Mixed Carboxylate–Bis(dimethylphosphino)methane Complexes of Dirhenium(II,II) and -(III,II)

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

The reactions between $Re_2(O_2CR)_4X_2$ (X = Cl, Br; R = CH$_3$, C$_2$H$_5$) and the bridging phosphine ligand $Me_2PCH_2PMe_2$ (dmpm) in ethanol/toluene afford the dirhenium(II) complexes [Re$_2$(O$_2$CR)X$_2$(dmpm)$_3$]X, which undergo anion exchange with *n*-Bu$_4$NPF$_6$ to give [Re$_2$(O$_2$CR)X$_2$(dmpm)$_3$]PF$_6$. The complex [Re$_2$(O$_2$CCH$_3$)Cl$_2$(dmpm)$_3$]Cl has also been prepared by the reaction of Re$_2$Cl$_4$(dmpm)$_3$ with LiO$_2$CCH$_3$ in methanol. The formation of these complexes from Re$_2$(O$_2$CR)$_4$X$_2$ proceeds through the intermediacy of the paramagnetic species *trans*-[Re$_2$(O$_2$CR)$_2$X$_2$(dmpm)$_2$]$^+$, as shown by the isolation of this cation (as its PF$_6^-$ salt) in the case of X = Cl and R = CH$_3$. The structural identity of these complexes has been established by a single-crystal X-ray analysis of a crystal of composition [Re$_2$(O$_2$CCH$_3$)Cl$_2$(dmpm)$_3$]Cl·2H$_2$O·CH$_2$Cl$_2$. Crystal data (at 20° C) are as follows: tetragonal space group $P\bar{4}2_1c$, $a = 26.941$ (1) Å, $b = 26.941$ (1) Å, $c = 9.931$ (1) Å, $V = 7208$ (2) Å^3, and $Z = 8$. The structure was refined to $R = 0.033$ ($R_w = 0.041$) for 2084 data with $I > 3.0\sigma(I)$. The Re–Re bond distance is 2.304 (1) Å, and the structure contains four bridging ligands (one acetate and three dmpm ligands) and two axially bound chlorides. The acetate complexes [Re$_2$(O$_2$CCH$_3$)X$_2$(dmpm)$_3$]PF$_6$ (X = Cl, Br) have been oxidized by NOPF$_6$ to the paramagnetic 1:2 salts [Re$_2$(O$_2$CCH$_3$)X$_2$(dmpm)$_3$](PF$_6$)$_2$.

Introduction

In a previous report[1] we described the synthesis and structural characterization of the triply bonded dirhenium(II) complex Re$_2$Cl$_4$(μ-dmpm)$_3$ (dmpm = Me$_2$PCH$_2$PMe$_2$). We have in subsequent studies been examining ways in which the reactivity of this complex differs from that of the coordinatively unsaturated dirhenium(II) complexes that contain the bis(diphenylphosphino)methane ligand, viz., Re$_2$X$_4$(μ-dppm)$_2$ (X = Cl, Br, I).[2] For example, we have discovered[3] that the conversion of Re$_2$Cl$_4$(μ-dmpm)$_3$ to the novel polyhydride species [Re$_2$(μ-H)H$_4$(μ-dmpm)$_3$]$^+$ is accompanied by the unprecedented loss of a direct Re–Re interaction and the formation of an electronically unsaturated dimetal complex. In order to more fully explore the effect of changing from dppm to the more basic dmpm ligand, we have set out to synthesize dirhenium compounds that contain other ligands in combination with dmpm. Herein we report the preparation and characterization of several mixed alkyl carboxylate–dmpm complexes that are derivatives of the dirhenium(II,II) and -(III,II) cores.

Experimental Section

Starting Materials. The complexes Re$_2$(O$_2$CR)$_4$X$_2$ (X = Cl, Br; R = CH$_3$, C$_2$H$_5$) were synthesized as described in the literature.[4] The Me$_2$PCH$_2$PMe$_2$ ligand was purchased from Quantum Design, Inc. 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.

(i) Preparation of [Re$_2$(O$_2$CR)X$_2$(dmpm)$_3$]X (a) [Re$_2$(O$_2$CCH$_3$)Cl$_2$-(dmpm)$_3$]Cl. A suspension of Re$_2$(O$_2$CCH$_3$)$_4$Cl$_2$ (0.30 g, 0.44 mmol) in 15 mL of ethanol was treated with 1 mL of a solution of dmpm in toluene (1.3 M, 1.32 mmol). The reaction mixture was refluxed for 15 h, and the green solution that resulted was evaporated. The residue was dissolved in a few milliliters of dichloromethane and the solution layered with hexane. After a few days a crop of green crystals was filtered off; yield 0.21 g (45%). Anal. Calcd for C$_{18}$H$_{51}$Cl$_5$O$_4$P$_6$Re$_2$ (i.e. [Re$_2$-(O$_2$CCH$_3$)Cl$_2$(dmpm)$_3$]Cl·2H$_2$O·CH$_2$Cl$_2$): C, 20.26; H, 4.78. Found: C, 19.32; H, 4.52. The presence of lattice CH$_2$Cl$_2$ and H$_2$O was suggested by ^{1}H NMR spectroscopy (δ +5.3 in CDCl$_3$) and IR spectroscopy (ν(O–H) at 3400 cm^{-1} in Nujol mull) and confirmed by X-ray crystallography (vide infra).

