The Interaction of Hydrogen with Tri-μ-chloro-hexakis(trimethylsilylmethyl)-*triangulo*-trirhenium(III), its Adducts with Carbon Monoxide, Triphenylphosphine, and Pyridine and with Tri-μ-chloro-chloropentakis-(trimethylsilylmethyl)-*triangulo*-trirhenium(III). The *X*-ray Crystal Structures of Hydridononakis(trimethylsilylmethyl)bis[tri-μ-chloro-*triangulo*-trirhenium(III)],† Tri-μ-chloro-chlorohydridotetrakis(trimethylsilylmethyl)(triphenylphosphine)-*triangulo*-trirhenium(III), and *syn,syn,-anti*-Trichloro-tris(μ-trimethylsilylmethyl)-tris(trimethylsilylmethyl)-*triangulo*-trirhenium(III) ‡

By **Konstantinos Mertis, Peter G. Edwards,** and **Geoffrey Wilkinson,*** Chemistry Department, Imperial College of Science and Technology, London SW7 2AY
K. M. Abdul Malik and **Michael B. Hursthouse,*** Chemistry Department, Queen Mary College, London E1 4NS

The interaction of tri-μ-chloro-hexakis(trimethylsilylmethyl)-*triangulo*-trirhenium(III), $Re_3(\mu\text{-}Cl)_3(CH_2SiMe_3)_6$, with dihydrogen in tetrahydrofuran leads to a hexanuclear hydrido-alkyl $(Me_3SiCH_2)_5(\mu\text{-}Cl)_3Re_3{-}Re_3(\mu\text{-}Cl)_3H(CH_2SiMe_3)_4$, (1), whose structure has been determined by *X*-ray diffraction. Crystals are triclinic, space group $P\bar{1}$, with $a = 15.950(5)$, $b = 16.351(6)$, $c = 16.386(6)$ Å, $\alpha = 62.31(2)$, $\beta = 94.25(3)$, $\gamma = 99.77(3)°$, and $Z = 2$. The structure was solved and refined to an R of 0.055 using 6 796 unique observed data (out of 10 203 measured). The two Re_3 triangles are linked by a single Re–Re bond of length 2.993(1) Å which constitutes, in each case, one of the terminal, out-of-plane bonds on six-co-ordinated Re. The Re–Re distances in the Re_3 triangle [2.390—2.420(1) Å] are slightly disturbed by the asymmetry of the co-ordinated ligands.

Hydrogenation of $Re_3Cl_3(CH_2SiMe_3)_6$ in benzene, by contrast, produces a hexanuclear hydrido-alkyl, $Re_6(\mu\text{-}Cl)_6H_6(CH_2SiMe_3)_6$, (2), for which a structure with two *triangulo*-Re_3Cl_3 units linked by alkyl bridges and with terminal hydrogen atoms is proposed.

The interaction of the alkyl $Re_3(\mu\text{-}Cl)_3Cl(CH_2SiMe_3)_5$, which has a terminal Re–Cl group, with hydrogen in the presence of triphenylphosphine gives a green complex, $Re_3(\mu\text{-}Cl)_3ClH(CH_2SiMe_3)_4(PPh_3)$, (3), whose structure has been determined by *X*-ray diffraction. These crystals are also triclinic, space group $P\bar{1}$ with $a = 17.732(3)$, $b = 13.212(3)$, $c = 11.723(4)$ Å, $\alpha = 90.95(3)$, $\beta = 95.04(3)$, $\gamma = 83.74(2)°$, and $Z = 2$. The final R value is 0.063 for 3 704 (8 536) observed data. The Re–Re distances in the Re_3 triangle [2.382(1)—2.411(2) Å] show the expected variation with rhenium co-ordination number. The phosphine is quite weakly bound [Re–P = 2.617(7) Å].

The interaction of hydrogen with the adducts $Re_3(\mu\text{-}Cl)_3(CH_2SiMe_3)_6L_3$, L = CO, PPh_3, pyridine (py), and H_2O, has been studied. For L = CO and PPh_3, reductive cleavage of the cluster occurs to give the rhenium(II) metal–metal bonded dimers $Re_2Cl_2(CH_2SiMe_3)_2(CO)_2$, (4), and $Re_2Cl_2(CH_2SiMe_3)_2(PPh_3)_2$, (5). For L = py the *triangulo*-trirhenium cluster is retained in the paramagnetic rhenium(II) alkyl $Re_3(\mu\text{-}Cl)_3(CH_2SiMe_3)_3(py)_3$, (6), whose e.s.r. spectrum is discussed. For L = H_2O, a polynuclear cluster, probably $[Re_3(\mu\text{-}Cl)_3(CH_2SiMe_3)_3(OH_2)_3]_6$, (7), is obtained.

The hydride (2) isomerises alk-1-enes under nitrogen and hydrogenates them under hydrogen, but the catalytic reaction decays due to the formation of a non-hydride hexanuclear species, $Re_6(\mu\text{-}Cl)_6(CH_2SiMe_3)_6$, (8). Thermal decomposition of (2) leads to a dodecameric species, $Re_{12}(\mu\text{-}Cl)_{12}(CH_2SiMe_3)_6$, (9).

The hydrogenation of the red supernatant from the synthesis of $Re_3(\mu\text{-}Cl)_3(CH_2SiMe_3)_6$ leads to a red isomer of this blue species, which *X*-ray structural determination shows to have bridging alkyl groups and to be $Re_3Cl_3(\mu\text{-}CH_2SiMe_3)_3(CH_2SiMe_3)_3$, (10), and *syn,syn,anti*-terminal chlorine atoms. The compound is monoclinic, space group $P2_1/n$, with $a = 17.939(2)$, $b = 11.280(1)$, $c = 22.933(4)$ Å, $\beta = 109.98(1)°$, and $Z = 4$. The final R value is 0.048 for 5 293 (8 487) observed data. The Re–Re distances here are 2.337—2.359(1) Å and are shorter than in the isomeric chloride-bridged species. Small distortions in the Re_3C_3 cluster are attributed to intramolecular crowding.

New aryl *triangulo*-clusters $Re_3(\mu\text{-}Cl)_3R_6$, R = C_6H_5, (11), and C_6H_4Me-*p*, (12), and the bridged methyl $Re_3(\mu\text{-}CH_3)_3(CH_2SiMe_3)_6$ (13), are described.

We have described [1,2] the synthesis and characterisation of *triangulo*-trirhenium-(III) and -(IV) alkyls such as $(Re_3Me_9)_n$, $Re_3(\mu\text{-}Cl)_3(CH_2SiMe_3)_6$, and $Re_3(CH_2SiMe_3)_{12}$, as well as carboxylato- and other derivatives [3] of rhenium(III) such as $Re_6(\mu\text{-}Cl)_6(\mu\text{-}CO_2Me)_6Me_6$. The structure of $Re_3(\mu\text{-}Cl)_3(CH_2SiMe_3)_6$,[4] of $Re_3(\mu\text{-}Me)_3Me_6(PEt_2Ph)_2$,[2] and of $Re_3(\mu\text{-}Cl_3)(CH_2SiMe_3)_5[ON(CH_2SiMe_3)NO]$ [2] have been confirmed by *X*-ray diffraction studies.

We now report the synthesis and characterisation of a number of polynuclear alkyl compounds [5] derived from $Re_3Cl_3(CH_2SiMe_3)_6$ (hereafter CH_2SiMe_3 = R), and of aryl analogues of the latter.

N.m.r. data for the new compounds are given in Table 1 and analytical data in Table 2.

1. *Interaction of Hydrogen with Tri-μ-chloro-hexakis-(trimethylsilylmethyl)-*triangulo*-trirhenium*(III).—(a) *In tetrahydrofuran.* Hydrogenation of $Re_3Cl_3R_6$ in tetrahydrofuran (thf) at 2 atm § pressure and ambient temperature gives a solution from which a green, thermally

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† 3-Hydrido-1,1,1′,1′,2,2,2′,2′,3′-nonakis(trimethylsilylmethyl)-3,3′-bis(tri-μ-chloro-*triangulo*-trirhenium).

‡ No reprints available.

§ Throughout this paper: 1 atm = 101 325 Pa; 1 G = 10^{-4} T; 1 B.M. ≈ 9.27×10^{-4} A m²; 1 mmHg ≈ 13.6 × 9.8 Pa.

stable hydrido-alkyl complex, $Re_6(\mu\text{-}Cl)_6HR_9$, (1), can be isolated.

