The redox chemistry of the triply bonded compounds $Re_2X_4(\mu\text{-}dmpm)_3$ (X = Cl or Br; dmpm = $Me_2PCH_2PMe_2$) and the isolation and characterization of the nitrosyl complex $Re_2Cl_5(\mu\text{-}dmpm)_2(NO)$

Irene Ara* and Richard A. Walton**
Department of Chemistry, Purdue University, West Lafayette, IN 47907 (USA)

Abstract

The current literature on multiply bonded dirhenium complexes that contain the bis(dimethylphosphino)methane ligand (abbreviated dmpm) is reviewed. New procedures are described for the synthesis of the complex $Re_2Cl_4(\mu\text{-}dmpm)_3$. The analogous bromide and iodide complexes of stoichiometry $Re_2X_4(\mu\text{-}dmpm)_3$ have been prepared by the reactions of $Re_2Br_4(\mu\text{-}dppm)_2$ (dppm = $Ph_2PCH_2PPh_2$) and $Re_2X_4(PR_3)_4$ (X = Br or I; R = Et or Pr^n) with dmpm. The reactions of $Re_2X_4(\mu\text{-}dmpm)_3$ (X = Cl or Br) with $NOPF_6$ in dichloromethane give the paramagnetic species $[Re_2X_4(\mu\text{-}dmpm)_3]PF_6$. The chloro complex reacts further with $NOPF_6$ to afford the diamagnetic complex $Re_2Cl_5(\mu\text{-}dmpm)_2(NO)$. This is the first triply bonded dimetal complex that contains a nitrosyl ligand and is stabilized to fission of the metal–metal bond. The identity of this complex has been confirmed by a single crystal X-ray structure determination. Crystal data at 20 °C: orthorhombic space group *Iba*2 (No. 45), $a = 14.278(3)$, $b = 23.966(3)$, $c = 13.880(3)$ Å, $V = 4749(3)$ Å, $Z = 8$. The structure was refined by full matrix least-squares to $R = 0.036$ ($R_w = 0.047$) for 1427 data with $I > 3\sigma(I)$. The structure, which can be represented as $Cl_3Re(\mu\text{-}dmpm)_2ReCl_2(NO)$, contains a terminally bound NO ligand and a *cis, trans* disposition of the pairs of phosphorus donor atoms at the two metal centers. The Re–Re bond distance is 2.379(1) Å.

Introduction

The triply bonded dirhenium(II) complexes of the types $Re_2X_4(PR_3)_4$ (X = Cl, Br or I; PR_3 represents a monodentate tertiary phosphine) and $Re_2X_4(LL)_2$ (X = Cl, Br or I; LL represents a chelating or bridging bidentate phosphine) are the most extensively studied class of dimetal complexes that possess the electron-rich metal–metal triple bond [1–5], while the subset of compounds $Re_2X_4(\mu\text{-}dppm)_2$ (dppm = $Ph_2PCH_2Ph_2$) are the ones that to date have been shown to display the richest and most varied chemistry [4, 6–9]. Our attempts to prepare the analogous complex that contains the bis(dimethylphosphine)methane (dmpm) ligand, viz. $Re_2Cl_4(\mu\text{-}dmpm)_2$, were unsuccessful [10]. Instead, the much more stable tris-dmpm complex $Re_2Cl_4(\mu\text{-}dmpm)_3$ was isolated in all instances. In the present report we (i) review briefly the current literature on dirhenium dmpm complexes, (ii) describe other strategies we have used in our attempts to prepare $Re_2Cl_4(\mu\text{-}dmpm)_2$, (iii) report on the synthesis of the bromo and iodo derivatives of the type $Re_2X_4(\mu\text{-}dmpm)_3$, and (iv) describe details of the redox chemistry of $Re_2X_4(\mu\text{-}dmpm)_3$ (X = Cl, Br or I) that have led to the isolation and structural characterization of the nitrosyl complex $Re_2Cl_5(dmpm)_2(NO)$. A preliminary report on some aspects of this work has been communicated previously [11].

Experimental

Starting materials

The following dirhenium(II) complexes were prepared by standard literature procedures: $Re_2Cl_4(PMe_3)_4$ [12], $Re_2X_4(PEt_3)_4$ (X = Cl or I) [3, 13], $Re_2Br_4(PPr_3^n)_4$ [3], $Re_2Cl_4(PMe_3)_2(\mu\text{-}dppm)$ [12], $Re_2X_4(\mu\text{-}dppm)_2$ (X = Cl or Br) [8] and $Re_2Cl_4(\mu\text{-}dppm)(\mu\text{-}dppe)$ (dppe = $Ph_2PCH_2CH_2PPh_2$) [14]. The paramagnetic dirhenium(III, II) complex $Re_2(\mu\text{-}O_2CCH_3)Cl_4(\mu\text{-}dmpm)_2$ was obtained as described previously [15]. The phosphine $Me_2PCH_2PMe_2$ was purchased from Quantum Design, Inc. or Strem Chemicals and was dispensed as a solution in toluene of known molarity. The other reagents and solvents were obtained from commercial sources and were used without further purification. Solvents were deoxygenated prior to use.

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*Permanent address: Departmento De Quimica Inorganica, Universidad De Zaragoza, 50009 Zaragoza, Spain.

**Author to whom correspondence should be addressed.

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Reaction procedures

All reactions were performed under an atmosphere of dry nitrogen gas with the use of standard Schlenk techniques.