(b) [Re$_2$(O$_2$CCH$_3$)Br$_2$(dmpm)$_3$]Br. A procedure similar to that described in section i(a) was used; yield 58%.

(c) [Re$_2$(O$_2$CC$_2$H$_5$)Cl$_2$(dmpm)$_3$]Cl. A mixture of Re$_2$(O$_2$CC$_2$H$_5$)$_4$Cl$_2$ (0.20 g, 0.27 mmol) in 15 mL of ethanol and 0.63 mL of a solution of dmpm in toluene (1.3 M, 0.82 mmol) was refluxed for 10 h. The green solution was evaporated, the residue was washed with acetone, and the green solid that resulted was recrystallized from dichloromethane/diethyl ether; yield 0.18 g (61%). Anal. Calcd for C$_{19}$H$_{53}$Cl$_5$O$_4$P$_6$Re$_2$ (i.e. [Re$_2$(O$_2$CC$_2$H$_5$)Cl$_2$(dmpm)$_3$]Cl·2H$_2$O·CH$_2$Cl$_2$): C, 21.11; H, 4.90. Found: C, 21.03; H, 5.00. The presence of lattice CH$_2$Cl$_2$ and H$_2$O was

supported by IR and NMR spectroscopy.

(d) [Re$_2$(O$_2$CC$_2$H$_5$)Br$_2$(dmpm)$_3$]Br. A procedure similar to that described in section i(c) was used; yield 64%.

(ii) Preparation of [Re$_2$(O$_2$CR)X$_2$(dmpm)$_3$]PF$_6$. (a) [Re$_2$(O$_2$CCH$_3$)-Cl$_2$(dmpm)$_3$]PF$_6$. A quantity of Re$_2$(O$_2$CCH$_3$)$_4$Cl$_2$ (0.30 g, 0.44 mmol) was mixed with 0.84 mL of a dmpm/toluene solution (1.57 M, 1.32 mmol), *n*-Bu$_4$NPF$_6$ (0.17 g, 0.44 mmol), and 20 mL of ethanol, and the mixture was refluxed for 4 h. The insoluble green solid was filtered off and washed with ethanol. Following the partial evaporation of the mother liquor a further quantity of product precipitated; total yield 0.32 g (68%). Anal. Calcd for C$_{17}$H$_{45}$Cl$_2$O$_2$P$_7$F$_6$Re$_2$: C, 19.34; H, 4.26. Found: C, 18.87; H, 4.30.

The following compounds were prepared by a procedure similar to that described above.

(b) [Re$_2$(O$_2$CCH$_3$)Br$_2$(dmpm)$_3$]PF$_6$. Yield: 74%.

(c) [Re$_2$(O$_2$CC$_2$H$_5$)Cl$_2$(dmpm)$_3$]PF$_6$. Yield: 70%.

(d) [Re$_2$(O$_2$CC$_2$H$_5$)Br$_2$(dmpm)$_3$]PF$_6$. Yield: 86%. Anal. Calcd for C$_{18}$H$_{47}$Br$_2$F$_6$O$_2$P$_7$Re$_2$: C, 18.88; H, 4.10. Found: C, 19.05; H, 4.14.

(iii) Reaction of Re$_2$Cl$_4$(μ-dmpm)$_3$ with Lithium Acetate. A mixture of Re$_2$Cl$_4$(dmpm)$_3$ (0.06 g, 0.065 mmol) and LiO$_2$CCH$_3$ (0.40 g, 6.06 mmol) was refluxed in 10 mL of methanol for 18 h. The green solution was evaporated, the residue was dissolved in ca. 5 mL of dichloromethane and this solution was layered with hexane. A crop of green crystalline [Re$_2$(O$_2$CCH$_3$)Cl$_2$(dmpm)$_3$]Cl·CH$_2$Cl$_2$·2H$_2$O was harvested after a few days; yield 0.04 g (58%). This product was identified by a comparison of its spectroscopic and electrochemical properties with those of a sample prepared as in section i(a).

(iv) Reaction of [Re$_2$(O$_2$CCH$_3$)Cl$_2$(dmpm)$_3$]PF$_6$ with Trimethylsilyl Chloride. An excess of Me$_3$SiCl (0.5 mL) was added to a solution of [Re$_2$(O$_2$CCH$_3$)Cl$_2$(dmpm)$_3$]PF$_6$ (0.06 g, 0.057 mmol) in 10 mL of acetone. The solution immediately changed color from green to red and was allowed to stand at room temperature for 30 min before the solvent was evaporated. The addition of an excess of diethyl ether to the residue gave Re$_2$Cl$_4$(μ-dmpm)$_3$ in microcrystalline form; yield 0.03 g (57%). Its identity was established on the basis of its cyclic voltammetric properties.[1]

(v) Oxidation of [Re$_2$(O$_2$CCH$_3$)X$_2$(dmpm)$_3$]PF$_6$. (a) X = Cl. A quantity of [Re$_2$(O$_2$CCH$_3$)Cl$_2$(dmpm)$_3$]PF$_6$ (0.05 g, 0.047 mmol) was reacted with 0.01 g of NOPF$_6$ (0.057 mmol) in 10 mL of dichloromethane at room temperature for 5 h. Thereupon, the dark red solution was taken to dryness and the residue treated with ethanol to give [Re$_2$-(O$_2$CCH$_3$)Cl$_2$(dmpm)$_3$](PF$_6$)$_2$; yield 0.03 g (53%). Anal. Calcd for C$_{17}$H$_{45}$Cl$_2$F$_{12}$O$_2$P$_8$Re$_2$: C, 17.00; H, 3.75. Found: C, 16.44; H, 3.91.

