Improved Syntheses of Tetrachloro-oxorhenium(VI) and Chlorotrioxorhenium(VII). Synthesis of Alkoxo- and Dialkylamido-rhenium Compounds. The Crystal and Molecular Structures of Di-μ-methoxo-tetramethoxo-μ-oxo-dioxodirhenium(VI) (*Re–Re*), Bis[lithium pentaisopropoxo-oxorhenate(VI)–lithiumchloride–tetrahydrofuran(1/1/2)], and *trans*-Tetraphenoxobis(trimethylphosphine)rhenium(IV) †

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Much improved synthetic procedures for $ReOCl_4$, ReO_3Cl, $ReOMe_4$, $Li_2[ReMe_8]$, and $ReMe_6$ are described. Interaction of $ReOCl_4$ with methanol in the presence of amine gives the unusual alkoxo-compound $(MeO)_2ORe(\mu\text{-}O)(\mu\text{-}OMe)_2ReO(OMe)_2$, (A), while $LiOBu^t$ gives $ReO(OBu^t)_4$, and $LiOPr^i$ gives an unusual dimeric species $\{Li[ReO(OPr^i)_5].LiCl(thf)_2\}_2$, (B) (thf = tetrahydrofuran). The interaction with phenol in the presence of trimethylphosphine leads to the compound *trans*-$Re(OPh)_4(PMe_3)_2$, (C), while with lithium bis(trimethylsilyl)-amide a unique four-co-ordinate rhenium(V) compound, $ReO\{N(SiMe_3)_2\}_3$, is obtained. The crystal and molecular structures of (A)—(C) have been determined by *X*-ray crystallography. Compound (A) is monoclinic, space group $P2_1/n$, $a = 12.142(1)$, $b = 15.369(1)$, $c = 7.311(1)$ Å, $\beta = 90.22(1)°$, and $Z = 4$. Compound (B) is triclinic, space group P_1, $a = 14.602(5)$, $b = 13.363(3)$, $c = 9.244(6)$ Å, $\alpha = 98.39(4)$, $\beta = 102.35(5)$, $\gamma = 68.71(2)°$, and $Z = 1$. Compound (C) is monoclinic, space group $P2_1/c$, $a = 10.079(2)$, $b = 10.527(3)$, $c = 14.443(3)$ Å, $\beta = 97.28(2)°$, and $Z = 2$. The structures have been refined to *R* values of 0.059 (A), 0.069 (B)' and 0.055 (C) using respectively 1 965, 4 061, and 1 797 observed intensities, measured on a diffractometer.

WITH the exception of the triply alkoxo-bridged carbonyl anions,[1] $[(OC)_3Re(\mu\text{-}OR)_3Re(CO)_3]^-$ (R = Et or Pr^i), other alkoxo-species have only one alkoxo-group and contain tertiary phosphine ligands [2] as in $ReO(OEt)Cl_2(PPh_3)_3$ or methyl and acetate groups as in the insoluble $\{ReMe(OMe)(O_2CMe)\}_n$.[3] We have been unable to confirm the compounds said [4] to have stoicheiometry $Re(OR)_3$ (R = Et or Pr^i). Although we have as yet failed to isolate alkoxide or dialkylamido-compounds starting with $ReCl_5$ and $ReCl_4(thf)_2$ (thf = tetrahydrofuran), we have isolated products from $ReOCl_4$ namely $Re_2O_3(OMe)_6$, whose *X*-ray structure was determined, and $ReO(OBu^t)_4$, $Li[ReO(OPr^i)_5]$, and $ReO[N(SiMe_3)_2]_3$, which were described in a preliminary note; [5] full details of this work are now given. We have subsequently [6] synthesised the trirhenium cluster alkoxide $Re_3Cl_3(OBu^t)_6$ while trimethylsilyloxo-compounds with *N*-t-butylimido-groups $Re(NBu^t)_3(OSiMe_3)$ and $Re_3O_5(NBu^t)_4(OSiMe_3)_3$, the latter having bridging $OSiMe_3$, O, and $OReO_3$ groups, have been recently described.[7]

We also describe improved syntheses of the starting material, $ReOCl_4$, and of ReO_3Cl.

RESULTS AND DISCUSSION

Syntheses.—(1) *Tetrachloro-oxorhenium*(VI) *and chlorotrioxorhenium*(VII). Methods for the synthesis of $ReOCl_4$ are (i) the oxidation of rhenium metal or rhenium halides in thionyl chloride [8] or sulphuryl chloride; [9] or (ii) the interaction of $ReCl_5$ with oxygen in a sealed tube at elevated temperature.[10] These are impractical on a large scale and purification of the oxohalide can be tedious.

Rhenium pentachloride is readily made in large quantities in high yield [11] and we find that direct oxidation with dioxygen just below the melting point (261 °C) in an open system at 1 atm ‡ pressure gives yields of up to 90% $ReOCl_4$, an overall yield from rhenium of over 75%. The loss is due to formation of Re_3Cl_9 on thermal decomposition of $ReCl_5$. Oxygenation at higher temperatures where the $ReCl_5$ burns gives lower yields. The $ReOCl_4$ is readily purified by vacuum distillation or sublimation and quantities *ca.* 25 g have been made in one run. The major contaminant in the product is chlorotrioxorhenium(VII) (per-rhenyl chloride, ReO_3Cl), but this is readily removed as it is a liquid (m.p. 4.5 °C).

By direct oxidation of Re_3Cl_9 which again can be obtained in high yield from $ReCl_5$,[11] ReO_3Cl can be obtained in high yield. Thus, on heating Re_3Cl_9 in a stream of oxygen so that it inflames, the ReO_3Cl can be collected in a cold trap to give, after vacuum distillation, a colourless product in yields exceeding 80% based on rhenium metal. Early routes [12] to ReO_3Cl are tedious and difficult for large quantities while a recent procedure [13] requires chlorine monoxide to react with rhenium halides.

(2) *Interaction of tetrachloro-oxorhenium*(VI) *with alcohols*. (*a*) *Methanol*. The interaction of $ReOCl_4$ with methanol and tertiary amine in diethyl ether leads to an orange diamagnetic complex that crystallises from light petroleum as oxygen- and moisture-sensitive rhombs. The compound can be sublimed with some decomposition at 90 °C (10^{-3} Torr). Analytical and molecular-weight data indicate a stoicheiometry Re_2O_3-

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† No reprints available.

‡ Throughout this paper: 1 atm = 101 325 Pa; 1 Torr = (101 325/760) Pa; 1 B.M. ≈ 9.27×10^{-24} A m².

$(OMe)_6$, (A). Although the molecular ion is not observed, the mass spectrum shows the highest peak at m/e 342, corresponding to $ReO_2(OMe)_4$, while peaks at lower mass correspond to loss of CH_3 and O from this fragment.

The spectroscopic data (Table 1) are consistent with the structure $(MeO)_2ORe(\mu\text{-}O)(\mu\text{-}OMe)_2ReO(OMe)_2$, determined by X-ray study (Figure 1 and below). Thus the ^1H n.m.r. shows two singlets at δ 5.03 and 0.20 p.p.m. (area 2 : 1) indicating two types of MeO groups; the high-field peak is assigned to μ-OMe. The i.r. spectrum has bands expected for OMe groups [ν(CO) at 1 025 cm^{-1}], together with sharp bands at 968 and 982 cm^{-1} assigned to ν(Re=O), and a band at 756 cm^{-1} assigned to ν(Re–O–Re) as found in other species containing the O=Re–O–Re=O unit.[14] Although a linear Re_2O_3 unit occurs in several rhenium complexes,[15] the lower symmetry of the bent unit observed here explains the splitting of the ν(Re=O) band.

