

The synthesis of the triply bonded tetramethyl complex $\text{Re}_2(\text{CH}_3)_4(\mu\text{-dppm})_2$ and its reaction with carbon monoxide to afford $\text{Re}_2(\mu\text{-CH}_2)_2(\text{CO})_4(\mu\text{-dppm})_2$

Mani Ganesan, Phillip E. Fanwick, Richard A. Walton*

Department of Chemistry, Purdue University, Brown Laboratories, 425 Central Drive, West Lafayette, IN 47907-2018, USA

Received 13 January 2003; received in revised form 5 February 2003; accepted 5 February 2003

Abstract

The reaction of $\text{Re}_2\text{Cl}_4(\mu\text{-dppm})_2$ ($\text{dppm} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$) with CH_3Li in toluene affords $\text{Re}_2(\text{CH}_3)_4(\mu\text{-dppm})_2$ (**1**) in high yield. This is the first simple alkyl complex of the triply bonded dirhenium(II) core. The crystal structure of **1** ($\text{Re}\text{--}\text{Re} = 2.2841(7) \text{ \AA}$) shows it to be very closely related to that of $\text{Re}_2\text{Cl}_4(\mu\text{-dppm})_2$. Compound **1** reacts with CO to produce the di- μ -methylene complex $\text{Re}_2(\mu\text{-CH}_2)_2(\text{CO})_4(\mu\text{-dppm})_2$ (**2**) which is shown to have an edge-sharing bioctahedral structure on the basis of X-ray crystal structure determinations on crystals of composition $2 \cdot 2\text{THF}$ and $2 \cdot 1.734\text{CH}_2\text{Cl}_2$. The dirhenium units have $\text{Re}\text{--}\text{Re}$ single bond distances $2.9931(5)$ and $2.8930(5) \text{ \AA}$ in these two crystals, and the $[\text{Re}_2(\mu\text{-dppm})_2]$ units possess chair and boat conformations, respectively.

© 2003 Elsevier Science B.V. All rights reserved.

Keywords: Dirhenium(II) complexes; Methyl complexes; μ -Methylene complexes; Crystal structures

1. Introduction

In spite of the extensive array of chemistry that has been developed for the electron-rich triple bond in complexes based upon the dirhenium $[\text{Re}\equiv\text{Re}]^{4+}$ core [1], only two simple alkyl complexes have been reported to date, namely, the compounds $\text{Re}_2\text{Cl}_2(\text{CH}_2\text{SiMe}_3)_2(\text{PR}_3)_4$ ($\text{PR}_3 = \text{PMe}_3$ or PMe_2Ph) which are formed by degradation of the trinuclear cluster $\text{Re}_3\text{--Cl}_3(\text{CH}_2\text{SiMe}_3)_6$ upon its reaction with these phosphines [2]. In neither case was the product characterized by X-ray crystallography. Although a few alkyl-containing complexes of quadruply bonded dirhenium(III) exist, such as the salt $\text{Li}_2[\text{Re}_2(\text{CH}_3)_8]$ [3], several complexes of the type $\text{Re}_2(\text{CH}_3)_6(\text{PR}_3)_2$ [2], and an assortment of mixed alkyl-acetato complexes [4,5], the dearth of dirhenium(II) species has led us to examine the possibility of expanding this chemistry with a view to obtaining structurally characterizable species. In the present report

we describe the synthesis and characterization of $\text{Re}_2(\text{CH}_3)_4(\mu\text{-dppm})_2$ ($\text{dppm} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$) and its reaction with carbon monoxide to afford the unexpected bis- μ -methylene complex dirhenium(II) $\text{Re}_2(\mu\text{-CH}_2)_2(\text{CO})_4(\mu\text{-dppm})_2$ in which a $\text{Re}\text{--}\text{Re}$ single bond is present.

2. Experimental

2.1. Starting materials and reaction procedures

The dirhenium complexes $\text{Re}_2\text{Cl}_4(\mu\text{-dppm})_2$ and $\text{Re}_2\text{Cl}_6(\mu\text{-dppm})_2$ ($\text{dppm} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$) were prepared by procedures we have described previously [6,7], while $[(\mu^5\text{-C}_5\text{H}_5)_2\text{Fe}]\text{BF}_4$ was obtained by use of the standard literature method [8]. A 1.4 M solution of CH_3Li in diethyl ether was purchased from Aldrich Chemical Co. and carbon monoxide was obtained from Matheson Gas Products; both were used as received. Solvents were obtained from commercial sources and were generally dried and distilled under a dinitrogen

* Corresponding author. Tel.: +1-765-4945464; fax: +1-765-4940239.

