppm)_2$[1,8] and α-$Re_2Cl_4(dppp)_2$,[9] respectively; isolated yields ca. 40%. No attempt was made to optimize the product yields, since other more convenient methods exist for preparing these compounds.

X-ray Crystal Structure Determination. A batch of red crystals of composition $Re_2O_3Cl_2(dmpm)_2$ was obtained by the slow evaporation of a solution of this complex in CH_2Cl_2/acetone (ca. 1:3 by volume). The basic crystallographic parameters for this complex are listed in Table I. The cell constants are based on 25 reflections with $22 < \theta < 23°$. Three standard reflections were measured after every 5000 s of beam exposure during data collection. Calculations were performed on a microVAX II computer using the Enraf-Nonius structure determination package. The crystal was found to belong to the monoclinic space group $P2_1/c$ (No. 14). With $Z = 8$, there are two independent molecules in the asymmetric unit. Lorentz and polarization corrections were applied to the data. An empirical absorption correction was applied,[9] the linear absorption coefficient being 125.85 cm^{-1}. No corrections were made for extinction.

The structure was solved by the use of the Patterson heavy-atom method, which revealed the positions of the Re atoms of the dirhenium molecule. The remaining non-hydrogen atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms of the dmpm ligands were included at fixed positions with the value of B(H), i.e., the isotropic equivalent thermal parameter for the hydrogen atoms, taken as $1.3[B_{eqv}(C)]$ at the time of the inclusion of this parameter in the refinement procedure. While these hydrogen atoms were used in the calculation of F_c, their positions were not refined. The structure was refined in a full-matrix least-squares procedure where the function minimized was $\sum w(|F_o| - |F_c|)^2$, where w is the weighting factor defined as $w = 1/\sigma^2(F_o)$. All non-hydrogen atoms were refined anisotropically, and corrections for anomalous scattering were applied.[10]

Positional parameters and their errors for the non-hydrogen atoms of the compound are listed in Table II. Important intramolecular bond distances and angles are given in Table III. Tables giving full details of the crystal data and data collection parameters (Table S1), positional parameters for the hydrogen atoms (Table S2), thermal parameters (Table

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(8) Walton, R. A. *Polyhedron* **1989**, *8*, 1689 and references cited therein.

(9) Cole, N. F.; Cotton, F. A.; Powell, G. L.; Smith, T. J. *Inorg. Chem.* **1983**, *22*, 2618.

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

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

Table III. Selected Bond Distances (Å) and Bond Angles (deg) for $Re_2O_3Cl_2(dmpm)_2$[a]

	Distances		
Re(1)–Re(2)	2.4705 (5)	Re(2)–Cl(22)	2.483 (2)
Re(1)–O(11)	1.716 (7)	Re(2)–P(21)	2.449 (3)
Re(1)–O(12)	1.717 (7)	Re(2)–P(22)	2.422 (3)
Re(1)–O(13)	1.729 (7)	Re(2)–P(23)	2.459 (2)
Re(2)–Cl(21)	2.553 (2)	Re(2)–P(24)	2.427 (2)
	Angles		
Re(2)–Re(1)–O(11)	107.2 (2)	Cl(21)–Re(2)–P(22)	90.70 (9)
Re(2)–Re(1)–O(12)	107.9 (3)	Cl(21)–Re(2)–P(23)	90.68 (8)
Re(2)–Re(1)–O(13)	108.0 (3)	Cl(21)–Re(2)–P(24)	89.87 (8)
O(11)–Re(1)–O(12)	110.1 (4)	Cl(22)–Re(2)–P(21)	138.21 (8)
O(11)–Re(1)–O(13)	111.2 (4)	Cl(22)–Re(2)–P(22)	73.78 (9)
O(12)–Re(1)–O(13)	112.3 (4)	Cl(22)–Re(2)–P(23)	139.51 (8)
Re(1)–Re(2)–Cl(21)	178.95 (6)	Cl(22)–Re(2)–P(24)	73.93 (8)
Re(1)–Re(2)–Cl(22)	95.69 (6)	P(21)–Re(2)–P(22)	65.83 (9)
Re(1)–Re(2)–P(21)	93.58 (6)	P(21)–Re(2)–P(23)	80.89 (9)
Re(1)–Re(2)–P(22)	88.49 (7)	P(21)–Re(2)–P(24)	146.69 (8)
Re(1)–Re(2)–P(23)	90.37 (6)	P(22)–Re(2)–P(23)	146.55 (9)
Re(1)–Re(2)–P(24)	90.44 (6)	P(22)–Re(2)–P(24)	147.41 (9)
Cl(21)–Re(2)–Cl(22)	83.43 (8)	P(23)–Re(2)–P(24)	66.02 (8)
Cl(21)–Re(2)–P(21)	86.71 (8)		