TABLE 1

Spectroscopic data for the rhenium alkoxides and rhenium dialkylamide

	^1H n.m.r.		Infrared (cm^{-1})	
Compound	δ/p.p.m.[a]	Assignment	ν(Re=O)	Other vibrations
$Re_2O_3(OMe)_6$	5.03 (s, 2 H) 0.20 (s, 1 H)	Re–OMe μ-(Re–OMe)	982m, 986s 755w [b]	2 950m, 2 910s, 2 860w, 150m, 1 025s, 575s, 548s, 520m [c] 1
$ReO(OBu^t)_4$	1.15	Re–OCMe$_3$	992m	1 380m, 1 358s, 1 230m, 1 167s, 1023w, 917s, 898s, 770m, 730w, 588m, 421m [d]
$Li[ReO(OPr^i)_5]\cdot LiCl$	1.35	Re–OCHMe_2	987m	1 360m, 1 340w, 1 315w, 1 260m, 1 167m, 1 115s, 937s, 832s, 638m, 612s, 570m, 467w, 420w [d]
$ReO[N(SiMe_3)_2]_3$	0.20	N–SiMe$_3$	978	1 400m, 1 248m, 1 100w, 885s, 840s, 772m, 693w, 660m, 432w [d]

[a] Relative to $SiMe_4$ δ = 0.0 p.p.m. [b] ν(Re–O). [c] In carbon disulphide. [d] In Nujol.

(*b*) *Isopropyl and t-butyl alcohols.* Using Pr^iOH brown solutions are obtained but no crystalline product could be isolated. t-Butyl alcohol also gives brown solutions, but from light petroleum low yields of very air-sensitive blue crystals were obtained. Similar blue crystals can be obtained in high yield, however, by interaction of $ReOCl_4$ with $LiOBu^t$, but these are thermally unstable above 0 °C, decomposing to give a black tar and a colourless liquid (mainly C_8 monounsaturated hydrocarbon plus a little Bu^tOH).

The complex is monomeric, and paramagnetic, showing a poorly resolved e.s.r. signal in frozen benzene, consistent with a monomeric, d^1, rhenium(VI) species. The ^1H n.m.r. spectrum shows a broadened singlet at δ 1.15 p.p.m. while the i.r. shows bands at 917 (C–O) and 992 (Re=O) cm^{-1}. It seems reasonable to suggest that this unstable compound is $ReO(OBu^t)_4$.

The reaction of $LiOPr^i$ with $ReOCl_4$ leads to the isolation of green, light petroleum-soluble, paramagnetic crystals of stoicheiometry $Li[ReO(OPr^i)_5]\cdot LiCl$. Crystallisation from thf gives $\{Li[ReO(OPr^i)_5]\cdot LiCl(thf)_2\}_2$, (B), whose structure has been determined by X-ray crystallography (Figure 3 and below). The conductivity in thf is very low (*ca.* 5 cm^2 ohm^{-1} mol^{-1}), evidently due to close ion-pair formation. The complex reacts with moisture but not dry air. The ^1H n.m.r. spectrum has a broad signal at δ = 1.35 p.p.m., while the i.r. shows alkoxo-bands (C–O, 1 115) and ν(Re–O) at 987 cm^{-1}.

The e.s.r. spectrum of a frozen benzene solution of the compound at 9.2 GHz consists of several fairly well resolved features spread over the region 0.15—0.64 T. It is typical of a rhenium(VI) complex with a very large hyperfine structure. It is very difficult to pick out the three sets of six lines expected for $S = \frac{1}{2}$, $I = \frac{5}{2}$ because, as with other rhenium(VI) spectra,[16] the hyperfine lines are not equally spaced and their intensities vary markedly; they are thus easily masked by the 'forbidden' lines which abound. As yet a good interpretation of the spectrum is not feasible but the principal values of the A tensor for rhenium seem to be between about 0.04 and 0.06 cm^{-1}, while those of the g tensor are probably below 2.0. The high solubility of this salt in benzene indicates strong ion pairing, but there is no sign of hyperfine interaction from $Li^+(I = \frac{3}{2})$ in the spectrum of the anion.

(*c*) *Phenol.* The interaction of $ReOCl_4$ with LiOPh gives a purple solution from which no clean product could be isolated. However, the addition of trimethylphosphine gives a black powder insoluble in diethyl ether, benzene, and light petroleum and extraction of this with CH_2Cl_2 leads to a low yield of red, air-stable crystals. X-Ray diffraction studies confirm the structure as *trans*-$Re(OPh)_4(PMe_3)_2$ (C) (Figure 4 and below). The reduction to an octahedral rhenium(IV) complex is presumably due to the phosphine.

(3) *Interaction of* $ReOCl_4$ *with lithium dialkylamides.* With the exception of $LiN(SiMe_3)_2$, the interaction of lithium dialkylamides has so far not lead to the isolation of well defined compounds. However, with $LiN(SiMe_3)_2$ a red, light petroleum-soluble, diamagnetic and volatile (sublimes 60 °C, 10^{-3} Torr) compound that crystallises from petroleum as red tetragonal plates is obtained. Analytical and spectroscopic data clearly show that the compound is $ReO[N(SiMe_3)_2]_3$ which has rhenium(V) in the previously unknown [17] co-ordination of four. The ^1H n.m.r. spectrum has only a sharp singlet at δ = 0.2 p.p.m. due to CH_3 groups, while the i.r. spectrum has a band at 1 248 cm^{-1} due to Si–C and one at 978 cm^{-1} due to Re=O.

(4) *Synthesis of methylrhenium compounds.* The oxotetrachloride is a useful starting material for the synthesis of known rhenium(VI) alkyls, $ReOMe_4$,[14] $ReMe_6$,

and $Li_2[ReMe_8]$,[16,18] giving higher yields than the previous methods starting with $ReOCl_3(PPh_3)_3$, which were somewhat irreproducible and gave very variable yields. Thus, $ReOMe_4$ is obtained by action of a stoicheiometric amount of methyl-lithium on $ReOCl_4$ at low temperatures followed by addition of water after warming. The use of excess of LiMe gives $Li_2[ReMe_8]$ directly and this in turn can be used to generate $ReMe_6$ by addition of water.

Structures.—(1) $Re_2O_3(OMe)_6$. The structure of $Re_2O_3(OMe)_6$, (A), is illustrated in Figure 1, which also indicates the atom labelling used. Interatomic distances and angles are given in Table 2. The molecule contains two rhenium atoms bridged by one oxo- and two methoxo-groups and has the overall geometry of a confacial bioctahedron with considerable distortion. It does not possess any crystallographic symmetry, but has an approximate mirror plane passing through the bridging oxygen atoms. The Re–O–Re bridge angles are all acute, with that involving the oxo-group *ca.* 10° wider than those with the methoxo-groups (83.8 *vs.* 74.4 and 74.7°). The acute angles at the bridging atoms and the short Re–Re distance (2.559 Å) are consistent with the presence of a Re–Re single bond, as required by the observed diamagnetism of the compound.

