Preliminary communication

SYNTHESIS AND STRUCTURE OF A NOVEL BIS-μ-OXO RHENIUM(VI) DIMER: $Re_2O_2(\mu\text{-O})_2(CH_2CMe_2Ph)_4$

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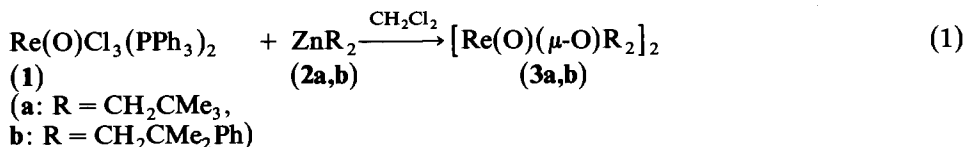
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Summary

The complex $Re(O)Cl_3(PPh_3)_2$ reacts with dialkyl zinc reagents in CH_2Cl_2 to give the novel bis-μ-oxo rhenium(VI) dimer $[Re(O)(\mu\text{-O})R_2]_2$. The molecular structure has been determined by single-crystal X-ray diffraction methods.

Structurally characterized oxo alkyl complexes of the transition metals are few, and only recently have synthetically useful methods for their preparation been developed [1]. An early example was the observation by Wilkinson and coworkers that reaction of either $ReOCl_4$ or $Re(O)Cl_3(PPh_3)_2$ (1) with excess RLi or RMgX reagents in ether gives the complexes $ReOR_4$ and $Re_2O_3R_6$ (R = Me, CH_2SiMe_3). This was shown to involve air oxidation of a reduced intermediate [2]. Other have noted that metal oxo complexes are prone to reduction by alkylating reagents especially in the presence of ether solvents [3]. Thus we set out to examine the alkylation chemistry of metal oxo complexes using less strongly reducing zinc reagents in non-coordinating solvents. Herein we wish to report the synthesis of novel bis-μ-oxo dimers $[ReO(\mu\text{-O})(R_2)]_2$ (R = CH_2CMe_3 and CH_2CMe_2Ph) from the reaction of 1 with dialkyl zinc reagents in dichloromethane.

The readily available oxo complex $Re(O)Cl_3(PPh_3)_2$ (1) [4] was observed to react with the dialkyl zinc reagents 2a,b in CH_2Cl_2 to give as the major isolable product the complexes 3a,b in 22–38% isolated yield following chromatography (eq. 1). In a typical reaction a solution of 205 mg (1 mmol) $Zn(CH_2CMe_3)_2$ (2a) [5] in 20 ml CH_2Cl_2 was added dropwise to a suspension of 835 mg (1 mmol) 1 in 100 ml CH_2Cl_2 at 0°C. The solution was warmed to 34°C for 1 h, filtered and the solvent removed. The resulting residue was chromatographed on Florisil eluting the product with pentane/CH_2Cl_2 (1/1) as a fast moving yellow band. If more than two

equivalents of zinc reagent were used the yield decreased with some increase in the yield of a minor red byproduct [12].

$$\text{Re(O)Cl}_3(\text{PPh}_3)_2 \quad + \quad \text{ZnR}_2 \xrightarrow{\text{CH}_2\text{Cl}_2} \left[\text{Re(O)}(\mu\text{-O})\text{R}_2\right]_2 \tag{1}$$

$$\begin{array}{lll} \textbf{(1)} & \textbf{(2a,b)} & \textbf{(3a,b)} \end{array}$$

(**a**: R = CH$_2$CMe$_3$,
b: R = CH$_2$CMe$_2$Ph)

Compounds **3a,b** are readily soluble in all conventional organic solvents and were obtained as diamagnetic air-stable yellow needles by crystallization from ether [6]. Elemental analyses indicated the absence of both phosphorus and chlorine and the molecular formula [ReO$_2$R$_2$]$_n$. In the ^{1}H NMR spectra all alkyl groups are equivalent, but the α-protons as well as the geminal methyls in **3b** are diastereotopic, suggesting a dissymmetric metal environment with a plane of symmetry. The infrared spectra contain absorptions characteristic of terminal oxo ligands at ca. 1020 cm^{-1} and a weaker band at ca. 740 cm^{-1} which may be the bridging μ-oxo ligands [9]. Mass spectra (electron impact), however, yielded only ions derived from the mononuclear fragments ReO$_2$R$_2$.

Conclusive evidence for the dinuclear bis-μ-oxo structure of these complexes was obtained from a single-crystal X-ray diffraction analysis of compound **3b** [8]. ORTEP drawings of the full molecule and the Re$_2$O$_4$C$_4$ core are shown in Figs. 1 and 2. The most remarkable feature of this molecule is the *cis* arrangement of the terminal oxo ligands and the concave butterfly arrangement of the two bridging oxo ligands. The angle between the two planes defined by the two metals and each of the μ-oxo ligands 141°. The Re–Re separation of 2.61 Å and the observed diamagnetism of these complexes are consistent with the presence of a Re–Re single bond and a formal oxidation state of +6 for each rhenium.