Reactions of bis(dimethylphosphino)methane with dirhenium halide complexes. The preparation of $Re_2X_4(\mu\text{-dmpm})_3$

(i) $Re_2Cl_4(PEt_3)_4$. A quantity of $Re_2Cl_4(PEt_3)_4$ (0.311 g, 0.32 mmol) was placed in a round bottom flask equipped with a condenser and a sidearm. The system was purged with N_2 and a mixture of 10 ml of ethanol and 10 ml of toluene was added to the flask. This was followed by the addition of 0.64 ml of a 1.5 M solution of dmpm in toluene (0.95 mmol), and the reaction mixture was heated to reflux for 24 h. The solvent was evaporated to one half its original volume under a stream of N_2 gas and the product was isolated by addition of an excess of hexanes. The red solid was filtered off, washed with hexanes, recrystallized from $CHCl_3$/hexanes, and dried under vacuum; yield 0.241 g (83%). The product was shown to be $Re_2Cl_4(\mu\text{-dmpm})_3$ on the basis of its spectroscopic and electrochemical properties which were identical with those reported previously for this complex [10].

(ii) $Re_2Cl_4(PMe_3)_4$. A similar reaction to (i) but with use of only one equivalent of dmpm led to a brown residue upon evaporation of the reaction mixture. This was shown by cyclic voltammetry to consist of a mixture of starting material and $Re_2Cl_4(\mu\text{-dmpm})_3$.

(iii) $Re_2Cl_4(dppm)_2$. A mixture of $Re_2Cl_4(dppm)_2$ (0.079 g, 0.062 mmol) and dmpm (0.4 ml of a 0.66 M solution in toluene, 0.26 mmol) was combined with 10 ml of n-butanol and heated for 1–2 days. The mixture was stripped to dryness, and the residue was treated with ethanol and filtered. The rose colored solid was washed with ethanol and diethyl ether and vacuum dried; yield 0.024 g (42%). The product was shown to be $Re_2Cl_4(\mu\text{-dmpm})_3$ by cyclic voltammetry and IR spectroscopy.

(iv) $Re_2Cl_4(PMe_3)_2(dppm)$. With the use of a procedure similar to (i), 0.063 g of $Re_2Cl_4(PMe_3)_2(dppm)$ (0.060 mmol) was reacted with 0.10 ml of a 1.5 M solution of dmpm in toluene (0.15 mmol) and 10 ml of EtOH at reflux for 17 h. This solution was observed to change color from brown to red. The solvent was evaporated and the residue was recrystallized from $CHCl_3$ and hexanes; yield 0.044 g (80%). The product was identified as $Re_2Cl_4(\mu\text{-dmpm})_3$ on the basis of its cyclic voltammetric properties. A decrease in the quantity of dmpm used led to a lowered yield of the tris-dmpm product.

(v) $Re_2Cl_4(dppm)(dppe)$. A quantity of Re_2Cl_4(dppm)(dppe) (0.050 g, 0.039 mmol) was mixed with dmpm (0.03 ml of a 1.5 M solution in toluene, 0.045 mmol) and 10 ml of n-butanol. The mixture was heated for 17 h during which time most of the starting material failed to dissolve although the solution acquired a rose colored tint. Cyclic voltammetry showed that the solid was mainly Re_2Cl_4(dppm)(dppe) along with a small amount of $Re_2Cl_4(\mu\text{-dmpm})_3$.

(vi) $Re_2Br_4(PPr_3{}^n)_4$. A mixture of $Re_2Br_4(PPr_3{}^n)_4$ (0.149 g, 0.112 mmol) and dmpm (0.70 ml of a 0.66 M solution in toluene, 0.46 mmol) was refluxed in 10 ml of a 1:1 ethanol/toluene solution for 24 h. After allowing the reaction mixture to cool to room temperature, the red crystalline product was filtered off, washed with ethanol and diethyl ether, and dried under vacuum; yield 0.074 g (60%). *Anal.* Calc. for $C_{15}H_{42}Br_4P_6Re_2$ (i.e. $Re_2Br_4(dmpm)_3$): C, 16.37; H, 3.85; Br, 29.05. Found: C, 16.35; H, 3.80; Br, 28.48%.

(vii) $Re_2Br_4(dppm)_2$. $Re_2Br_4(dppm)_2$ (0.057 g, 0.039 mmol) was combined with dmpm (0.25 ml of a 0.66 M solution in toluene, 0.165 mmol) in 10 ml of refluxing ethanol. After 1–2 days, the mixture was cooled and filtered. The rose colored complex $Re_2Br_4(dmpm)_3$ was washed with diethyl ether and dried *in vacuo*; yield 0.028 g (65%). The same product was obtained, but in lower yield, when n-butanol was used as the reaction solvent.

(viii) $Re_2I_4(PEt_3)_4$. The reaction between $Re_2I_4(PEt_3)_4$ and dmpm in ethanol/toluene was carried out through use of a procedure essentially identical to that described in (i). Addition of hexanes gave a green–brown solid; yield *c.* 25%. *Anal.* Calc. for $C_{19}H_{54}I_4O_2P_6Re_2$ (i.e. $Re_2I_4(dmpm)_3 \cdot 2C_2H_5OH$): C, 16.52; H, 3.94. Found: C, 17.04; H, 3.96%. The presence of lattice ethanol is supported by the ^1H NMR spectrum of this complex which shows resonances at $\delta + 3.73$ (quartet) and $\delta + 1.25$ (triplet).