TABLE 2

Intramolecular interatomic distances and angles for $Re_2O_3(OMe)_6$ (A). The estimated standard deviations are given in parentheses

Bond lengths (Å)

Re(2)–Re(1)	2.559(1)	O(1)–Re(1)	2.094(11)
O(2)–Re(1)	2.097(11)	O(3)–Re(1)	1.917(13)
O(4)–Re(1)	1.874(12)	O(5)–Re(1)	1.903(11)
O(6)–Re(1)	1.690(11)	O(1)–Re(2)	2.139(10)
O(2)–Re(2)	2.121(10)	O(3)–Re(2)	1.916(13)
O(7)–Re(2)	1.867(12)	O(8)–Re(2)	1.891(12)
O(9)–Re(2)	1.703(12)	C(1)–O(1)	1.436(17)
C(2)–O(2)	1.427(18)	C(4)–O(4)	1.499(20)
C(5)–O(5)	1.419(23)	C(7)–O(7)	1.476(20)
C(8)–O(8)	1.443(23)		

Bond angles (°)

O(1)–Re(1)–Re(2)	53.6(3)	O(2)–Re(1)–Re(2)	53.1(3)
O(2)–Re(1)–O(1)	69.9(4)	O(3)–Re(1)–Re(2)	48.1(4)
O(3)–Re(1)–O(1)	73.4(5)	O(3)–Re(1)–O(2)	100.5(5)
O(4)–Re(1)–Re(2)	131.3(4)	O(4)–Re(1)–O(1)	100.9(5)
O(4)–Re(1)–O(2)	165.1(5)	O(4)–Re(1)–O(3)	87.5(6)
O(5)–Re(1)–Re(2)	127.8(4)	O(5)–Re(1)–O(1)	86.9(5)
O(5)–Re(1)–O(2)	84.2(4)	O(5)–Re(1)–O(3)	156.4(5)
O(5)–Re(1)–O(4)	83.6(5)	O(6)–Re(1)–Re(2)	102.2(5)
O(6)–Re(1)–O(1)	153.4(6)	O(6)–Re(1)–O(2)	86.9(6)
O(6)–Re(1)–O(3)	99.4(6)	O(6)–Re(1)–O(4)	104.4(7)
O(6)–Re(1)–O(5)	104.0(6)	O(1)–Re(2)–Re(1)	52.0(3)
O(2)–Re(2)–Re(1)	52.2(3)	O(2)–Re(2)–O(1)	68.6(4)
O(3)–Re(2)–Re(1)	48.1(4)	O(3)–Re(2)–O(1)	72.3(5)
O(3)–Re(2)–O(2)	99.6(5)	O(7)–Re(2)–Re(1)	130.7(4)
O(7)–Re(2)–O(1)	101.7(5)	O(7)–Re(2)–O(2)	165.5(5)
O(7)–Re(2)–O(3)	86.9(6)	O(8)–Re(2)–Re(1)	126.5(4)
O(8)–Re(2)–O(1)	87.1(5)	O(8)–Re(2)–O(2)	83.9(5)
O(8)–Re(2)–O(3)	155.8(5)	O(8)–Re(2)–O(7)	84.9(6)
O(9)–Re(2)–Re(1)	103.0(5)	O(9)–Re(2)–O(1)	152.7(6)
O(9)–Re(2)–O(2)	87.7(6)	O(9)–Re(2)–O(3)	99.8(6)
O(9)–Re(2)–O(7)	103.9(7)	O(9)–Re(2)–O(8)	104.2(6)
Re(2)–O(1)–Re(1)	74.4(3)	C(1)–O(1)–Re(1)	126.4(10)
C(1)–O(1)–Re(2)	124.8(10)	Re(2)–O(2)–Re(1)	74.7(3)
C(2)–O(2)–Re(1)	125.1(11)	C(2)–O(2)–Re(2)	124.7(11)
Re(2)–O(3)–Re(1)	83.8(5)	C(4)–O(4)–Re(1)	128.4(13)
C(5)–O(5)–Re(1)	131.3(10)	C(7)–O(7)–Re(2)	128.5(13)
C(8)–O(8)–Re(2)	130.7(12)		

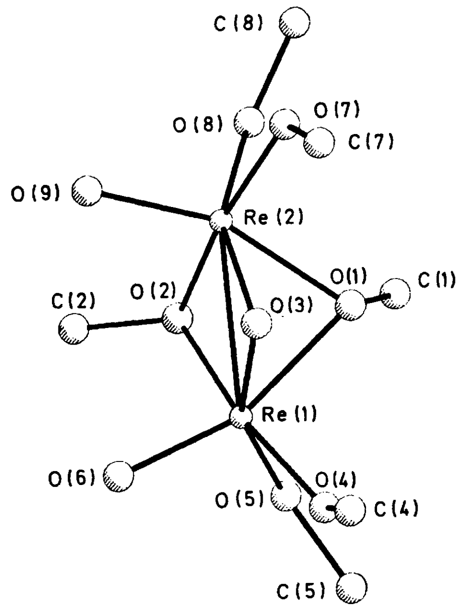

FIGURE 1 Molecular structure of $Re_2O_3(OMe)_6$, (A), showing the atom-numbering

The structural parameters in the two ReO_6 octahedra are nearly the same, but each octahedron shows considerable distortions from idealised geometry. The $O_3Re(O_3)ReO_3$ bioctahedron retains the basic feature of eclipsing of the atoms occupying the corners of the two terminal triangles, but the triangle formed by the three bridging atoms is shifted so that although the Re–Re is still perpendicular to the O(2) · · · O(3) edge, it almost intersects it. The extent of this distortion is expressed by the dihedral angles between the planes Re(1)–O(1)–Re(2)/Re(1)–O(2)–Re(2) 91.1°, Re(1)–O(1)–Re(2)/Re(1)–O(3)–Re(2) 79.4°, and Re(1)–O(2)–Re(2)/Re(1)–O(3)–Re(2) 11.7°, and is well demonstrated by the view chosen for Figure 2.

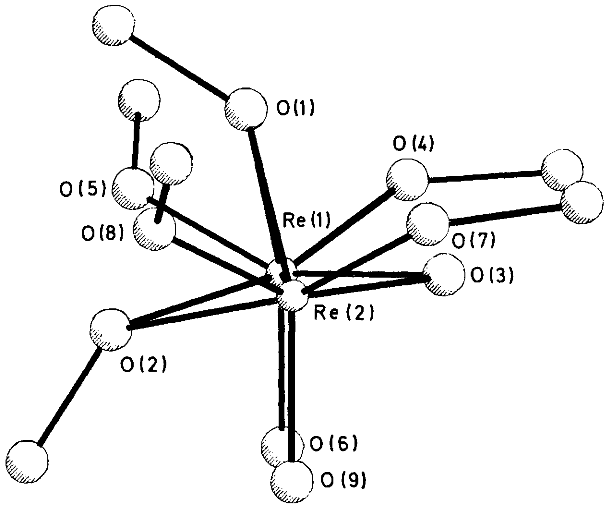

FIGURE 2 View of the $Re_2O_3(OMe)_6$ molecule showing the eclipsing of the terminal ligands and staggering of the bridging oxo-group [O(3)] with the two terminal alkoxo-oxygen atoms [O(4) and O(7)]

One possible explanation for the distortion is the existence of a bent, off-centre, Re···Re interaction, stereochemically active in the space between O(6), O(9), and O(3). This would to some extent explain the uneven distribution of intramolecular O···O contacts (Table 3), where O(3)···O(6), O(9), whilst still very short, are longer than O(3)···O(4),O(7) and O(2)···O(6),O(9).

In fact, one characteristic of this molecule is the considerable intramolecular crowding, as evidenced by the values listed in Table 3. In particular, we note the contacts O(2)···C(1), O(5)···C(1), O(8)···C(1), O(6)···C(2), and O(9)···C(2) which could actually be relieved by the oxygens O(1) and O(2) becoming planar. That this does not happen is probably a reflection of the strain which would occur in the bridges if the oxygen bridging orbitals were sp^2 rather than sp^3 hybridised.

