The Chemistry of Rhenium Alkyls. Part III. The Synthesis and Reactions of Hexamethylrhenium(VI), *cis*-Trimethyldioxorhenium(VII), and the Octamethylrhenate(VI) Ion †

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The green, crystalline, paramagnetic (d^1) hexamethylrhenium, $ReMe_6$, has been prepared by interaction of tetramethyloxorhenium(VI), $ReOMe_4$, with trimethylaluminium. It is characterised by mass, i.r., and e.s.r. (reported separately) spectra. It reacts with dioxygen to give $ReOMe_4$ and with nitric oxide to give *cis*-trimethyldioxorhenium(VII), ReO_2Me_3; the latter is best prepared by the action of NO on $ReOMe_4$. The mechanism of this reaction is discussed and an intermediate of stoicheiometry $ReO(CH_3)_3(CH_3NO)$ is characterised. N.m.r. spectra of the oxo-species are reported.

Interaction of hexamethylrhenium with methyl-lithium forms the octamethylrhenate(VI) ion, which can be isolated as the tetramethylethylenediamine (tmed) salt $Li_2[ReMe_8]\cdot$tmed.

An improved synthesis of $ReOMe_4$ is given.

In previous papers, the synthesis[1] and electronic and e.s.r. spectra[2] of the oxotetra-alkyls of rhenium, $ReOR_4$ (R = Me and CH_2SiMe_3), have been described. The red tetramethyloxorhenium(VI) has now been converted by action of trimethylaluminium into green hexamethylrhenium(VI). This compound is only the second hexamethyl of a transition metal, the other being hexamethyltungsten(VI).[3] It is probably also only the second example of an ReX_6 compound. Although the gaseous hexafluororhenium(VI) is well characterised, there is no positive evidence[4] that the hexachloride exists despite claims of its synthesis. In view of the stability of hexamethylrhenium, there seems good reason to anticipate that the hexa-alkoxides and hexadialkylamides will also be stable.

This paper describes the synthesis of hexamethylrhenium and some of its properties. Also reported is the reaction with nitric oxide of $ReMe_6$ and $ReOMe_4$ to give the diamagnetic compound *cis*-ReO_2Me_3, the first transition metal alkyl with the metal in the VII oxidation state. The synthesis of the octamethylrhenate(VI) ion is also described. The e.s.r. spectra of $ReMe_6$ and the $[ReMe_8]^{2-}$ ion are discussed in Part IV.[5]

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† No reprints available. Preliminary note. L. Galyer, K. Mertis, and G. Wilkinson, *J. Organometallic Chem.*, 1975, **85**, C37.

[1] K. Mertis, D. H. Williamson, and G. Wilkinson, *J.C.S. Dalton*, 1975, 607.

[2] J. F. Gibson, K. Mertis, and G. Wilkinson, *J.C.S. Dalton*, 1975, 1093.

[3] A. J. Shortland and G. Wilkinson, *J.C.S. Dalton*, 1973, 372.

[4] J. Burgess, C. J. W. Fraser, I. Haigh, and R. D. Peacock, *J.C.S. Dalton*, 1973, 501.

[5] J. F. Gibson, G. Lack, K. Mertis, and G. Wilkinson, *J.C.S. Dalton*, following paper.

Hexamethylrhenium(VI) *and Its Properties.*—The interaction of petroleum solutions of $ReOMe_4$ (or ReO_2Me_3) with trimethylaluminium in light petroleum gives an intense green solution from which hexamethylrhenium can be readily isolated. The compound can also be obtained, though in low yield, by interaction of trimethylaluminium with a suspension of dirhenium heptaoxide, Re_2O_7, in light petroleum. Attempts to synthesise mixed alkyls by treating $ReOMe_4$ with etherates of triethylaluminium and tris(trimethylsilylmethyl)-aluminium were unsuccessful. In the first case only decomposition occurred, while in the second, an exchange reaction gave the previously characterised [1] blue compound $ReO(CH_2SiMe_3)_4$.