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

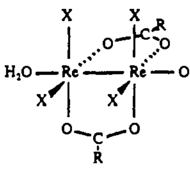
S3), and complete bond distances (Table S4) and bond angles (Table S5) are available as supplementary material.

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. Electronic absorption spectra were recorded with the use of a Cary 17 spectrophotometer. 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-300 spectrometer. Resonances were referenced internally to the residual protons in the incompletely deuteriated $CDCl_3$ solvent (δ +7.27). $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian XL-200 spectrometer operated at 80.98 MHz with an internal deuterium lock using aqueous 85% H_3PO_4 as an external standard. X-Band ESR spectra were recorded at −160 °C with the use of a Varian E-109 spectrometer. FAB mass spectra were recorded in 3:1 dithiothreitol/dithioerythreitol matrices using a Kratos MS-50 spectrometer.

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

Results

The reactions of the quadruply bonded dirhenium(III) complexes *cis*-$Re_2(O_2CR)_2X_4(H_2O)_2$ (**1**),[3] where X = Cl or Br and R = CH_3 or C_2H_5, with $Me_2PCH_2PMe_2$ (dmpm) at room temperature for ca. 15 min afford the paramagnetic dirhenium(III,II) complexes $Re_2(\mu\text{-}O_2CR)X_4(\mu\text{-dmpm})_2$ (**2**) as the major identifiable products (isolated yields 35–40%). Small amounts of the known triply bonded dirhenium(II) compounds $Re_2X_4(\mu\text{-dmpm})_3$ (**3**),[6,7] which are also present in these reaction mixtures, are apparently formed through the reaction of **2** with dmpm, since the yield of **3** increases with much longer reaction times. A better procedure for the synthesis of **2** is the reaction of the bis(pyridine) adducts *cis*-$Re_2(O_2CR)_2X_4(py)_2$ with dmpm, as demonstrated by the preparation of $Re_2(O_2CCH_3)X_4(\mu\text{-dmpm})_2$ (X = Cl, Br) in ca. 80% yield through the use of this method.



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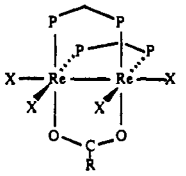

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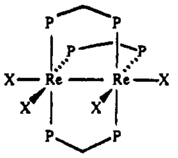

3

We find that the direct reaction of a sample of pure **2** (X = Cl, R = CH_3) with 1 equiv of dmpm in hot ethanol gives **3** (X = Cl). Complex **2** (X = Cl, R = CH_3) also reacts with an excess of $Ph_2PCH_2PPh_2$ (dppm) and $Ph_2P(CH_2)_3PPh_2$ (dppp) to give the known triply bonded complexes $Re_2Cl_4(dppm)_2$[1,8] and α-$Re_2Cl_4(dppp)_2$;[9] these reactions proceed through a similar reductive decarboxylation pathway, following exchange of dppm and dppp for dmpm. Accordingly, the conversions of $Re_2(O_2CR)X_4(\mu\text{-dmpm})_2$ to $Re_2X_4(\mu\text{-dmpm})_3$, $Re_2Cl_4(dppm)_2$, and α-$Re_2Cl_4(dppp)_2$ resemble the thermolysis of $Re_2(\mu\text{-}O_2CR)X_4(\mu\text{-dppm})_2$ to give $Re_2X_4(\mu\text{-dppm})_2$.[1]

The reaction of **1** (X = Cl, R = CH_3) with dmpm differs from the others in that small quantities of the oxo complex of composition $Re_2O_3Cl_2(dmpm)_2$ (**4**) are also isolated. While this product was obtained reproducibly, we found no evidence for its formation (or that of its bromide analogue) when the other derivatives of type **1** were used.