E-mail address: rawalton@purdue.edu (R.A. Walton).

atmosphere before use. All reactions were carried out under an atmosphere of dinitrogen.

2.2. Synthesis of $\text{Re}_2(\text{CH}_3)_4(\mu\text{-dppm})_2$ (**1**)

A solution of $\text{Re}_2\text{Cl}_4(\mu\text{-dppm})_2$ (0.50 g, 0.39 mmol) in 60 ml of toluene was treated at room temperature with an excess of CH_3Li (1.3 ml of a 1.4 M solution in Et_2O , 1.82 mmol). The resulting red reaction mixture was stirred for 18 h and then filtered. The solvent was evaporated from the filtrate to leave a dark red residue and **1** was obtained as a dark orange needle from a concentrated solution in toluene; yield 0.44 g (90%). Anal. Calc. for $\text{C}_{57.5}\text{H}_{60}\text{P}_4\text{Re}_2$ (i.e. $1 \cdot 0.5\text{C}_7\text{H}_8$): C, 55.32; H, 4.81. Found: C, 55.47; H, 4.87%.

This same product was isolated when $\text{Re}_2\text{Cl}_6(\mu\text{-dppm})_2$ (0.26 g, 0.18 mmol) was reacted with CH_3Li (1.1 ml, 1.54 mmol) in toluene for 3 days. Work-up was as described above; yield 0.17 g (74%). The spectroscopic and electrochemical properties are identical to those of the product obtained from $\text{Re}_2\text{Cl}_4(\mu\text{-dppm})_2$.

IR spectra (Nujol mull, 1600–400 cm^{-1}): 1586w, 1571w, 1495w, 1482(w), 1435s, 1306w, 1261w, 1186w, 1158w, 1132w, 1090m-s, 1027m-w, 999w, 907m-w, 801w, 764m-w, 750s, 734s, 713m-s, 695vs, 670w, 618vw, 518vs, 494w, 478w, 462vw, 446vw, 429m, 420m-w. ^1H -NMR (CDCl_3 , δ): 8.13–7.20 (m, $\sim 42\text{H}$, C_6H_5), 5.34 (m, 4H, $-\text{CH}_2-$ of dppm), 2.35 (s, 1.5H, CH_3 of toluene solvent), 0.75 (p, br, 12H, CH_3). $^{31}\text{P}\{^1\text{H}\}$ -NMR (CDCl_3 , δ): +8.2(s). Cyclic voltammogram (0.1 M $n\text{-Bu}_4\text{NPF}_6\text{-CH}_2\text{Cl}_2$, Pt-bead electrode, $\nu = 200 \text{ mV s}^{-1}$): $E_{1/2} = -0.14$ ($E_p = 90 \text{ mV}$) and $E_{p,a} = +0.59 \text{ V}$ versus Ag/AgCl.

2.3. Synthesis of $\text{Re}_2(\mu\text{-CH}_2)_2(\text{CO})_4(\mu\text{-dppm})_2$ (**2**)

A slow stream of CO(g) was bubbled through a solution of **1** (0.09 g, 0.072 mmol) in 30 ml of toluene for 1 h during which time the reaction solution became yellow–orange in color. The reaction solvent was removed by evaporation and the residue extracted with 10 ml of THF. The extract was filtered and the filtrate layered with hexanes to afford crystals of composition $2 \cdot 2\text{THF}$ as established by X-ray crystallography; yield 0.055 g (54%). The THF molecules were lost upon drying these crystals under a vacuum. Anal. Calc. for $\text{C}_{56}\text{H}_{48}\text{O}_4\text{P}_4\text{Re}_2$: C, 52.48; H, 3.75. Found: C, 53.18; H, 4.54%. X-ray quality crystals were also obtained from a concentrated solution of **2** in CH_2Cl_2 and were found to be of composition $2 \cdot 1.734\text{CH}_2\text{Cl}_2$.