(b) X = Br. The reaction of [Re$_2$(O$_2$CCH$_3$)Br$_2$(dmpm)$_3$]PF$_6$ (0.10 g, 0.087 mmol) with NOPF$_6$ (0.016 g, 0.094 mmol) in dichloromethane for 15 h gave red-purple [Re$_2$(O$_2$CCH$_3$)Br$_2$(dmpm)$_3$](PF$_6$)$_2$. This complex was filtered off and washed with dichloromethane; yield 0.09 g (80%).

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(2) (a) Walton, R. A. *Polyhedron* **1989**, *8*, 1689 and references cited therein. (b) Price, A. C.; Walton, R. A. *Polyhedron* **1987**, *6*, 729 and references cited therein.

(3) Meyer, K. E.; Fanwick, P. E.; Walton, R. A. *J. Am. Chem. Soc.* **1990**, *112*, 8586.

(4) Cotton, F. A.; Oldham, C.; Robinson, W. R. *Inorg. Chem.* **1966**, *5*, 1798.

†Fulbright Postdoctoral Fellow.

Table I. Crystallographic Data for
[Re$_2$(O$_2$CCH$_3$)Cl$_2$(dmpm)$_3$]Cl·2H$_2$O·CH$_2$Cl$_2$

chem formula	Re$_2$Cl$_5$P$_6$O$_4$C$_{18}$H$_{51}$	T, °C	20
fw	1067.11	λ(Mo Kα), Å	0.71073
space group	$P\bar{4}2_1c$ (No. 114)	ρ_{calcd}, g cm^{-3}	1.966
a, Å	26.941 (1)	μ(Mo Kα), cm^{-1}	74.65
b, Å	26.941 (1)	transm coeff	1.00–0.76
c, Å	9.931 (1)	R^a	0.033
V, Å^3	7208 (2)	$R_w{}^b$	0.041
Z	8		

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

Table II. Positional Parameters and Equivalent Isotropic Displacement Parameters (Å^2) for the Non-Hydrogen Atoms of [Re$_2$(O$_2$CCH$_3$)Cl$_2$(dmpm)$_3$]Cl·2H$_2$O·CH$_2$Cl$_2$ and Their Estimated Standard Deviations^a

atom	x	y	z	B
Re(1)	0.53770 (2)	0.75281 (3)	0.79086 (8)	2.32 (1)
Re(2)	0.47589 (2)	0.74770 (3)	0.63119 (8)	2.28 (1)
Cl(1)	0.6017 (2)	0.7576 (2)	0.9852 (2)	4.5 (1)
Cl(2)	0.3986 (2)	0.7423 (2)	0.4774 (6)	5.1 (1)
Cl(11)	$^1/_2$	$^1/_2$	$^1/_2$	5.6 (2)
Cl(12)	$^1/_2$	1	0.450 (1)	6.3 (2)
Cl(13)	1	1	$^1/_2$	8.6 (3)
Cl(1001)^b	0.1966 (3)	0.2826 (3)	0.216 (1)	10.8 (3)
Cl(1002)^b	0.3031 (3)	0.2826 (3)	0.209 (1)	10.1 (3)
P(11)	0.5521 (2)	0.6642 (2)	0.8282 (6)	3.8 (1)
P(12)	0.6056 (2)	0.7687 (2)	0.6422 (6)	4.0 (1)
P(13)	0.5252 (2)	0.8410 (2)	0.8371 (6)	4.2 (1)
P(21)	0.4625 (2)	0.6588 (2)	0.6530 (6)	3.3 (1)
P(22)	0.5296 (2)	0.7405 (2)	0.4428 (5)	3.9 (1)
P(23)	0.4606 (2)	0.8366 (2)	0.5970 (6)	3.4 (1)
O(14)	0.4812 (4)	0.7437 (6)	0.944 (1)	4.3 (3)
O(1T)^b	0.508 (1)	0.9294 (8)	0.205 (2)	12.4 (8)
O(24)	0.4218 (4)	0.7539 (5)	0.790 (1)	3.2 (3)
O(2T)^b	0.5049 (7)	0.5724 (6)	0.251 (2)	7.8 (5)
C(1B)	0.5180 (7)	0.6231 (7)	0.708 (2)	4.2 (5)
C(2B)	0.5832 (7)	0.7809 (8)	0.469 (2)	4.0 (5)
C(3B)	0.5051 (7)	0.8749 (8)	0.683 (2)	4.3 (5)
C(41)	0.4347 (7)	0.7487 (8)	0.907 (2)	4.8 (5)
C(42)	0.3978 (7)	0.748 (1)	1.023 (2)	6.6 (6)
C(111)	0.5285 (9)	0.643 (1)	0.995 (3)	6.4 (7)
C(112)	0.6127 (9)	0.6341 (8)	0.831 (3)	5.8 (6)
C(121)	0.6565 (8)	0.724 (1)	0.620 (4)	8.4 (8)
C(122)	0.6443 (8)	0.8245 (9)	0.673 (3)	6.5 (7)
C(131)	0.4752 (8)	0.8550 (7)	0.957 (3)	5.2 (6)
C(132)	0.5767 (8)	0.8772 (9)	0.914 (3)	7.6 (7)
C(211)	0.4409 (8)	0.6224 (8)	0.505 (2)	5.4 (5)
C(212)	0.4137 (8)	0.6399 (8)	0.769 (2)	4.6 (5)
C(221)	0.5050 (9)	0.759 (1)	0.278 (2)	7.5 (8)
C(222)	0.5616 (9)	0.683 (1)	0.400 (3)	7.0 (7)
C(231)	0.4579 (8)	0.865 (1)	0.428 (2)	6.1 (6)
C(232)	0.3984 (8)	0.8562 (8)	0.657 (2)	5.6 (6)
C(1002)^b	0.2436 (9)	0.279 (1)	0.339 (3)	21.4 (8)