Attempted thermolysis of $Re_2(\mu\text{-}O_2CCH_3)Cl_4(dmpm)_2$

A suspension of this complex was refluxed for several hours in toluene but there was no evidence for the occurrence of reductive decarboxylation to give $Re_2Cl_4(dmpm)_2$. The starting material was recovered unchanged.

Oxidation reactions of $Re_2X_4(\mu\text{-}dmpm)_3$

(i) $[Re_2Cl_4(dmpm)_3]PF_6$. A mixture of $Re_2Cl_4(dmpm)_3$ (0.10 g, 0.108 mmol) and $NOPF_6$ (0.023 g, 0.130 mmol) in 10 ml of dichloromethane was stirred at room temperature for 15 min, the purple solution evaporated to dryness, and ethanol added to the residue to afford the microcrystalline complex $[Re_2Cl_4(\mu\text{-}dmpm)_3]PF_6$; yield 0.08 g (70%). *Anal.* Calc. for $C_{15}H_{42}Cl_4F_6P_7Re_2$: C, 16.88; H, 3.95. Found: C, 16.36; H, 4.14%.

(ii) $Re_2Cl_5(dmpm)_2(NO)$. The reaction between $Re_2Cl_4(dmpm)_3$ (0.21 g, 0.228 mmol) and $NOPF_6$ (0.080 g, 0.455 mmol) in 15 ml of dichloromethane for 4 h at room temperature led to a color change from red to purple to brown. The reaction mixture was filtered, evaporated to dryness, and the residue treated with ethanol to give crystals of dark red–brown $Re_2Cl_5(dmpm)_2(NO)$; yield 0.08 g (41%). *Anal.* Calc. for $C_{10}H_{28}Cl_5NOP_4Re_2$: C, 14.10; H, 3.29. Found: C, 14.62; H, 3.08%.

An alternative procedure involved the reaction between $[Re_2Cl_4(dmpm)_3]PF_6$ and one equivalent of $NOPF_6$ in dichloromethane.

(iii) $[Re_2Br_4(dmpm)_3]PF_6$. The dark green complex was obtained by the reaction between $Re_2Br_4(dmpm)_3$ (0.05 g, 0.045 mmol) and $NOPF_6$ (0.0085 g, 0.048 mmol) in 10 ml of dichloromethane; yield 0.03 g (53%). *Anal.* Calc. for $C_{15}H_{42}Br_4F_6P_7Re_2$: C, 14.47; H, 3.37. Found: C, 15.23; H, 3.64%.

X-ray crystallography

Crystals of the complex of composition $Re_2Cl_5(dmpm)_2(NO)$ were grown by the slow diffusion of hexane vapor into a dichloromethane solution. The structure of a crystal of this complex was determined by the application of standard procedures. The basic crystallographic parameters for this complex are listed in Table 1. The cell constants are based on 25 reflections with $18 < \theta < 22°$. Three standard reflections were measured after every 5000 s of beam exposure during data collection. There were no systemmatic variations in intensity. Calculations were performed on a microVAX II computer using the Enraf-Nonius structure determination package. The crystal was found to belong to the orthorhombic space group *Iba*2 (No. 45). 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 complex. The remaining non-hydrogen atoms were located in succeeding difference Fourier syntheses. The hydrogen atoms of the dmpm ligands were included at fixed positions with $B(H) = 1.3B(C)$. An empirical absorption correction was applied [16], but no correction for extinction was made. The structure was refined in full-matrix least-squares where the function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where w is the weighting factor defined as $w = 1/\sigma^2(F_o)$. The non-hydrogen atoms of the dirhenium complex were refined anisotropically; corrections for anomalous scattering were applied to these atoms [17]. The final residuals were $R = 0.036$ ($R_w = 0.047$) and $GOF = 1.399$ for 1427 data with $I > 3\sigma(I)$. Refinement in the other enantiomorph gave $R = 0.040$ ($R_w = 0.052$) and $GOF = 1.544$.

TABLE 1. Crystallographic data and data collection parameters for $Re_2Cl_5(\mu\text{-}dmpm)_2(NO)$

Formula	$Re_2Cl_5P_4ONC_{10}H_{28}$
Formula weight	851.90
Space group	*Iba*2 (No. 45)
a (Å)	14.278(3)
b (Å)	23.966(3)
c (Å)	13.880(3)
V	4749(3)
Z	8
D_c (g cm^{-3})	2.383
Crystal dimensions (mm)	0.38×0.17×0.13
Temperature (°C)	20
Radiation (wavelength)	Mo Kα (0.71073 Å)
Monochromator	graphite
Linear absorption coefficient (cm^{-1})	111.64
Absorption correction applied	empirical[a]
Transmission factors: min., max.	0.79, 1.00
Diffractometer	Enraf-Nonius CAD4
Scan method	ω
h, k, l limits	0 to 15, 0 to 25, 0 to 14
2θ Range (°)	4.00–45.00
Scan width (°)	$0.92 + 0.35\tan(\theta)$
Take-off angle (°)	2.95
Programs used	Enraf-Nonius SDP
$F(000)$	3184.0
p-Factor used in weighting	0.040
Data collected	1743
Unique data	1743
Data with $I > 3.0\sigma(I)$	1427
No. variables	207
Largest shift/e.s.d. in final cycle	0.09
R[b]	0.036
R_w[c]	0.047
GOF[d]	1.399

[a] See ref. 16. [b] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(F_o)$. [d] Goodness of fit $= [\Sigma w(|F_o| - |F_c|)^2/(N_{obs} - N_{parameters})]^{1/2}$.