IR spectrum (KBr pellet, 2000–400 cm^{-1}): 1985w, 1915vs, 1903m, 1887s, $\sim 1850\text{sh}$, 1587w, 1573w, 1484m-w, 1434 m-s, 1360w, 1306w, 1187w, 1158vw, 1123vw, 1092m, 1059m-w, 1028w, 1001w, 942vw, 909m-w, br, 1845vw, 780m, 752vw, 736m, 720w, 691m-s, 610vw, 579w, 561w, 522m-w, 504w, 483m, 455w, 419w. ^1H -

NMR (CDCl_3 , δ): 8.42 (p, 4H, $\mu\text{-CH}_2$), 7.64–7.08 (m, 40H, C_6H_5), 2.79 (p, 4H, $-\text{CH}_2-$ of dppm). $^{31}\text{P}\{^1\text{H}\}$ -NMR (CDCl_3 , δ): $-4.4(\text{s})$. Cyclic voltammogram (0.1 M $n\text{-Bu}_4\text{NPF}_6\text{-CH}_2\text{Cl}_2$, Pt-bead electrode, $\nu = 200 \text{ mV s}^{-1}$): $E_{1/2} = +0.36$ ($E_p = 100 \text{ mV}$) and $E_{p,a} = +0.86 \text{ V}$ (with a coupled product wave at $E_{p,c} \sim -0.11 \text{ V}$) versus Ag/AgCl.

2.4. Reaction of **2** with $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}]\text{BF}_4$

A solution of **2** (0.10 g, 0.07 mmol) in 20 ml of dichloromethane was treated with a slight stoichiometric excess of $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}]\text{BF}_4$ (0.022 g, 0.081 mmol) and then stirred for 2 days. The reaction mixture was centrifuged to remove an insoluble suspension, and the clear solution layered with hexanes which afforded a few dark green crystals ($\sim 10 \text{ mg}$). Characterization of this product by NMR spectroscopy and cyclic voltammetry indicated that it was a mixture and contained both diamagnetic and paramagnetic materials. Based upon the X-ray crystallographic characterization of one of the crystals, it is apparent that one of the components of this mixture is a salt of the $[\text{Re}_2(\mu\text{-CH}_2)_2(\text{CO})_4(\mu\text{-dppm})_2]^+$ cation (see Section 2.5).

2.5. X-ray crystallography

Crystals of $\text{Re}_2(\text{CH}_3)_4(\mu\text{-dppm})_2$ (**1**) were grown from a concentrated solution in toluene, while single crystals of compositions $\text{Re}_2(\mu\text{-CH}_2)_2(\text{CO})_4(\mu\text{-dppm})_2 \cdot 2\text{THF}$ (**2**·2THF) and $\text{Re}_2(\mu\text{-CH}_2)_2(\text{CO})_4(\mu\text{-dppm})_2 \cdot 1.734\text{CH}_2\text{Cl}_2$ (**2**·1.734 CH_2Cl_2) were obtained from THF–hexane and dichloromethane, respectively. A crystal of apparent composition $[\text{Re}_2(\mu\text{-CH}_2)_2(\text{CO})_4(\mu\text{-dppm})_2]\text{Cl}_{0.53}(\text{BF}_4)_{0.47}$ (**3**) was selected from the batch of crystals isolated in Section 2.4. Data collections were performed at 150 ($\pm$)K with graphite-monochromated Mo– K_α radiation ($\lambda = 0.71073 \text{ \AA}$) on a Nonius–Kappa CCD diffractometer. Lorentz and polarization corrections were applied to the data sets. The important crystallographic data for **1**, **2**·2THF and **2**·1.734 CH_2Cl_2 are given in Table 1.

The structure of **1** was solved using the structure solution program PATTY in DIRDIF-92 [9], the structures of **2**·2THF and **3** with the use of PATTY in DIRDIF-99 [10], while that of **2**· CH_2Cl_2 was solved by direct methods using SIR-97 [11]. The remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were placed in calculated positions according to idealized geometries with $\text{C-H} = 0.95 \text{ \AA}$ and $U(\text{H}) = 1.3U_{\text{eq}}(\text{C})$. They were included in the refinement but constrained to ride on the atom to which they are bonded. An empirical absorption correction using SCALEPACK [12] was applied in all instances except **2**·2THF. The final refinements were performed by the use of the program SHELXL-97 [13]. All non-

Table 1

Crystallographic data for crystals of composition $\text{Re}_2(\text{CH}_3)_4(\mu\text{-dppm})_2$ (**1**), $\text{Re}_2(\mu\text{-CH}_2)_2(\text{CO})_4(\mu\text{-dppm})_2 \cdot 2\text{THF}$ (**2**·2THF) and $\text{Re}_2(\mu\text{-CH}_2)_2(\text{CO})_4(\mu\text{-dppm})_2 \cdot 1.734\text{CH}_2\text{Cl}_2$ (**2**·1.734CH₂Cl₂)