The structure of this complex, which has been determined by *X*-ray diffraction study as described later, is shown in Figure 1. The two Re_3Cl_3 *triangulo* units are linked by a long Re–Re single bond and there are formally four Re^{III} d^4 and two Re^{II} d^5 atoms, the latter being the ones formed by the metal–metal bond so that the compound has an even number of electrons and is diamagnetic. The ^1H n.m.r. spectrum shows a sharp singlet at δ 0.4 p.p.m. (CH_2SiMe_3) and a singlet at δ −4.0 p.p.m. assignable to Re–H. The $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum has two rather broad peaks at δ 1.5 and 0.2 p.p.m. that can be assigned to CH_2 and CH_3 resonances, but the unique alkyl group bound to the formally Re^{II} atom cannot be distinguished spectroscopically nor can the Re–H stretch be detected in the i.r. spectrum. Although in the crystal the H and R groups are *trans* about the Re–Re bond, in solution there will presumably be free or almost free rotation.

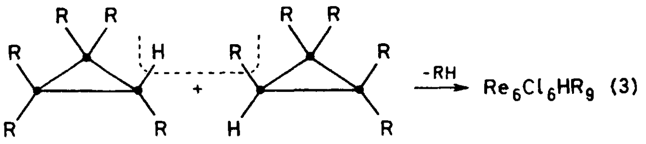
The formation of $Re_6Cl_6HR_9$ according to the stoicheiometry shown in equation (1) probably involves the initial

$$2Re_3Cl_3R_6 + 2H_2 \longrightarrow Re_6Cl_6HR_9 + 3SiMe_4 \quad (1)$$

oxidative addition of hydrogen to one rhenium of the triangle followed by intramolecular hydrogen transfer and reductive elimination of tetramethylsilane [equation (2)]. This is followed by intermolecular elimination of

$$Re_3Cl_3R_6 \xrightarrow{H_2} Re_3^{III,III,V}Cl_3H_2R_6 \xrightarrow{-RH} Re_3Cl_3HR_5 \quad (2)$$

$SiMe_4$ as in equation (3) (the μ-Cl atoms are omitted in this and other similar diagrams and Re=Re double bonds in the triangles are not indicated).



This reaction is to be contrasted with that in benzene discussed below which leads to $Re_6Cl_6H_6R_6$, where bridging alkyl groups appear to be formed. The reason for the difference may be that thf co-ordinates more strongly to the vacant end sites on rhenium intermediates, thus inhibiting the formation of alkyl bridges between two Re_3Cl_3 units.

(b) *In benzene or light petroleum.* The interaction of the blue *triangulo* cluster in benzene or light petroleum solutions, or in the solid state, with dihydrogen at 2 atm pressure at ambient temperatures yields a mixture of products from which the major product, a green crystalline complex, can be isolated. Analytical, molecular weight, and spectroscopic data indicate that this is $[Re_3(\mu\text{-}Cl)_3H_3R_3]_2$, (2).

This hydride is moderately stable in air and is slightly unstable thermally in solution at room temperature (half-life in benzene about 30 h) but it can be stored for months at −20 °C under nitrogen. The compound is extremely soluble in aliphatic and aromatic hydrocarbons, diethyl ether, dichloromethane, *etc.*, but is less soluble in more polar solvents such as acetone, acetonitrile, or methanol. Although it can be crystallised at low temperatures from light petroleum as needles, we have not yet obtained crystals suitable for *X*-ray structural determination due to clustering and twinning. The compound is not volatile.

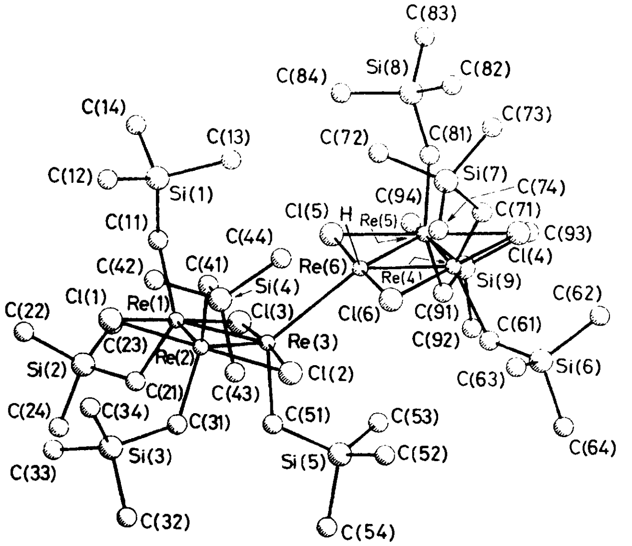


FIGURE 1 Molecular structure of $Re_6(\mu\text{-}Cl)_6H(CH_2SiMe_3)_9$ showing the atom-numbering system

The i.r. spectrum of (2) shows bands characteristic of the CH_2SiMe_3 group, a band at 2 030 cm^{-1} (Re–H), and a weak band at 350 cm^{-1} probably due to the CH_2SiMe_3 ligand.

The ^1H n.m.r. spectrum has only a broad singlet centred at δ 0.3 p.p.m. and a singlet at δ −5.85 p.p.m. The former can be assigned to CH_2SiMe_3 where the CH_3 and CH_2 resonances are coincident, as has been commonly observed for other trimethylsilylmethyl compounds,[1,2] and the high-field line to a terminal Re–H.

The $^{13}C\text{-}\{^1H\}$ spectrum has two broad peaks at δ 2.2 and 0.1 p.p.m. (relative to $SiMe_4$ δ 0.0 p.p.m.) due to CH_2 and CH_3 respectively.

The reaction of $Re_3Cl_3R_6$ and hydrogen can be followed by ^1H n.m.r. A peak due to $SiMe_4$ appears and after *ca.* 10 min this is of intensity equal to that of the CH_2SiMe_3 resonance, suggesting that there is hydrogenolysis of one alkyl group per rhenium. Mass-spectrometric examination of the gas collected in the reaction shows not only $SiMe_4$, but smaller amounts of CH_4, C_2H_4, $SiHMe_3$, and $(SiMe_3)_2$, suggesting that there are side reactions leading to species other than the main product but so far we have been unable to isolate them. On reaction of (2) with chlorine in CCl_4 only $CH_2ClSiMe_3$ and HCl are formed, confirming that no carbene or carbyne groups are present.

The spectroscopic data are consistent with a polynuclear structure (I) with terminal hydrides and bridging alkyl groups. Any Re_3 intermediates of stoicheiometry $Re_3(\mu\text{-}Cl)_3H_3R_3$ would not only have a co-ordinatively and electronically (16-e) unsaturated rhenium atom but also a very small ligand, *i.e.* H, replacing the bulky alkyl in $Re_3Cl_3R_6$, so that it is not surprising that dimerisation *via* bridging alkyls occurs to increase the co-ordination at rhenium.

There is no necessity for Re–Re bonding between the two Re_3 units although there will be the usual Re–Re double bonding in each triangle. The triangles may either be eclipsed as shown in (Ia) or staggered as in (Ib).

The formation of the hydride can be accounted for by stepwise oxidative addition of hydrogen to rhenium followed by reductive elimination of tetramethylsilane as in equation (2), successively at the three rhenium centres. It does not follow that $Re_3Cl_3H_3R_3$ necessarily is an intermediate since alkyl-bridged Re_6 intermediates could be formed after the first eliminations. However, the mechanism will probably be as in reaction (4), leading to the overall equation (5).

$$Re_3^{III,III,III}Cl_3R_6 \xrightarrow{H_2} Re_3^{III,III,V}Cl_3(H_2)R_6 \xrightarrow{-RH} Re_3^{III,III,III}Cl_3HR_5$$

$$Re_3Cl_3HR_5 \xrightarrow{H_2} Re_3Cl_3H(H_2)R_5 \xrightarrow{-RH} Re_3Cl_3(H_2)R_4,\ etc., \quad (4)$$

$$2Re_3Cl_3R_6 + 6H_2 \longrightarrow Re_6(\mu\text{-}Cl)_6H_6R_6 + 6RH \quad (5)$$

The other unisolated products may arise from intermolecular reactions of intermediate hydrido-species and their isomeric forms.

