The Chemistry of Rhenium Alkyls. Part I. Synthesis and Properties of Oxorhenium(VI) Methyl and Trimethylsilylmethyl Compounds †

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The interaction of [ReO(Cl)$_3$(PPh$_3$)$_2$] and [ReOCl$_4$] with methyl-lithium forms the paramagnetic d^1 complex [ReOMe$_4$]. Interaction of [ReO(Cl)$_3$(PPh$_3$)$_2$] with Me$_3$SiCH$_2$MgCl gives the blue paramagnetic [ReO(CH$_2$SiMe$_3$)$_4$] and the diamagnetic [Re$_2$O$_3$(CH$_2$SiMe$_3$)$_6$].

Both oxotetra-alkyl compounds are thermally very stable; although [ReOMe$_4$] is air-sensitive, [ReO(CH$_2$SiMe$_3$)$_4$] is unaffected by air. E.s.r. and electronic absorption spectra (reported separately) and i.r. spectra are consistent with a square-based pyramidal structure for the oxotetra-alkyls. The i.r. spectrum of [Re$_2$O$_3$(CH$_2$SiMe$_3$)$_4$] is consistent with a structure containing linear Re–O–Re and *cis* Re=O groups.

In 1934, Druce[1] claimed to have prepared the volatile trimethylrhenium by the interaction of methylmagnesium iodide with rhenium trichloride. However, Gilman *et al.* were unable to repeat the synthesis.[2] Since then, the only σ-alkyls of rhenium have contained π-bonding ligands, *viz.*, [Re(CO)$_5$Me],[3] [(η^5-C$_5$H$_5$)ReMe(CO)$_2$Br],[4] [(η^5-C$_5$H$_5$)(η^2-C$_5$H$_4$Me)ReMe$_2$],[5] and [{ReAr(PR$_3$)$_2$}$_2$] and [{ReAr(PR$_3$)$_2$}$_n$] (Ar = Ph and *p*-MeC$_6$H$_4$, PR$_3$ = PPh$_3$ or PPhEt$_2$).[6]

We have now prepared the methyl[7] and trimethylsilylmethyl compounds, [ReOMe$_4$] and [ReO(CH$_2$SiMe$_3$)$_4$], by interaction of either trichloro-oxobis(triphenylphosphine)rhenium(V) or tetrachloro-oxorhenium(VI) with the lithium or Grignard reagent.

Oxoalkyls are so far uncommon, being confined to [VO(CH$_2$SiMe$_3$)$_3$],[8] [WO(Me)Cl$_3$] and [WO$_2$(Me)Cl],[9] and complexes [MO(Me)X$_2$L$_2$], M = Nb or Ta, X = Cl or Br, L = OSMe$_2$, OP(NMe$_2$)$_3$, OP(OMe)$_3$, and PPh$_3$.[10]

We here describe the synthesis, i.r. and n.m.r. spectra of the compounds; e.s.r. and electronic absorption spectra are discussed in a subsequent paper.[11]

RESULTS AND DISCUSSION

Synthesis of Tetramethyloxorhenium(VI).—The interaction of [ReO(Cl)$_3$(PPh$_3$)$_2$] with methyl-lithium in diethyl ether can give high yields of the alkyl. Clearly some oxidative step is required to produce the rhenium(VI) oxoalkyl from the rhenium(V) complex. Although some [ReOMe$_4$] can be isolated when a [ReO(Cl$_3$)(PPh$_3$)$_2$]: MeLi ratio of 1 : 4 is used in absence of oxygen, the yield becomes essentially quantitative when traces of oxygen are present in the solvents added after the primary reaction has taken place. The use of 1—3 equivalents of methyl-lithium gave brown solutions from which no well-defined product could be obtained, while use of an excess of MeLi gave yellow-brown precipitates, evidently of lithium salts as etherates, but no volatile rhenium species. From these solids [ReOMe$_4$] could be isolated by (*a*) thermal decomposition (*ca.* 100 °C) *in vacuo*, (*b*) treating them with traces of oxygen when the colour changes to red and [ReOMe$_4$] can be sublimed out in high vacuum, and (*c*) extracting them with hexane or light petroleum containing traces of oxygen when red solutions of [ReOMe$_4$] are obtained.