Hexamethylrhenium is a green crystalline solid that can be kept indefinitely at −20 °C but which decomposes at about 10 °C to give a black residue and methane. The crystalline solid should be handled with caution since in one case admission of nitrogen to a sample *in vacuo* caused a violent detonation. The compound is extremely air sensitive (see below) and is also somewhat light sensitive so that it should be protected from extended exposure to light. It is very volatile, though less so than $ReOMe_4$, and sublimes at −30 °C and 10^{-3} mmHg. The compound is very soluble in n-hexane, from which it can be crystallised, and in CS_2, CCl_4, diethyl ether, *etc.*; in these solvents there is slow decomposition in light at room temperature to give dark residues and light brown solutions. The solutions in benzene and other aromatic hydrocarbons are more stable, decomposing only after several days.

The mass spectrum (Table 1) gives ions identified by the correct rhenium isotopic distribution and mass number. All ions $ReMe_n^+$ (n = 6—0) were observed at both 70 and 16 eV. The i.r. spectrum (Table 2) shows only the expected methyl group vibrations and a band at 500 cm^{-1} assignable as the Re–C stretching frequency. Attempts to obtain the Raman spectrum failed due to decomposition in the laser beam even at low temperatures.

TABLE 1

Mass spectra of hexamethylrhenium(VI) (70 eV)

Ion	*m/e*	Ratio
$ReMe_6^+$	277, 275	9.8
$ReMe_5^+$	262, 260	79
$ReMe_4^+$	247, 245	100
$ReMe_3^+$	232, 230	23
$ReMe_2^+$	217, 215	7.5
$ReMe^+$	202, 200	17.5
Re^+	187, 185	22.5

Hexamethylrhenium is only slowly decomposed by water. It is particularly reactive towards radical species. With controlled amounts of oxygen, the carmine $ReOMe_4$ is formed. This reaction can be followed at liquid-nitrogen temperature by e.s.r. spectra.[5] In the reaction of $ReOMe_4$ with dioxygen the e.s.r. spectra [2] were consistent with the formation of a rhenium(VII) superoxo-complex, $Me_4Re(O)O_2\cdot$, having a single unpaired electron located on an oxygen atom. However, no e.s.r. signal for a similar species $Me_6ReOO\cdot$ could be detected at −178 °C which suggests direct attack of oxygen *via* a four-centre transition state. Methyl transfer to an oxygen atom in a way similar to that discussed later for methyl transfer to the nitrogen atom of NO could then lead to formation of a Re=O bond, and possibly dimethyl ether.

TABLE 2

I.r. spectra of hexamethylrhenium(VI) and *cis*-trimethyldioxorhenium(VII) (in cm^{-1})

$ReMe_6$		*cis*-ReO_2Me_3	
a	Assignments	*b*	*c*
2 958 2 910 m 2 820	C–H str	2 985 2 920 m 2 890	2 980 2 942 2 919 m 2 840
1 370m	C–H def	1 390 1 360 m 1 150	1 380 1 188 m
	Re=O str	992s 951vs	992s 951vs
680m, sh	CH_3 rock	752m	752s
500w, sh	Re–C str	512w	512w

[a] Nujol and CS_2 solutions. [b] Nujol and as a liquid film between KBr plates. [c] CS_2 and CCl_4 solutions.

There is a rapid reaction between $ReMe_6$ and nitric oxide and small yields of a volatile yellow compound were obtained. This appeared to be identical with that obtained [1] by interaction of $ReOMe_4$ but not reported in detail.

cis-*Trimethyldioxorhenium*(VII) *and Its Properties.*—This yellow compound is best prepared by the action of nitric oxide on a diethyl ether solution of $ReOMe_4$ at −78 °C. Although it is an oil at room temperature, it can be obtained as pale yellow needles, m.p. *ca.* 10 °C, from light petroleum at low temperatures. The compound is volatile, readily distilling *in vacuo*, and it is reasonably stable at room temperature. The only other similar dioxorhenium species is ReO_2F_3.[6]

I.r. and n.m.r. spectra are consistent with the trigonal bipyramidal structure (E) shown in the Scheme. Thus the i.r. (Table 2) has bands due to methyl vibrations together with two strong bands attributable to the *cis*-ReO_2 group at 992 and 951 cm^{-1}. The n.m.r. spectrum in CS_2 or deuteriotoluene has two sharp resonances at τ 7.5 and 7.93, ratio 2 : 1, so that the higher field line is presumable due to the axial methyl group. There is no significant line broadening in the spectrum on cooling toluene solutions to −78 °C or heating to 85 °C, so that the molecule appears to be rigid. The mass spectrum shows peaks due to the ions $ReO_2Me_2^+$, ReO_2Me^+, and ReO^+, but the molecular ion was not observed even at 17 eV.