2. *Interaction of Hydrogen and Triphenylphosphine with* $Re_3(\mu\text{-}Cl)_3Cl(CH_2SiMe_3)_5$. *The Hydride* $Re_3(\mu\text{-}Cl)_3ClH(CH_2SiMe_3)_4(PPh_3)$, (3). When the complex $Re_3(\mu\text{-}Cl)_3ClR_5$ that has one terminal chlorine atom [2] is carefully hydrogenated (2 atm, 20 °C, 5 min) in benzene in the presence of triphenylphosphine, a green hydrido-alkyl of stoicheiometry $Re_3(\mu\text{-}Cl)_3ClHR_4(PPh_3)$ (3) can be isolated. The structure determined by *X*-ray diffraction is shown in Figure 2. It will be noted that the triphenylphosphine is co-ordinated to the rhenium atom carrying the hydrogen and chlorine atoms so that co-ordination is maximised for this particular metal atom.

The ^1H n.m.r. spectrum has a poorly resolved multiplet at δ 0.3 p.p.m. due to CH_2SiMe_3 groups, a broad peak at δ 7.4 p.p.m. due to PPh_3, and a weak high-field line due to Re–H at δ −5.2.

The $^{31}P\text{-}\{H\}$ spectrum is a singlet. The i.r. spectrum has a Re–H stretch at 2 010 cm^{-1}.

Prolonged hydrogenation leads to loss of more alkyl groups as $SiMe_4$ but no clean products could be isolated. On following the initial reaction by n.m.r. the peak due to $SiMe_4$ grows rapidly to *ca.* 20% of the total due to CH_2SiMe_3 groups in about 5 min, and thereafter more slowly until after 30 min about half of the CH_2SiMe_3 groups appear as $SiMe_4$.

3. *Hydrogenation of the Adducts* $Re_3(\mu\text{-}Cl)_3(CH_2SiMe_3)_6L_3$.—When either the adducts [1,2] of $Re_3Cl_3R_6$ or this complex in the presence of the ligands are hydrogenated, disruption of the *triangulo*-rhenium(III) unit may occur to give dinuclear complexes of rhenium(II).

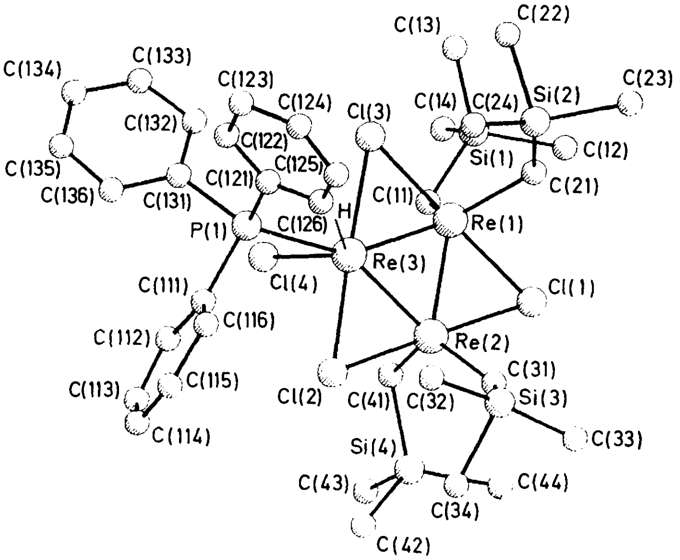
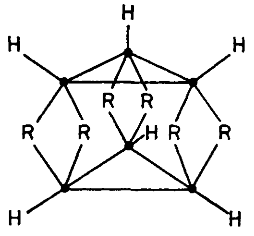


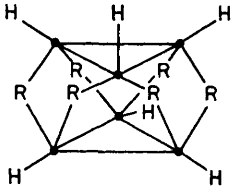
FIGURE 2 The molecular structure of $Re_3(\mu\text{-}Cl)_3ClH(CH_2SiMe_3)_4(PPh_3)$

(a) *Carbon monoxide and triphenylphosphine.* $Re_3Cl_3R_6(CO)_3$ in benzene at 20 °C reacts with hydrogen (2 atm) to give the complex $Re_2Cl_2R_2(CO)_2$, (4). This has all terminal groups and evidently a metal–metal multiple bond [*cf.* the dimeric compound [2] $Re_2Cl_2R_2(PMe_3)_4$]. There is only one CO stretching frequency in the i.r. spectrum suggesting a linear OC–Re–Re–CO grouping.

When $Re_3Cl_3R_6$ is hydrogenated in the presence of triphenylphosphine a similar dimer, $Re_2Cl_2R_2(PPh_3)_2$ (5) is obtained. Although the configurations of (4) and (5) cannot be ascertained without a crystal-structure

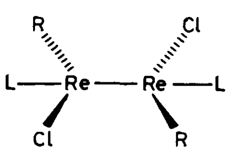


(Ia)



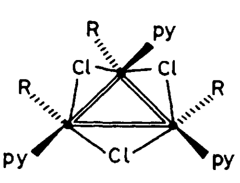
(Ib)

• = Re, μ-Cl omitted



(II)

L = CO or PPh3



(III)

• = Re

TABLE 1

Hydrogen-1 and ^{13}C n.m.r. data for rhenium cluster alkyl complexes

	Compound	^1H n.m.r., δ/p.p.m.[a]		Assignment	^{13}C-{^1H} n.m.r.[b] δ/p.p.m.	Assignment
	$Re_3(\mu\text{-}Cl)_3(CH_2SiMe_3)_6$	1.27s	(2 H)	$\mathrm{C}\mathit{H}_2\mathrm{SiMe_3}$	70.23s	$\mathit{C}\mathrm{H_2SiMe_3}$
		0.37s	(9 H)	$\mathrm{CH_2Si}\mathit{Me}_3$	4.26s	$\mathrm{CH_2Si}\mathit{Me}_3$
(1)	$Re_6(\mu\text{-}Cl)_6H(CH_2SiMe_3)_9$	0.4s [c]		$\mathrm{C}\mathit{H}_2\mathrm{Si}\mathit{Me}_3$	1.5s,br	$\mathit{C}\mathrm{H_2SiMe_3}$
		−4.0s		Re–H	0.2s,br	$\mathrm{CH_2Si}\mathit{Me}_3$
(2)	$Re_6(\mu\text{-}Cl)_6H_6(CH_2SiMe_3)_6$	0.3s		$\mathrm{C}\mathit{H}_2\mathrm{Si}\mathit{Me}_3$	0.3s,br [d]	$\mathrm{CH_2Si}\mathit{Me}_3$
		−5.8s		Re–H		
(3)	$Re_3(\mu\text{-}Cl)_3ClH(CH_2SiMe_3)_4(PPh_3)$	7.4s,br	(5 H)	PPh_3	^{31}P-{^1H} [e]	
		0.3	(15 H)	$\mathrm{C}\mathit{H}_2\mathrm{Si}\mathit{Me}_3$	5.0s	PPh_3
		−5.2		Re–H		
(4)	$Re_2Cl_2(CH_2SiMe_3)_2(CO)_2$	0.3s		$\mathrm{C}\mathit{H}_2\mathrm{Si}\mathit{Me}_3$		
(5)	$Re_2Cl_2(CH_2SiMe_3)_2(PPh_3)_2$	0.2s	(11 H)	$\mathrm{C}\mathit{H}_2\mathrm{Si}\mathit{Me}_3$		
		7.5m,br	(15 H)	PPh_3		
(6)	$Re_3(\mu\text{-}Cl)_3(CH_2SiMe_3)_3(py)_3$	0.2s [e]	(11 H)	$\mathrm{C}\mathit{H}_2\mathrm{Si}\mathit{Me}_3$	−12.11s,br	$\mathrm{CH_2Si}\mathit{Me}_3$
(7)	$[Re_3(\mu\text{-}Cl)_3(CH_2SiMe_3)_3(OH_2)_3]_6$	0.3s		$\mathrm{C}\mathit{H}_2\mathrm{Si}\mathit{Me}_3$	2.6s	$\mathrm{CH_2Si}\mathit{Me}_3$
					2.0s,br	
(8)	$Re_6(\mu\text{-}Cl)_6(CH_2SiMe_3)_6$	0.2s		$\mathrm{C}\mathit{H}_2\mathrm{Si}\mathit{Me}_3$	2.3s	$\mathrm{CH_2Si}\mathit{Me}_3$
					1.0s	
(9)	$Re_{12}(\mu\text{-}Cl)_{12}(CH_2SiMe_3)_6$	0.2s		$\mathrm{C}\mathit{H}_2\mathrm{Si}\mathit{Me}_3$		
(10)	$Re_3Cl_3(\mu\text{-}CH_2SiMe_3)_3(CH_2SiMe_3)_3$	0.20s	(2 H)	$\mathrm{C}\mathit{H}_2\mathrm{SiMe_3}$		
		0.35s	(9 H)	$\mathrm{CH_2Si}\mathit{Me}_3$		
		0.64s	(9 H)	$\mu\text{-}\mathrm{CH_2Si}\mathit{Me}_3$		
		0.70s	(2 H)	$\mu\text{-}\mathrm{C}\mathit{H}_2\mathrm{SiMe_3}$		
(11)	$Re_3(\mu\text{-}Cl)_3(C_6H_5)_6$	7.25m,br	[f]	Ph		
(12)	$Re_3(\mu\text{-}Cl)_3(C_6H_4Me\text{-}p)_6$	1.55s	(3 H) [f]	$\mathrm{C_6H_4}\mathit{Me}$		
		7.21m,br	(4 H)	C_6H_4		
(13)	$Re_3(\mu\text{-}CH_3)_3(CH_2SiMe_3)_6$	4.22s	(3 H)	$\mu\text{-}\mathrm{C}\mathit{H}_3$	−14.8s	$\mu\text{-}\mathit{C}\mathrm{H_3}$
		0.22s	(9 H)	$\mathrm{CH_2Si}\mathit{Me}_3$	4.6s	$\mathrm{CH_2Si}\mathit{Me}_3$
		−0.38s	(2 H)	$\mathrm{C}\mathit{H}_2\mathrm{SiMe_3}$	47.4s	$\mathit{C}\mathrm{H_2SiMe_3}$

