The Oxygenation of the Electron-rich Triple Bond in the Complexes $[Re_2X_4(\mu\text{-dppm})_2]$ [X = Cl or Br; dppm = bis(diphenylphosphino)methane]. Multielectron Redox Behaviour involving Retention of the $Re_2X_4P_4$ Unit

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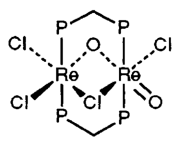
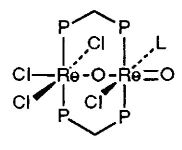
The reactions of the triply bonded complexes $[Re_2X_4(\mu\text{-dppm})_2]$ (X = Cl or Br; dppm = $Ph_2PCH_2PPh_2$) with O_2 proceed to give the products $[Re_2(\mu\text{-O})(\mu\text{-X})(O)X_3(\mu\text{-dppm})_2]$ and $[Re_2(\mu\text{-O})(O)_2X_4(dppm)_2]$ in high yield in which net four- and six-electron redox reactions have occurred and the integrity of the ligand sets of the precursor complex is preserved.

The triply-bonded dirhenium(II) complexes $[Re_2X_4(\mu\text{-dppm})_2]$ **1** (**1a** X = Cl, **1b** X = Br),[1,2] which are useful synthons in dirhenium chemistry,[3] have found application in a variety of redox reactions including the reductive coupling of organic molecules,[4,5] the oxidative additions of reagents such as CS_2,[6] H_2S[7] and Ph_2PH[8] across the Re≡Re bond, and the formation of charge-transfer complexes.[9] In these reactions, **1** delivers up to two electrons in the redox process, which in all instances proceed with retention of the $[Re_2(\mu\text{-dppm})_2]$ unit. We now report the reactions of **1** with O_2, which are unprecedented in the field of multiply bonded dimetal chemistry[10] in that *both* four- and six-electron metal-based redox reactions ensue to give the dimetal complexes $[Re_2(\mu\text{-O})(\mu\text{-X})(O)X_3(\mu\text{-dppm})_2]$ **2** (**2a** X = Cl, **2b** X = Br) and $[Re_2(\mu\text{-O})(O)_2X_4(\mu\text{-dppm})_2]$ **3** (**3a** X = Cl, **3b** X = Br), with complete retention of the ligand sets present in **1a** and **1b**.†

The exposure of a stirred solution of **1a** (0.10 g; 0.078 mmol) in 2 ml of $CHCl_3$ to an atmosphere of O_2 for *ca.* 7 h leads to the precipitation of brown $[Re_2(\mu\text{-O})(\mu\text{-Cl})(O)Cl_3(\mu\text{-dppm})_2]$ **2a** in high yield (*ca.* 70%). A similar reaction course occurs when dichloromethane, acetone, tetrahydrofuran, benzene or toluene are used as the reaction solvents. The analogous bromide complex **2b** is likewise formed from **1b** (isolated yield *ca.* 70%). The reactions of solutions of **1** or **2** in the aforementioned solvents with O_2 for longer periods (several hours or several days depending upon the particular starting material and solvent used) lead to the precipitation of green crystalline $[Re_2(\mu\text{-O})(O)_2X_4(\mu\text{-dppm})_2]$ **3**, which can be isolated in yields of up to 75%. These reactions do not proceed in the absence of



2a



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† Earlier studies have shown that four-electron and six-electron redox reactions can occasionally occur, as in the conversions of $[Ru_2R_6]$ to $[Ru_2(\mu\text{-O})_2R_6]$[11] and $[Mo_2(S_2CNEt_2)_4]$ to $[Mo_2O_3(S_2CNEt_2)_4]$,[12] but these have not previously been coupled in the same system.