TABLE 3

Selected non-bonded short contacts (Å) in $Re_2O_3(OMe)_6$

(*a*) Intramolecular			
O(1)···O(2)	2.40	O(3)···C(7)	2.81
O(1)···O(3)	2.40	O(4)···O(5)	2.52
O(1)···O(4)	3.06	O(4)···C(5)	2.75
O(1)···O(5)	2.75	O(4)···O(6)	2.82
O(1)···O(7)	3.11	O(5)···O(6)	2.83
O(1)···O(8)	2.78	O(5)···C(1)	2.99
O(2)···O(3)	3.09	O(5)···C(2)	3.52
O(2)···O(5)	2.69	O(5)···C(4)	3.31
O(2)···O(6)	2.62	O(6)···C(2)	2.89
O(2)···O(8)	2.69	O(6)···O(9)	3.30
O(2)···O(9)	2.67	O(7)···O(8)	2.54
O(2)···C(1)	2.85	O(7)···O(9)	2.81
O(3)···O(4)	2.62	O(7)···C(8)	2.77
O(3)···O(6)	2.75	O(8)···O(9)	2.84
O(3)···O(7)	2.60	O(8)···C(1)	2.99
O(3)···O(9)	2.77	O(8)···C(2)	3.52
O(3)···C(4)	2.86	O(8)···C(7)	3.33
(*b*) Intermolecular			
O(1)···C(2^{I})	3.48	O(6)···C(8^{III})	3.34
O(5)···C(4^{II})	3.31	O(8)···C(7^{II})	3.33
O(5)···C(8^{III})	3.46	O(9)···C(4^{V})	3.46
O(6)···C(1^{IV})	3.06	O(9)···C(5^{IV})	3.49

Symmetry code:
I $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$; II $x, y, -1+z$;
III $\frac{1}{2}-x, -\frac{1}{2}+y, -\frac{1}{2}-z$; IV $-\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$;
V $-\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$

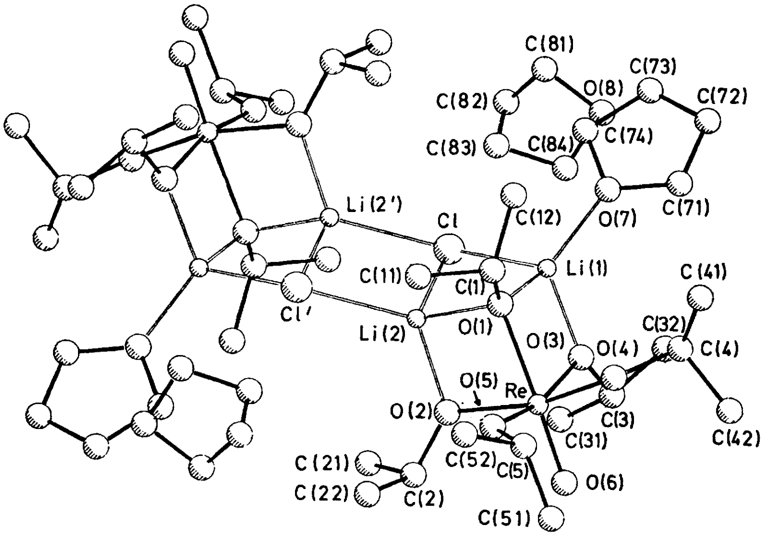

FIGURE 3 Structure of $\{Li[ReO(OPr^i)_5]\cdot LiCl(thf)_2\}_2$, (B), showing the atom numbering in the asymmetric unit. The primed atoms are generated by the centre of symmetry at (0, $\frac{1}{2}$, $\frac{1}{2}$)

The distribution of Re-O distances is as expected. The terminal Re=O lengths (1.690, 1.703 Å) are similar to that found in the compound [acetone benzoylhydrazonido-(1—)-*N'O*]dichloro-oxo(triphenylphosphine)rhenium(V), 1.685 Å.[19] The bridging Re-O-Re bonds are longer at 1.916, 1.917 Å and are similar to those involving the terminal OMe groups (1.867—1.903 Å). The bonds to the bridging methoxides are longest, at 2.094—2.139 Å.

The dimensions of the methoxide ligands are normal, with a mean C-O distance of 1.450 Å and, perhaps surprisingly, a fairly constant Re-O-C angle of 125—130°. The shorter intermolecular contacts (Table 3) involve oxygen atoms and indicate a fairly tight packing.

(2) $\{Li[ReO(OPr^i)_5]\cdot LiCl(thf)\}_2$. The structure of this centrosymmetric dimer, (B), and the atom-numbering scheme are illustrated in Figure 3. Each half of the dimer contains an octahedral $[ReO(OPr^i)_5]^-$ ion in which three alkoxo-oxygen atoms [O(1), O(2), and O(3)] are involved in forming bridges with two Li^+ ions to produce Re-O-Li-O heterocycles in a manner similar to that found previously for two alkoxides of Cr^{III} and Fe^{III}.[20] One OPr^i group is also involved in forming a Li-O-Li-Cl ring.

Some of the more important bond lengths and angles are given in Table 4, and present interesting comparisons with those found for compound (A). Thus, Re=O here is 1.707 Å; Re-O distances to the two terminal alkoxides are 1.898 and 1.899 Å, and to those alkoxides involved in Re-O-Li bridging, 1.987 and 2.023 Å. The Re-O bond to the unique four-co-ordinate oxygen atom is longest, at 2.083 Å. Even so, it is shorter than those to the three-co-ordinate oxygens in (A). In neither compound is there any evidence of a *trans* influence weakening by the Re–O bond such as is found for other metal–oxo-functions.[21] Nevertheless, in (B) there is the usual bending away of the ' equatorial ' ligands from the Re=O group, with the metal atom lying some 0.23 Å above the equatorial O_4 plane towards the oxo-atom. Naturally, the the disposition of the Re–O(2) and Re–O(3) bonds is also affected by the heterocycle formation.

The environment about the chloride ions is interesting in that it appears to be pyramidally three-co-ordinate. The ' empty ' side of the co-ordination sphere is blocked by a second thf molecule, but there are no contacts to the chloride <4.0 Å. In fact this thf molecule is not bonded to any other portion of the complex and is rather poorly defined.

Dimensions of the OPr^i ligands are normal with average C–O and C–C distances of 1.425 and 1.517 Å respectively. Intermolecular contacts are all >3.71 Å and correspond to normal van der Waals packing.

TABLE 4

Selected intramolecular distances and angles for $\{Li[ReO(OPr^i)_5]\cdot LiCl(thf)_2\}_2$, (B)*

Bond lengths (Å)

Re–O(1)	2.083(6)	Re–O(2)	1.987(8)
Re–O(3)	2.023(7)	Re–O(4)	1.898(8)
Re–O(5)	1.899(8)	Re–O(6)	1.707(9)
Li(1)–Cl	2.389(24)	Li(2)–Cl	2.422(18)
Li(2)–Cl′	2.379(25)	Li(1)–O(1)	1.976(23)
Li(2)–O(1)	1.995(22)	Li(2)–O(2)	1.919(21)
Li(1)–O(3)	1.855(22)	Li(1)–O(7)	1.959(21)

Bond angles (°)