The compound reacts with $AlMe_3$ in light petroleum to give $ReMe_6$, in high yield.

Mechanism of Reaction of Methyl Compounds with Nitric Oxide.—The reactions of $ReOMe_4$ and $ReMe_6$ with nitric oxide and dioxygen both give compounds with an

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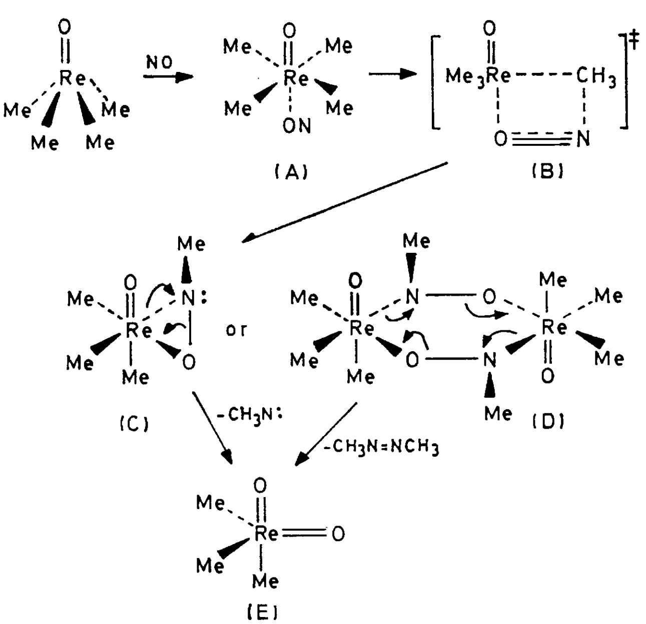
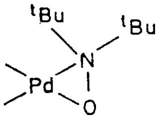
[6] E. E. Aynsley, R. D. Peacock, and P. L. Robinson, *J. Chem. Soc.*, 1950, 1622.

Re=O bond, in contrast to the reaction of WMe$_6$ where insertion occurs to give, respectively, Me$_4$W{ON(Me)NO}$_2$ and W(OMe)$_6$.[3] This difference can be attributed to the fact that the rhenium methyls are paramagnetic with a single unpaired electron and that the reaction pathway is accordingly different. The cleavage of the N–O bond of nitric oxide under very mild conditions does not normally occur in reactions involving transition-metal compounds, although NO reacts with triphenylphosphine at 140 °C to give Ph$_3$PO, which is also formed by the action of Ph$_3$P on nitrosyl complexes such as {Co(NO)$_2$Cl}$_2$.[7] Interaction of (η^5-C$_5$H$_5$)Mo(CO)$_2$NO with Ph$_3$P in a CO atmosphere under u.v. irradiation also gives Ph$_3$PO together with (η^5-C$_5$H$_5$)Mo(CO)$_2$(PPh$_3$)(NCO).[8]