Table 2 lists the atomic positional parameters and their errors for the non-hydrogen atoms, while Tables 3 and 4 provide the more important intramolecular bond distances and angles for the dirhenium cation. See also 'Supplementary material'.

Physical measurements

IR spectra (4000–200 cm^{-1}) were recorded as Nujol mulls supported on KBr or polyethylene plates with a

TABLE 2. Positional parameters for non-hydrogen atoms of $Re_2Cl_5(\mu\text{-dmpm})_2(NO)$ and their e.s.d.s[a]

Atom	x	y	z	$B(Å^2)$
Re(1)	0.20819(6)	0.15600(3)	0	2.34(2)
Re(2)	0.24543(6)	0.08806(3)	−0.11893(9)	2.46(2)
Cl(11)	0.1126(4)	0.2345(2)	0.0872(4)	2.4(1)
Cl(12)	0.3242(5)	0.1614(3)	0.1221(5)	4.4(2)
Cl(21)	0.3458(5)	0.0150(3)	−0.1886(4)	4.0(1)
Cl(22)	0.1070(5)	0.0334(3)	−0.1483(5)	4.3(2)
Cl(23)	0.2170(6)	0.1275(3)	−0.2758(5)	4.9(2)
P(11)	0.2879(5)	0.2352(3)	−0.0724(5)	3.7(1)
P(12)	0.1270(5)	0.0950(3)	0.1150(6)	3.2(1)
P(21)	0.3953(5)	0.1358(3)	−0.1411(5)	3.6(2)
P(22)	0.2648(4)	0.0210(2)	0.0093(5)	3.2(1)
O(1)	0.046(1)	0.1640(8)	−0.133(2)	6.1(5)
N(1)	0.118(2)	0.1577(7)	−0.077(1)	4.3(5)
C(1B)	0.385(2)	0.213(1)	−0.147(2)	5.3(8)
C(2B)	0.184(2)	0.026(1)	0.111(2)	4.9(6)
C(111)	0.339(2)	0.288(1)	0.009(4)	10.6(9)
C(112)	0.205(3)	0.263(2)	−0.165(3)	12(1)
C(121)	0.128(3)	0.114(1)	0.240(3)	8.5(9)
C(122)	0.005(2)	0.087(1)	0.089(3)	6.9(8)
C(211)	0.454(3)	0.125(1)	−0.255(2)	9.2(9)
C(212)	0.493(2)	0.124(1)	−0.057(3)	8(1)
C(221)	0.245(2)	−0.053(1)	−0.015(3)	6.0(8)
C(222)	0.384(2)	0.020(1)	0.067(2)	6.0(8)

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

TABLE 3. Some important bond distances (Å) for $Re_2Cl_5(\mu\text{-dmpm})_2NO$[a]

Re(1)–Re(2)	2.379(1)	P(11)–C(111)	1.84(4)
Re(1)–Cl(11)	2.622(4)	P(11)–C(112)	1.87(4)
Re(1)–Cl(12)	2.373(6)	P(12)–C(2B)	1.84(2)
Re(1)–P(11)	2.431(6)	P(12)–C(121)	1.79(3)
Re(1)–P(12)	2.455(6)	P(12)–C(122)	1.79(3)
Re(1)–N(1)	1.68(3)	P(21)–C(1B)	1.85(3)
Re(2)–Cl(21)	2.461(6)	P(21)–C(211)	1.81(3)
Re(2)–Cl(22)	2.406(6)	P(21)–C(212)	1.83(3)
Re(2)–Cl(23)	2.408(6)	P(22)–C(2B)	1.83(2)
Re(2)–P(21)	2.446(6)	P(22)–C(221)	1.82(2)
Re(2)–P(22)	2.414(6)	P(22)–C(222)	1.88(3)
P(11)–C(1B)	1.81(3)	O(1)–N(1)	1.28(3)

[a] Numbers in parentheses are e.s.d.s in the least significant digits.

TABLE 4. Some important bond angles (°) for $Re_2Cl_5(\mu\text{-dmpm})_2(NO)$[a]