The complexes of type **2** (X = Cl when R = CH_3 or C_2H_5; X = Br when R = CH_3), which are the dmpm analogues of the previously characterized complexes $Re_2(\mu\text{-}O_2CR)X_4(\mu\text{-dppm})_2$ (X = Cl when R = CH_3 or C_2H_5; X = Br when R = CH_3),[1] possess broad X-band ESR signals (CH_2Cl_2 glasses at −160 °C) centered at ca. 2900 G ($g \approx 2.21$) which show only broad, poorly resolved hyperfine structure. As expected, none of these paramagnetic complexes give well-defined ^1H NMR spectra. The electronic absorption spectra of CH_2Cl_2 solutions of $Re_2(O_2CCH_3)X_4(dmpm)_2$ show intense bands ($\epsilon \approx 1000\ cm^{-1}\ M^{-1}$) at 1185 nm (X = Cl) and 1210 nm (X = Br), which are characteristic of the $\delta \rightarrow \delta^*$ transition of complexes that contain the multiply bonded Re_2^{5+} core.[1] Their solutions in 0.1 M TBAH/CH_2Cl_2 show cyclic voltammograms that are very similar to those of the dppm analogues. For $Re_2(O_2CCH_3)Cl_4(dmpm)_2$, a reversible one-electron oxidation at $E_{1/2} = +0.39$ V, with $E_{p,a} - E_{p,c} = 100$ mV, and an irreversible reduction at $E_{p,c} = -0.69$ V vs Ag/AgCl are analogous to processes at +0.52 and −0.60 V, respectively, reported for $Re_2(O_2CCH_3)Cl_4(dppm)_2$.[1] In the cases of $Re_2(O_2CCH_3)Br_4(dmpm)_2$ and $Re_2(O_2CC_2H_5)Cl_4(dmpm)_2$, the values for the corresponding redox processes are $E_{1/2}(ox) = +0.42$ V, $E_{p,c} = -0.64$ V and $E_{1/2}(ox) = +0.40$ V, $E_{p,c} = -0.70$ V, respectively.

The oxo complex (**4**) of composition $Re_2O_3Cl_2(dmpm)_2$ was shown by single-crystal X-ray crystallography to have the unsymmetrical structure $O_3ReReCl_2(dmpm)_2$. An ORTEP representation of the structure is shown in Figure 1. The important details of the crystallographic and structural parameters are given in Tables I–III. The most abundant molecular ion in the FAB mass spectrum of **4** is at m/z 765 and corresponds to the protonated ion $(M + H)^+$. A less abundant cluster of peaks centered around m/z 729 is assigned to the fragment ion $(M - Cl)^+$. There was no evidence for ions such as $[ReO_3]^+$ and $[ReCl_2(dmpm)_2]^+$ that could originate through fission of the Re–Re bond. The Nujol mull IR spectrum of the complex shows five sharp bands of medium-strong intensity clustered between 950 and 880 cm^{-1}, which presumably include the $\nu(ReO_3)$ modes.

The ^1H NMR spectrum of **4** (recorded in $CDCl_3$ at room temperature) displays multiplets at δ +4.8 and +3.6 (–CH_2– of dmpm) and four doublets of doublets at δ +2.13, +2.03, +1.93, and +1.91 (–CH_3 of dmpm, J(P–H) ≈ 5.5 Hz), while the $^{31}P\{^1H\}$ spectrum is an AA′BB′ pattern with the most intense components at δ −59.3 and δ −66.6. The solutions of this complex are very stable, as demonstrated by the invariance of the NMR spectra after the solutions had been set aside for 2 weeks.