The mechanism of the alkyl formation from [ReOCl$_3$(PPh$_3$)$_2$] is obscure—it could well involve de-oxygenation and then subsequent oxidation of species in a lower oxidation state by molecular oxygen.

The reaction of methyl-lithium with [ReOCl$_4$] is evidently also complicated; the yields are only *ca.* 20%. The initial dark red solution of [ReOCl$_4$] in ether becomes dark brown in a few minutes and addition of MeLi gives red-brown solutions. The use of oxygen-containing solvents as above does not give an increased yield.

No [ReOMe$_4$] could be obtained using dry reactions with solid MeLi.

Properties of Tetramethyloxorhenium.—This is a red-purple (carmine) crystalline solid, m.p. *ca.* 45 °C. It is extremely volatile subliming readily even at −35 °C and 10^{-3} mmHg. It co-distils even at low temperatures with ether or petroleum and in the syntheses some losses always occur on removal of solvents. The compound is air sensitive (see later and ref. 11) but thermally very stable. It can be stored indefinitely *in vacuo* and on heating there is no evident decomposition below *ca.*

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† No reprints available.

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[10] C. Santini-Scampucci and J. G. Riess, *J.C.S. Dalton*, 1974, 1433.

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150 °C. The compound is extremely soluble in petroleum, ethers, CS_2, CCl_4 *etc.* but these solutions slowly decompose with time even in absence of air; the solutions in tetrahydrofuran and aromatic hydrocarbons are more stable.

The complex is surprisingly unreactive in diethyl ether solution at room temperature, and is unaffected by water, dilute mineral acids, alcohols, hydrogen, carbon dioxide, sulphur dioxide, gaseous HCl, butadiene, tetramethylthiuram disulphide, 1,1-diphenyl-2-picrylhydrazyl, tertiary phosphines, amines, and carbon monoxide. However, reaction with oxygen is very fast. Solid [$ReOMe_4$] fumes instantly in air, but solutions in benzene are oxidised slowly to give yellow-orange products.[11]

TABLE 1

Mass spectra of rhenium alkyls

[$ReOMe_4$]			[$C_{16}H_{44}OSiRe$]			[$C_{24}H_{66}O_3Si_6Re_2$]		
				% *m/e* 551			% *m/e* 944	
Ion	% 70 eV	% 16 eV	*m/e*	Obs.[a]	Calc.[b]	*m/e*	Obs.[a]	Calc.[b]
$ReOMe_4^+$	6·5	31·5	549	58	53	940	32	24
$ReOMe_3CH_2^+$		90	550	15	20	941	17	14
ReO_3Me^+	100		551	100	100	942	88	90
$ReOMe_3^+$	53	100	552	33	38	943	54	51
$ReOMe_2^+$	88	97	553	17	19	944	100	100
$ReOMe^+$	29	56	554	8	5	945	59	52
ReO^+	43					946	33	29
Re^+	40					947	10	11
						948	7	4

[a] At 70 eV *m/e* 555—560 and 949—954 not observed, calculated <2%. [b] We thank Mr. A. L. Galyer for computer calculations of isotopic distribution.