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

(vi) Preparation of *trans*-[Re$_2$(O$_2$CCH$_3$)$_2$Cl$_2$(dmpm)$_2$]PF$_6$. The acetate complex Re$_2$(O$_2$CCH$_3$)$_4$Cl$_2$ (0.75 g, 1.1 mmol) was treated with 1.2 mL of a dmpm/toluene solution (1.84 M, 2.2 mmol) and 0.42 g of *n*-Bu$_4$NPF$_6$ (1.08 mmol) in 20 mL of ethanol and the mixture refluxed for 14 h. The pale green solid that precipitated was filtered off and washed with ethanol; yield 0.55 g (51%). Anal. Calcd for C$_{14}$H$_{38}$Cl$_2$F$_6$O$_6$P$_5$Re$_2$ (i.e. [Re$_2$(O$_2$CCH$_3$)$_2$Cl$_2$(dmpm)$_2$]PF$_6$·2H$_2$O): C, 16.58; H, 3.74. Found: C, 15.82; H, 3.61. The presence of lattice water was confirmed by IR spectroscopy.

When a similar reaction was carried out in acetone/toluene but with Re$_2$(O$_2$CCH$_3$)$_4$Cl$_2$ and dmpm in only 1:1 mole proportions, the product consisted of a separable mixture of insoluble starting material and soluble *trans*-[Re$_2$(O$_2$CCH$_3$)$_2$Cl$_2$(dmpm)$_2$]PF$_6$.

(vii) Reaction of *trans*-[Re$_2$(O$_2$CCH$_3$)$_2$Cl$_2$(dmpm)$_2$]PF$_6$ with Bis(dimethylphosphino)methane. The reaction between the title complex (0.08 g, 0.082 mmol) and 0.068 mL of a dmpm/toluene solution (1.45 M, 0.098 mmol) for 18 h gave a green solution. This was evaporated, the

Table III. Selected Bond Distances (Å) and Bond Angles (deg) for [Re$_2$(O$_2$CCH$_3$)Cl$_2$(dmpm)$_3$]Cl·2H$_2$O·CH$_2$Cl$_2{}^a$

	Distances		
Re(1)–Re(2)	2.304 (1)	Re(2)–P(21)	2.431 (7)
Re(1)–Cl(1)	2.592 (5)	Re(2)–P(22)	2.374 (6)
Re(1)–P(11)	2.447 (7)	Re(2)–P(23)	2.453 (6)
Re(1)–P(12)	2.390 (7)	Re(2)–O(24)	2.16 (1)
Re(1)–P(13)	2.442 (7)	O(14)–C(41)	1.31 (3)
Re(1)–O(14)	2.17 (1)	O(24)–C(41)	1.22 (4)
Re(2)–Cl(2)	2.588 (6)	C(41)–C(42)	1.52 (4)

	Angles		
Re(2)–Re(1)–Cl(1)	175.4 (2)	Re(1)–Re(2)–Cl(2)	172.7 (2)
Re(2)–Re(1)–P(11)	99.3 (2)	Re(1)–Re(2)–P(21)	96.0 (2)
Re(2)–Re(1)–P(12)	98.0 (2)	Re(1)–Re(2)–P(22)	96.1 (1)
Re(2)–Re(1)–P(13)	95.0 (2)	Re(1)–Re(2)–P(23)	99.1 (2)
Re(2)–Re(1)–O(14)	88.2 (4)	Re(1)–Re(2)–O(24)	88.9 (4)
Cl(1)–Re(1)–P(11)	80.2 (2)	Cl(2)–Re(2)–P(21)	82.9 (2)
Cl(1)–Re(1)–P(12)	86.7 (2)	Cl(2)–Re(2)–P(22)	91.2 (2)
Cl(1)–Re(1)–P(13)	84.5 (2)	Cl(2)–Re(2)–P(23)	80.7 (2)
Cl(1)–Re(1)–O(14)	87.1 (4)	Cl(2)–Re(2)–O(24)	83.8 (4)
P(11)–Re(1)–P(12)	98.4 (2)	P(21)–Re(2)–P(22)	94.6 (2)
P(11)–Re(1)–P(13)	160.4 (2)	P(21)–Re(2)–P(23)	161.6 (2)
P(11)–Re(1)–O(14)	84.0 (5)	P(21)–Re(2)–O(24)	84.8 (5)
P(12)–Re(1)–P(13)	92.7 (2)	P(22)–Re(2)–P(23)	94.2 (2)
P(12)–Re(1)–O(14)	172.8 (4)	P(22)–Re(2)–O(24)	175.0 (4)
P(13)–Re(1)–O(14)	83.1 (5)	P(23)–Re(2)–O(24)	85.0 (5)