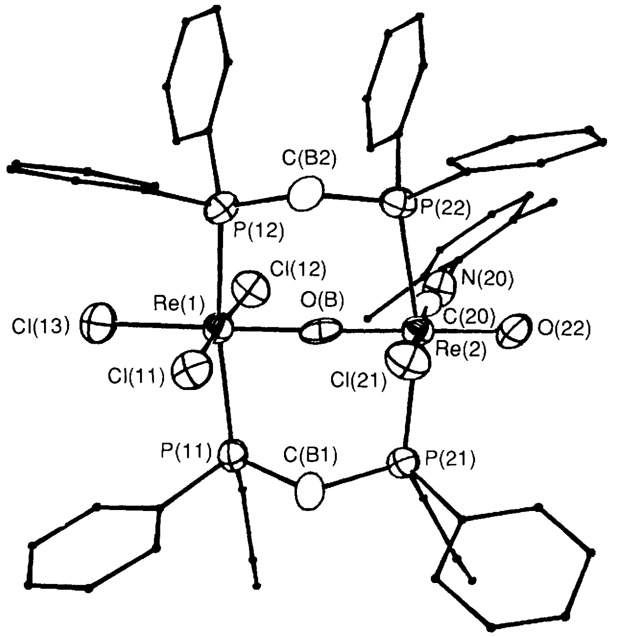

Fig. 1 ORTEP representation of the structure of the $[Re_2(\mu\text{-}O)(O)Cl_4(\mu\text{-dppm})_2(CNxyl)]$ **4a** molecule. Thermal ellipsoids are drawn at the 50% probability level except for the phenyl and xylyl group carbon atoms which are circles of arbitrary radius. Selected bond distances (Å) and bond angles (°): Re(1)–Cl(11) 2.389(5), Re(1)–Cl(12) 2.403(5), Re(1)–Cl(13) 2.345(5), Re(1)–P(11) 2.459(5), Re(1)–P(12) 2.446(5), Re(1)–O(B) 1.94(1), Re(2)–Cl(21) 2.424(5) Re(2)–P(21) 2.484(5), Re(2)–P(22) 2.492(5), Re(2)–O(B) 1.79(1), Re(2)–O(22) 1.76(1), Re(2)–C(20) 2.07(2), N(20)–C(20) 1.12(2); Cl(13)–Re(1)–O(B) 176.9(3), Re(1)–O(B)–Re(2) 176.0(7), O(B)–Re(2)–O(22) 177.6(5), P(11)–Re(1)–P(12) 163.7(2), P(21)–Re(2)–P(22) 162.3(2), N(20)–C(20)–Re(2) 172(2).

a source of gaseous O_2 under the present reaction conditions. Furthermore, we can rule out small amounts of water as being the source of the oxygen in either of these redox processes since the course of the reactions proceed in the same fashion under anhydrous conditions and the presence of small controlled amounts of water; H_2 is not a reaction byproduct, thereby ruling out the occurrence of the following reaction: $\mathbf{1} + H_2O \rightarrow \mathbf{2} + H_2$.

The IR spectra of **2** show characteristic ν(Re=O) and ν(Re–O–Re) modes at *ca.* 910m-s and *ca.* 775m cm^{-1}, respectively, and a crystal structure determination of **2a** reveals an edge sharing bioctahedral structure; the Re–Re distance of 3.363(2) Å accords with the absence of a Re–Re bond.‡ This structure is supported by the derivatization of **2a** upon its reaction with organic isocyanides (RNC) to produce 1 : 1 adducts of the type $[Re_2(\mu\text{-}O)(O)Cl_4(\mu\text{-dppm})_2(CNR)]$ **4**. The single crystal X-ray structure of the compound with R = $C_6H_3\text{-}2,6\text{-}Me_2$ (xyl) **4a** is shown in Fig. 1.§ Coordination of RNC leads to an opening up of the [Re(μ-O)(μ-Cl)Re] unit of **2a** to produce a corner-sharing bioctahedral structure. Of particular interest in this structure is the disparity of the Re–O distances within the bridging Re–O–Re unit; the distances Re(1)–O(B) and Re(2)–O(B) differ by 0.15 Å. The two Re–O distances about Re(2) are very similar [1.76(1) and 1.79(1) Å], so that the linear Cl–Re–O–Re=O unit can be represented formally as $Cl\text{–}Re^{III}\cdots O\text{=}Re^{V}\text{=}O$ or, at least, have a major contribution from this form. Accordingly, it appears that the four-electron oxidation of **1** proceeds primarily through oxygenation at one metal centre with a concomitant structural rearrangement (including loss of the Re–Re bond) and some degree of charge equalization between the two metal centres.