Re(2)–Re(1)–Cl(11)	158.2(1)	Re(1)–Re(2)–Cl(23)	108.7(2)
Re(2)–Re(1)–Cl(12)	112.1(2)	Re(1)–Re(2)–P(21)	87.9(2)
Re(2)–Re(1)–P(11)	98.2(2)	Re(1)–Re(2)–P(22)	88.2(1)
Re(2)–Re(1)–P(12)	98.5(1)	Cl(21)–Re(2)–Cl(22)	91.4(2)
Re(2)–Re(1)–N(1)	75.3(6)	Cl(21)–Re(2)–Cl(23)	91.2(2)
Cl(11)–Re(1)–Cl(12)	89.7(2)	Cl(21)–Re(2)–P(21)	76.9(2)
Cl(11)–Re(1)–P(11)	82.7(2)	Cl(21)–Re(2)–P(22)	75.5(2)
Cl(11)–Re(1)–P(12)	83.2(2)	Cl(22)–Re(2)–Cl(23)	85.5(2)
Cl(11)–Re(1)–N(1)	82.9(6)	Cl(22)–Re(2)–P(21)	162.2(2)
Cl(12)–Re(1)–P(11)	85.7(2)	Cl(22)–Re(2)–P(22)	81.8(2)
Cl(12)–Re(1)–P(12)	84.1(2)	Cl(23)–Re(2)–P(21)	81.4(2)
Cl(12)–Re(1)–N(1)	172.5(6)	Cl(23)–Re(2)–P(22)	161.3(2)
P(11)–Re(1)–P(12)	162.7(2)	P(21)–Re(2)–P(22)	107.7(2)
P(11)–Re(1)–N(1)	94.4(6)	Re(1)–N(1)–O(1)	174(1)
P(12)–Re(1)–N(1)	93.8(6)	P(11)–C(1B)–P(21)	109(1)
Re(1)–Re(2)–Cl(21)	152.9(2)	P(12)–C(2B)–P(22)	111(1)
Re(1)–Re(2)–Cl(22)	107.9(2)		

[a] Numbers in parentheses are e.s.d.s in the least significant digits.

Perkin–Elmer 1800 FTIR spectrometer. Electrochemical experiments were carried out by using a Bioanalytical Systems Inc. model CV-1A instrument on dichloromethane solutions that contained 0.1 M tetra-n-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte. $E_{1/2}$ values, determined as $(E_{p,a}+E_{p,c})/2$, were referenced to the Ag/AgCl electrode at room temperature and are uncorrected for junction potentials. Under our experimental conditions $E_{1/2}=+0.47$ V for the ferrocenium/ferrocene couple, which was used as an internal standard. ^1H NMR spectra were recorded on Varian XL-200 or Nicolet NT-470 spectrometers. Resonances were referenced internally to the residual protons in the incompletely deuteriated 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 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 and discussion

Previous studies on bis(dimethylphosphino)methane complexes that contain a multiple bonded dirhenium unit

Our first study [10] involved the synthesis and structural characterization of the tris-dmpm dirhenium(II) product $Re_2Cl_4(\mu\text{-dmpm})_3$, during unsuccessful attempts to prepare $Re_2Cl_4(\mu\text{-dmpm})_2$. A representation of the structure of this complex is given in Fig. 1. We subsequently found that the reaction of this chloride complex with lithium acetate in methanol produces the salt $[Re_2(\mu\text{-}O_2CCH_3)Cl_2(\mu\text{-dmpm})_3]^+Cl^-$, in which there are four bridging ligands and two axially bound chlorides [18]. This compound, and others like it, viz. $[Re_2(\mu\text{-}O_2CR)X_2(\mu\text{-dmpm})_3]X$ (X = Cl or Br; R = CH_3 or C_2H_5) can be prepared from the redox reactions between the dirhenium(III) carboxylates $Re_2(\mu\text{-}O_2CR)_4X_2$ and dmpm in ethanol/toluene. These reactions proceed through the intermediacy of the bis-dmpm dirhenium(III,II) species *trans*-$[Re_2(\mu\text{-}$

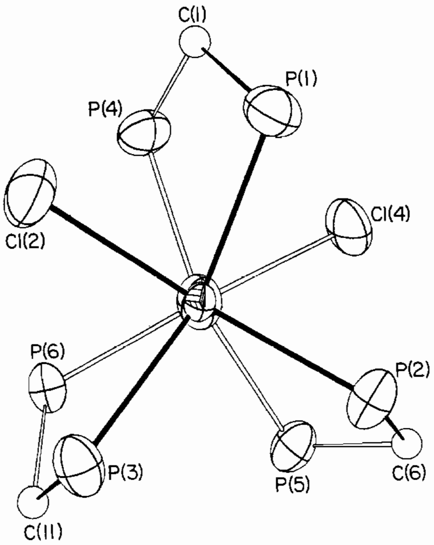

Fig. 1. View of the staggered $Re_2Cl_4(\mu\text{-dmpm})_3$ molecule along the Re–Re vector, showing the disposition of the equatorial ligands and the conformations of the three bridging dmpm ligands. There are also two axially bound chloride ligands. See ref. 10.

$O_2CR)_2X_2(\mu\text{-dmpm})_2]^+$ [18]. Anion exchange reactions occur between $[Re_2(\mu\text{-}O_2CR)X_2(\mu\text{-dmpm})_3]X$ and $Bu_4{}^nNPF_6$ to produce the analogous salts of composition $[Re_2(\mu\text{-}O_2CR)X_2(\mu\text{-dmpm})_3]PF_6$.