TABLE 2

Infrared spectra of oxorhenium alkyls (in cm^{-1})

[$ReOMe_4$]				
Solid[a]	Nujol	CS_2[b]	[$ReO(CH_2SiMe_3)_4$][c,d]	[$Re_2O_3(CH_2SiMe_3)_4$][c,e]
2974s (CH str)		2980s	2950s	2940s
			2890m	2880m
1231s (CH def)		1370m	1400w	1400w
			1245s	1240s
1016s (Re=O str)	1009s	1002s	1005s (Re=O str)	1008m 990s (Re=O str)
			920m	935m
1004sh, br			825s, br	825s, br
746m (Me rock)		749w	750s	
552m 529s (ReC str)	520m	520m	700s	690s
			680s	670s
			500w (ReC str)	540w 515w (ReC str)

[a] In argon matrix at −250 °C. [b] With time, bands due to oxidation begin to appear at 2825, 1110, 952, and 669 cm^{-1}. [c] From Nujol, and CS_2 solutions, KBr discs and for [$ReO(CH_2SiMe_3)_4$] liquid film. Unspecified bands are due to the CH_2SiMe_3 group. [d] Other peaks at 1440w, 1340w, 1295w, 1257s, and 605w. [e] Other peaks at 1340w and 1250s.

Reaction with iodine in benzene produces quantitatively methyl iodide and a black non-identified product {presumably [$ReOI_4$]}. Reaction with chlorine in carbon tetrachloride at −75 °C gives a very unstable red product which decomposes at room temperature. Treatment of an ethereal solution of [$ReOMe_4$] at −78 °C with nitric oxide produces an unstable yellow diamagnetic oil which is under investigation.

In the mass spectrum, Table 1, ions were identified by the rhenium isotopic distribution (^{185}Re, 37%, ^{187}Re, 63%) as well as by mass number. For [$ReOMe_4$] at −78 °C in the external inlet and an ionisation potential of 70 eV, only a weak parent ion (<0·5%) was detected, but at 16 eV the abundance increases to 31·5%. In the fragmentation pattern, all the species [$ReOMe_n$]$^+$ n = 4, 3, 2, 1, and 0 are observed, as well as ReO_3Me^+ and Re^+ and, at 16 eV, $ReOMe_3CH_2^+$. A detailed analysis has not been attempted since different ions can occur at the same mass number; thus $ReOMe_3^+$ (246, 248), $ReMe_4^+$ (245, 247), $ReOMe_3H^+$ (247, 249), and $ReOMe_3H_2^+$ (248, 250) resulting from oxidative reactions of [$ReOMe_4$] in the spectrometer. Oxidation products have also been found in the mass spectrum of [$ReOCl_4$].[12]

The i.r. spectrum in the solid state at −250 °C cocondensed with argon * (Table 2) shows a very strong,

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* We are indebted to Dr. S. Ogden, Inorganic Chemistry Laboratories, Oxford, for the spectrum.

[12] D. L. Singleton and F. E. Stafford, *Inorg. Chem.*, 1972, **11**, 1208.

sharp, band at 1016 cm^{-1} that is readily assigned as the Re=O stretch. The broader shoulder at 1004 cm^{-1} may be due to an aggregated species since such shoulders have been found in related molecules; thus [ReOCl$_4$] has bands at 1028 and 1017 cm^{-1}.[13] Apart from the methyl stretches, deformation and rocking modes the only other bands at 529 and 553 cm^{-1} can be assigned as Re–C vibrations. The intensity ratio, 529(6) and 553(1) cm^{-1} suggests a square-based pyramidal structure (C_{4v}) for [ReOMe$_4$] [Re–C $= A_1 + E +$ (inactive)B_1] in which the Me–Re–O angles are close to 90° (see also ref. 11). For a trigonal bipyramidal molecule with C_{3v} symmetry, four bands in both i.r. and Raman ($2A_1 + B_1 + B_2$) are expected.

I.r. spectra in de-oxygenated Nujol and CS$_2$ solutions have been obtained. The solutions are difficult to protect from oxidation and the colour changes from deep red to orange while bands originally present decrease in intensity and new ones appear. Attempts to obtain Raman spectra of the solid or of tetrahydrofuran solutions at −78 °C failed due to decomposition.