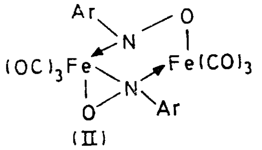


Scheme Interaction of NO with ReOMe$_4$

The reaction of NO with a paramagnetic metal methyl compound could be expected to differ from the reaction with a diamagnetic methyl since the latter, of necessity, must initially form a radical species. Thus for hexamethyltungsten it was proposed [3] that there is a methyl transfer to the nitrogen atom of co-ordinated NO * and that the radical species Me$_5$WO$\dot{N}$(Me) then reacts rapidly with more NO to generate an N–N bond in the *N*-methyl-*N*-nitrosohydroxylaminato-chelate ring of the compound, Me$_5$W{ON(Me)NO}. Since the tungsten atom in the latter is but seven-co-ordinate, the reaction with NO proceeds further to give a second chelate ring and the co-ordinatively saturated, eight-co-ordinate species, Me$_4$W{ON(Me)NO}$_2$. The same argument applies to the reaction of NO with Me$_3$TaCl$_2$ [9] and (η^5-C$_5$H$_5$)$_2$ZrMe$_2$ [10]; although the resulting compound in the latter case was not so formulated, it probably has a chelate ring.[3] For a paramagnetic alkyl with a single unpaired electron the interaction with nitric oxide presumably occurs initially with spin pairing. Hence further reaction with NO to generate an –N–N– bond and the ligand –ON(Me)NO– is precluded. The reaction sequence shown in the Scheme seems reasonable. We suggest initial co-ordination of nitric oxide and concomitant electron transfer to rhenium to give a diamagnetic, formally rhenium(v) species (A). Whether the NO is bound by oxygen, is at an angle or is sideways, is immaterial, but since there are no filled orbitals on the metal π-bonding is unlikely. Rapid methyl transfer to the nitrogen atom *via* a four-centre transition state, (B), leads to the formally rhenium(VII) species (C) or the similar bridged dimeric species (D). While RNO species of the type (C) do not appear to be known,† palladium complexes that have di-t-butyl nitroxide bound in a three-membered metallocycle ring (I) have been described.[11] A bridged nitroso aryl iron complex (II) has been characterised [12] and provides a reasonable model for species (D), although in (D) co-ordination of the nitrogen atom to the metal through its lone pair seems unlikely since this would lead to seven-co-ordination for the rhenium; this possibility cannot, however, be excluded and would appear to facilitate N=N bond formation. Intramolecular collapse of the ring in (C) would generate the nitrene CH$_3\ddot{N}$:, which would presumably rapidly dimerise to CH$_3\ddot{N}$=$\ddot{N}$CH$_3$ and *cis*-ReO$_2$Me$_3$. Similarly in (D) intramolecular collapse with cleavage of N–O bonds could produce azomethane directly by N=N bond formation. Although we cannot be certain whether the intermediate has structure (C),



(I)



(II)

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* Matrix isolation techniques indicate that below −196 °C no adducts of WMe$_6$ with NO, CO, H$_2$, or O$_2$ are formed (C. W. DeKock, 19th Ann. Rep. on Research, Petroleum Research Fund, Amer. Chem. Soc., 1975, p. 212) so that reaction of NO with WMe$_6$ possibly proceeds without prior co-ordination of NO.

† Radical nitroxide compounds L$_n$MN(R)O· have been characterised by e.s.r. study at low-temperature and metal centred radicals added to nitroso-compounds, *e.g.* irradiation of (CO)$_5$MnR and nitrosodurene gives (CO)$_5$MnN(Ar)O· (see A. Hudson *et al.*, *J.C.S. Chem. Comm.*, 1974, 966). The use of RNO as spin traps may be misleading, since it is quite likely that oxidative addition of RNO alone to species such as Pt(PPh$_3$)$_3$ can occur giving metallocycles of type C(*cf.* P. K. Wong, K. S. Y. Lau, and J. K. Stille, *J. Amer. Chem. Soc.*, 1974, **96**, 5956). In PhNO$_2$PdCl$_2$, nitrosobenzene is bound through the N atom (R. G. Little and R. J. Doedens, *Inorg. Chem.*, 1973, **12**, 537).

[7] W. Hieber and K. Heinicke, *Z. anorg. Chem.*, 1962, **316**, 305; W. Hieber and R. Kramolowsky, *Z. anorg. Chem.*, 1963, **321**, 94.

[8] A. T. McPhail, *J. Chem. Soc.* (*A*), 1971, 205.

[9] J. D. Wilkins and M. G. B. Drew, *J. Organometallic Chem.*, 1974, **69**, 111.

[10] P. C. Wailes, H. Weigold, and A. P. Bell, *J. Organometallic Chem.*, 1972, **34**, 155.

[11] W. Beck and K. Schmidtner, *Chem. Ber.*, 1967, **100**, 3363; M. Okunaka, G. Matsubayashi, and T. Tanaka, *Bull. Chem. Soc. Japan*, 1975, **48**, 1826.

[12] M. S. Barrow and O. S. Mills, *J. Chem. Soc.* (*A*), 1971, 864. See also G. P. Khave and R. J. Doedens, *Inorg. Chem.*, 1976, **15**, 86.

(D), or type II, nevertheless convincing evidence for the general correctness of the Scheme is the isolation of a yellow crystalline compound that is stable at low temperatures, but which begins to decompose above 0 °C and rapidly at 20 °C to give orange-brown residues from which *cis*-ReO_2Me_3 can be sublimed. The mass spectrum of the gas evolved shows a fragmentation pattern in good agreement with that reported for azomethane.[13] Thus under our experimental conditions, the most abundant fragments were $C_2H_3N_2^+$, $CH_3N_2^+$, $CH_2N_2^+$, CH_2N^+, N_2^+, $C_2H_4^+$, and CH_3^+.