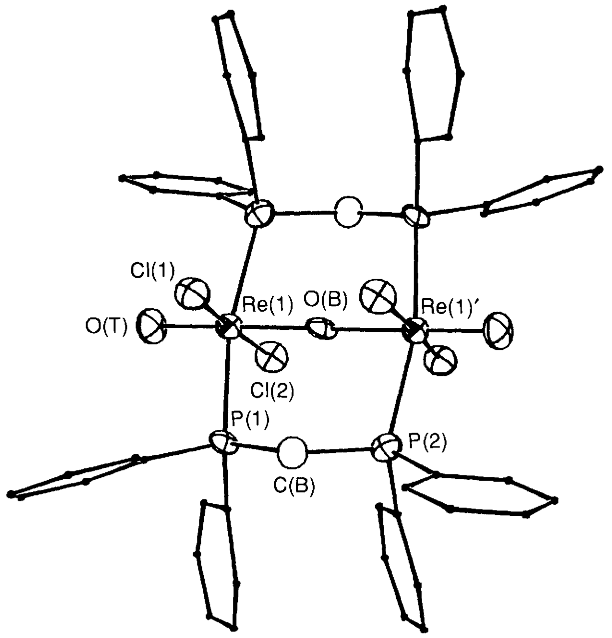

Fig. 2 ORTEP representation of the structure of the $[Re_2(\mu\text{-}O)(O)_2Cl_4(\mu\text{-dppm})_2]$ **3a** molecule. Thermal ellipsoids are drawn at the 50% probability level except for the phenyl group carbon atoms, which are circles of arbitrary radius. Selected bond distances (Å) and bond angles (°): Re(1)–Cl(1) 2.387(4), Re(1)–Cl(2) 2.435(4), Re(1)–P(1) 2.488(4), Re(1)–P(2) 2.454(4), Re(1)–O(B) 1.910(1), Re(1)–O(T) 1.68(1); Re(1)–O(B)–Re(1)′ 180.0, O(B)–Re(1)–O(T) 175.3(4).

Both **2** and **4** exhibit Knight-shifted ^1H NMR spectra and are weakly paramagnetic; for example, crystalline **2a** has a μ_{eff} value of 1.13 BM at 280 K (1 BM = 9.27402×10^{-24} J T^{-1}), which decreases to 0.42 BM at 5 K. We might anticipate that the 'lower valent' rhenium centre in **4** would be readily oxidized, and, in accord with this, we find that a reversible one-electron oxidation at *ca.* +0.3 V (*vs.* Ag/AgCl, by cyclic voltammetry in 0.1 mol dm^{-3} $Bu^n{}_4NPF_6\text{–}CH_2Cl_2$), can be accessed by $[(\eta^5\text{-}C_5H_5)_2Fe]PF_6$ in CH_2Cl_2 to give paramagnetic $[Re_2(\mu\text{-}O)(O)Cl_4(\mu\text{-dppm})_2(CNR)]PF_6$ **5**. A magnetic moment of *ca.* 2.7 BM was measured for a CH_2Cl_2 solution of **5a** (R = $C_6H_3\text{-}2,6\text{-}Me_2$), while for a solid sample a superconducting quantum interference device (SQUID) measurement gave μ_{eff} = 3.23 BM at 280 K and 2.47 BM at 5 K.

The reaction of **2** with more O_2 leads to further oxidation of the dirhenium unit to form the symmetrical, diamagnetic dirhenium(V) complexes of type **3**, in which the very stable linear O=Re–O–Re=O unit is present. The crystal structure of **3a** (Fig. 2)§ shows that the dppm ligands retain their *trans*

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‡ Although the structural refinement is complicated by a disorder involving the terminal oxo and chloro ligands the structure has been modelled satisfactorily. At the present stage of refinement $R = 0.068$ ($R_w = 0.082$). Full details will be published in due course.