[a] C_6H_6 as solvent and internal reference (δ 7.27) at 60 MHz; δ $SiMe_4$ = 0. [b] C_6D_6 as solvent and internal reference (δ 128.7), relative to $SiMe_4$ (δ 0.0) at 28 °C and 25.2 MHz. The ^{31}P-{^1H} chemical shift of $Re_3(\mu\text{-}Cl)_3ClH(CH_2SiMe_3)_4(PPh_3)$ is relative to 85% aqueous H_3PO_4. [c] In CCl_4. [d] In [$^2H_8$]toluene. [e] In CCl_2D_2. [f] In C_6D_6.

determination, the structures are probably of the type (II).

It is to be noted that in both compounds there is only one CO or PPh_3 per metal, whereas in trimethylphosphine complexes[2] there are two ligands per metal. This difference is probably attributable to the stronger π bonding of CO and the steric bulk of PPh_3 respectively. The yields of (4) and (5) are relatively low but insoluble uncharacterised material is also formed in the cleavage of the trimer.

(b) *Pyridine.* Hydrogenation of the adduct $Re_3Cl_3R_6(py)_3$ (py = pyridine), by contrast, produces a complex $Re_3(\mu\text{-}Cl)_3R_3(py)_3$ (6) in which the Re_3 unit is retained, according to molecular-weight data. The compound thus is a *triangulo*-rhenium(II) species. There is no evidence for any Re–H groups in either the i.r. or n.m.r. spectra and treatment of the complex with CCl_4 gives no chloroform. The only other *triangulo*-trirhenium(II) species are those containing amine ligands[6] such as $[Re_3Cl_6(py)_3]_n$ and these are polymeric, presumably *via* halogen bridges between the Re_3 units.

The e.s.r. spectrum (9.148 GHz) of a dilute frozen thf solution of (6), although weak, consisted of four well resolved features between 2 kG and 4 kG with an indication of two broad features to higher field. The spectrum is too simple to be interpreted in terms of hyperfine structure from rhenium ($I = \frac{5}{2}$); this usually shows up as three well resolved patterns of six lines for a

TABLE 2

Analytical data for rhenium cluster alkyls

			Analysis[a] %				
	Compound	Colour	C	H	Cl	Re	*M*[b]
(1)	$Re_6(\mu\text{-}Cl)_6H(CH_2SiMe_3)_9$	Green	19.3 (20.4)	4.4 (4.7)	10.4 (9.95)	53.0 (53.1)	1 850 [c] (2 115)
(2)	$Re_6(\mu\text{-}Cl)_6H_6(CH_2SiMe_3)_6$	Green	15.5 (15.2)	3.5 (4.7)	11.4 (11.4)	58.2 (59.5)	1 860 (2 040)
(3)	$Re_3(\mu\text{-}Cl)_3ClH(CH_2SiMe_3)_4(PPh_3)$	Green	34.7 (34.0)	5.2 (5.0)	11.3 (11.8)	44.6 (46.5)	1 070 (1 200)
(4)	$Re_2Cl_2(CH_2SiMe_3)_2(CO)_2$	Brown	18.2 (17.8)	3.3 (3.3)	10.0 (10.4)	56.5 (55.5)	650 [d] (674)
(5)	$Re_2Cl_2(CH_2SiMe_3)_2(PPh_3)_2$	Brown	46.6 (46.2)	4.3 (4.5)	6.3 (6.1)	33.5 (32.7)	840 [d] (1 142)
(6)	$Re_3(\mu\text{-}Cl)_3(CH_2SiMe_3)_3(py)_3$	Brown	27.3 (27.8)	3.2 (4.1)	8.8 (9.0)	47.2 (48.0)	1 130 [d] (1 164)
(7)	$[Re_3(\mu\text{-}Cl)_3(CH_2SiMe_3)_3(OH_2)_3]_6$	Green	16.8 (14.7)	3.9 (4.0)	10.1 (10.7)	59.7 (57.5)	5 400 (5 586)
(8)	$Re_6(\mu\text{-}Cl)_6(CH_2SiMe_3)_6$	Green	15.6 (15.2)	4.0 (4.7)	11.5 (11.4)	60.0 (59.5)	1 950 (2 034)
(9)	$Re_{12}(\mu\text{-}Cl)_{12}(CH_2SiMe_3)_6$	Green	9.7 (9.1)	2.6 (2.1)	14.1 (13.4)		3 100 [e] (3 183)
(10)	$Re_3Cl_3(\mu\text{-}CH_2SiMe_3)_3(CH_2SiMe_3)_3$	Red	24.3 (24.0)	5.5 (5.5)	9.0 (8.8)	46.0 (47.2)	1 150 (1 185)
(11)	$Re_3(\mu\text{-}Cl)_3(C_6H_5)_6$	Green	31.6 (32.0)	3.1 (2.7)	8.8 (9.4)		1 160 (1 126)
(12)	$Re_3(\mu\text{-}Cl)_3(C_6H_4Me\text{-}p)_6$	Green	42.3 (41.7)	3.7 (3.5)	8.6 (8.7)		1 160 (1 210)
(13)	$Re_3(\mu\text{-}CH_3)_3(CH_2SiMe_3)_6$	Red	29.2 (28.8)	6.8 (6.6)		49.0 (49.6)	1 000 [d] (1 128)

[a] Calculated values are given in parentheses. Difficulties have been experienced in obtaining really pure samples of some compounds due to ease of retention of solvent, non-crystallinity, *etc.* Rhenium was determined by plasma-arc atomic absorption. [b] Osmometrically in benzene unless otherwise stated. [c] Osmometrically in dichloromethane. [d] Osmometrically in chloroform. [e] Cryoscopically in benzene.

system with $S = \frac{1}{2}$. Further, it is too complicated to be interpreted in terms of three principal g values without hyperfine structure. However, a coupling between three unpaired electrons on three separated Re^{II} atoms resulting in a $\frac{3}{2}$ spin state can explain the spectrum, which would be centred on the $g = 2$ region but widely split by zero-field splitting. A zero-field splitting would be expected from separated spins whatever the local geometry; the observed splitting into five features is consistent with overall axial symmetry.