A single-scan cyclic voltammogram of a solution of **4** in 0.1 M TBAH/CH_2Cl_2 (ν = 200 mV s^{-1}) showed oxidations at $E_{p,a}$ = +0.81 and +1.29 V vs Ag/AgCl when the scan was extended

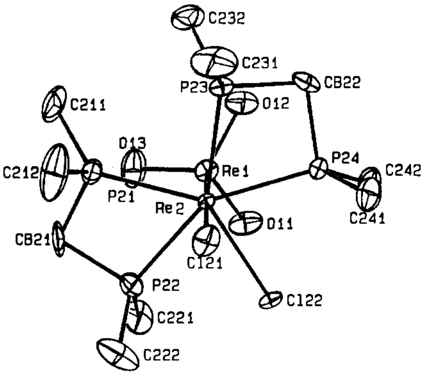

Figure 1. ORTEP view of one of crystallographically independent molecules of the dirhenium complex $O_3ReReCl_2(dmpm)_2$ with the hydrogen atoms of the dmpm ligands omitted. The thermal ellipsoids are drawn at the 50% probability level.

to +1.6 V; the coupled reduction waves were very weak and signified a lack of chemical reversibility. The process at $E_{p,a}$ = +1.29 V has a much greater current associated with it than the more accessible oxidation (at +0.81 V) and is clearly an irreversible multielectron oxidation. When a value for the switching potential of +1.1 V was used (i.e. intermediate between the two oxidations), the first oxidation was now found to be reversible, as evidenced by the observation of a coupled reduction at $E_{p,c}$ = +0.72 V and $i_{p,a}/i_{p,c}$ = 1.0.

Discussion

Our original motivation for studying the reactions between *cis*-$Re_2(O_2CCH_3)_2X_4(H_2O)_2$ and dmpm, *using 1:2 stoichiometric proportions of reagents*, had been to devise a route to the elusive dirhenium(II) complexes $Re_2X_4(\mu\text{-dmpm})_2$ through use of a strategy that works quite satisfactorily for the synthesis of $Re_2X_4(\mu\text{-dppm})_2$.[1] Unfortunately, even with the use of mild conditions and short reaction times, we were unsuccessful in our initial objective although these reactions proved to be of interest for other reasons.

While the reactions of *cis*-$Re_2(O_2CCH_3)_2X_4(H_2O)_2$ (**1**; X = Cl, Br) with $Me_2PCH_2PMe_2$ (dmpm) in ethanol/toluene afford mixtures of $Re_2(\mu\text{-}O_2CCH_3)X_4(\mu\text{-dmpm})_2$ (**2**) and $Re_2X_4(\mu\text{-dmpm})_3$ (**3**), the most interesting reaction is that between *cis*-$Re_2(O_2CCH_3)_2Cl_4(H_2O)_2$ and dmpm, since the novel mixed-valent complex $O_3ReReCl_2(dmpm)_2$ (**4**) is also formed in this case. Even when the amount of dmpm ligand was reduced, as in the reaction between *cis*-$Re_2(O_2CC_2H_5)_2Cl_4(H_2O)_2$ and an equimolar quantity of dmpm, the reaction course was the same, with the major product being $Re_2(O_2CC_2H_5)Cl_4(dmpm)_2$ (ca. 40% yield). A higher yield route to the dirhenium(III,II) complexes $Re_2(\mu\text{-}O_2CCH_3)X_4(\mu\text{-dmpm})_2$ utilizes the pyridine adduct *cis*-$Re_2(O_2CCH_3)_2X_4(py)_2$ in place of *cis*-$Re_2(O_2CCH_3)_2X_4(H_2O)_2$. These reactions should be carried out for relatively short periods (<2 h), since prolonged reaction times slowly lead to the formation of $Re_2X_4(\mu\text{-dmpm})_3$ contaminants even when the reactions are conducted at room temperature. Since complexes **2** have properties that are strikingly similar to those of the previously characterized dppm analogues $Re_2(\mu\text{-}O_2CR)X_4(\mu\text{-dppm})_2)$,[1] they presumably have the same symmetrical structures.