	1	2 ·2THF	2 ·1.734CH ₂ Cl ₂
Empirical formula	C ₅₄ H ₅₆ P ₄ Re ₂	C ₆₄ H ₆₄ O ₆ P ₄ Re ₂	C _{57.73} H _{51.47} Cl _{3.47} O ₄ P ₄ Re ₂
Formula weight	1201.34	1425.52	1428.57
Space group	<i>Pbcn</i> (No. 60)	<i>I</i> 4 ₁ / <i>a</i> (No. 88)	<i>P</i> $\bar{1}$ (No. 2)
<i>a</i> (Å)	11.7245(3)	31.3724(10)	12.5246(4)
<i>b</i> (Å)	27.4137(5)	31.3724(10)	13.4041(4)
<i>c</i> (Å)	16.2428(8)	11.3650(2)	18.8627(7)
α (°)	90	90	103.9548(14)
β (°)	90	90	97.6111(14)
γ (°)	90	90	111.675(2)
<i>V</i> (Å ³)	5220.6(4)	11185.8(9)	2768.4(4)
<i>Z</i>	4	8	2
ρ_{calcd} (g cm ^{−3})	1.528	1.693	1.714
$\mu(\text{Mo-K}\alpha)$ (mm ^{−1})	4.849	—	4.755
<i>R</i> (<i>F</i> _o) ^a	0.058	0.039	0.053
<i>R</i> _w (<i>F</i> _o ²) ^b	0.148	0.081	0.120
Goodness-of-fit	1.016	0.975	0.952

^a $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$ with $F_o^2 > 2\sigma(F_o^2)$.

^b $R_w = [\Sigma w(|F_o^2| - |F_c^2|)^2 / \Sigma w|F_o^2|^{1/2}]^{1/2}$.

hydrogen atoms were refined with anisotropic thermal parameters unless otherwise indicated. The highest peak in the final difference Fouriers of **1**, **2**·2THF, **2**·1.734CH₂Cl₂ and **3** had a height of 1.95, 1.57, 2.41 and 2.10 e Å^{−3}, respectively.

The structure solution and refinement of **1** proceeded routinely. A small amount of disordered lattice solvent (presumably toluene) could not be satisfactorily modeled and was removed with the squeeze option in PLATON [14]. The dirhenium unit is located on a twofold rotation axis that bisects the Re–Re bond. The dirhenium unit that is present in crystals of **2**·2THF is located on a center of inversion and the asymmetric unit also contains a full molecule of THF solvent. The second crystal of **2**, of composition **2**·1.734CH₂Cl₂, contains two independent molecules of CH₂Cl₂ solvent that were allowed to refine freely to occupancies of 0.931 and 0.803. The dirhenium unit has no crystallographically imposed symmetry. In the case of **3**, several problems were encountered in the refinement. The dirhenium cation itself posed no special problems although three of the carbon atoms of one of the phenyl rings of a $\mu\text{-dppm}$ ligand were disordered; the resulting six ‘half’ carbon atoms (with multiplicities of 0.55 or 0.45) were refined with isotropic thermal parameters. An unidentified and badly disordered solvent molecule was present in this crystal but the disorder could not be adequately modeled. Accordingly, the molecule was removed with the squeeze option in PLATON [14]. The most significant problem arose in the modeling and refinement of the counter anions that were present in the asymmetric unit. There are two independent anions located at special positions, one of which refined satisfactorily as Cl[−] at 0.50 occupancy and the other that was treated as a

compositional disorder between [BF₄][−] (0.47) and a small amount of Cl[−] (0.03). The charge balance for **3** is satisfactory and is confirmed by the conductivity properties of these crystals (1:1 electrolyte). The source of Cl[−] is probably from the CH₂Cl₂ solvent. Although the treatment of the anion refinement is not entirely satisfactory, the identity of the chemically important dirhenium cation is clearly established. Crystallographic data for **3** are as follows: formula weight, 1342.00; space group, *C*2/*c* (No. 15); *a* = 21.3403(4); *b* = 14.3708(3); *c* = 35.9259(8) Å, β = 104.9700(10)°; *V* = 10643.7(7) Å³; *Z* = 8; ρ_{calcd} = 1.675 g cm^{−3}; μ = 4.802 mm^{−1}, data collected 27 877, data with *I* > 2.0 σ (*I*) 6511; *R*(*F*_o) = 0.050; *R*_w(*F*_o²) = 0.100; Goodness-of-fit = 0.930.