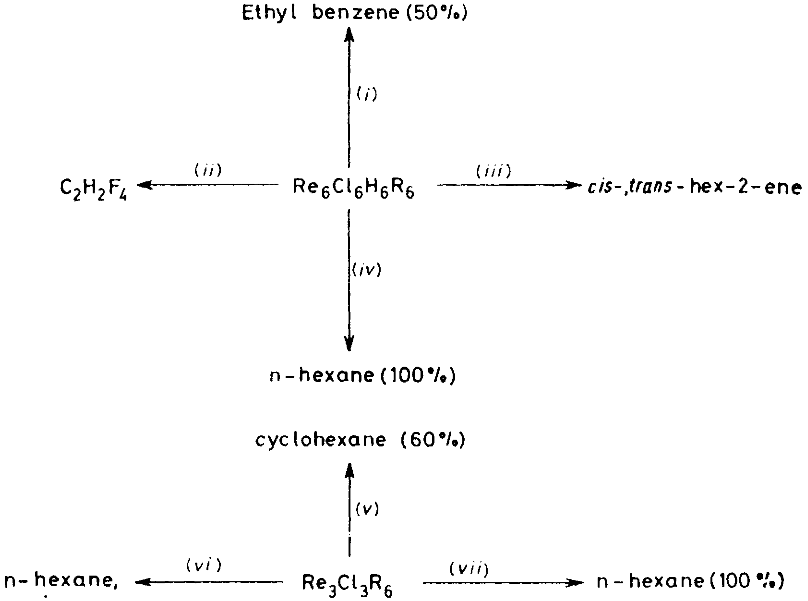
The hyperfine structure expected from a trinuclear species would be 16 lines with an intensity ratio 1 : 3 : 6 : 10 : 15 : 21 : 25 : 27 : 27 : 25 : 21 : 15 : 10 : 6 : 3 : 1 and with a splitting reduced to one third of the corresponding value from a monomeric species. Such a peaked distribution combined with a smaller splitting can reasonably account for our failure to resolve it.

The data are thus consistent with the *triangulo*-trirhenium structure (III) which formally has Re=Re double bonds and three Re^{II} atoms.

The magnetic susceptibility measured in solution by the Evans' n.m.r. method, on the assumption that the substance obeys Curie's law, corresponded to a magnetic moment per Re_3 unit of 0.9 B.M. Such a low value is not unexpected from second and third row metal ions, which have very high spin–orbit coupling constants, and in the absence of variable-temperature magnetic susceptibility measurements the result is not incompatible with the $S = \frac{3}{2}$ ground state proposed above.

(c) *Water*. Finally, the green aquo-complex[1] $Re_3(\mu\text{-}Cl)_3R_6(OH_2)_3$ in benzene reacts with hydrogen to give a green oligomeric complex. On the basis of analytical, molecular-weight, and spectroscopic data this appears to be $[Re_3(\mu\text{-}Cl)_3R_3(OH_2)_3]_6$, (7). The ^1H and ^{13}C n.m.r. and i.r. spectra are essentially identical to those of $Re_3Cl_3R_6$, except for the presence of the band due to water at 3 620 cm^{-1}. The water can be replaced by pyridine to give $[Re_3(\mu\text{-}Cl)_3R_3(py)_3]_6$. So far, crystals suitable for *X*-ray study have not been obtained.

4. *Isomerisation and Hydrogenation of Alkenes by* $Re_6(\mu\text{-}Cl)_6H_6(CH_2SiMe_3)_6$. *The Hexanuclear Cluster* $Re_6(\mu\text{-}Cl)_6(CH_2SiMe_3)_6$.—The hexanuclear hydrido-alkyl, (2), slowly catalyses the isomerisation of alkenes in the absence of hydrogen, and in presence of hydrogen their hydrogenation to alkanes. As far as we are aware these are the first homogeneous catalytic reactions of this type by rhenium complexes. The blue cluster $Re_3Cl_3R_6$ can, of course, be used directly without isolation of $Re_6Cl_6H_6R_6$. The reactions are summarised in Scheme 1.



SCHEME 1 Reactions of $Re_6Cl_6H_6R_6$ and $Re_3Cl_3R_6$ with hydrogen (2 atm) and alkenes (20 °C). (*i*) H_2, styrene, 30 min; (*ii*) C_2F_4; (*iii*) hex-1-ene in C_6H_6, 15 min; (*iv*) H_2, hex-1-ene in C_6H_6, 15 min; (*v*) cyclohexane in C_6H_6, 2 h; (*vi*) H_2, *cis-,trans*-hex-2-enes in C_6H_6, 2 h; (*vii*) H_2, hex-1-ene in C_6H_6, 2 h

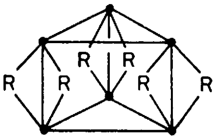
The catalytic reaction is relatively short-lived due to destruction of hydrido-species by alkene as discussed below. The hydrogenation reaction is completely inhibited by the presence of tertiary phosphines or pyridine which evidently block the site on rhenium required for alkene co-ordination. The hydride does not catalyse the hydroformylation reaction of alkenes under CO and H_2 and indeed reacts rapidly with CO to give carbonyl species that have not yet been characterised.

With alkenes alone, such as tetrafluoroethylene (which gives $C_2F_4H_2$) and styrene, (2) is slowly converted to a green light petroleum soluble cluster which does not react with hydrogen in benzene.

The analytical, molecular-weight, and spectroscopic data suggest that the non-hydridic cluster is $Re_6(\mu\text{-}Cl)_6(CH_2SiMe_3)_6$ (8), formed as in equation (6). Such removal of hydrogen atoms is tantamount to reduction

$$Re_6Cl_6H_6R_6 + 3C_2F_4 \longrightarrow Re_6Cl_6R_6 + 3C_2F_4H_2 \quad (6)$$

of Re^{III} to Re^{II} and we suggest that this is accompanied by Re–Re single bond formation between *triangulo*-Re_3 units since $Re_6Cl_6R_6$ is diamagnetic. Although crystals suitable for *X*-ray study have not been obtained the structure (IV) seems reasonable.



(IV)

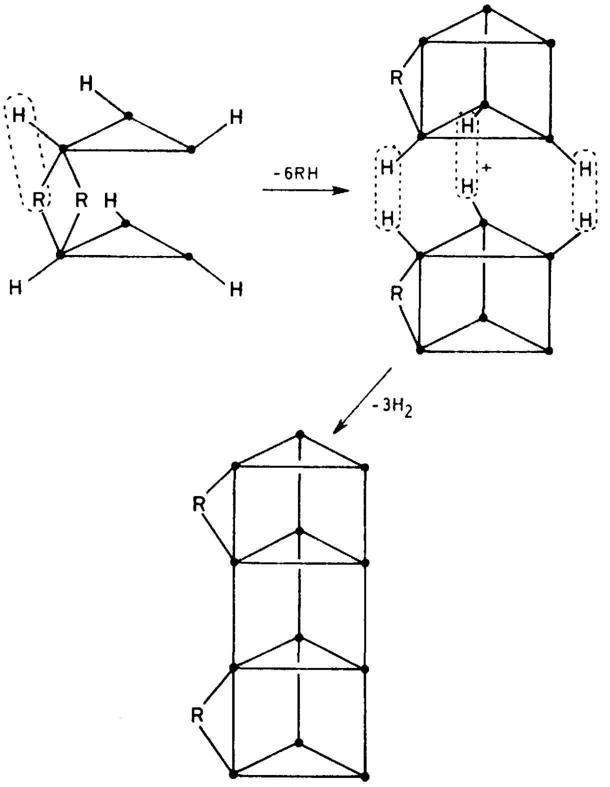
In the catalytic hydrogenation of alkenes using $Re_3(\mu\text{-}Cl)_3(CH_2SiMe_3)_6$ it is quite probable that hydrido-species of the type $Re_3Cl_3H_nR_{6-n}$ are involved, although we have been unable to isolate them.

A second green cluster alkyl is formed by thermal decomposition of $Re_6Cl_6H_6R_6$ in benzene over a period of several days. In this case, tetramethylsilane, detected by n.m.r., in an amount corresponding to half of the number of alkyl groups is formed. The green product has no Re–H bonds and analytical, molecular-weight, and spectroscopic data suggest that it is $Re_{12}(\mu\text{-}Cl)_{12}R_6$, (9), so that the stoicheiometric reaction appears to be as in equation (7).

$$2Re_6Cl_6H_6R_6 \longrightarrow Re_{12}Cl_{12}R_6 + 6RH + 3H_2 \quad (7)$$

The average formal oxidation state of rhenium is therefore 1.5. Scheme 2 shows a possible route to this compound and one possibility, (V), for its structure. The latter would involve Re=Re double bonds in the Re_3Cl_3 triangles and single bonds between the triangles. Stacked *triangulo*-units of this type have been confirmed in a number of platinum carbonylate anions.[7] In a stack such as (V), as well as bridging chlorines in the triangles, the alkyl groups must also be bridging as otherwise the co-ordination number of some rhenium atoms would be unreasonably low. There are, of course, other possible structures with Re_6 units linked by a corner or by one edge with appropriate increases in multiple bonding within the Re_6 units.