Synthesis of Oxotetrakis(trimethylsilylmethyl)rhenium(VI) *and μ-Oxo-bis[oxotris(trimethylsilylmethyl)rhenium*(VI)] (I).—Treatment of [ReOCl$_3$(PPh$_3$)$_2$] with five equivalents of Me$_3$SiCH$_2$MgCl in diethyl ether at room temperature gives the blue paramagnetic [ReO(CH$_2$SiMe$_3$)$_4$] as the major product, and a red diamagnetic compound [Re$_2$O$_3$(CH$_2$SiMe$_3$)$_6$] in minor amounts. Interaction of [ReOCl$_3$(PPh$_3$)$_2$] with three equivalents of the Grignard reagent at low temperatures produces mainly the red species.

Interaction of Me$_3$SiCH$_2$Li in ether with [ReOCl$_3$(PPh$_3$)$_2$] gives a dark brown solution from which we have not been able to isolate a definite product. Reduced species, probably lithium salts, appear to be formed since careful introduction of dry air turns the solution green; [ReO(CH$_2$SiMe$_3$)$_4$] may then be isolated though in small yield. Interactions of Me$_3$SiCH$_2$Li with [ReOCl$_4$] and [Re$_2$Cl$_{10}$] give similar results.

Properties of Oxotetrakis(trimethylsilylmethyl)rhenium(VI).—This compound forms dark blue crystals, m.p. 35 °C. It is completely unaffected by air in either the solid state or in solutions in organic solvents during periods of several weeks. The difference from [ReOMe$_4$] is probably attributable to the greater steric bulk of the Me$_3$SiCH$_2$ groups which could prevent a sideways approach of the oxygen molecule. It is interesting that nitric oxide reacts quite readily as discussed later, probably because of an end-on approach. The thermal stability of the compound is high and decomposition (in a sealed tube) begins only at *ca.* 200 °C. It is very soluble in all common organic solvents and is readily sublimed *in vacuo* at room temperature.

Like the methyl, the compound shows no evidence of adduct formation or reaction with tertiary phosphines, amines, or carbon monoxide *etc.* The e.s.r. spectrum[11] in frozen benzene is similar to that of [ReOMe$_4$] and both compounds are considered to be square pyramidal. Further, the spectrum in pyridine is identical to that in benzene suggesting that there is no interaction in the axial position.

The Re=O bond is unreactive and attempts to prepare nitrido- and imido-derivatives analogous to those derived from [ReOCl$_3$(PPh$_3$)$_2$][14] led only to slight decomposition even after prolonged reaction times.

The complex will react with radical species like NO and NO$_2$ and with compounds capable of producing radicals like Br$_2$ even at −78 °C but the products have not been investigated except in the case of NO which gives [Re$_2$O$_3$(CH$_2$SiMe$_3$)$_6$]. In CCl$_4$, where CCl$_3$ radicals can be generated, there is also slow decomposition especially in light.

Reduction of [ReO(CH$_2$SiMe$_3$)$_4$] with sodium amalgam in tetrahydrofuran, sodium in liquid ammonia, or electrochemically in acetone gives what appears to be the diamagnetic anion [ReO(CH$_2$SiMe$_3$)$_4$]$^-$. Polarographic reduction in acetone gave a one-electron reduction wave with a half-wave potential of −0·41 V *vs.* the S.C.E. The anion decomposes quite rapidly and attempts to isolate a crystalline salt failed but freshly reduced solutions can be re-oxidised by air to [ReO(CH$_2$SiMe$_3$)$_4$].

Properties of [Re$_2$O$_3$(CH$_2$SiMe$_3$)$_4$].—The red, diamagnetic, needles, m.p. 139 °C, obtained either directly from [ReO(Cl)$_3$(PPh$_3$)$_2$] or by interaction of [ReO(CH$_2$SiMe$_3$)$_4$] with NO, are identical. The volatility is much less than [ReO(CH$_2$SiMe$_3$)$_4$] and the compounds are readily separated by fractional sublimation. The compound is less stable to air than is [ReO(CH$_2$SiMe$_3$)$_4$]; the solid decomposes over about a day while solutions turn from deep red to yellow in several hours.