3. Results and discussion

The reaction of Re₂Cl₄($\mu\text{-dppm}$)₂ with CH₃Li in toluene affords the tetramethyl complex Re₂(CH₃)₄($\mu\text{-dppm}$)₂ (**1**) in high yield. Interestingly, this same product is formed from the reaction of the edge-sharing bioctahedral dirhenium(III) complex Re₂Cl₆($\mu\text{-dppm}$)₂ with CH₃Li with the use of similar reaction conditions albeit with a longer reaction time. The latter reaction may proceed through the intermediacy of an unstable intermediate Re₂(CH₃)₆($\mu\text{-dppm}$)₂ which reductively eliminates ethane. The characterization of **1** was straightforward. The ¹H-NMR spectrum (recorded in CDCl₃) has a broad pentet at δ +0.75 that is assigned to the four methyl groups; in toluene-*d*₈ this resonance is at δ +1.14 and is better resolved (³*J*_{H–P} = 3.6 Hz). Compound **1** shows a singlet in its ³¹P-NMR spectrum (recorded in CDCl₃) at δ +8.2, similar to that reported

for the $\text{Re}_2\text{Cl}_4(\mu\text{-dppm})_2$ precursor [7]. In the cyclic voltammogram of **1** (recorded for a solution in 0.1 M $n\text{-Bu}_4\text{NPF}_6\text{-CH}_2\text{Cl}_2$) there are two one-electron redox processes associated with the $[\text{Re}_2]^{5+}/[\text{Re}_2]^{4+}$ and $[\text{Re}_2]^{6+}/[\text{Re}_2]^{5+}$ couples that are characterized by values of $E_{1/2} = -0.14$ and $E_{\text{p,a}} = +0.59$ V versus Ag/AgCl, respectively. For the complex $\text{Re}_2\text{Cl}_4(\mu\text{-dppm})_2$ both processes are reversible and have $E_{1/2}$ values of $+0.27$ and $+0.80$ V versus SCE [7]. The shift in potentials presumably reflects the effect of replacing Cl^- by CH_3^- , the latter being a better σ -donor which leads to a more electron-rich dirhenium core that is more easily oxidized.

A single crystal X-ray structure determination of **1** confirms its close structural relationship to $\text{Re}_2\text{Cl}_4(\mu\text{-dppm})_2$ [15,16]. The asymmetric unit contains one-half of the dirhenium unit. An ORTEP representation [17] of the structure of **1** is shown in Fig. 1 along with the important bond distances and bond angles. The Re–Re triple bond distance of 2.284(7) Å is similar to the values reported for different crystalline forms of $\text{Re}_2\text{Cl}_4(\mu\text{-dppm})_2$ (range 2.231–2.250 Å) [15,16]. Complex **1**, like $\text{Re}_2\text{Cl}_4(\mu\text{-dppm})_2$, has a staggered rotational geometry, which is typical of triply-bonded complexes of the type $\text{Re}_2\text{X}_4(\mu\text{-dppm})_2$. The four torsion angles Cl(1)–Re–Re(a)–C(1a), C(2)–Re–Re(a)–C(2a), P(1)–Re–Re(a)–P(2a) and P(2)–Re–Re(a)–P(1a) average to 42.2°; the average torsion angle in the non-disordered structure of $\text{Re}_2\text{Cl}_4(\mu\text{-dppm})_2$ is 50.3° [16]. The structures of the quadruply bonded dimolybdenum(II) complexes

$\text{Mo}_2(\text{CH}_3)_4(\text{PR}_3)_4$ ($\text{PR}_3 = \text{PMe}_3$ or PMe_2Ph) have been reported [18] but, as might be expected [19], these compounds have eclipsed rotational geometries.

The tetramethyl complex **1** reacts in toluene solution with CO at room temperature to give an orange–yellow complex **2** identified as the di- μ -methylene complex $\text{Re}_2(\mu\text{-CH}_2)_2(\text{CO})_4(\mu\text{-dppm})_2$. The IR spectrum of **2** shows the presence of $\nu(\text{CO})$ modes (1920–1850 cm^{-1}) that can be assigned to terminal carbonyl ligands and precludes the presence of bridging carbonyls. The presence of two equivalent $\mu\text{-CH}_2$ groups in **2** is evidenced in the ^1H -NMR spectrum (recorded in CDCl_3) by a pentet at $\delta +8.42$ (integrating to 4H and with $^3J_{\text{H-P}} = 7.8$ Hz). This chemical shift is similar to those reported for the *cis* and *trans* isomers of $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Rh}_2(\mu\text{-CH}_2)_2(\text{CH}_3)_2$ ($\delta +8.03$ and $+8.10$, respectively) [20]. The $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum of **2** (recorded in CDCl_3) has a singlet at $\delta -4.4$ that reflects its symmetrical structure. This is confirmed by X-ray structure determinations of crystals of compositions **2**·2THF and **2**·1.734 CH_2Cl_2 that contain different crystallization solvent molecules. Both edge-sharing bioctahedral structures are similar but not identical. The ORTEP representation [17] of the dirhenium molecule present in **2**·2THF is shown in Fig. 2; the important bond distances and angles are given in the caption to this figure. Full details of the structure of **2**·1.734 CH_2Cl_2 are