5. *New Rhenium*(III) *Cluster Alkyls and Aryls.*—(a) syn,syn,anti-*Trichloro-tris*(μ-*trimethylsilylmethyl*)-*tris*-(*trimethylsilylmethyl*)-triangulo-*trirhenium*(III). In the synthesis of blue $Re_3(\mu\text{-}Cl)_3R_6$ from $Re_3Cl_9(thf)_3$ in diethyl ether a red supernatant was always observed after crystallisation of the main product from light petroleum. No pure complex could be obtained from these red solutions. However, treatment of the red material in thf with hydrogen (2 atm) for 10 min gave a solution from which a red compound can be crystallised. This light petroleum soluble species has analyses and molecular weight that suggest it is also $Re_3Cl_3R_6$ (10) and is an isomer of the blue $Re_3Cl_3R_6$. The ^1H n.m.r. spectrum shows four peaks in the CH_2SiMe_3 region at δ 0.7 (2), 0.64 (9), 0.35 (9), and 0.20 (2) p.p.m. which can be ascribed to two non-equivalent types of alkyl groups in equal ratios, one terminal, one bridging. Conclusive assignment of the peaks is somewhat difficult, but by analogy with the relative positions of terminal and bridge methyl resonances in $Re_3Me_9L_3$ complexes we suggest that the bridging alkyls appear at lower shifts than terminal ones. The low-field peak (0.7 p.p.m.) can thus be ascribed to the CH_2 protons of the $\mu\text{-}CH_2SiMe_3$ group and the peak at 0.2 p.p.m. to CH_2 protons of the terminal alkyl. The latter thus are at higher fields than the methyl resonances which is the reverse of the situation for $Re_3(\mu\text{-}Cl)_3R_6$. The i.r. spectrum is similar to that of the blue isomer but has a terminal Re-Cl stretch at 350 cm^{-1}.



(V)

SCHEME 2 Thermal decomposition of $Re_6(\mu\text{-}Cl)_6H_6R_6$ to $Re_{12}(\mu\text{-}Cl)_{12}R_6$ (μ-Cl and some R groups omitted)

The compound reacts only slowly with hydrogen under the conditions stated and the reason we have been able to isolate it is presumably that other isomers in the initial red solution are removed more rapidly.

The molecular structure has been confirmed by an *X*-ray diffraction study (Figure 3).

(b) *Hexaphenyl- and hexa*(p-*tolyl*(-*tri*)-μ-*chloro*-triangulo-*trirhenium*(III). The interaction of $Re_3Cl_9(thf)_3$ with phenylmagnesium bromide yields a green microcrystalline complex for which analytical and molecular-weight data agree with the formula $Re_3(\mu\text{-}Cl)_3Ph_6$, (11). The ^1H n.m.r. shows a complex multiplet due to phenyl groups at δ 7.3 p.p.m. while the i.r. spectrum has aromatic C–H (3 050 cm^{-1}) and C–C (1 570, 1 557 cm^{-1}) bands, together with other typical phenyl-ring deformation bands. The analogous *p*-tolyl complex $Re_3(\mu\text{-}Cl)_3(C_6H_4Me\text{-}p)_6$ (12), which forms needles from toluene, shows in the ^1H n.m.r. a multiplet δ 7.2 p.p.m., and a CH_3 singlet δ 2.2 p.p.m., in a ratio 4 : 3 respectively, whilst the i.r. spectrum is similar to that of the hexaphenyl derivatives but with aliphatic C–H stretches at 2 925 and 2 850 cm^{-1}.

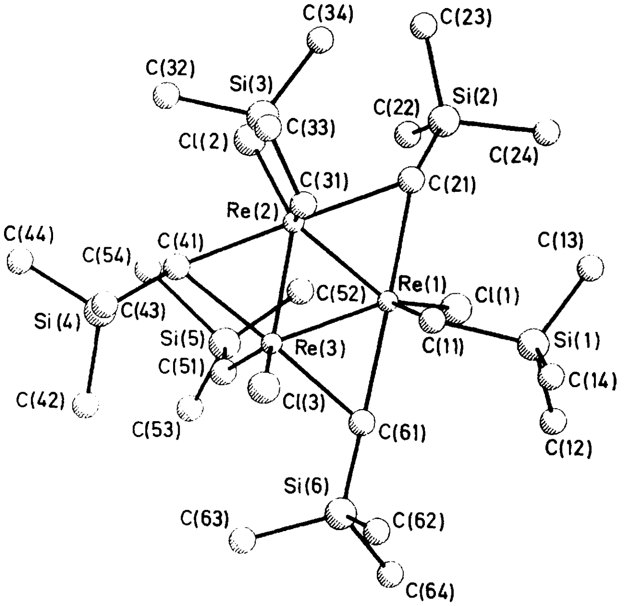


FIGURE 3 The molecular structure of $Re_3Cl_3(\mu\text{-}CH_2SiMe_3)_3(CH_2SiMe_3)_3$

(c) *Tris*(μ-*methyl*)-*hexakis*(*trimethylsilylmethyl*)-*trirhenium*(III). The interaction of $Re_3(\mu\text{-}Cl)_3R_6$ with methyl-lithium in diethyl ether in the absence of triphenylphosphine leads to carmine red polynuclear species not yet fully characterised. However, in the presence of triphenylphosphine what is believed to be an intermediate is obtained. This is the compound $Re_3(\mu\text{-}CH_3)_3(CH_2SiMe_3)_6$ (13), in which the bridging Cl groups in $Re_3(\mu\text{-}Cl)_3R_6$ are replaced by methyl groups.

The compound is extremely soluble in hydrocarbons and sublimes to a cold probe at 50 °C (10^{-3} mmHg); in the mass spectrum, the appropriate molecular ion is observed.

The ^1H n.m.r. spectrum shows three resonances in the ratio 3 : 9 : 2 at δ 4.22, 0.22, and −0.38 which can be assigned respectively to the bridging CH_3 and the alkyl CH_3 and CH_2 protons. The $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum also shows three sharp peaks at δ 47.4, 4.6, and −14.8 p.p.m. The first two can be assigned to CH_2 and CH_3 groups of CH_2SiMe_3 by analogy with those in $Re_3(\mu\text{-}Cl)_3R_6$ and the high-field peak to the $\mu\text{-}CH_3$ group. The i.r. spectrum is similar to that of $Re_3Cl_3R_6$.

Attempts to prepare other alkyls from $Re_3Cl_3R_6$ in which μ-Cl was replaced by H, Ph, CH_2CMe_3, or OMe did not give analogues of the tris(μ-methyl) compound, but formed red polynuclear species that are still under investigation.

6. *Crystallographic Studies*.—For the purposes of comparison it is most convenient to consider the results of the crystal structure analyses of compounds (1), (3), and (10) all together.

Conventional molecular-structure diagrams have already been presented (Figures 1—3); in Figures 4—6 are shown the more important geometric parameters for the three molecules.

Before analysing the data given in Figure 4, it is worth noting that in blue $Re_3(\mu\text{-}Cl)_3R_6$ the Re_3 triangle is equilateral (Re–Re = 2.386 ± 0.002 Å), but the Re–μ-Cl distances vary in the range 2.412—2.440 (5) Å. These differences were ascribed to an unsymmetrical array of Me · · · Cl short contacts.[4]

As mentioned previously, compound (10) is an isomer of blue $Re_3(\mu\text{-}Cl_3)R_6$, with switching of the bridging chlorines and three of the terminal alkyls. The arrangement of the chlorines (two on one side of the Re_3 triangle, one on the other) can be denoted *syn, syn, anti*. The orientations of the bridging and terminal CH_2SiMe_3 groups also adopt a very unsymmetrical pattern (relative to the potential three-fold symmetry of the Re_3C_3 group) and this is probably the cause of the fairly wide variation in Re–μ-C distances and a smaller, but still significant distortion in the Re_3 triangle where the Re–Re distances show a wider variation than in other chemically symmetrical systems. In addition, however, the three Re–Re distances here are significantly shorter than those in the blue cluster. This can perhaps be ascribed to differences in electron density on the metal atoms caused by the switching of the chlorines (formally considered as a three-electron ligand when bridging) and the alkyls (one-electron ligand). Similarly, the Re–C distances to the terminal alkyl groups are also shorter than those in the blue isomer.