In our earlier study on $Re_2Cl_4(\mu\text{-dmpm})_3$, we had shown [10] by the use of cyclic voltammetry that this complex possesses a reversible one-electron oxidation although, at the time, salts of the $[Re_2Cl_4(\mu\text{-dmpm})_3]^+$ cation were not isolated. However, the acetate complexes $[Re_2(\mu\text{-}O_2CCH_3)X_2(\mu\text{-dmpm})_3]PF_6$ (X = Cl or Br), which also have an accessible oxidation ($E_{1/2}$(ox) $\approx +0.75$ V versus Ag/AgCl in 0.1 M TBAH–CH_2Cl_2 [18]), are oxidized by $NOPF_6$ to give the dirhenium(III, II) species $[Re_2(\mu\text{-}O_2CCH_3)X_2(\mu\text{-dmpm})_3](PF_6)_2$ [18]. Another set of mixed carboxylate–dmpm complexes that contain the dirhenium(III,II) core have also been isolated; these are the neutral compounds of composition $Re_2(\mu\text{-}O_2CR)X_4(\mu\text{-dmpm})_2$ (X = Cl or Br; R = CH_3 or C_2H_5) which have been isolated in moderate yield from the reactions between $Re_2(\mu\text{-}O_2CR)_2X_4L_2$ (L = H_2O or py) and dmpm [15, 19]. In the case of the reaction of $Re_2(\mu\text{-}O_2CCH_3)_2Cl_4(H_2O)_2$ with dmpm, the novel mixed-valent dirhenium complex $O_3ReReCl_2(dmpm)_2$ was isolated in low yield along with $Re_2(\mu\text{-}O_2CCH_3)Cl_4(\mu\text{-dmpm})_2$ [15].

Attempted synthesis of $Re_2Cl_4(\mu\text{-dmpm})_2$ and methods for the synthesis of $Re_2X_4(\mu\text{-dmpm})_3$ (X = Cl, Br or I)

Our original synthesis of $Re_2Cl_4(\mu\text{-dmpm})_3$ involved a procedure in which either $(Bu_4{}^nN)_2Re_2Cl_8$ or $Re_2Cl_4(PPr_3{}^n)_4$ were reacted with dmpm [10]. It has also been reported that the reaction of $[Re_2(\mu\text{-}O_2CCH_3)Cl_2(\mu\text{-dmpm})_3]PF_6$ with Me_3SiCl gives $Re_2Cl_4(\mu\text{-dmpm})_3$ as the major product [18], and this compound is formed, along with $Re_2(\mu\text{-}O_2CCH_3)Cl_4(\mu\text{-dmpm})_2$ and $O_3ReReCl_2(dmpm)_2$, in a complex redox reaction between $Re_2(\mu\text{-}O_2CCH_3)_2Cl_4(H_2O)_2$ and dmpm [15]. However, neither of the latter procedures constitutes an especially useful means of preparing $Re_2Cl_4(\mu\text{-dmpm})_3$. In the present work we have found that the reactions of dmpm with the dirhenium(II) complexes $Re_2Cl_4(PMe_3)_4$, $Re_2Cl_4(PEt_3)_4$, $Re_2Cl_4(\mu\text{-dppm})_2$ and $Re_2Cl_4(PMe_3)_2(\mu\text{-dppm})$ provide alternative means of preparing $Re_2Cl_4(\mu\text{-dmpm})_3$. In no instances were we able to prepare $Re_2Cl_4(\mu\text{-dmpm})_2$ by adjusting the reaction conditions (the use of room temperature reactions, different solvents and different reaction stoichiometries). We also examined the possibility that $Re_2(\mu\text{-}O_2CCH_3)Cl_4(\mu\text{-dmpm})_2$ [15] would undergo thermal reductive decarboxylation to afford $Re_2Cl_4(\mu\text{-dmpm})_2$, but to no avail.

The reactions of $Re_2Br_4(PPr_3{}^n)_4$ and $Re_2Br_4(\mu\text{-dppm})_2$ with dmpm proceed in good yield to afford $Re_2Br_4(\mu\text{-dmpm})_3$ [20], while $Re_2I_4(PEt_3)_4$ gives $Re_2I_4(\mu\text{-dmpm})_3$. The latter product is the most unstable of the three halide complexes $Re_2X_4(\mu\text{-dmpm})_3$, and we were able to isolate it only as a solid in which lattice ethanol was present (based upon microanalytical data and NMR spectroscopy).

The spectral properties of the chloride and bromide complexes are very similar, thereby signifying a close similarity in structure. The $^{31}P\{^1H\}$ NMR spectrum of $Re_2Br_4(\mu\text{-dmpm})_3$ in $CDCl_3$ exhibits two broad resonances in a 2:1 intensity ratio at $\delta -32.4$ and $\delta -44.3$. As is the case for $Re_2Cl_4(\mu\text{-dmpm})_3$ [10], this implies that there are two sets of phosphorus atoms, i.e. those which can be classified as being approximately *trans* to other phosphorus atoms (four) and those *trans* to halogen atoms (two) (see Fig. 1). The 470 MHz ^1H NMR spectrum in $CDCl_3$ is rather complex. It displays six doublets at $\delta +2.27$, $+2.23$, $+2.09$, $+2.08$, $+1.87$ and $+1.81$ (^2J(HP) = 8.7 Hz) of approximately equal intensity (the doublets at $\delta +2.09$ and $+2.08$ overlap one another). Six resonances would be expected for a complex containing six pairs of inequivalent methyl groups. This pattern was seen for the structurally characterized chloro complex and thus provides further support for $Re_2Br_4(\mu\text{-dmpm})_3$ having the same structure. The methylene protons are seen as three resonances in a 1:1:1 intensity ratio in the ^1H NMR spectrum. A triplet (^2J(HP) = 9.7 Hz) at $\delta +4.35$ is attributed to the methylene protons on the unique dmpm, i.e. the one that has each of its phosphorus atoms *trans* to another phosphorus atom. On the other hand, the methylene protons on the dmpm ligands that have one phosphorus atom *trans* to a Br atom and one *trans* to a P atom give rise to a pair of doublets of triplets. The doublets of triplets are centered at $\delta + 4.42$ ($^2J(\mathrm{HP}) = 8.3$ Hz and $^2J(\mathrm{H_AH_B}) = 14.1$ Hz) and at $\delta + 5.13$ ($^2J(\mathrm{HP}) = 11.6$ Hz and $^2J(\mathrm{H_AH_B}) = 14.0$ Hz).