Spectroscopic Properties of the Trimethylsilylmethyl Compounds.—Infrared spectra. Both compounds show absorptions characteristic of the trimethylsilylmethyl group; these can be assigned as before.[8] The Re–C stretches are weak and can be observed only in concentrated Nujol mulls.

For [M$_2$O$_3$L$_n$] complexes with linear M–O–M groups, three configurations have been recognised, linear, O=M–O–M=O, and isomers with *cis*- or *trans*-dioxo-groups. A structure for [Re$_2$O$_3$(CH$_2$SiMe$_3$)$_6$] with a bent Re–O–Re bridge can be excluded as this would require an absorption band in the 400—550 cm^{-1} region.[15,16] The *cis*- or *trans*-isomers usually can be differentiated by the frequencies of the M–O–M vibration which is in the range 730—950 cm^{-1} compared to 650—700 cm^{-1} in the linear case.[16,17] Unfortunately, absorptions in these regions of the spectrum of [Re$_2$O$_3$(CH$_2$SiMe$_3$)$_6$] are very similar both in frequency and intensity to those in [ReO(CH$_2$SiMe$_3$)$_4$] assigned to the trimethylsilylmethyl vibrations and no

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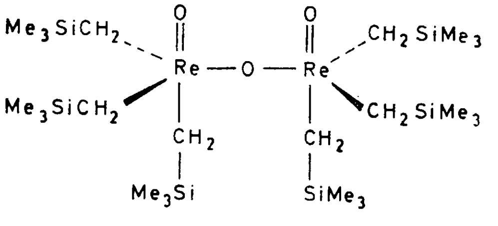
additional peaks or shoulders could be observed. However, it may be noted that (*a*) in *cis*-complexes of [Mo_2O_3] there are two strong bands assigned as terminal Mo=O stretches whereas in *trans* and linear complexes there is only one;[18] (*b*) in linear complexes,[16] the Re=O frequencies are in the 910—950 cm^{-1} region whereas they are 950—1050 cm^{-1} in non-linear isomers. Since [$Re_2O_3(CH_2SiMe_3)_6$] has two bands at 1008 and 990 cm^{-1} the *cis*-form (I) is thus indicated and consistent with this


(I)

there are also two Re–C stretches. Complexes containing the Re_2O_3 unit whose structures are confirmed by *X*-ray diffraction study are the rhenium(V) complexes [$Re_2O_3(CN)_8$]$^{4-}$ and [$Re_2O_3(S_2CNEt_2)_4$]; both have a linear O=Re–O–Re=O grouping.[19]

Mass spectrum. Weak molecular ions are observed for both compounds with the isotopic distributions expected for $ReOC_{16}H_{44}Si_4^+$ and $Re_2O_3C_{24}H_{66}Si_6^+$ respectively (Table 1).

The base peak in each spectrum occurs at *m*/*e* 464 corresponding to [$ReO(CH_2SiMe_3)_3$]$^+$. The molecular ions observed at 70 eV are 2% and nil respectively for [$ReO(CH_2SiMe_3)_4$] and [$Re_2O_3(CH_2SiMe_3)_6$]. These intensities are enhanced at lower electron voltages, 4% at 20 eV for [$ReO(CH_2SiMe_3)_4$] and 6% at 12 eV for 70 eV spectra show similar complicated patterns, due presumably to fragmentation of the CH_2SiMe_3 ligands. Sequential loss of further CH_2SiMe_3 groups from [$ReO(CH_2SiMe_3)_3$]$^+$ is not observed in either case.