O(1)–Re–(O(2)	77.8(3)	O(1)–Re–O(3)	75.7(3)
O(1)–Re–O(4)	89.2(3)	O(1)–Re–O(5)	91.0(3)
O(1)–Re–O(6)	163.1(4)	O(2)–Re–O(3)	91.5(3)
O(2)–Re–O(4)	165.8(3)	O(2)–Re–O(5)	88.7(3)
O(2)–Re–O(6)	92.0(4)	O(3)–Re–O(4)	90.7(3)
O(3)–Re–O(5)	166.3(3)	O(3)–Re–O(6)	91.4(4)
O(4)–Re–O(5)	85.9(3)	O(4)–Re–O(6)	101.9(4)
O(5)–Re–O(6)	102.3(4)	Li(1)–Cl–Li(2′)	142.5(8)
Li(1)–Cl–Li(2)	69.5(7)	Li(2)–Cl–Li(2′)	83.2(8)
O(1)–Li(1)–Cl	100.6(9)	O(1)–Li(2)–Cl	99.0(8)
O(3)–Li(1)–Cl	113.7(12)	O(2)–Li(2)–Cl	120.2(10)
O(1)–Li(1)–O(3)	82.2(7)	Cl′–Li(2)–Cl	96.8(9)
O(7)–Li(1)–Cl	104.6(10)	Cl′–Li(2)–O(1)	137.5(8)
O(7)–Li(1)–O(1)	132.3(15)	Cl′–Li(2)–O(2)	122.6(8)
O(7)–Li(1)–O(3)	121.5(12)	O(1)–Li(2)–O(2)	81.5(7)
Re–O(2)–C(2)	126.2(8)	Re–O(5)–C(5)	128.7(8)
Li(2)–O(2)–C(2)	130.5(10)	Li(2)–O(2)–Re	102.9(7)
Li(1)–O(3)–Re	104.2(8)	C(3)–O(3)–Re	123.8(7)
C(4)–O(4)–Re	131.6(8)	Li(1)–O(3)–C(3)	129.0(11)
Li(1)–O(1)–Re	97.9(7)	C(1)–O(1)–Re	121.4(7)
Li(2)–O(1)–Re	97.0(7)	Li(1)–O(1)–C(1)	126.9(9)
Li(2)–O(1)–Li(1)	87.3(9)	Li(2)–O(1)–C(1)	118.2(9)

* The primed atoms belong to the same dimer, and are generated by the centre of symmetry at $(0,\frac{1}{2},\frac{1}{2})$.

(3) *trans*-$Re(OPh)_4(PMe_3)_2$. The molecular structure of (C) is shown in Figure 4, together with the atom numbering. Important interatomic distances and angles are given in Table 5. The monomeric molecules lie on crystallographic inversion centres, and the Re atom shows a distorted octahedral geometry with the phosphine ligands in *trans* positions. The Re–P distance (2.488 Å) is normal and comparable with those (2.472, 2.481, and 2.485 Å) in $ReOCl_2(PPh_3)[Ph(O)CNNCMe_2]$,[19] $ReCl_3(NMe)(PEtPh_2)_2$,[22] and $ReCl_3(NC_6H_4COMe)(PEt_2Ph)_2$,[23] while the mean Re–O distance (1.965 Å) is comparable with the mean $Re-O(OPr^i)$ (terminal) distance (1.959 Å) in (B).

The ligand-geometry parameters are normal but some angular distortions are observed which can be attributed to interligand congestion. Thus, the Re–P–C(1) angle becomes considerably wider than the other two Re–P–C angles (122.5 *vs.* 108.9 and 114.6°) as a result of several C(1) ··· Ph short contacts (Table 5). These contacts in turn widen the Re–O(1)–C(11) angle compared with the Re–O(2)–C(22) angle (141.3 *vs.* 131.9°). Also the octahedral P–Re–O(1′) and P–Re–O(2′) angles became larger than the P–Re–O(2) angles (97.4 and 96.3 *vs.* 82.6 and 83.7°). The intermolecular contacts (Table 5) are normal for van der Waals packing, with one contact of 3.57 and others greater than 3.70 Å.

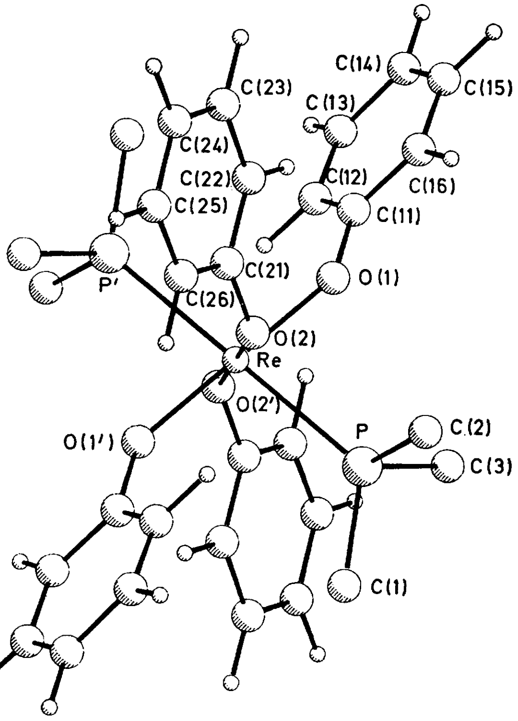

FIGURE 4 Molecular structure of $Re(OPh)_4(PMe_3)_2$, (C), showing the atom numbering in the asymmetric unit. The primed atoms are generated by the centre of symmetry at (0,0,0)

EXPERIMENTAL

Microanalyses were by Butterworth Microanalytical Consultancy Ltd., Pascher, Bonn, and Imperial College Laboratories. Spectrometers: Perkin-Elmer R32 (^1H, 90 MHz), 597 and 325 (i.r.), and VG Micromass 7070 (mass spectra). Molecular weights were obtained cryoscopically and using an Hitachi–Perkin-Elmer 115 osmometer. Melting points were determined in capillaries sealed under nitrogen and magnetic moments in solution by Evans' method.

All operations except the syntheses of $ReOCl_4$ and ReO_3Cl were carried out under dry oxygen-free nitrogen or *in vacuo*. All hydrocarbons and ethers were dried by refluxing over sodium–benzophenone under nitrogen; dichloromethane and acetonitrile were dried by refluxing over calcium hydride under nitrogen, alcohols by refluxing over the corresponding magnesium alkoxide under nitrogen, triethylamine by refluxing over sodium under nitrogen, and phenol was recrystallised from dry high-boiling light petroleum. All solvents were distilled immediately prior to use. The light petroleum used had b.p. 40—60 °C.

(1) *Tetrachloro-oxorhenium*(VI).—In a distillation flask (100 cm^3) with a U tube to act as a cold trap sealed to the side arm, was placed rhenium pentachloride (25 g), under N_2. A gas-inlet tube of a length such that oxygen could be passed directly onto the surface of the $ReCl_5$ was fitted in the neck of the distillation flask. The exhaust from the cold trap was connected to a bubbler and trap to avoid suck back and the U tube was cooled to −35 °C. Teflon sleeves were used in ground joints as $ReOCl_4$ reacts with greases.