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

residue was dissolved in ca. 2 mL of dichloromethane, and the solution was layered with hexane. After a few days, a crop of crystalline [Re$_2$-(O$_2$CCH$_3$)Cl$_2$(dmpm)$_3$]PF$_6$ was harvested; yield 0.04 g (42%).

X-ray Crystal Structure Determination. A batch of green crystals of composition [Re$_2$(O$_2$CCH$_3$)Cl$_2$(dmpm)$_3$]Cl·2H$_2$O·CH$_2$Cl$_2$ were grown by the slow diffusion of hexane into a solution of the complex in dichloromethane. A representative "lozenge-shaped" crystal was selected and the structure determined by the application of standard procedures. The basic crystallographic parameters for this complex are listed in Table I. The cell constants are based on 25 reflections with $14 < \theta < 20°$. 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 tetragonal space group $P\bar{4}2_1c$ (No. 114). Lorentz and polarization corrections were applied to the data. The structure was solved by the use of the Patterson heavy-atom method, which revealed the positions of the Re atoms of the dirhenium cation. The remaining non-hydrogen atoms were located in succeeding difference Fourier syntheses. The outer-sphere chloride anions were located at three crystallographically independent special positions and were refined with occupancy factors of $^1/_4$ for Cl(11) and Cl(13) and $^1/_2$ for Cl(12). During the course of the refinement, regions of electron density that were at nonbonding distances to the cation were refined as lattice water or dichloromethane. These were located about general positions and were refined with full occupancy such that the stoichiometry of the complex conformed to [Re$_2$(O$_2$CCH$_3$)Cl$_2$-(dmpm)$_3$]Cl·2H$_2$O·CH$_2$Cl$_2$. This conclusion was substantiated by the IR and ^{1}H NMR spectral properties of the crystals. The water molecules are involved in a complex hydrogen-bonding network with the Cl$^-$ anions. An empirical absorption correction was applied,[5] the linear absorption coefficient being 74.65 cm^{-1}. No corrections were made for extinction. The structure was refined in full-matrix least squares where the function minimized was $\sum w(|F_o| - |F_c|)^2$, where w is the weighting factor defined as $w = 1/\sigma^2(F_o)$. All non-hydrogen atoms were refined anisotropically, and corrections for anomalous scattering were applied.[6] Hydrogen atoms were not included. Since the space group $P\bar{4}2_1c$ is enantiomorphic, refinement was performed on both possible enantiomorphs. Refinement was completed on the enantiomorph with the lowest R factor. The refined values for the other enantiomorph were $R = 0.046$ and $R_w = 0.056$ with the goodness-of-fit = 1.265.

Positional parameters and their errors for the non-hydrogen atoms of the compound are listed in Table II. Important intramolecular bond

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

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

Table IV. Electrochemical Data and NMR Spectral Properties for Salts of the $[Re_2(O_2CR)X_2(dmpm)_3]^+$ Cations

complex[a]	voltammetric half-wave potentials,[b] V		^1H NMR,[d] δ			$^{31}P\{^1H\}$ NMR,[f] δ
	$E_{1/2}(ox)^c$	$E_{p,c}$	R	CH_3-P[e]	P-CH_2-P[e]	dmpm
$[Re_2(O_2CCH_3)Cl_2(dmpm)_3]Cl$	+0.75 (90)	-1.48	+2.81 s	+1.99 m (1), +1.80 s, br (2)	+5.16 (1), +4.70 m, br (2)	-12.6 (2), -22.8 (1)
$[Re_2(O_2CCH_3)Br_2(dmpm)_3]Br$	+0.74 (90)	-1.52	+2.78 s	+2.03 m (1), +1.91 m, +1.82 m (2)	+5.53 (1), +5.10 m,[g] +4.75 m[g] (2)	-19.3 (2), -27.7 (1)
$[Re_2(O_2CC_2H_5)Cl_2(dmpm)_3]Cl$	+0.69 (90)	-1.55	+3.15 q, +1.43 t	+1.97 m (1), +1.79 m (2)	+5.20 t (1), +4.72,[g] +4.60 m[g] (2)	-12.8 (2), -22.8 (1)
$[Re_2(O_2CC_2H_5)Br_2(dmpm)_3]Br$	+0.73 (100)	-1.48	+3.13 q, +1.41 t	+2.02 s (1), +1.91 s, +1.81 s (2)	+5.40 m (1), +4.95 m,[g] +4.78 m[g] (2)	-17.4 (2), -25.7 (1)
$[Re_2(O_2CCH_3)Cl_2(dmpm)_3]PF_6{}^h$	+0.74 (110)	-1.50				
$[Re_2(O_2CCH_3)Br_2(dmpm)_3]PF_6{}^h$	+0.73 (120)	-1.50				