§ *Crystal data* for $[Re_2(\mu\text{-}O)(O)Cl_4(\mu\text{-dppm})_2(CNxyl)]\cdot CH_2Cl_2\cdot H_2O$ **4a** at +20 °C: space group $P\bar{1}$ with $a = 14.316(3)$, $b = 14.818(2)$, $c = 16.840(2)$ Å, $\alpha = 99.60(1)$, $\beta = 106.38(1)$, $\gamma = 97.26(1)°$, $Z = 2$, $D_c = 1.548$ g cm^{-3}. An empirical absorption correction was applied and hydrogen atoms of the dppm and xylNC ligands were included at fixed positions and constrained to ride on their C atoms. The final residuals were $R = 0.056$ ($R_w = 0.082$) and goodness of fit 2.639 for 5978 data with $I > 3.0\sigma(I)$.

For $[Re_2(\mu\text{-}O)(O)_2Cl_4(\mu\text{-dppm})_2]\cdot 2CH_2Cl_2$ **3a** at +20 °C: space group $P\bar{1}$ with $a = 11.264(4)$, $b = 11.317(4)$, $c = 12.966(7)$ Å, $\alpha = 103.86(4)$, $\beta = 104.24(4)$, $\gamma = 113.54(3)°$, $Z = 1$, $D_c = 1.834$ g cm^{-3}. An empirical absorption correction was applied and hydrogen atoms of the dppm ligands were included at fixed positions and constrained to ride on their C atoms. The final residuals were $R = 0.052$ ($R_w = 0.072$) and goodness of fit 1.793 for 2872 data with $I > 3.0\sigma(I)$.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

bridging disposition, in spite of the very long Re···Re distance (*ca.* 3.83 Å) that is spanned. This behaviour demonstrates the considerable stability of the [Re(μ-dppm)$_2$Re] unit in its role as a template for multi-electron redox chemistry. What is even more remarkable in the case of the oxygenation reactions, is that the ligand set present in **1** is retained through this series of reactions. Further studies are underway to examine in detail the properties and reactivities of the unusual unsymmetrical complexes of types **2**, **4** and **5**.

Support from the National Science Foundation (Grant No. CHE91-07578 to R. A. W. and CHE89-14915 to K. R. D.) is gratefully acknowledged.

Received, 28th August 1992; Com. 2/04644J

References

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

2 T. J. Barder, F. A. Cotton, K. R. Dunbar, G. L. Powell, W. Schwotzer and R. A. Walton, *Inorg. Chem.*, 1985, **24**, 2550.

3 R. A. Walton, *Polyhedron*, 1989, **8**, 1689.

4 D. Esjornson, D. R. Derringer, P. E. Fanwick and R. A. Walton, *Inorg. Chem.*, 1989, **28**, 2821.

5 K.-Y. Shih, P. E. Fanwick and R. A. Walton, unpublished results.

6 J.-S. Qi, P. W. Schrier, P. E. Fanwick and R. A. Walton, *Inorg. Chem.*, 1992, **31**, 258.

7 K.-Y. Shih, P. E. Fanwick and R. A. Walton, *J. Chem. Soc., Chem. Commun.*, 1992, 375.

8 I. Ara, P. E. Fanwick and R. A. Walton, *Polyhedron*, 1992, **11**, 1277; *J. Cluster Sci.*, 1992, in the press.

9 S. L. Bartley and K. R. Dunbar, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 448.

10 F. A. Cotton and R. A. Walton, *Multiple Bonds Between Metal Atoms*, Wiley, New York, 1982 and references cited therein; F. A. Cotton and R. A. Walton, *Struct. Bonding (Berlin)*, 1985, **62**, 1 and references cited therein.

11 R. P. Tooze, G. Wilkinson, M. Motevalli and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1986, 2711.

12 D. F. Steele and T. A. Stephenson, *Inorg. Nucl. Chem. Lett.*, 1973, **9**, 777; P. Vella and J. Zubieta, *J. Inorg. Nucl. Chem.*, 1978, **40**, 477.

Typeset and printed by Black Bear Press Limited, Cambridge, England