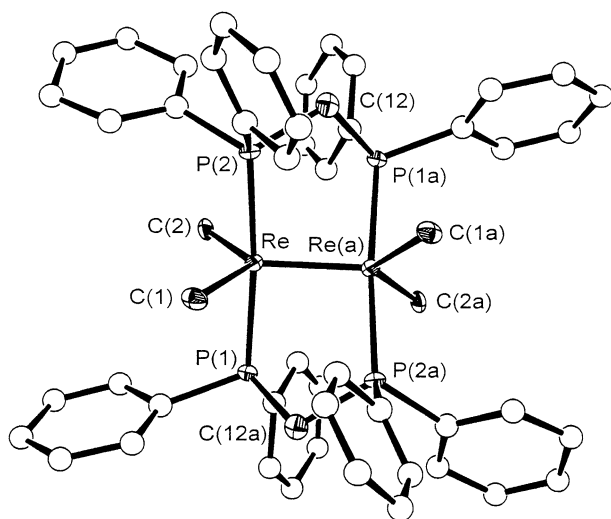


Fig. 1. ORTEP [17] representation of the structure of the dirhenium(II) complex $\text{Re}_2(\text{CH}_3)_4(\mu\text{-dppm})_2$ (**1**). Thermal ellipsoids are drawn at the 50% probability level except for the carbon atoms of the phenyl rings which are circles of arbitrary radius. This molecule contains a two-fold rotation axis that bisects the Re–Re bond. Selected bond distances (Å) and bond angles (°) are as follows: Re–Re(a) 2.2841(7), Re–C(1) 2.169(8), Re–C(2) 2.154(9), Re–P(1) 2.380(2), Re–P(2) 2.378(2); C(1)–Re–C(2) 121.9(4), C(1)–Re–Re(a) 118.6(3), C(2)–Re–Re(a) 119.5(2), P(1)–Re–P(2) 173.88(8).

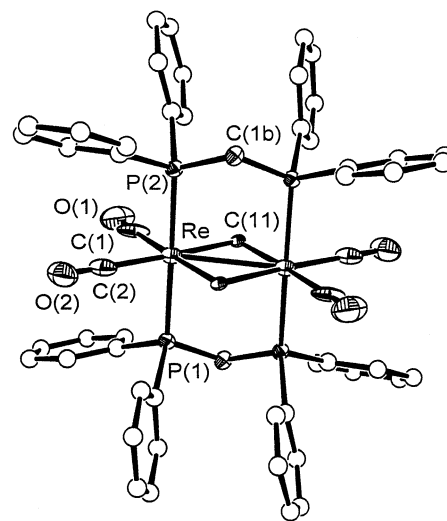


Fig. 2. ORTEP [17] representation of the structure of the dirhenium(II) complex $\text{Re}_2(\mu\text{-CH}_2)_2(\text{CO})_4(\mu\text{-dppm})_2$ as present in crystals of **2**·2THF. Thermal ellipsoids are drawn at the 50% probability level except for the carbon atoms of the phenyl rings which are circles of arbitrary radius. Unlabeled atoms are related to the equivalent labeled atoms by an inversion center. Selected bond distances (Å) and bond angles (°) are as follows: Re–Re(a) 2.9931(5), Re–C(1) 1.947(7), Re–C(2) 1.945(7), Re–C(11) 2.257(6), Re(a)–C(11) 2.361(5), Re–P(1) 2.4023(14), Re–P(2) 2.4205(14), C(1)–O(1) 1.099(7), C(2)–O(2) 1.099(7); Re–C(11)–Re(a) 80.77(18), C(1)–Re–C(2) 86.7(3), C(1)–Re–C(11) 79.8(3), C(1)–Re–C(11a) 178.3(2), C(2)–Re–C(11) 165.8(2), C(2)–Re–C(11a) 94.4(2), P(1)–Re–P(2) 175.33(4), Re–C(1)–O(1) 172.7(7), Re–C(2)–O(2) 175.3(6).