[a] Lattice solvent has been omitted from the formulations of the complexes. [b] Versus Ag/AgCl. Recorded on solutions in 0.1 M TBAH/CH_2Cl_2 by the use of a Pt-bead electrode. Data obtained at ν = 200 mV s^{-1}. Under our experimental conditions $E_{1/2}$ for the ferrocenium/ferrocene couple is +0.47 V vs Ag/AgCl. [c] Numbers of parentheses are ΔE_p values (i.e., $E_{p,a} - E_{p,c}$). [d] Spectra recorded at room temperature in $CDCl_3$. Abbreviations are as follows: s = singlet; t = triplet; q = quartet; m = multiplet; br = broad. [e] Relative intensities are given in parentheses for resonances arising from the chemically inequivalent dmpm ligands. [f] Spectra recorded at room temperature in $CDCl_3$. All resonances are singlets, and numbers in parentheses are relative intensities. [g] Components of an ABX_4 splitting pattern. [h] Cyclic voltammetric data for this complex were obtained on a solution in CH_2Cl_2/acetone (ca. 10:1 by volume) because of its low solubility in CH_2Cl_2.

distances and angles are given in Table III. Tables giving full details of the crystal data and data collection parameters (Table S1) and the thermal parameters (Table S2) and complete listings of bond distances (Table S3) and bond angles (Table S4) 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 or dichloromethane/acetone (10:1 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 Varian XL-200 spectrometer. Resonances were referenced internally to the residual protons in the incompletely deuterated solvent. $^{31}P\{^1H\}$ 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 of acetone solutions were recorded at −160 °C with the use of a Varian E-109 spectrometer.

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

Results

The reactions between $Re_2(O_2CR)_4X_2$ (R = CH_3, C_2H_5; X = Cl, Br) and approximately 3 equiv of bis(dimethylphosphino)methane in a mixed ethanol/toluene solvent system give the green diamagnetic dirhenium(II) complexes $[Re_2(O_2CR)X_2(dmpm)_3]X$. In the presence of n-Bu_4NPF_6, these same reactions afford the hexafluorophosphate salts $[Re_2(O_2CR)X_2(dmpm)_3]PF_6$. The presence of the PF_6^- anion is shown by a ν(P–F) mode at ca. 840 cm^{-1} in the IR spectra of these complexes. Note that the yield of the halide salts is lower than for the analogous PF_6^- species since halide must be sacrificed by some of the dirhenium molecules to provide the outer-sphere halide anion. Elemental microanalyses, spectroscopic data, and an X-ray crystal structure determination in the case of R = CH_3 and X = Cl, have shown that when these complexes are recrystallized from dichloromethane, the crystals contain lattice solvent and are best formulated as being of composition $[Re_2(O_2CR)X_2(dmpm)_3]X\cdot2H_2O\cdot CH_2Cl_2$. Solutions of $[Re_2(O_2CCH_3)X_2(dmpm)_3]X\cdot2H_2O\cdot CH_2Cl_2$ in acetone (0.5 × 10^{-3} M) had conductivities (Λ_m = 100 Ω^{-1} cm^2 mol^{-1} for X = Cl and 110 Ω^{-1} cm^2 mol^{-1} for X = Br) in accord with their formulation as 1:1 electrolytes.[7] The important details of the crystallographic and structural parameters for $[Re_2(O_2CCH_3)Cl_2(dmpm)_3]Cl\cdot2H_2O\cdot CH_2Cl_2$ are presented in Tables I–III, while an ORTEP representation of the structure of the cation is given in Figure 1. The important NMR spectral data and electrochemical
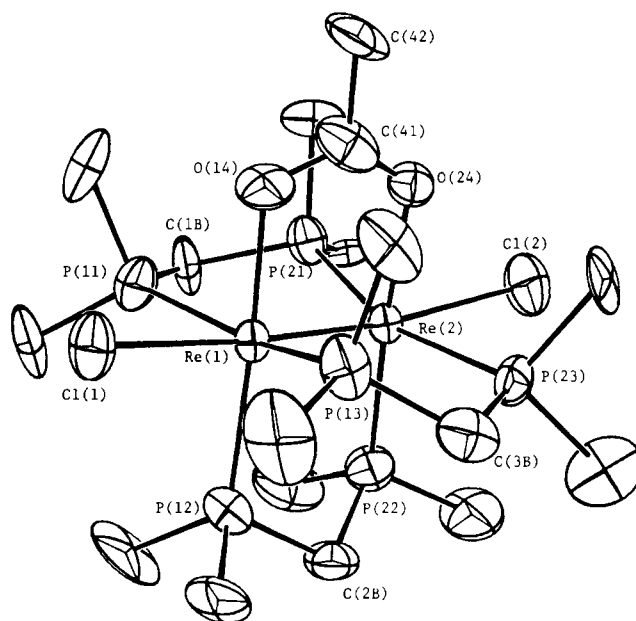
Figure 1. ORTEP representation of the structure of the dirhenium cation in the salt $[Re_2(O_2CCH_3)Cl_2(dmpm)_3]Cl\cdot2H_2O\cdot CH_2Cl_2$. The thermal ellipsoids are drawn at the 50% probability level.

properties of these complexes are summarized in Table IV.