TABLE 5

Important interatomic distances and angles for $Re(OPh)_4(PMe_3)_2$, (C)

Bond lengths (Å)

P–Re	2.488(3)	O(1)–Re	1.939(9)
O(2)–Re	1.992(9)	C(1)–P	1.822(14)
C(2)–P	1.845(13)	C(3)–P	1.821(12)
C(11)–O(1)	1.336(13)	C(21)–O(2)	1.338(13)
C(12)–C(11)	1.394(14)	C(16)–C(11)	1.376(16)
C(13)–C(12)	1.344(15)	C(14)–C(13)	1.398(19)
C(15)–C(14)	1.387(18)	C(16)–C(15)	1.364(17)
C(22)–C(21)	1.364(16)	C(26)–C(21)	1.376(15)
C(23)–C(22)	1.412(17)	C(24)–C(23)	1.398(21)
C(25)–C(24)	1.357(22)	C(26)–C(25)	1.361(18)

Bond angles (°)

O(1)–Re–P	82.6(3)	O(2)–Re–P	83.7(2)
O(2)–Re–O(1)	88.7(3)	C(1)–P–Re	122.5(5)
C(2)–P–Re	108.9(5)	C(2)–P–C(1)	102.4(8)
C(3)–P–Re	114.6(5)	C(3)–P–C(1)	103.0(7)
C(3)–P–C(2)	103.4(7)	C(11)–O(1)–Re	141.3(8)
C(21)–O(2)–Re	131.9(7)	C(12)–C(11)–O(1)	122.6(10)
C(16)–C(11)–O(1)	119.4(10)	C(16)–C(11)–C(12)	118.0(11)
C(13)–C(12)–C(11)	120.7(12)	C(14)–C(13)–C(12)	120.9(13)
C(15)–C(14)–C(13)	119.0(13)	C(16)–C(15)–C(14)	118.9(14)
C(15)–C(16)–C(11)	122.4(13)	C(22)–C(21)–O(2)	120.2(11)
C(26)–C(21)–O(2)	121.2(11)	C(26)–C(21)–C(22)	118.5(11)
C(23)–C(22)–C(21)	120.7(12)	C(24)–C(23)–C(22)	118.4(13)
C(25)–C(24)–C(23)	120.0(15)	C(26)–C(25)–C(24)	120.3(16)
C(25)–C(26)–C(21)	122.0(14)		

Non-bonded short contacts ⩽3.80 Å

Intramolecular		Intermolecular	
$C(1) \cdots C(11^{I})$	3.59	$C(2) \cdots C(3^{II})$	3.80
$C(1) \cdots C(12^{I})$	3.46	$C(2) \cdots C(12^{III})$	3.75
$C(1) \cdots C(22^{I})$	3.55	$C(13) \cdots C(23^{IV})$	3.80
$C(3) \cdots C(21^{I})$	3.49	$C(16) \cdots C(24^{V})$	3.80
$C(3) \cdots C(22^{I})$	3.79	$C(16) \cdots C(25^{V})$	3.71
$C(3) \cdots C(26^{I})$	3.75	$C(26) \cdots C(26^{VI})$	3.57

Symmetry code:

I $-x, -y, -z$; II $-x, -\frac{1}{2} + y, \frac{1}{2} - z$;
III $-x, \frac{1}{2} + y, \frac{1}{2} - z$; IV $1 - x, -y, -z$;
V $x, \frac{1}{2} - y, \frac{1}{2} + z$; VI $-x, 1 - y, -z$

Oxygen was passed slowly over the rhenium chloride and the distillation flask was heated to 250 °C. Tetrachloro-oxorhenium began to reflux in the distillation flask and the oxygen flow was adjusted so that the oxohalide collected in the U tube, but was not flushed completely through the system. When no more oxohalide distilled the flask was allowed to cool and the apparatus was isolated under oxygen and transferred to a vacuum line. The more volatile ReO_3Cl was first condensed into a separate flask (cooled in liquid nitrogen) and the $ReOCl_4$ then collected. The product is quite pure after one distillation but can be further purified by sublimation or trap-to-trap distillation. The initial product is satisfactory for syntheses. Yields after purification are typically *ca.* 19 g (80% based on $ReCl_5$).

(2) *Chlorotrioxorhenium*(VII).—In the apparatus described above was placed trirhenium nonachloride (25 g). The U tube was cooled to −35 °C and oxygen was passed slowly over the halide. The distillation flask was heated gently with a bunsen burner until the Re_3Cl_9 inflamed. The oxygen flow was adjusted so that the combustion was maintained without external heating and the chlorotrioxorhenium produced was not flushed through the system. The ReO_3Cl rapidly collects in the cold trap and freezes to a solid varying in colour from green-yellow to red. When all the Re_3Cl_9 had burned the flask was allowed to cool and the apparatus was isolated under oxygen and transferred to a vacuum line. The ReO_3Cl was distilled very slowly under vacuum into a separate flask cooled in liquid nitrogen. If the distillation is too rapid the product is coloured (yellow or red) and another distillation is necessary to obtain a colourless product, *ca.* 20 g (87% based on Re_3Cl_9).

(3) *Di-μ-methoxo-tetramethoxo-μ-oxo-dioxodirhenium*(VI) (Re–Re), (A).—A solution (red) of tetrachloro-oxorhenium(VI) (1 g) in diethyl ether (10 cm^3) was added with vigorous stirring to a cooled (−78 °C) solution of methanol (5 cm^3) and triethylamine (2 cm^3) in diethyl ether (20 cm^3). The violet solution was allowed to warm to ambient temperatures with stirring when a white precipitate formed. The solvent was removed *in vacuo* and the orange residue extracted with light petroleum (4 × 50 cm^3). The orange solution was filtered, concentrated to *ca.* 75 cm^3, and held at −20 °C overnight to give orange diamond-shaped crystals. A second crop of crystals was obtained by further concentration of the supernatant and cooling. The crystals were collected, washed with light petroleum (2 × 5 cm^3), and dried under vacuum. Yield 0.64 g (74% based on $ReOCl_4$), m.p. 76—78 °C (Found: C, 12.7; H, 3.2; O, 23.5%; *M* 580. $C_4H_{12}O_6Re$ requires C, 11.9; H, 3.0; O, 23.8%; *M* 606).

(4) *Oxotetra-t-butoxorhenium*(VI).—To a solution of $ReOCl_4$ (1 g, 2.9 mmol) in diethyl ether (20 cm^3) cooled to −78 °C was added dropwise a solution of lithium t-butoxide [1.05 mol dm^{-3} in light petroleum (11.1 cm^3), 11.6 mmol] with vigorous stirring. The resulting red solution was allowed to warm slowly to 10 °C, when it was green. The solvent was removed *in vacuo* and the residue extracted with light petroleum (3 × 20 cm^3). The green solution was filtered, concentrated to *ca.* 20 cm^3, and held at −20 °C overnight. The large blue crystals were collected, washed with cold light petroleum (2 × 5 cm^3), and stored at −20 °C. Yield 1.2 g (84% based on $ReOCl_4$); decomp. *ca.* 0 °C, *M* 400 (calc. 494).

A small sample of the butoxide (*ca.* 0.1 g) was allowed to decompose at room temperature in a sealed flask with side tube for introducing samples into the mass spectrometer *via* a vacuum line. Both flasks were cooled in liquid nitrogen, evacuated, and connected in a closed system. The volatile products were then allowed to condense in the sample tube which was subsequently isolated from the vacuum line.

(5) *Lithium Pentaisopropoxo-oxorhenate*(VI)–*Lithium Chloride*, (B).—To a solution of $ReOCl_4$ (1 g, 2.9 mmol) in diethyl ether (20 cm^3) cooled to −78 °C was added dropwise a solution of lithium isopropoxide [1 mol dm^{-3} in light petroleum (14.5 cm^3), 14.5 mmol] with vigorous stirring. The red solution was allowed to warm slowly to room temperature when the colour had changed through brown to

pale green. The solvent was removed *in vacuo* and the green residue extracted with light petroleum (5 × 20 cm^3). The solution was filtered, concentrated to *ca.* 30 cm^3, and held at −20 °C overnight. The green needles were collected, washed with light petroleum, and dried *in vacuo*. Yield 1.1 g (69% based on $ReOCl_4$), decomp. > 50 °C (Found: C, 33.2; H, 6.6; Cl, 5.8; O, 18.0. $C_{15}H_{35}ClLi_2O_6Re$ requires C, 33.0; H, 6.4; Cl, 6.4; O, 17.6%). Magnetic moment (298 K, Gouy method) $\mu_{eff.}$ *ca.* 0.9 B.M. Crystallisation from thf gave the solvate $\{Li[ReO(OPr^i)_5]\cdot LiCl(thf)_2\}_2$, (B).