available as Section 4. The Re–Re bond distances for **2**·2THF and **2**·1.734CH₂Cl₂ are 2.9931(5) and 2.8930(5) Å, respectively, values that are consistent with the presence of Re–Re single bonds which in turn accord with 18-electron counts for the Re atoms in these compounds. The Re–C bond lengths within the [Re(μ-CH₂)₂Re] units are 2.257(6) and 2.361(5) Å for **2**·2THF, and are in the range 2.148(12)–2.243(8) Å in the case of **2**·1.734CH₂Cl₂. Other parameters are similar between these two structures with one notable exception, namely, the conformation of the [Re₂(μ-dppm)₂] unit (Fig. 3). In the case of **2**·2THF, which has a crystallographic inversion center, this conformation is required to be chair-like (Fig. 3a). For **2**·1.734CH₂Cl₂, which has no crystallographically imposed symmetry, a boat conformation is present (Fig. 3b). These different ring conformation, and associated differences in ring strain, could explain the variations in Re–CH₂ distances between these two structures. This is only the second time, as far as we are aware, that such boat and chair isomeric forms have been found for compounds that contain a [M₂(μ-dppm)₂] unit. The previous example was encountered in the case of salts of the unsymmetrical edge-sharing bioctahedral cation [Re₂(μ-Br)₂(μ-dppm)₂Br(CO)(CNXyl)₂]⁺ [21]. This difference in conformation presumably accounts (at least in part) for the difference found for the Re–Re distance in these two structures (~0.10 Å). The NMR spectral properties of these two crystalline forms are identical. Since the –CH₂– groups of the dppm ligands appear as a pentet in the NMR spectrum (²J_{H-P} = 4.5 Hz) this is consistent with only the chair isomer being present in solution or with the occurrence of rapid inversion about the bridge-

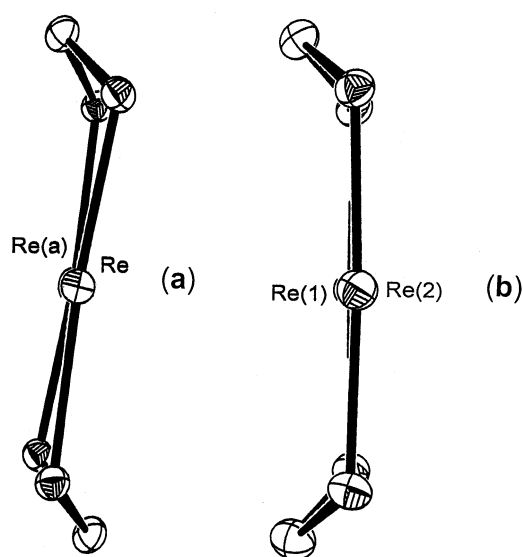
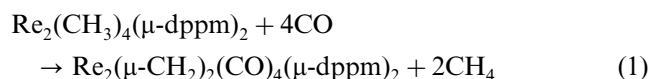


Fig. 3. A comparison of the [Re₂(μ-dppm)₂] units present in the crystals of: (a) **2**·2THF; and (b) **2**·1.734CH₂Cl₂ as viewed down the Re–Re axis to show the chair conformation in (a) and boat conformation in (b).

head methylene carbon atoms of the dppm ligands that renders the –CH₂– protons equivalent.

In the conversion of **1** to **2** we observed no other rhenium-containing intermediates or products (as monitored by ¹H-NMR in toluene-*d*₈). Furthermore, the formation of acetone, a possible reaction by-product, was not detected by ¹H-NMR spectroscopy or GS/MS but the initial appearance of a weak singlet at δ +0.18 in the ¹H-NMR spectrum of the reaction solution, that decreased in intensity with reaction time, could be due to the formation of CH₄ or C₂H₆ as a by-product. Since H₂ was not detected we suggest that the reaction stoichiometry may be that shown in Eq. (1).