The most striking feature of **4** is its grossly unsymmetrical structure (Figure 1). Note that there are two independent molecules in the asymmetric unit but these are structurally indistinguishable (see supplementary material); accordingly, the structural parameters of only one of them will be discussed (Table III). The molecule consists of two Re atoms in quite different environments, namely, tetrahedral 4-coordinate and pentagonal-bipyramidal 7-coordinate, that are joined by a very short, unsupported Re–Re bond (2.4705 (5) Å). While the molecule possesses no crystallographically imposed symmetry, it has virtual C_s symmetry, with the mirror plane encompassing the two Re atoms and the two Cl atoms, as well as atom O(11) of the ReO_3 fragment. In accord with this, the Cl(21)–Re(2)–Re(1) unit is essentially linear (178.95 (6)°) and the Cl(22)–Re(2)–Re(1)–O(11) torsional angle is 0.1 (3)°. The Re–O bond lengths and O–Re–O angles associated with the ReO_3 unit are similar to those reported for other $(L)ReO_3$ species (where L represents a *single* donor atom such as F, Cl, O, or N from a monoanionic ligand),[12-14] although the angles (110.1 (4)–112.3 (4)°) are at the higher end of the range reported previously. A further unusual feature is the presence of two dmpm ligands in a chelating rather than the more usual bridging mode, as present in **2** and **3**. Why **4** does not assume the more symmetrical, non metal–metal bonded structure $Cl(O)Re(\mu\text{-}O)(\mu\text{-dmpm})_2Re(O)Cl$ is unclear, since the symmetric dirhenium(IV) complex $Cl_3Re(\mu\text{-}O)(\mu\text{-dppm})_2ReCl_3$ is easily prepared and is very stable.[15]

Complex **4** represents the first case where the ReO_3 unit has been found to partake in direct metal–metal bonding. While **4** bears a close relationship to Herrmann's half-sandwich complexes $(\eta^5\text{-}C_5R_5)ReO_3$,[16,17] the trioxorhenium unit in **4** is *formally* Re(VI) rather than Re(VII). The Re–Re interaction can be viewed in its simplest terms as arising from the coupling of d^1 and d^5 fragments to give a strong σ bond. However, Costas and Benard[18] have recently carried out ab initio SCF and CI studies on the model complex $O_3ReReCl_2(H_2PCH_2PH_2)_2$ and concluded that a more realistic description of the charge distribution in this molecule is Re^VRe^{III} (i.e. d^2–d^4) with the short, strong metal–metal bond represented in terms of a σ-donation from $[ReO_3]^-$ to $[ReCl_2(H_2PCH_2PH_2)_2]^+$. Interestingly, complexes of the type *trans*-$ReX_2[R_2P(CH_2)_2PR_2]_2$, which contain a *two*-carbon fragment between the phosphorus atoms, as well as their one-electron-oxidized congeners,[19] are stable species that have not previously been found[20] to undergo reactions in which the metal stereochemistry deviates from pseudooctahedral. It may be that the smaller bite of the chelating $Me_2PCH_2PMe_2$ ligand permits an expansion of the metal coordination number from 6 to 7 and, hence, the formation of a Re–Re bond.

One compound that shows a close relationship to **4** is the ditungsten complex $(\eta^5\text{-}C_5Me_5)O_2WW(CO)_3(\eta^5\text{-}C_5Me_5)$,[21] in which there is an unsupported W–W bond connecting W(V) and W(I) centers. While this complex is isoelectronic with $O_3ReReCl_2(dmpm)_2$, the W–W bond length of 2.877 (3) Å is much longer (by ca. 0.4 Å) than the Re–Re bond length in **4**.