(6) *Tris[bis(trimethylsilyl)amido]oxorhenium*(V).—To a solution of $ReOCl_4$ (1 g, 2.9 mmol) in diethyl ether (20 cm^3) cooled to −78 °C was added with vigorous stirring a solution of $LiN(SiMe_3)_2$ [1 mol dm^{-3} in light petroleum (11.6 cm^3), 11.6 mmol]. The solution was allowed to warm slowly to ambient temperatures when it was bright red. The solvent was removed *in vacuo* and the residue extracted with light petroleum (2 × 20 cm^3), concentrated to *ca.* 5 cm^3, and held at −20 °C overnight. The red plates were collected and recrystallised from light petroleum to remove traces of $LiN(SiMe_3)_2$. The complex could also be purified by sublimation at 60 °C (10^{-3} Torr). Yield of recrystallised material 1.25 g (63% based on $ReOCl_4$), m.p. 184—185 °C (Found: C, 31.5; H, 7.7; N, 6.0%; *M* 690. $C_{18}H_{54}N_3OReSi_6$ requires C, 31.7; H, 7.9; N, 6.2%; *M* 682).

(7) trans-*Tetraphenoxobis(trimethylphosphine)rhenium*(IV), (C).—To $ReOCl_4$ (0.7 g) in diethyl ether (20 cm^3) at −78 °C was added a solution of NaOPh (0.9 g, 4 equivalents) in thf (10 cm^3). The dark brown-purple solution was allowed to warm to room temperature when NaCl separated. Addition of trimethylphosphine (*ca.* 2 cm^3) caused a change in colour to red, and a brown insoluble precipitate was formed. After removal of solvent, the brown residue was extracted first with diethyl ether (discarded) and then with dichloromethane. Concentration of the dichloromethane solution gave diamond-shaped crystals in *ca.* 15% yield (Found: C, 47.8; H, 3.9; O, 9.7. $C_{30}H_{38}O_4P_2Re$ requires C, 48.0; H, 4.0; O, 9.7%).

TABLE 6

Crystal data and details of structure analyses

(*i*) Crystal Data	Compound (A) [a]	Compound (B) [b]	Compound (C) [b]
Formula	$Re_2O_3(OMe)_6$	$\{Li[ReO(OPr^i)_5]\cdot LiCl(thf)_2\}_2$	$Re(OPh)_4(PMe_3)_2$
M	606.6	1 382.5	710.8
Crystal system	Monoclinic	Triclinic	Monoclinic
a/Å	12.142(1)	14.602(5)	10.079(2)
b/Å	15.369(1)	13.363(3)	10.527(3)
c/Å	7.311(1)	9.244(6)	14.443(3)
α/°	90	98.39(4)	90
β/°	90.22(1)	102.35(5)	97.28(2)
γ/°	90	68.71(2)	90
U/Å^3	1 364.4	1 637.1	1 520.1
Space group	$P2_1/n$ (no. 14)	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)
Z	4	1	2
D_c/g cm^{-3}	2.953	1.402	1.553
F(000)	1 104	704	710
Linear absorption coefficient, μ(Mo-*K*α)/cm^{-1}	179.7	38.5	41.5
Crystal size/mm	0.33 × 0.33 × 0.08	0.30 × 0.25 × 0.22	0.24 × 0.12 × 0.08
(*ii*) Data Collection			
Scan mode	ω/2θ	ω/2θ	ω/2θ
$\theta_{min.}, \theta_{max.}$/°	1.5, 27	1.5, 24	1.5, 25
ω scan-width parameters *A*, *B* in $\omega = A + B\tan\theta$	0.85, 0.35	0.85, 0.35	0.85, 0.35
Horizontal aperture parameters *A*, *B* in aperture $= A + B\tan\theta$	4.0, 0.0	4.0, 0.0	4.0, 0.0
Total data	3 212	4 855	2 894
Total unique data	2 966	4 761	2 670
Observed data, $F_o > 4\sigma(F_o)$	1 965	4 061	1 797
Crystal decay during data collection	5.8% (linear)	32.8% (linear)	None
(*iii*) Refinement			
No. of parameters	154	317	170
Weighting scheme coefficient *g*, in $w = 1/[\sigma^2(F_o) + g(F_o)^2]$	0.0022	0.0028	0.0012
Final $R = \Sigma\Delta F/\Sigma(F_o)$	0.059	0.069	0.055
$R' = (\Sigma w\Delta F^2/\Sigma wF_o^2)^{\frac{1}{2}}$	0.072	0.086	0.071

[a] Crystallographic measurements at 298 K. [b] Crystallographic measurements at 270 K.

(8) *Synthesis of Methylrhenium Compounds*.—(*a*) $ReOMe_4$. To a solution of $ReOCl_4$ (1 g, 2.9 mmol) in diethyl ether (20 cm^3) at −100 °C was added dropwise a cooled (−100 °C) solution of methyl-lithium [1.4 mol dm^{-3} in diethyl ether (8.3 cm^3), 11.6 mmol] with vigorous stirring. The solution was allowed to warm slowly (1 h) to ambient temperature when it was red. Degassed water (10 cm^3) was added dropwise with vigorous stirring, the solution cooled to −78 °C and allowed to stand until excess of water had frozen, and filtered. The red-purple solution was evaporated to dryness at −40 °C *in vacuo* and $ReOMe_4$ sublimed at 20 °C (10^{-3} Torr); yield 0.51 g (67% based on $ReOCl_4$). Although the reaction is probably quantitative, loss of $ReOMe_4$ occurs on removal of solvent. This can be collected in a cold trap and more $ReOMe_4$ recovered by fractionation.

(*b*) $Li_2[ReMe_8]$. To a solution of $ReOCl_4$ (1 g, 2.9 mmol) in diethyl ether (20 cm^3) at −78 °C was added dropwise with stirring a solution of methyl-lithium [1.4 mol dm^{-3} in diethyl ether (20.8 cm^3), 29 mmol]. The red solution was allowed to warm to, and held at, −10 °C for 30 min, when it was evaporated *in vacuo* and the residue extracted at −10 °C with toluene (3 × 20 cm^3). The solution was filtered, concentrated to *ca.* 15 cm^3, and held at −78 °C overnight. The thermally unstable red crystals were separated, washed with cooled light petroleum (10 °C, 2 × 5 cm^3), and stored at −20 °C; yield 0.77 g (83% based on $ReOCl_4$).

(*c*) $ReMe_6$. **CAUTION:** The red solution obtained from the reaction of $ReOCl_4$ with excess of methyl-lithium (above) was cooled to −78 °C and degassed water (10 cm^3) was added dropwise with vigorous stirring. The solution was allowed to warm (until the ice melted) when it was green, re-coooled to −78 °C, filtered, concentrated at −40 °C *in vacuo* until green crystals appeared (*ca.* 5 cm^3), and then held at −78 °C overnight. The crystals were collected and stored at −20 °C. The compound may also be produced from $Li_2[ReMe_8]$ by the same procedure and since it is potentially hazardous and should be treated with great caution it is better to prepare it from $Li_2[ReMe_8]$ in small quantities as required. In all operations with $ReMe_6$, oxygen and moisture should be rigorously excluded.