The CV of a solution of **2** in 0.1 M *n*-Bu₄NPF₆–CH₂Cl₂ shows a reversible one-electron oxidation with an *E*_{1/2} value of –0.14 V versus Ag/AgCl. Treatment of a solution of **2** in dichloromethane with [(η⁵-C₅H₅)₂Fe]BF₄ afforded the oxidized species [**2**]⁺ in low yield, admixed with other unidentified species. Although this reaction is obviously complex we were able to structurally characterize a crystal of composition close to [Re₂(μ-CH₂)₂(CO)₄(μ-dppm)₂]Cl_{0.5}(BF₄)_{0.5} (**3**). Full structural details are not reported here since we are not entirely satisfied with our modeling of the anion; however this structural information is available as Section 4. The structure of the edge-sharing bioctahedral cation is similar to that present in the crystal of **2**·1.734CH₂Cl₂, in which the [Re₂(μ-dppm)₂] unit assumes a boat conformation. The Re–Re distance of 2.8204(4) Å in **3** is shorter (by 0.07 Å) than that present in this crystal of **2**, implying that the electron removed in the oxidation of **2** to **3** is lost from a non-bonding or weakly anti-bonding metal based orbital.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 200914–200917 for compounds **1**, **2**·2THF, **2**·1.734CH₂Cl₂ and **3**, respectively. Copies of the information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

Acknowledgements

We thank the John A. Leighty Endowment Fund for support of this work.

References

- [1] See, for example, F.A. Cotton, R.A. Walton, *Multiple Bonds Between Metal Atoms*, 2nd ed., Oxford University Press, Oxford, 1993, pp. 69–111.
- [2] P. Edwards, K. Mertis, G. Wilkinson, M.B. Hursthouse, K.M. Abdul Malik, *J. Chem. Soc. Dalton Trans.* (1980) 334.
- [3] F.A. Cotton, L.D. Gage, K. Mertis, L.W. Shive, G. Wilkinson, *J. Am. Chem. Soc.* 98 (1976) 6922.
- [4] R.A. Jones, G. Wilkinson, *J. Chem. Soc. Dalton Trans.* (1978) 1063.
- [5] R.A. Jones, G. Wilkinson, *J. Chem. Soc. Dalton Trans.* (1979) 472.
- [6] A.R. Cutler, D.R. Derringer, P.E. Fanwick, R.A. Walton, *J. Am. Chem. Soc.* 110 (1988) 5024.
- [7] T.J. Barder, F.A. Cotton, D. Lewis, W. Schwotzer, S.M. Tetrack, R.A. Walton, *J. Am. Chem. Soc.* 106 (1984) 2882.
- [8] D.N. Hendrickson, Y.S. Sohn, H.B. Gray, *Inorg. Chem.* 10 (1971) 1560.
- [9] P.T. Beurskens, G. Admirall, G. Beurskens, W.P. Bosman, S. Garcia-Granda, R.O. Gould, J.M.M. Smits, C. Smykalla, *The DIRDIF-92 Program System*, Technical Report, Crystallography Laboratory, University of Nijmegen, Netherlands, 1992.
- [10] P.T. Beurskens, G. Beurskens, R. de Gelder, S. Garcia-Granda, R.O. Gould, R. Israel, J.M.M. Smits, *The DIRDIF-99 Program System*, Crystallography Laboratory, University of Nijmegen, Netherlands, 1998.
- [11] A. Altomare, M.C. Burla, M. Camalli, G.L. Cascarano, C. Giacovazzo, A. Guagliardi, A.G.G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Cryst.* 32 (1999) 115.
- [12] Z. Otwinowski, W. Minor, *Methods Enzymol.* 276 (1996) 307.
- [13] G.M. Sheldrick, *SHELXL-97*, A Program for Crystal Structure Refinement, University of Göttingen, Germany, 1997.
- [14] P.V.D. Sluis, A.L. Spek, *Acta Crystallogr. Sect. A* 46 (1990) 194.
- [15] T.J. Barder, F.A. Cotton, K.R. Dunbar, G.L. Powell, W. Schwotzer, R.A. Walton, *Inorg. Chem.* 24 (1985) 2550.
- [16] J.K. Bera, P.E. Fanwick, R.A. Walton, *Inorg. Chim. Acta* 31 (2000) 138.
- [17] C.K. Johnson, *ORTEP-II*, Rep. ORNL-5138, Oak Ridge National Laboratory, TN, 1976.
- [18] F.A. Cotton, K.J. Wiesinger, *Inorg. Chem.* 29 (1990) 2594.
- [19] See, for example, F.A. Cotton, R.A. Walton, *Multiple Bonds Between Metal Atoms*, 2nd ed., Oxford University Press, Oxford, 1993, pp. 19–20.
- [20] P.M. Maitlis, *J. Organomet. Chem.* 500 (1995) 239.
- [21] (a) W. Wu, P.E. Fanwick, R.A. Walton, *J. Chem. Soc. Chem. Commun.* (1997) 755;
(b) W. Wu, P.E. Fanwick, R.A. Walton, *Inorg. Chem.* 37 (1998) 3122.