The n.m.r. spectrum of the yellow compound in CS_2 and deuteriotoluene at -35 °C is consistent with either structure (C) or (D). There are three single resonances at τ 5.7, 7.4, and 8.0 in a ratio 1 : 1 : 2. The lowest field resonance is assigned to the CH_3 group bound to nitrogen since the CH_3 groups in *cis*-ReO_2Me_3 are at τ 7.5 and 7.93. Although the methyl groups *trans* to the N and O atoms of the CH_3NO moiety should be different, they could well have a similar chemical shift and appear as a peak of relative intensity 2, as is observed. When the solution is allowed to warm the intensity of the lines due to the intermediate begin to decrease at *ca.* 5 °C and have disappeared at 35 °C, while lines of *cis*-ReO_2Me_3 simultaneously grow. The azomethane formed is not evident in the n.m.r. spectra since as a gas it may be lost from the solution, though a small transient peak at τ 7.85 could be due to this compound.

Dilithium Octamethylrhenate(VI).—Hexamethylrhenium reacts readily with methyl-lithium at -78 °C to give red solutions. From diethyl ether red-orange, and from toluene, bright red crystals can be obtained. These are pyrophoric and decompose rapidly both in the solid state and in solution at room temperature. The solution reacts with both dimethylpiperazine and 1,10-phenanthroline but with tetramethylethylenediamine (tmed) light yellow pyrophoric thermally unstable crystals were obtained and were shown to be $Li_2[ReMe_8]\cdot$tmed where the lithium ion is presumably solvated. The e.s.r. spectrum discussed separately [5] is consistent with square antiprismatic co-ordination of rhenium(VI).

EXPERIMENTAL

Microanalyses were by the Imperial College and Bernhardt, Mülheim, laboratories. Rhenium and lithium analyses were made in this Department by Mr. John Gulton using a plasma arc emission absorption instrument.

I.r. spectra were recorded on Perkin-Elmer 325 and 475 spectrometers and n.m.r. spectra on Perkin-Elmer R12A or R14 spectrometers at 60 or 100 MHz. Mass spectra were obtained using an AEI-MS9 with direct inlet technique.

All syntheses and manipulations were carried out *in vacuo* or under oxygen-free nitrogen or argon. All solvents and reagents were carefully purified, dried, and deoxygenated. In handling $ReMe_6$, the glassware was thoroughly flamed under vacuum.

The rhenium was B.D.H. reagent quality (99.5%), the trimethylaluminium from the Ethyl Corporation, and nitric oxide from Matheson Co. The NO was passed through concentrated sulphuric acid, 50% potassium hydroxide, a trap at -78 °C, and a P_2O_5 drying tube before collection at liquid-nitrogen temperature; head fractions were discarded. The petroleum used had b.p. 30—40 °C.

Hexamethylrhenium.—(**CAUTION** *This material may detonate and a protective screen should be used in handling pure substance.*) To tetramethyloxorhenium (*ca.* 0.5 g) in petroleum (40 cm³) at 0 °C was added dropwise, slowly with rapid stirring, a petroleum solution of trimethylaluminium (*ca.* 1M). It is essential that the solution of $ReOMe_4$ be *extremely dry* otherwise the reaction gives brown decomposition products. The addition of $AlMe_3$ was stopped when the red colour changed to deep green. The stirring was maintained for 30 min; the solution was then cooled to -78 °C and the excess of $AlMe_3$ was destroyed by dropwise injection of water (*ca.* 10 cm³). The stirred solution was left to warm slowly to room temperature after which it was again cooled to -78 °C. The petroleum layer was decanted from ice and aluminium hydroxide, filtered through a frit at -78 °C, and the solvent slowly removed under vacuum at -45 °C. The residue was then sublimed to a probe at -78 °C at 10^{-3} mmHg to give the green crystalline *hexamethylrhenium* (yield, *ca.* 60%), decomp. 10—12 °C.

The compound can be crystallised from hexane or petroleum. It is readily freed from its oxidation products, principally $ReOMe_4$, by trap-to-trap sublimation (the $ReOMe_4$ sublimes at *ca.* -20 °C).

The compound *cis*-ReO_2Me_3 can be used in place of $ReOMe_4$.