An alternative synthetic strategy to $[Re_2(O_2CR)X_2(dmpm)_3]X$ involved the reaction between $Re_2Cl_4(\mu$-dmpm$)_3{}^1$ and an excess of LiO_2CCH_3 in methanol. This reaction affords the complex $[Re_2(O_2CCH_3)Cl_2(dmpm)_3]Cl\cdot2H_2O\cdot CH_2Cl_2$ upon recrystallization from dichloromethane/hexane. The reversibility of this reaction was demonstrated by the reaction between $[Re_2(O_2CCH_3)Cl_2(dmpm)_3]PF_6$ and Me_3SiCl in acetone at room temperature which produces $Re_2Cl_4(dmpm)_3$ in good yield.

When the reactions between $Re_2(O_2CR)_4X_2$ and dmpm are carried out with the use of 1:≤2 mole proportions of these reagents, the reaction product is different. Thus, when $Re_2(O_2CCH_3)_4Cl_2$ is treated with 1 or 2 equiv of dmpm in refluxing ethanol/toluene in the presence of n-Bu_4NPF_6, the paramagnetic Re_2^{5+} complex $trans$-$[Re_2(O_2CCH_3)_2Cl_2(dmpm)_2]PF_6$ is the main product. Its formulation as the trans isomer is based upon the similarity of its cyclic voltammetric properties ($E_{1/2}$(ox) = +0.76 V and $E_{1/2}$ = −0.42 V vs Ag/AgCl for a solution in 0.1 M n-Bu_4NPF_6/CH_2Cl_2) to those of $trans$-$[Re_2(O_2CCH_3)_2Cl_2(dppm)_2]PF_6$ (dppm = $Ph_2PCH_2PPh_2$).[8] This compound also displays an X-band ESR

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spectrum (−160 °C in acetone) that is similar to those exhibited by *cis*- and *trans*-[Re$_2$(O$_2$CR)$_2$X$_2$(dppm)$_2$]Y (X = Cl, Br; Y = X or PF$_6$.[8] A very broad complex pattern is centered at $g \simeq 2.16$. The intermediacy of the *trans*-[Re$_2$(O$_2$CCH$_3$)$_2$Cl$_2$(dmpm)$_2$]$^+$ cation in the conversion of Re$_2$(O$_2$CCH$_3$)$_4$Cl$_2$ to [Re$_2$-(O$_2$CCH$_3$)Cl$_2$(dmpm)$_3$]$^+$ is shown by the reaction of *trans*-[Re$_2$(O$_2$CCH$_3$)$_2$Cl$_2$(dmpm)$_2$]PF$_6$ with 1 equiv of dmpm to give [Re$_2$(O$_2$CCH$_3$)Cl$_2$(dmpm)$_3$]PF$_6$.

The cyclic voltammetric properties of [Re$_2$(O$_2$CR)X$_2$-(dmpm)$_3$]X and [Re$_2$(O$_2$CR)X$_2$(dmpm)$_3$]PF$_6$ are very similar to one another (Table IV). All show a reversible one-electron oxidation close to +0.7 V that can be accessed both by bulk electrolysis (at ca. +0.8 V) or through the use of NOPF$_6$ as the oxidant. The latter reagent was used to oxidize [Re$_2$-(O$_2$CCH$_3$)X$_2$(dmpm)$_3$]PF$_6$ to paramagnetic [Re$_2$(O$_2$CCH$_3$)X$_2$-(dmpm)$_3$](PF$_6$)$_2$ (X = Cl, Br) in dichloromethane. The X-band ESR spectra of these complexes were recorded at −160 °C in acetone rather than in dichloromethane, in which the purified complexes have limited solubility. Each signal spans the range 1.5-5.5 kG and is centered at $g \simeq 2.1$. Resolvable Re hyperfine splitting ($A^{Re} \simeq 300$ G) is present in the higher field region of these signals, but the overall splitting pattern is too complex to be fully interpreted without recourse to computer simulation. The oxidized species can be rereduced to [Re$_2$(O$_2$CCH$_3$)X$_2$-(dmpm)$_3$]PF$_6$ upon their treatment with ferrocene.

Discussion

The preparation of salts of the dirhenium(II) cations [Re$_2$-(O$_2$CR)X$_2$(dmpm)$_3$]$^+$ (R = CH$_3$, C$_2$H$_5$; X = Cl, Br), both by the reaction of Re$_2$(O$_2$CR)$_4$Cl$_2$ with dmpm (via the intermediacy of *trans*-[Re$_2$(O$_2$CR)$_2$X$_2$(dmpm)$_2$]$^+$) and the substitution of chloride by acetate in Re$_2$Cl$_4$(μ-dmpm)$_3$, demonstrates the considerable stability of the Re$_2$(μ-dmpm)$_3$ unit. The lability of two of the chloride ligands of Re$_2$Cl$_4$(μ-dmpm)$_3$ is not surprising in view of the X-ray structural results for this complex,[1] which show that the two axial Re–Cl bonds (colinear with the Re–Re bond) are much longer (by ca. 0.18 Å) and presumably weaker than the two equatorial Re–Cl bonds. While we have previously obtained dirhenium complexes that contain one or two μ-O$_2$CR ligands in combination with two μ-R$_2$PCH$_2$PR$_2$ ligands,[8-10] this is the first time that a set of four bridging ligands comprises one μ-O$_2$CR and three μ-R$_2$PCH$_2$PR$_2$ ligands.