(9) *X-Ray Crystallography.*—Crystals of compounds (A)—(C) were sealed under nitrogen in Lindemann capillaries. The determination of unit-cell constants and recording of intensity data were done using a Nonius CAD4 diffractometer and (Mo-K_α) radiation (λ = 0.710 69 Å) in a manner previously described in detail,[24] at room temperature (289 K) for (A) and at 270 K for both (B) and (C). The crystal data, important data-collection parameters, and refinement results are summarised in Table 6. The monoclinic space groups $P2_1/n$ for (A) and $P2_1/c$ for (C) were determined from systematic absences.

TABLE 7

Fractional co-ordinates (Re × 10^5, others × 10^4) of the non-hydrogen atoms for $Re_2O_3(OMe)_6$, (A)

	x	*y*	*z*
Re(1)	29 200(5)	20 564(5)	−511(8)
Re(2)	27 471(5)	37 146(5)	866(8)
O(1)	4 185(8)	2 959(7)	−483(14)
O(2)	2 502(8)	2 893(8)	−2 211(14)
O(3)	2 881(10)	2 852(8)	1 967(18)
O(4)	3 624(9)	1 265(9)	1 515(15)
O(5)	3 580(9)	1 373(9)	−1 920(13)
O(6)	1 589(9)	1 737(10)	−63(19)
O(7)	3 286(9)	4 513(9)	1 794(16)
O(8)	3 262(9)	4 517(9)	−1 675(15)
O(9)	1 359(10)	3 873(10)	119(22)
C(1)	4 844(13)	3 041(13)	−2 101(23)
C(2)	1 509(16)	2 848(14)	−3 257(30)
C(4)	3 669(16)	1 271(17)	3 563(25)
C(5)	4 256(17)	621(15)	−1 824(27)
C(7)	3 423(19)	4 402(16)	3 787(24)
C(8)	3 768(15)	5 360(14)	−1 456(30)

The centrosymmetric space group $P\bar{1}$ was confirmed for (B) by successful refinement. During data collection, compounds (A) and (B) suffered losses of 5.8 and 32.8% respectively in the intensities of their standard reflections, while (C) remained quite stable. All data sets were corrected for Lorentz, polarisation, and absorption effects, and those of (A) and (B) also for the crystal decay. The total number of reflections measured and those used in the refinement, $F_o > 4\sigma(F_o)$, are given in Table 6.

TABLE 8

Fractional co-ordinates (Re × 10^5, others × 10^4) of the non-hydrogen atoms for $\{Li[ReO(OPr^i)_5]\cdot LiCl(thf)_2\}_2$, (B)

	x	*y*	*z*
Re	24 180(3)	17 657(3)	61 969(5)
Cl	1 086(2)	5 142(3)	4 568(4)
O(1)	1 839(5)	3 330(5)	7 139(8)
O(2)	1 116(6)	2 344(6)	4 860(9)
O(3)	3 019(6)	2 623(6)	5 300(9)
O(4)	3 502(5)	1 480(6)	7 816(10)
O(5)	1 773(6)	1 258(6)	7 357(9)
O(6)	2 824(7)	683(7)	4 973(10)
C(1)	1 705(9)	3 531(10)	8 626(14)
C(11)	648(11)	3 669(13)	8 767(17)
C(12)	2 001(17)	4 513(13)	9 306(21)
C(2)	642(11)	1 737(12)	3 788(18)
C(21)	12(15)	2 430(17)	2 541(20)
C(22)	15(23)	1 366(25)	4 554(32)
C(3)	3 463(9)	2 255(12)	3 961(15)
C(31)	2 724(15)	2 401(22)	2 595(20)
C(32)	4 224(20)	2 787(24)	4 030(25)
C(4)	4 431(9)	1 642(11)	8 052(15)
C(41)	4 706(12)	1 992(16)	9 648(18)
C(42)	5 163(12)	560(14)	7 507(24)
C(5)	2 211(11)	512(12)	8 485(16)
C(51)	2 650(14)	−627(12)	7 759(22)
C(52)	1 375(15)	697(18)	9 396(23)
O(7)	3 335(7)	4 904(8)	6 884(14)
C(71)	4 372(14)	4 530(17)	7 588(26)
C(72)	4 742(15)	5 472(18)	7 662(35)
C(73)	3 889(21)	6 361(20)	7 079(44)
C(74)	2 988(15)	6 044(16)	6 695(37)
Li(1)	2 497(16)	4 017(16)	6 131(30)
Li(2)	641(14)	3 835(15)	5 562(26)
O(8)	3 232(17)	7 291(33)	2 840(43)
C(81)	2 372(56)	8 176(33)	3 190(57)
C(82)	1 789(47)	8 094(60)	1 721(104)
C(83)	1 710(42)	7 341(50)	2 157(96)
C(84)	2 697(56)	6 776(41)	1 885(78)

The rhenium atoms were determined from an *E* map in (A) and Patterson syntheses in both (B) and (C). The non-hydrogen atoms were then located and refined by successive electron-density syntheses and full-matrix least-squares refinement. In the final stages of refinement all the non-hydrogen atoms were assigned anisotropic temperature factors. None of the hydrogen atoms in any structure could be located from difference maps. These were ignored, except for the methine hydrogens in (B) and phenyl hydrogens in (C), which were inserted in idealised positions and included in the calculations of F_c. A common $U_{iso.}$ refined to 0.08(2) and 0.09 (2) Å^2 respectively for the two groups of hydrogens in (B) and (C). The weighting scheme used was $w = 1/[\sigma^2(F_o) + g(F_o)^2]$, with the parameter *g* chosen to give nearly flat analyses of variances with

TABLE 9

Fractional co-ordinates (× 10^4) of the non-hydrogen atoms for $Re(OPh)_4(PMe_3)_2$, (C)

	x	*y*	*z*
Re	0	0	0
P	−1 594(3)	215(3)	1 172(2)
O(1)	1 271(9)	−281(7)	1 105(6)
O(2)	239(9)	1 863(8)	197(5)
C(1)	−3 395(14)	352(17)	842(11)
C(2)	−1 199(17)	1 681(14)	1 851(11)
C(3)	−1 457(14)	−1 023(13)	2 059(10)
C(11)	2 363(11)	−957(10)	1 406(7)
C(12)	2 629(11)	−2 136(11)	1 031(8)
C(13)	3 712(13)	−2 808(12)	1 379(9)
C(14)	4 621(15)	−2 326(14)	2 105(12)
C(15)	4 362(13)	−1 160(14)	2 493(9)
C(16)	3 237(13)	−512(13)	2 144(9)
C(21)	1 202(11)	2 662(10)	9(7)
C(22)	2 506(13)	2 420(12)	339(8)
C(23)	3 528(14)	3 265(14)	156(10)
C(24)	3 173(18)	4 355(15)	−372(11)
C(25)	1 869(19)	4 585(15)	−688(14)
C(26)	903(13)	3 761(11)	−489(9)

$(F_o/F_{max.})^{\frac{1}{2}}$ and sin θ. Final fractional atomic co-ordinates of the non-hydrogen atoms are given in Tables 7—9. Anisotropic temperature factors of these atoms, hydrogen-atom parameters, lists of observed and calculated structure factors, and a table containing all the bond lengths and angles in (B) have been deposited in Supplementary Publication No. SUP 22891 (39 pp.).*

Neutral-atom scattering factors were taken from refs. 25 (H), 26 (Re), and 27 (others), with those of the heavier elements being modified for anomalous dispersion, taking the $\Delta f'$ and $\Delta f''$ values from ref. 28. All calculations were performed on the ICL2980 computer at Queen Mary College using the programs SHELX [29] (structure determination and refinement) and PLUTO [30] (diagrams).

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

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