Trimethyl(nitrosomethyl)oxorhenium(VII) *and* cis-*Trimethyldioxorhenium*(VII).—A solution of $ReOMe_4$ (*ca.* 0.5 g) in petroleum (*ca.* 40 cm³) at -78 °C was exposed to nitric oxide. The red colour disappeared and yellow crystals of the intermediate $ReOMe_3(MeNO)$ or $[ReOMe_3(MeNO)]_2$ were precipitated; these were collected on a frit at -78 °C, washed twice with petroleum (*ca.* 2 cm³ at -78 °C), and freed from solvent by pumping at -20 °C (10^{-3} mmHg) for several hours. The compound was too unstable to obtain satisfactory microanalyses.

For direct isolation of *cis*-trimethyldioxorhenium the reaction of $ReOMe_4$ and NO was carried out at -78 °C in ether and the solution left to warm to room temperature with stirring. After *ca.* 1 h, the ether was removed at -40 °C *in vacuo* and the yellow crystalline *compound* sublimed onto a probe at -78 °C, 10^{-3} mmHg (yield *ca.* 60%), m.p. 10—11 °C (Found: C, 13.4; H, 3.4%. $C_3H_9O_2Re$ requires C, 13.7; H, 3.4%). The compound can be crystallised from petroleum solutions on cooling to -78 °C.

Lithium Octamethylrhenate(VI).—A solution of $ReMe_6$ (*ca.* 0.25 g) in ether (10 cm³) was cooled to -78 °C and methyl-lithium in ether was slowly added with stirring until the green solution became orange-red. The solution was left to warm to 0 °C and stirring was then continued for 0.5 h, when the ether was removed at -10 °C *in vacuo*. To the residue was added toluene (15 cm³) and the deep red solution filtered at low temperature and concentrated to *ca.* 3 cm³ when red crystals were obtained. These were collected at low temperature and solvent pumped off at -10 °C (Found: Re : Li = 1 : 2.07 ± 0.1. $C_8H_{24}Li_2Re$ requires Re : Li = 1 : 2).

For the tetramethylenediamine salt, the red crystals from toluene were dissolved in ether (10 cm³) filtered at -78 °C and tmed added to the solution at 0 °C when a light yellow

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[13] L. J. Stief and P. Ausloos, *J. Phys. Chem.*, 1961, **65**, 877; Z. Prášil and W. Forst, *J. Amer. Chem. Soc.*, 1968, **90**, 3344.

crystalline solid was immediately precipitated. This was collected at −78 °C, washed twice with cold ether (15 cm^3), and dried at −10 °C *in vacuo* (Found: Re : Li = 1 : 1.9 ± 0.1; Li, 3.3%; Re, 42.8%. Li_2ReMe_8·tmed requires Re : Li = 1 : 2; Li, 3.2; Re, 42.68%). The compound is pyrophoric and thermally unstable at room temperature, but it can be quickly weighed out for analyses.

Tetramethyloxorhenium.—The following procedure is an improvement on the original[1] and gives high yields reproducibly.

A diethyl ether solution of MeLi *ca.* 1M (0.08 mol, 80 cm^3) was added slowly to a suspension of $ReOCl_3(PPh_3)_2$ (8.31 g, 0.01 mol) in diethyl ether (120 cm^3) at −78 °C and the mixture was allowed to warm slowly at room temperature. The dark brown solution was stirred for *ca.* ½ h when the excess of MeLi was destroyed by dropwise addition at −78 °C of water (*ca.* 10 cm^3). After being allowed to warm to room temperature the solution was cooled again to −30 °C and hydrogen peroxide (2.5 g, 30% H_2O_2 diluted in 20 cm^3 of H_2O) was added dropwise very slowly with vigorous stirring. The colour of the solution rapidly changed to red and stirring was continued after warming to room temperature for *ca.* ½ h. The solution was then cooled to −78 °C and the ether layer was filtered free from ice, and dried first with anhydrous calcium chloride at room temperature, and then with molecular sieves. The solution was cooled again to −78 °C, filtered, and the solvent was carefully removed at −50 °C. The crystalline $ReOMe_4$ was then sublimed onto a cold probe at −78 °C, 10^{-3} mmHg; yield 1.26 g, *ca.* 48% based on $ReOCl_3(PPh_3)_2$. Losses of $ReOMe_4$ occur mainly on removal of solvent *in vacuo*.

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