Although 2.61 Å is relatively short for a Re–Re single bond, the dominant influence on the intermetal separation appears to be the number of bridging groups. For example, Re$_2$(C$_5$Me$_5$)$_2$(CO)$_4$(μ-O) [10] compound **3b**, and Re$_2$(μ-O)(μ-OMe)$_2$-(OMe)$_4$ [11] with one, two and three bridging oxygens to have Re–Re distances of 2.82, 2.61 and 2.56 Å, respectively. A similar bis-μ-oxo butterfly dimer was recently reported by Herrmann and coworkers [10]. In their example a Re–Re double bond is present, yet the intermetal distance is quite similar, 2.65 Å and a butterfly angle of 122° was observed.

The mechanism of formation of these complexes is not clear, but requires the oxidation of an intermediate. We do not believe that molecular oxygen is involved. All attempts to rigorously exclude oxygen, or purposely introduce it, have had only a marginal influence on the yield. NMR spectra of the crude reaction mixture prior to chromatography reveal only PPh$_3$ and **3**. Moreover, yields are consistently less than 50% and no significant amounts of unreacted starting material or soluble side products are evident [12]. Together these observations suggest that the oxidant in these reactions is a second rhenium oxo complex.

The preparation of the complexes **3** and their unique bis-μ-oxo structure add to the rich organometallic chemistry of rhenium oxo complexes. Recent observations by a number of researchers have shown that these complexes display a varied oxidation-reduction chemistry, often initiated by such non-standard reagents as air, PPh$_3$ or alkynes [2,10,11,13]. The observation that alkylation leads to the expulsion
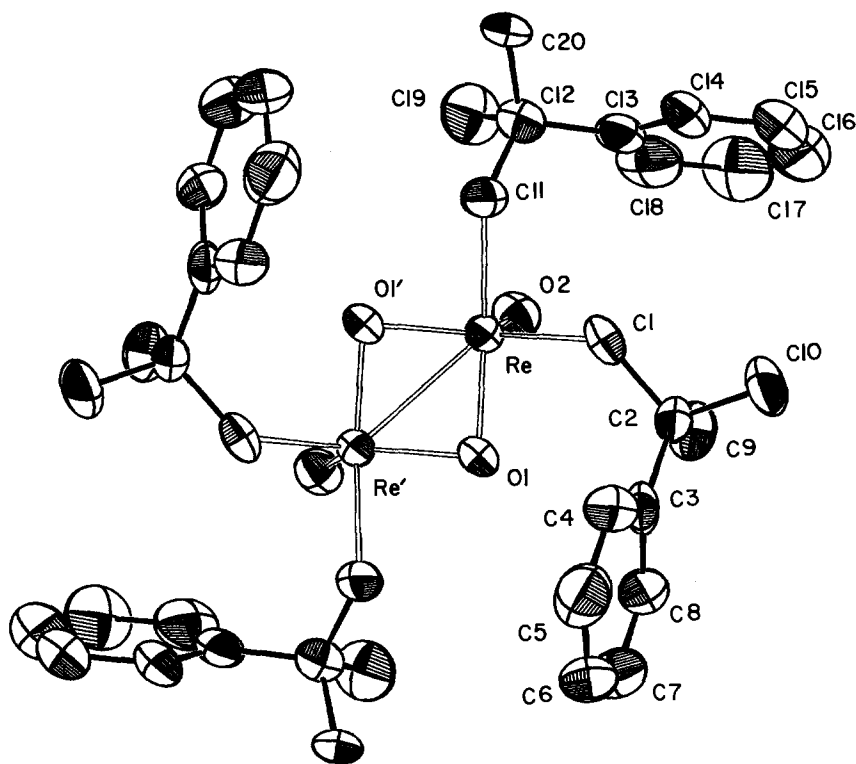
Fig. 1. ORTEP drawing of **3b** (50% probability, hydrogens excluded). Selected bond distances (Å) and angles (°): Re–Re 2.6116(7), Re–O(1) 1.934(6), Re′–O(1) 1.903(6), Re–O(2) 1.64(1), Re–C(1) 2.16(2), Re–C(11) 2.20(1), O(1)–Re–O(1) 87.3(3), Re–O(1)–Re′ 85.8(3), Re–Re′–O(2) 114.9(3), Re–Re′–C(1) 122.4(3), Re–Re′–C(11) 125.5(3), O(2)–Re–C(1) 106.9(4), O(2)–Re–C(11) 101.5(5), Re–C(1)–C(2) 122.7(7).
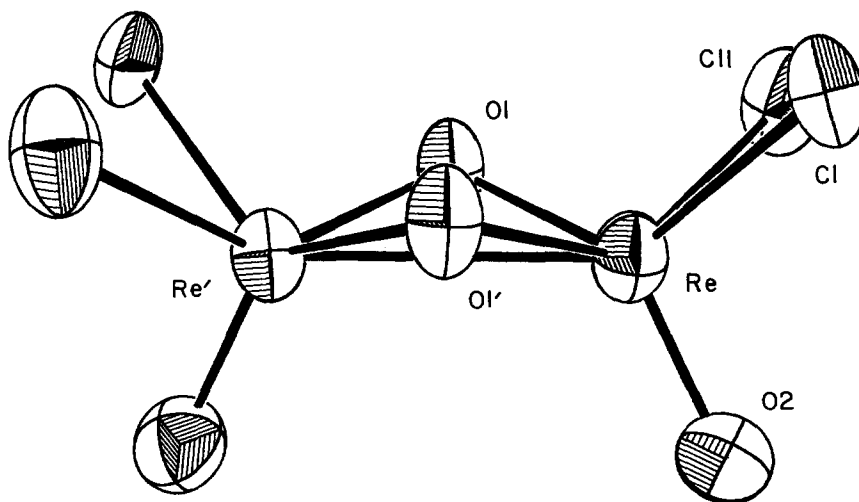

