Interaction of Oxotetrachlororhenium(VI) with Alcohols, Lithium Alkoxides, and Bis(trimethylsilylamido)lithium; *X*-Ray Crystal Structure of Tetramethoxodioxo-μ-dimethoxo-μ-oxo-dirhenium(VI)(*Re–Re*)†

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Summary The syntheses of $Re_2O_3(OMe)_6$, $ReO(OBu^t)_4$, $[ReO(OPr^i)_5]^-Li^+$, and $ReO[N(SiMe_3)_2]_3$ are reported; the structure of $Re_2O_3(OMe)_6$ has been determined by a single crystal *X*-ray analysis.

THE only rhenium alkoxides, none having more than one alkoxo ligand[1a] [except $Re_2(CO)_6(OR)_3$] have tertiary phosphine[1b] or methyl and acetate[2] groups. We have been unable to confirm the reported compounds $Re(OR)_3$ (R = Et, Pr^i),[3] and have also as yet failed to isolate alkoxide or dialkylamide compounds starting with $ReCl_5$, $Re_3Cl_9.L_n$ (L = H_2O, *n* = *ca.* 6; L = THF, *n* = 3[4]), $ReCl_4(THF)_2$, *etc.* (THF = tetrahydrofuran), although petroleum-soluble species were formed. The only fully characterised products have been obtained from oxotetrachlororhenium(VI).

When $ReOCl_4$ is dissolved in methanol in the presence of a tertiary amine, the orange crystalline petroleum-soluble complex $Re_2O_3(OMe)_6$ is obtained. The ^1H n.m.r. spectrum shows two singlets at δ 0·20 and 5·03 (area ratio 1 : 2) which can be assigned to bridging and terminal OMe units respectively. The i.r. spectrum shows the presence of terminal and bridging Re=O bands [at 968, 982 cm^{-1} ν(Re=O), and 756 cm^{-1} ν(Re–O)], as well as bands due to methoxo groups; ν(C–O) appears at 1025 cm^{-1}. The ν(Re=O) band is split into a doublet unlike previously reported linear O=Re–O–Re=O units[5] presumably owing to the lower symmetry of the bent Re_2O_3 unit (in the Figure) in our compound, of which we believe this is the first example. The highest peak in the mass spectrum occurs at *m/e* = 342 a.m.u., corresponding to the fragment $ReO_2(OMe)_4$. The molecular ion is not seen. The structure of this diamagnetic, air-sensitive complex (see Figure) has been determined by an *X*-ray crystallographic study.

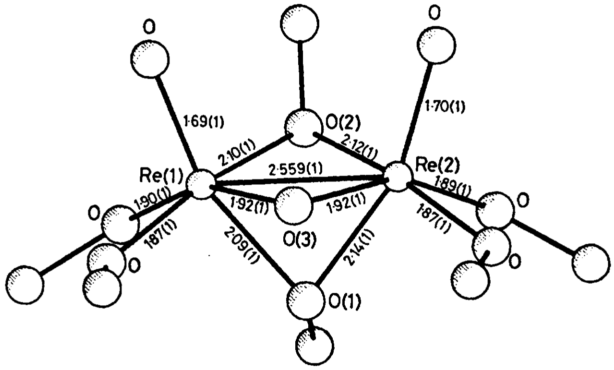

FIGURE. The molecular structure of $Re_2O_3(OMe)_6$.

Crystal data: $C_6H_{18}O_9Re_2$. *M* = 606·6, monoclinic, *a* = 12·142(1), *b* = 15·369(1), *c* = 7·311(1) Å, *β* = 90·22(1)°, *U* = 1364·4 Å^3, space group $P2_1/n$, *Z* = 4, D_C = 2·953 g cm^{-3}, *F*(000) = 1104, μ(Mo-K_α) = 179·7 cm^{-1}, λ(Mo-K_α) = 0·71069 Å.

Intensity data were collected on a Nonius CAD4 diffractometer with Mo-K_α radiation and corrected for Lorentz and polarisation and absorption effects. The structure was solved by direct methods and refined by least-squares to an *R* value of 0·059 for 1965 reflections with $F_o > 4\,\sigma(F_o)$.

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† No reprints available.

All atoms were treated anisotropically, but the hydrogen atoms were ignored.‡

The molecular structure and some important bond lengths are shown in the Figure. It contains two Re atoms bridged by one oxo and two methoxo groups and has an overall co-ordination geometry of a distorted confacial bioctahedron. All the Re–O–Re bridge angles are acute, with that involving the oxo groups *ca.* 10° wider than those with the methoxo groups [84·8 *vs.* 74·4 and 74·7(3)°]. The acute bridge angles and short Re–Re distance [2·559(1) Å] indicate the presence of a Re–Re single bond in the compound.

The interaction of $ReOCl_4$ with Bu^tOH, or better, $LiOBu^t$ leads to the isolation of the paramagnetic alkoxide $ReO(OBu^t)_4$ obtained as large air-sensitive blue crystals soluble in hydrocarbons and thermally unstable above 0 °C. The ^1H n.m.r. spectrum shows a very broad singlet at δ 1·15 and the i.r. spectrum has a ν(Re–O) band at 992 cm^{-1} and bands assigned to alkoxy vibrations, ν(C–O), appear at 1167 cm^{-1}. The e.s.r. spectrum is consistent with a monomeric Re^{VI} complex. The interaction of $ReOCl_4$ with $LiOPr^i$, however, leads to the isolation of the thermally stable, paramagnetic salt $[ReO(OPr^i)_5]^-Li^+$, obtained as pale green, moisture-sensitive needles from petroleum. In the ^1H n.m.r. spectrum a broad peak is seen at δ 1·35 although a peak due to the unique proton is not observed presumably owing to paramagnetic broadening. The i.r. spectrum shows ν(Re=O) and ν(C–O) bands at 965 and 1115 cm^{-1} respectively. The e.s.r. spectrum is again consistent with a monomeric Re^{VI} species. An *X*-ray crystal structure determination of this complex is in progress.

From the reaction of $ReOCl_4$ with $LiN(SiMe_3)_2$, the red, diamagnetic, crystalline, very petroleum-soluble $ReO[N(SiMe_3)_2]_3$ is obtained. The ^1H n.m.r. spectrum shows a sharp singlet at δ 0·33 and the i.r. spectrum shows the ν(Re=O) band at 970 cm^{-1}. Although rhenium amides have been made from $ReOCl_4$[6] our compound is the first example of a rhenium dialkylamide. This volatile (sub. 60 °C, 10^{-1} Torr) amide is moderately air-stable and no products have been isolated from its reactions with CO_2, CS_2, PMe_3, or Na/K alloy.

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‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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