The similarity between the chloride and bromide is further reinforced by their electronic absorption spectra; their solutions in dichloromethane show asymmetric peaks with $\lambda_{\max} = 488$ nm ($\epsilon \approx 150$) for X = Cl [10] and $\lambda_{\max} = 500$ nm ($\epsilon \approx 220$) for X = Br.

The $^{31}P\{^1H\}$ NMR spectrum of a solution of $Re_2I_4(\mu\text{-dmpm})_3 \cdot 2EtOH$ in $CDCl_3$ closely resembles the spectra of the chloride and bromide; broad resonances are present at $\delta - 38.0$ and -39.7 with an intensity ratio of 2:1. However, in contrast to the chloride and bromide, the ^1H NMR spectrum of $Re_2I_4(\mu\text{-dmpm})_3 \cdot 2EtOH$ was deceptively simple, with broad singlets in an intensity ratio of 2:1 at $\delta + 2.08$ and $+2.67$ for the methyl resonances of the dmpm ligands, and multiplets for the $-CH_2-$ groups at $\delta + 5.23$ and $+6.15$ (also in a 2:1 intensity ratio). The broadness of the resonances and the simplicity of the spectrum indicate that a fluxional process is occurring which preserves the 2:1 ratio of different types of bridging dmpm ligands. This motion is presumably a slow twist about the Re≡Re bond; this accords with there being no electronic barrier to rotation about a metal–metal triple bond [1, 2].

Redox chemistry of $Re_2X_4(\mu\text{-dmpm})_3$ (X = Cl or Br)

The electrochemical properties of $Re_2Br_4(\mu\text{-dmpm})_3$ closely resemble those reported previously for $Re_2Cl_4(\mu\text{-dmpm})_3$ [10]. The cyclic voltammogram of the bromide complex (measured in 0.1 M TBAH–CH_2Cl_2) displays a one-electron oxidation at $E_{1/2} = +0.58$ V and an irreversible oxidation at $E_{p,a} = +1.33$ V versus Ag/AgCl (compare with $E_{1/2} = +0.53$ V and $E_{p,a} = +1.30$ V versus Ag/AgCl for the chloride derivative [10]). The corresponding cyclic voltammetric data for $Re_2I_4(\mu\text{-dmpm})_3 \cdot 2EtOH$ are much more complicated and signify a lack of reversibility for the redox processes. A single scan cyclic voltammogram shows an oxidation at $E_{p,a} = +0.17$ V ($i_{p,c} < i_{p,a}$). Additional oxidation processes are found at $E_{p,a}$ *c.* $+0.7$ and *c.* $+1.2$ V; while these have coupled reduction waves, $i_{p,c} < i_{p,a}$ in both instances. Some of these redox processes may be associated with free I^- and other iodide-containing anions [21] that are formed from the decomposition of this compound in solution. There are also two closely spaced irreversible reductions with $E_{p,c}$ values of *c.* -1.15 and *c.* -1.35 V versus Ag/AgCl; the analogous chloride and bromide complexes do not display any such reductions at potentials more positive than -1.7 V (the limit of our measurements).

The reversible oxidation in the cyclic voltammograms of $Re_2X_4(\mu\text{-dmpm})_3$ (at $E_{1/2} = +0.53$ V (X = Cl) and $E_{1/2} = +0.58$ V (X = Br)) can be accessed both electrochemically and chemically, the latter with the use of $NOPF_6$ as oxidant. The identity of the salts $[Re_2X_4(\mu\text{-dmpm})_3]PF_6$ was established by their electrochemical and spectroscopic properties. Their cyclic voltammetric properties are identical to those of the parent $Re_2X_4(\mu\text{-dmpm})_3$ compounds, except that the reversible process at *c.* $+0.5$ V now corresponds to a reduction of the bulk complexes. Their IR spectra (Nujol mulls) show the presence of the $[PF_6]^-$ anion (ν(P–F) at 840 s cm^{-1}) and both compounds are ESR-active (X-band spectra in CH_2Cl_2 at -160 °C), with a broad signal at $g \approx 2.2$ which shows some poorly resolved hyperfine structure in the case of X = Cl.

A quite different reaction product is obtained if $Re_2Cl_4(\mu\text{-dmpm})_3$ is reacted with $NOPF_6$ using 1:2 mole proportions of these reagents, or if $[Re_2Cl_4(\mu\text{-dmpm})_3]PF_6$ is treated with a further equivalent of $NOPF_6$ in dichloromethane. In both instances the diamagnetic red–brown nitrosyl complex $Re_2Cl_5(\mu\text{-dmpm})_2(NO)$ is produced in yields of under 50%. A single intense ν(NO) mode is present at 1750 cm^{-1} in its IR spectrum, in accord with the presence of a terminally bound nitrosyl ligand. Its ^1H NMR spectrum (recorded in $CDCl_3$ at room temperature) exhibits a broad resonance (unresolved multiplet) at $\delta + 4.13$ (P–CH_2–P) and multiplets at $\delta + 2.46$, $+2.00$ and $+1.60$, in an intensity ratio of *c.* 1:1:2, which are assigned to CH_3–P. The resonance at $\delta + 1.60$ is composed of two overlapping multiplets. Overall these results indicate the presence of four inequivalent pairs of CH_3–P groups. A cyclic voltammogram of a solution of this complex in 0.1 M TBAH–CH_2Cl_2 shows a reversible oxidation at $E_{1/2} = +0.95$ V and an irreversible reduction at $E_{p,c} = -0.82$ V versus Ag/AgCl.