N.m.r. spectrum. Although [$Re_2O_3(CH_2SiMe_3)_6$] formally contains Re^{VI}, it is diamagnetic. Numerous examples of spin-pairing *via* π-bonding in complexes with linear M–O–M groups are well established.[20] A previous example [21] for rhenium(VI) is the anion [$Re_2O_3Cl_8$]$^{3-}$. There are two closely spaced singlets at τ 9·8, 9·9 in the ratio 9 : 2 (accurate integration is difficult due to the proximity of the lines) that can be assigned to methyl of $SiMe_3$ and the methylene Re–CH_2Si, respectively. On cooling the solution below 0 °C, considerable broadening of the peaks occurs but even at −90 °C resolution is not obtained. The non-equivalence of the Me_3SiCH_2 groups that is implied is consistent with the structure (I).

EXPERIMENTAL

Microanalyses by A. Bernhardt, Mulheim and Imperial College Laboratories.

Infrared spectra were obtained using Perkin-Elmer 325 and 475 spectrometers calibrated with polystyrene over the region 5000—200 cm^{-1}. Samples of [$ReOMe_4$] were distilled into Nujol *in vacuo* and the solution mounted between KBr plates in an inert-atmosphere box. Low-temperature solid-state spectra were obtained by condensation of the compound onto a cooled (20 K) caesium iodide window from an argon stream. N.m.r. spectra were recorded on a Perkin-Elmer R14 (60 MHz) or R12A (100 MHz) spectrometer. Mass spectra were obtained using an AEI MS9 instrument.

Polarograms of [$ReO(CH_2SiMe_3)_4$] in acetone with Bu^t_4NI as supporting electrolyte and against the S.C.E. were obtained on a Beckman Electroscan ^{TM}30 polarograph.

Syntheses.—All syntheses and manipulations were carried out normally in oxygen-free nitrogen or argon and all solvents or reagents were vigorously purified, dried, and degassed by freeze-pumping. For work with [$ReOMe_4$] all glass apparatus was heated to *ca.* 400 °C under high vacuum before use, since otherwise extensive reaction with the surface occurs to give yellow-orange products. The rhenium was reagent-quality powder (99·9% B.D.H.). [$ReOCl_3(PPh_3)_2$] Was prepared from perrhenic acid.[22] [$ReOCl_4$] Was prepared either from [Re_2O_7] (from Re and dry oxygen [23]) and thionyl chloride [24] or by interaction of metal and sulphuryl chloride in a sealed tube at 350 °C. In contrast to the previous report [25] the latter reaction was incomplete even after 5 days. The reaction products and excess SO_2Cl_2 were removed *in vacuo* and [$ReOCl_4$] purified by trap-to-trap distillation.

Methyl-lithium was prepared in diethyl ether from lithium and methyl chloride and $Me_3CH_2SiMgCl$ [26] from Me_3SiCH_2Cl (Peninsular Chem. Res. Inc.).

Tetramethyloxorhenium(VI).—*Method* 1. A diethyl ether solution of MeLi (8 mmol) was added slowly to a stirred suspension of [$ReO(Cl)_3(PPh_3)_2$] (1·66 g, 2 mmol) in diethyl ether (100 ml) at −78 °C. The mixture was allowed to warm slowly to 0 °C and stirring was continued for *ca.* 1 h. The reaction begins *ca.* −30 °C and the solution becomes brown. When exposed to traces of air admitted judiciously through a stop-cock the solution rapidly becomes red. The solution was filtered at low temperature, the ether was removed slowly under vacuum at −40 °C. The *product* then sublimed onto a cold probe (−78 °C, 10^{-3} mmHg) as a red-purple crystalline solid, m.p., *ca.* 45 °C. Yields may be as high as 70% based on [$ReOCl_3(PPh_3)_2$] but losses inevitably occur because of co-distillation during removal of ether.

Instead of admitting air as above, a saturated aqueous solution of NH_4Cl (*ca.* 25 ml) can be added to the brown solution, which then becomes red. The solution was then frozen at −78 °C and the ether layer filtered at this tempera-

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ture. The filtrate was dried with anhydrous Na_2SO_4 and after removal of ether the product was sublimed as before.