In compound (1) the chemical perturbation of the Re_3Cl_3 units is considerable. However, inspection of Figure 4 will show that the structural distortions are not as significant as might have been expected. The Re–Re distances in both triangles vary by similar amounts to those found in compound (10), but the actual values are, on average, larger than in either of the $Re_3Cl_3R_6$ isomers. Although there is an indication that the bond distances involving the formally rhenium(II) atoms, Re(3) and Re(6), are slightly longer than those involving the Re^{III} atoms, Re(1), Re(2), Re(4), and Re(5), the difference is really quite small. With regard to the Re–μ-Cl distances, however, there is a very interesting and at present inexplicable variation. In both triangles, the bridges between the Re^{III} and Re^{II} atoms are unsymmetrical with the Re^{II}–Cl distance averaging 2.418(4) Å and the Re^{III}–Cl distance averaging 2.389(4) Å. Then, however, the bridges between the two Re^{III} atoms are symmetrical but have the same (or even slightly larger) value, 2.421(4) Å, as the Re^{II}-Cl distances. What is perhaps even more interesting is the fact that the chemical differences between the two rings, with the terminal alkyl on one and the hydride on the

TABLE 3

Crystal data and details of data collection and structure analyses

	Compound (1)	Compound (3)	Compound (10)
(*a*) Crystal data			
Formula	$Re_6(\mu\text{-}Cl)_6H(CH_2SiMe_3)_9$	$Re_3(\mu\text{-}Cl)_3ClH(CH_2SiMe_3)_4(PPh_3)$	$Re_3Cl_3(\mu\text{-}CH_2SiMe_3)_3(CH_2SiMe_3)_3$
Formula weight	2 115.89	1 312.58	1 188.27
Crystal system	Triclinic	Triclinic	Monoclinic
a/Å	15.950(5)	17.732(3)	17.939(2)
b/Å	16.351(6)	13.212(3)	11.280(1)
c/Å	16.386(6)	11.723(4)	22.933(4)
α/°	62.31(2)	90.95(3)	90
β/°	94.25(3)	95.04(3)	109.98(1)
γ/°	99.77(3)	83.74(2)	90
U/Å^3	3 729.1	2 719.4	4 361.2
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
Z	2	2	4
D_c/g cm^{-3}	1.88	1.60	1.81
F(000)	1 988	1 258	2 280
μ(Mo-K_α)/cm^{-1}	101.8	70.5	87.5
(*b*) Data collection			
Crystal size/mm	0.50 × 0.30 × 0.10	0.45 × 0.37 × 0.06	0.30 × 0.12 × 0.10
Crystal faces	{0 0 1}, {1 0 0}, {0 1 0}	{0 0 1}, {0 1 0}, {1 0 0}	{0 0 1}, {1 0 0}, {0 1 0}
$\theta_{min.}$, $\theta_{max.}$/°	1.5, 23	1.5, 24	1.5, 25
ω scan parameters, A, B/° in width = $A + B\tan\theta$	0.80, 0.15	0.90, 0.35	0.80, 0.15
Horizonal aperture parameters A, B/mm in aperture = $A + B\tan\theta$	4.0, 0.0	4.0, 0.0	4.0, 0.0
Total data collected	10 760	8 660	8 487
Total unique data	10 203	8 536	7 670
Observed data $F_o > 4\sigma(F_o)$	6 796	3 704	5 293
Crystal decay	22.5% (linear)	21.2% (linear)	9.2% (linear)
(*c*) Refinement			
No. of parameters	514	415	325
Weighting scheme coefficient g in $w = 1/[\sigma^2(F_o) + g(F_o)^2]$	0.0012	0.0010	0.0008
Final $R = \Sigma\Delta F/\Sigma F_o$	0.055	0.063	0.048
$R' = [\Sigma w(\Delta F)^2/\Sigma w(F_o)^2]^{\frac{1}{2}}$	0.071	0.077	0.061

other, produce no structural differences: the two Re_3Cl_3 systems are virtually superimposable.

The structural features of compound (3) are also intriguing. This molecule now contains one seven-co-ordinate rhenium atom [Re(3)] and two six-co-ordinate Re atoms, and the bond lengths tend to reflect the expected[2] difference with the bond between the two six-co-ordinate atoms about 0.02 Å shorter than those between the six- and seven-co-ordinate atoms. In fact the molecule can be compared with that of the compound $Re_3(\mu\text{-}Cl)_3R_5\text{-}[ON(CH_2SiMe_3)NO]$ [2] and although in this case the seven-co-ordinate rhenium atom is bonded to 2 Re, 2 Cl, and then 1 C and 2 O, compared with 2 Re, 2 Cl and 1 Cl, 1 P, and 1 H in the present case, the differences in Re–Re bond lengths are very similar in the two molecules. The comparison can be taken much further however, when the chloride bridges are considered. For both cases there is a strong indication that the chlorine bridges between the two six-co-ordinate rhenium atoms have the longest distances with asymmetric bridges between the six- and seven-co-ordinate atoms (*cf.* Figure 5 and ref. 2, p. 339). Most interestingly this is the same kind of distortion found for compound (1) where the unique rhenium atoms did not differ from the others in terms of co-ordination number, but only in ligand environment. It seems clear therefore, that the symmetry of the Re_3 cluster is equally sensitive to electronic and steric influences, both of which can cause shifts away from a symmetrical structure.

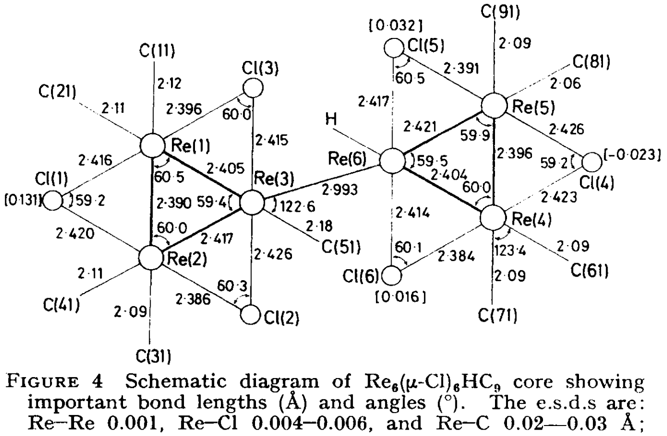


FIGURE 4 Schematic diagram of $Re_6(\mu\text{-}Cl)_6HC_9$ core showing important bond lengths (Å) and angles (°). The e.s.d.s are: Re–Re 0.001, Re–Cl 0.004–0.006, and Re–C 0.02—0.03 Å; Re–Re–Re, Re–Cl–Re 0.1 and C–Re–C 0.6—0.9°. Cl(bridging)–Re–Cl(bridging) angles are 177.8—179.4° except the Cl–Re(3)–Cl angle which has a value of 173.2(2)°. Re–C–Si angles are 115.4—134.7(12)°. The values in square brackets are the deviations of the bridging Cl atoms from the plane of the rhenium trangles. The angles between the Re(3)–Re(6) bond and normals to the Re(1)–Re(2)–Re(3) and Re(4)–Re(5)–Re(6) planes are 42.7 and 62.1° respectively

Compound (3) shows extreme variations in the Re–C–Si angles. Thus the two Re–C(21)–Si(2) angles are equal at 127° while the Re–C(41)–Si(4) and Re–C(61)–Si(6) angles are widely different and fall into two categories (156 and

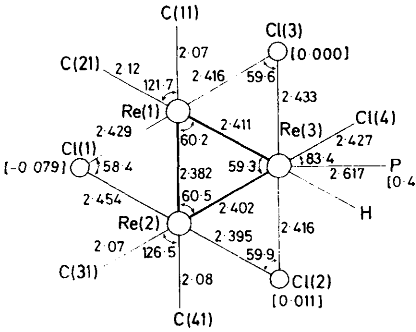


FIGURE 5 Schematic diagram of $Re_3(\mu\text{-}Cl)_3ClHC_4P$ core in complex (3) showing the important bond lengths (Å) and angles (°). The e.s.d.s are: Re–Re 0.001, Re–Cl 0.006—0.008, Re–C 0.02—0.04 Å; C–Re–C 0.12, and Cl–Re–P 0.2°. The values in the square brackets are deviations (Å) of the bridging and P atoms from the Re_3 plane. The Cl (bridging)–Re–Cl (bridging) and Re–C–Si angles are 177.3—178.7(3) and 117.1—139.1(23)° respectively

111°). Of the three terminal Re–C–Si angles, two are 115° while Re(3)–C(51)–Si(5) is 140°. All these variations are found to originate from intramolecular interligand crowding. The larger angles of 140 and 156° are most unusual for what are essentially sp^3 carbon atoms. It is interesting to speculate whether this size of angle results from a ' bent ' Re–C bond or whether the orbital energy levels of the carbon atoms are seriously affected by the bonding of the metal.