The crystal structure of $Re_2Cl_5(\mu\text{-dmpm})_2(NO)$ has been determined and an ORTEP view of the molecule is shown in Fig. 2. Not only is the presence of a linearly bound nitrosyl ligand confirmed, but so also is the presence of only two dmpm ligands. These are bound

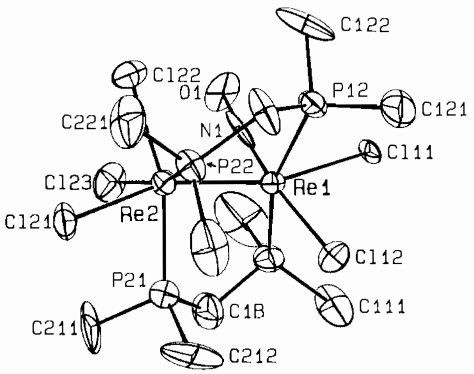

Fig. 2. ORTEP representation of the structure of $Re_2Cl_5(\mu\text{-dmpm})_2(NO)$ with the hydrogen atoms of the dmpm ligands omitted. The thermal ellipsoids are drawn at the 50% probability level.

such that there is a rarely encountered *cis*, *trans* disposition of phosphorus donor atoms at the two metal centers [22]; the angles P(22)–Re(2)–P(21) and P(21)–Re(1)–P(11) are 107.7(2) and 162.7(2)°, respectively. While this molecule possesses no crystallographically imposed symmetry, there is a virtual plane of symmetry containing the NO ligand and the atoms Cl(11), Cl(12), Re(1), Re(2) and Cl(21) that bisects the angles P(22)–Re(2)–P(21) and P(12)–Re(1)–P(11).

If we treat the nitrosyl ligand as being formally NO^+ we can consider this complex as a derivative of dirhenium(II,II). The Re–Re bond distance of 2.379(1) Å accords with this being a Re≡Re bond, although it is longer than the comparable distance in $Re_2Cl_4(\mu\text{-dmpm})_3$ (2.3157(4) Å) [10], and in many other dirhenium(II) halide complexes [6]. This bond lengthening is probably a consequence of a weakening of the π and/or δ components of the Re≡Re bond through $Re \rightarrow NO(\pi^*)$ backbonding. Note that the relative shortness of the Re–Cl bond that is *trans* to the nitrosyl ligand may support the occurrence of some degree of $Re \rightarrow NO(\pi^*)$ backbonding since this could enhance any $Cl(p\pi) \rightarrow Re(d)$ contribution to the Re(1)–Cl(12) bond as well as the σ bonding interaction. The disparity in the axial and equatorial Re–Cl bond distances at Re(1) (2.622(4) and 2.373(6) Å, respectively) is comparable to that seen in $Re_2Cl_4(\mu\text{-dmpm})_3$ [10]. However, a much smaller difference exists between the Re–Cl bonds about Re(2); in particular, the axial bond Re(2)–Cl(21) is surprisingly short (2.461(6) Å). Although the reason for this is not obvious it may reflect a disparity in charges at the two Re centers that renders Re(2) more positively charged and therefore leads to a shortening of this axial bond.

The formation of $Re_2Cl_5(\mu\text{-dmpm})_2(NO)$ from $Re_2Cl_4(\mu\text{-dmpm})_3$ is unusual in that it requires the loss of a dmpm ligand from the latter complex. Since $Re_2Cl_4(\mu\text{-dmpm})_3$ is normally very stable towards dissociation of the dmpm ligands, it is apparently the attack of NO^+ upon the more reactive oxidized species $[Re_2Cl_4(\mu\text{-dmpm})_3]^+$ that leads to the formation of $Re_2Cl_5(\mu\text{-dmpm})_2(NO)$. This is shown through the reaction of $[Re_2Cl_4(\mu\text{-dmpm})_3]PF_6$ with $NOPF_6$ to produce $Re_2Cl_5(\mu\text{-dmpm})_2(NO)$. However, this is obviously a complex reaction since some proportion of the dirhenium species must be sacrificed to provide the extra chloride ligand that becomes incorporated into the final product. Interestingly, when the reaction is carried out in the presence of added chloride ion we observed no increase in the yield of $Re_2Cl_5(\mu\text{-dmpm})_2(NO)$, so free Cl^- is not required.

The diamagnetic complex $Re_2Cl_5(\mu\text{-dmpm})_2(NO)$ constitutes the first example of a triply bonded dimetal compound that contains a nitrosyl ligand.

Supplementary material

Tables of anisotropic thermal parameters, full listings of bond distances and bond angles, and observed and calculated structure factors are available on request from R.A.W. Further details concerning the structure determination can be obtained from Dr P. E. Fanwick of this department.

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