Method 2. To a stirred solution of $[ReOCl_4]$ (1·02 g, 3 mmol) in diethyl ether (50 ml) at −78° C was slowly added methyl-lithium in ether (12 mmol). Rapid reaction occurs and the solution becomes dark brown; it was allowed to warm slowly to −10 °C and stirring was continued for *ca.* 30 min. The ether was removed at −40 °C *in vacuo* and the product was sublimed as above onto a cold probe; yield based on $[ReOCl_4]$ *ca.* 20%.

Oxotetrakis(*trimethylsilylmethyl*)*rhenium*(VI).—A suspension of $[ReOCl_3(PPh_3)_2]$ (2 g, 2·4 mmol) in diethyl ether (50 ml) at room temperature was stirred vigorously while a solution of trimethylsilylmethylmagnesium chloride (12 ml of 1M-solution) was run in from a syringe. An immediate dark blue colour appeared. Stirring was continued for *ca.* 1 h and the ether was removed under vacuum. The dark residue was washed with light petroleum (b.p. 40—60 °C, 3 × 15 ml). The undissolved material was largely triphenylphosphine. The washings were concentrated to *ca.* 5 ml and run onto a column of neutral alumina (activity I) under nitrogen. Elution with light petroleum gave a large blue band followed by a smaller red band. (Chromatography under nitrogen is not necessary for isolation of the blue compound but this prevents any decomposition of the red complex.) The red fraction was worked-up as detailed below.

Removal of solvent from the blue fraction left a blue oil which crystallised from acetone or ethanol solutions at −78 °C giving dark blue *needles* (1·33 g, 68%).

The product obtained by this procedure had m.p. 13 °C and appeared to contain traces of organic silicon derivatives (probably $Me_3SiCH_2CH_2SiMe_3$) which were not removed by repeated crystallisation from acetone. Further purification was achieved by fractional sublimation at 30 °C/10^{-4} mmHg when the impurities collected in the first fraction (*ca.* 10%). The second fraction after crystallisation from acetone at −78 °C had m.p. 35 °C and was used for analytical purposes (Found: C, 35·6; H, 7·9%. $C_{16}H_{44}OReSi_4$ requires C, 34·9; H, 8·0%).

μ-*Oxo-bis*[*oxotris*(*trimethylsilylmethyl*)*rhenium*(VI)].—*Method* 1. Trimethylsilylmethylmagnesium chloride (7·2 ml of 1M-solution in diethyl ether) was added to a suspension of $[ReOCl_3(PPh_3)_2]$ (2 g, 2·4 mmol) in diethyl ether (50 ml) at −78 °C. The mixture was stirred while slowly warming to room temperature. Chromatography in light petroleum (b.p. 40—60 °C) as described above gave a deep red solution which was concentrated and cooled to −25 °C overnight to give red *needles* (0·89 g, 53%), m.p. 139 °C, subl., 90 °C/10^{-4} mmHg [Found: C, 30·9; H, 7·2%; *M* (osmometric in C_6H_6 under nitrogen) 940 ± 90. $C_{24}H_{66}O_3Re_2Si_6$ requires C, 30·6; H, 7·1%; *M*, 944].

Method 2. A solution of $[ReO(CH_2SiMe_3)_4]$ in diethyl ether was exposed to an atmosphere of nitric oxide at −78 °C. The blue colour rapidly disappeared. Chromatography on alumina as above gave $[Re_2O_3(CH_2SiMe_3)_6]$ in yields of 90% or more. The fate of the NO and the trimethylsilylmethyl group was not determined. If the reaction mixture is first evaporated at −30 °C, a volatile yellow solid can be sublimed onto a probe at −78 °C. This rapidly decomposes on warming to give $[Re_2O_3(CH_2SiMe_3)_6]$. We have been unable to characterise this intermediate. There is a similar reaction sequence between $[ReO(CH_2SiMe_3)_4]$ and NO_2 leading to $[Re_2O_3(CH_2SiMe_3)]$.

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