The oxygen in the ReO_3 fragment apparently originates from the water molecules that are present in *cis*-$Re_2(O_2CCH_3)_2Cl_4(H_2O)_2$, since when the pyridine adduct $Re_2(O_2CCH_3)_2Cl_4(py)_2$ is used as the starting material, reaction with dmpm affords **2** as the only identified product (80% yield) after 12 h. When the reaction between *cis*-$Re_2(O_2CCH_3)_2Cl_4(H_2O)_2$ and dmpm was carried out under an atmosphere of air rather than dinitrogen or when the solvents were not deoxygenated prior to their

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(12) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley-Interscience: New York, 1988; Table 5.2, pp 176–177.

(13) McGilligan, B. S.; Arnold, J.; Wilkinson, G.; Hussain-Bates, B.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1990**, 2465.

(14) Roesky, H. W.; Hesse, D.; Rietzel, M.; Noltemeyer, M. *Z. Naturforsch.* **1990**, *45B*, 72.

(15) Shih, K.-Y.; Fanwick, P. E.; Walton, R. A. Unpublished results.

(16) Herrmann, W. A.; Herdtweck, E.; Floel, M.; Kulpe, J.; Kusthardt, U.; Okuda, J. *Polyhedron* **1987**, *6*, 1165 and references cited therein.

(17) Okuda, J.; Herdtweck, E.; Herrmann, W. A. *Inorg. Chem.* **1988**, *27*, 1254.

(18) Costas, M.; Benard, M. *J. Am. Chem. Soc.*, in press.

(19) For recent examples of such complexes see: (a) Bakir, M.; Fanwick, P. E.; Walton, R. A. *Polyhedron* **1987**, *6*, 907. (b) Esjornson, D.; Bakir, M.; Fanwick, P. E.; Jones, K. S.; Walton, R. A. *Inorg. Chem.* **1990**, *29*, 2055.

(20) Conner, K. A.; Walton, R. A. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon: Oxford, England, 1987; Chapter 43, pp 147–149.

(21) Alt, H. G.; Hayen, H. I.; Rogers, R. D. *J. Chem. Soc., Chem. Commun.* **1987**, 1795.

use, a small quantity of **3** was identified but there was no evidence for the formation of **4**. Accordingly, the formation of **4** does not appear to require the presence of gaseous O_2; neither does it proceed via $Re_2(\mu\text{-}O_2CCH_3)Cl_4(\mu\text{-dmpm})_2$ or $Re_2Cl_4(\mu\text{-dmpm})_3$. Also, we have been unable to prepare **4**, or its bromo analogue, from the reactions between *cis*-$Re_2(O_2CC_2H_5)_2Cl_4(H_2O)_2$ or *cis*-$Re_2(O_2CCH_3)_2Br_4(H_2O)_2$ and dmpm. It is unclear why **4** can be prepared reproducibly from *cis*-$Re_2(O_2CCH_3)_2Cl_4(H_2O)_2$ but not from other precursors of this type.

The complexity of the ^1H NMR spectrum of **4** accords with the retention of a relatively rigid structure in solution. The observation of four doublets of doublets for the $-CH_3$ groups of the two chelating dmpm ligands is consistent with the structure in Figure 1, in which there are four chemically and magnetically inequivalent pairs of methyl groups. This would be the case irrespective of whether the structure is completely rigid (Figure 1) or rapid rotation is occurring about the Re–Re bond.

Complex **4** is remarkably stable and shows prolonged stability in solution (several weeks in chloroform) and upon exposure to air. Unfortunately, the low yield in which it is obtained has precluded, for the time being at least, detailed studies of its reactivity, although, as noted, it does show an accessible one-electron oxidation ($E_{1/2}(\text{ox}) = +0.81$ V).

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Supplementary Material Available: Tables giving full details of the crystal data and data collection parameters (Table S1), positional parameters for the hydrogen atoms (Table S2), thermal parameters (Table S3), and complete bond distances (Table S4) and bond angles (Table S5) (12 pages); a listing of observed and calculated structure factors (20 pages). Ordering information is given on any current masthead page.