An X-ray crystal structure determination on a crystal of composition [Re$_2$(O$_2$CCH$_3$)Cl$_2$(dmpm)$_3$]Cl·2H$_2$O·CH$_2$Cl$_2$ established the complex to be a derivative of Re$_2$Cl$_4$(μ-dmpm)$_3$. An ORTEP representation of the structure of the dirhenium cation shows that is resembles quite closely the structure of Re$_2$Cl$_4$(μ-dmpm)$_3$, with the bridging acetate replacing the two equatorial chloride ligands. However, there is one important difference. Whereas the two equatorial Re–Cl bonds of Re$_2$Cl$_4$(μ-dmpm)$_3$ are in an anti disposition to one another on the two metal atoms, the bonding requirements of a bridging acetate ligand require a syn arrangement of oxygen atoms. This reduces the magnitude of the twist angle (χ) in [Re$_2$(μ-O$_2$CCH$_3$)Cl$_2$(dmpm)$_3$]$^+$, as reflected by values for the torsional angles O(14)–Re(1)–Re(2)–O(24),

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) of 10.7(5), 9.6 (2), 14.3 (2), and 12.5 (2)°, respectively. This behavior contrasts with the much greater twisting encountered in Re$_2$Cl$_4$(μ-dmpm)$_3$[1] and Re$_2$Cl$_4$(μ-dppm)$_2$ (dppm = Ph$_2$PCH$_2$PPh$_2$),[11] where the constraints imposed by a bridging acetate ligand are of course absent.

The acetate complex, which possesses a triple bond between the metal atoms, has a Re–Re bond length (2.304 (1) Å) that is very similar to those in Re$_2$Cl$_4$(μ-dmpm)$_3$ (2.309 (2) and 2.3157 (4) Å for the orthorhombic and monoclinic crystal forms) and the cis and trans isomers of Re$_2$(O$_2$CCH$_3$)$_2$Cl$_2$(dppm)$_2$ (2.315 (7) and 2.2763 (7) Å, respectively),[8,10] all of which contain weak axial Re–Cl bonds. The Re–Cl$_{ax}$ bond distances in the [Re$_2$-(O$_2$CCH$_3$)Cl$_2$(dmpm)$_3$]$^+$ cation (2.592 (5) and 2.588 (6) Å) are shorter than those in Re$_2$Cl$_4$(μ-dmpm)$_3$ (2.652 (2) and 2.647 (2) Å in the monoclinic form),[1] probably reflecting, in part, the cationic charge of the former species. The Re–Re–Cl units are a little closer to linearity in the acetate complex (175.4 (2) and 172.7 (2)°) than they are in Re$_2$Cl$_4$(μ-dmpm)$_3$ (167.63 (6) and 168.30 (6)° in the monoclinic form), but this difference is not significant chemically. A disparity in Re–P lengths of [Re$_2$-(O$_2$CCH$_3$)Cl$_2$(dmpm)$_3$]$^+$ is similar to that reported previously for Re$_2$Cl$_4$(μ-dmpm)$_3$.[1] The four Re–P bonds that are trans to another Re–P bond are longer (range 2.453 (6)–2.431 (7)Å) than the two that are trans to a Re–O bond (2.390 (7) and 2.374 (6)Å).

The ^{31}P{^{1}H} NMR spectra of the halide salts of [Re$_2$-(O$_2$CR)X$_2$(dmpm)$_3$]$^+$ (X = Cl, Br) in CDCl$_3$ (Table IV) exhibit fairly broad singlets in a 2:1 intensity ratio that are consistent with the results of the solid-state structure determination of the [Re$_2$(O$_2$CCH$_3$)Cl$_2$(dmpm)$_3$]$^+$ cation. The phosphine resonance of the dmpm ligand that is trans to acetate is upfield of the resonance due to the pair of trans dmpm ligands; a similar chemical shift difference was observed for Re$_2$Cl$_4$(μ-dmpm)$_3$.[1] The ^{1}H NMR spectra of the complexes (Table IV) also show separate discernible resonances for the two types of dmpm ligands. While the C*H$_3$*–P resonances appear as multiplets or broad "singlets", those for the bridgehead methylene groups usually consist of a triplet for the unique dmpm ligand and an AB pattern for the trans pair of dmpm ligands. The presence of a triplet for the former may reflect the occurrence of a dynamic process involving a fairly fast motion of this unique methylene group from one side of the molecule to the other.

Supplementary Material Available: Tables giving full details of the crystal data and data collection parameters (Table S1), thermal parameters (Table S2), and complete bond distances (Table S3) and bond angles (Table S4) (7 pages); tables of observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

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