Fig. 2. ORTEP drawing of **3b** showing only the $Re_2O_2(\mu\text{-}O_2)C_4$ core. The angle defined by the planes containing Re–Re′–O(1) and Re–Re′–O(1)′ is 140.9°.

of all soft ligands (i.e. PR_3) and the formation of a μ-oxo bridged structure indicates the preference of rhenium in these oxidation states for hard π-donor ligands. Indeed, **3** resists addition of neutral donor ligands such as PMe_3, but does react with hard bases such as t-butoxide. This property is likely crucial to much of the catalytic behavior of metal oxo complexes [14]. These and other reactions of metal oxo alkyls will be the subject of future investigations.

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5 **2a** and **2b** were prepared by the literature method [7] and identified spectroscopically. **2a**: ^{1}H NMR (C_6D_6): 1.06 (9H), 0.46 ppm (2H). ^{13}C NMR ($CDCl_3$): 37.02 (CH_2), 35.65 (CH_3), 32.11 ppm (CR_4). **2b**: ^{1}H NMR ($CDCl_3$): 7.2–7.5 (5H), 1.38 (6H), 0.88 ppm (2H). ^{13}C NMR (C_6D_6): 126.3, 125.0, 124.5 (C_6H_5), 37.51 (CR_4), 36.78 (CH_2), 34.23 ppm (CH_3).

6 Spectroscopic and anlytical data. **3a**: ^{1}H NMR (C_6D_6): 3.65 (d, J 11.8 Hz, 2H), 3.12 (d, J 11.8 Hz, 2H), 1.43 ppm (s, 9H). ^{13}C NMR ($CDCl_3$): 70.77 (CH_2), 37.46 (CMe_3), 33.44 ppm (CH_3). IR (KBr): 1017s (Re=O), 740 m cm^{-1} (Re–O–Re). MS: m/e 360.8 (0.55, $ReO_2R_2^+$, ^{187}Re), 358.8 (0.32, $ReO_2R_2^+$, ^{185}Re). m.p. 133–135°C. Anal. Found: C 33.90 H, 6.38. $C_{20}H_{44}O_4Re_2$ calcd.: C, 33.31, H, 6.15%. **3b**: ^{1}H NMR ($CDCl_3$): 7.15–7.40 (m, Ph's), 3.74 (d, J 12.2 Hz, 1H), 3.17 (d, J 12.2 Hz, 1H), 1.60 (s, 3H), 1.55 ppm (s, 3H). ^{13}C NMR ($CDCl_3$): 151.2, 128.0, 125.8, and 125.6 (C_6H_5), 69.65 (CH_2), 43.37 (CR_4); 32.47 and 31.97 ppm (CH_3's). IR (KBr): 1022s (Re=O), 760s cm^{-1} (Re–O–Re). MS: m/e 485 (0.01, $ReO_2R_2^+$, ^{187}Re), 483 (0.01, $ReO_2R_2^+$, ^{185}Re), 353, 352, 351, 350 (9 : 30 : 8 : 18, ReO_2R^+). m.p. 120–121°C. Anal. Found: C, 49.47; H, 5.44. $C_{40}H_{52}O_4Re_2$ calcd.: C, 49.56; H, 5.41%.

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8 Crystals of **3b** are orthorhombic space group $Fdd2$ with a 24.971(3) A, b 46.316(5), c 6.448(1) Å, V 7457 Å^3, $Z = 16$ and D 1.727 g cm^{-3}. A total of 3132 reflections were collected in the $3 < 2\theta < 52$ shell and analytical absorption corrections applied. Averaging then gave 2074 symmetry independent reflections, which were used to give a final $R = 0.032$ and $R_w = 0.046$. Data tables and details of the crystal structure determination have been deposited with the Cambridge Structural Database.

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