The phosphine ligand in (3) is quite weakly bound; the Re–P distance of 2.517(7) Å is much longer than the 2.546 and 2.569(3) Å distances in $Re_3Me_9(PEt_2Ph)_2$.[2] This is possibly due to steric factors as well as the higher co-ordination number for the relevant Re atom, since the terminal Re–Cl is also long at 2.427(5) Å, much longer than the terminal Re–Cl distances in compound (10).

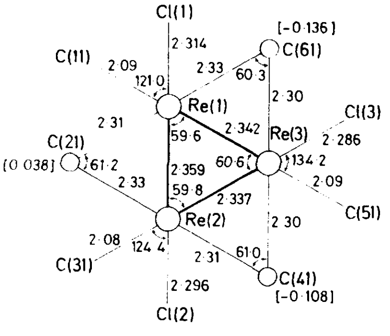


FIGURE 6 Schematic diagram of $Re_3(\mu\text{-}C)_3Cl_3C_3$ core in complex (10) showing the important bond lengths (Å) and angles (°). The e.s.d.s are: Re–Re 0.001, Re–Cl 0.003, and Re–C 0.01—0.02 Å; Re–Re–Re 0.1, -Re–C–Re 0.3—0.4, and Cl–Re–C 0.3—0.6°. The C (bridging) –Re–C (bridging) angles are 173.9—177.3(5)°. Re(1,2)–C(21)–Si(2) 127.0, 127.4(7)°; Re(2,3)–C(41)–Si(4) 155.6, 111.1(6)°; Re(1,3)–C(61)–Si(6) 156.2, 111.3(6)°; Re(1)–C(11)–Si(1) 115.4(6), Re(2)–C(31)–Si(3) 115.3(6), and Re(3)–C(51)–Si(5) 140.3(8)°

EXPERIMENTAL

Microanalyses were by the Imperial College, Butterworth, and Pascher Laboratories. The following spectrometers were used: i.r., Perkin-Elmer 325, 457, and 597 calibrated with polystyrene; n.m.r., Perkin-Elmer R12A (60 MHz) and R32 (90 MHz), and Varian Associates XL-100 (Fourier-transform mode with proton noise decoupling); e.s.r., Varian E-12 (*X*-band); mass, VG Micromass 7070.

Molecular weights in solution were determined cryoscopically under nitrogen or osmometrically using a Perkin-Elmer–Hitachi osmometer.

All syntheses and manipulations were carried out under oxygen-free nitrogen or argon. Diethyl ether, thf, light petroleum (b.p. 40—60 °C), toluene, and benzene were dried by refluxing over sodium–benzophenone under nitrogen, and were distilled immediately prior to use. Acetonitrile and dichloromethane were dried by refluxing over calcium hydride under nitrogen and were distilled immediately before use. When necessary, solvents were degassed by freeze-pumping, otherwise by nitrogen purge.

Rhenium Starting Materials.—Trirhenium nonachloride was prepared from Re metal (99.9%) *via* rhenium pentachloride. The compound $Re_3Cl_9(PPh_3)_3$ was prepared according to the literature;[8] $Re_3Cl_9(thf)_3$ was prepared as follows. Fresh Re_3Cl_9 (10 g, 11.4 mmol) was extracted from a Soxhlet thimble with thf (20 cm^3) until the solvent passing through the thimble was no longer coloured (*ca.* 2 d). The purple-red crystals were collected, washed with diethyl ether (2 × 20 cm^3), and dried carefully *in vacuo*. Yield, 11.7 g, 94% based on Re_3Cl_9; i.r. (Nujol), 1 335, 1 245, 1 130, 1 040, 1 012, 917, 850, 675, 570, and 335 cm^{-1}.

The compound $Re_3Cl_3(CH_2SiMe_3)_6$ can be prepared from aged trirhenium nonachloride,[1] $Re_3Cl_9{\cdot}ca.6H_2O$, but owing to the variability in reactivity of the hydrated chloride and hence large variations in yields from this material, it is best made from $Re_3Cl_9(PPh_3)_3$ or $Re_3Cl_9(thf)_3$ as follows.

(a) To $Re_3Cl_9(PPh_3)_3$ (1 g, 0.6 mmol) suspended in diethyl ether (20 cm^3) at −78 °C was added with vigorous stirring a solution of trimethylsilylmethylmagnesium chloride (1.0 mol dm^{-3} in diethyl ether, 3.0 cm^3, 6 mmol). The suspension was then allowed to warm slowly to room temperature. At −10 °C, the supernatant became blue in colour. When all the rhenium halide had dissolved (*ca.* 30 min at room temperature) the solvent was removed *in vacuo*. The grey residues were extracted with light petroleum (3 × 10 cm^3), cooled to −20 °C, and filtered to remove the majority of PPh_3. The solvent was removed and the blue residue was washed (3 × 10 cm^3) with cooled (−20 °C) acetonitrile to remove the remaining PPh_3. The blue compound was then recrystallised from light petroleum (3 cm^3, −78 °C). Yield, 0.53 g, 75% based on $Re_3Cl_9(PPh_3)_3$.

(b) To $Re_3Cl_9(thf)_3$ (10 g, 9.0 mmol) suspended in diethyl ether (300 cm^3) at −78 °C was added a solution of trimethylsilylmethylmagnesium chloride (1 mol dm^{-3} in diethyl ether, 69 cm^3, 22 mmol) with vigorous stirring. The suspension was allowed to warm slowly to 0 °C when the supernatant was blue. The mixture was stirred at 0 °C for 1 h and then at ambient temperature until the rhenium halide had dissolved. The solvent was then removed *in vacuo* and the grey residue extracted with light petroleum (3 × 30 cm^3), concentrated to *ca.* 15 cm^3, and held at −78 °C overnight to give blue crystals of the complex which were filtered and washed with cooled (−78 °C) light petroleum (2 × 5 cm^3). Yield, 7 g, 65% based on $Re_3Cl_9(thf)_3$. The yield is depressed by stirring the reaction mixture at ambient temperatures for long periods.

*Hydridononakis(trimethylsilylmethyl)bis[tri-μ-chloro-*triangulo-*trirhenium*(III)], $Re_6(\mu\text{-}Cl)_6H(CH_2SiMe_3)_9$, (1). $Re_3Cl_3R_6$ (1 g, 0.8 mmol) in thf (10 cm^3) was hydrogenated under 2 atm pressure in a glass pressure bottle for 10 min. The blue solution rapidly turns green and then, if left for longer than 10 min, brown. The green solution was filtered, and evaporated *in vacuo*. The green residue was extracted into light petroleum and the complex chromatographed on silica at −78 °C using diethyl ether as eluant. Yield 0.41 g, 53% based on $Re_3Cl_3R_6$. The compound is soluble in hydrocarbons, CH_2Cl_2, CS_2, *etc.*; i.r. (Nujol), 3 600w, 2 900vs,br, 1 495s, 1 375m, 1 300w, 1 245s, 920s,br, 825s,br, 745m, 720m, 675m, 610w, and 460m, br cm^{-1}.

Bis[tri-μ-chloro-trihydridotris(trimethylsilylmethyl)-triangulo-*trirhenium*(III)], $Re_6(\mu\text{-}Cl)_6H_6(CH_2SiMe_3)_6$, (2). $Re_3Cl_3R_6$ (5 g) in benzene (30 cm^3), was placed in a glass pressure bottle, evacuated, pressurised with hydrogen to 2 atm, and stirred vigorously for 8 min at room temperature. The resulting green solution was filtered and evaporated *in vacuo*. The green residue was chromatographed at −78 °C on silica with diethyl ether as eluant and, after evaporation, recrystallised from light petroleum (5 cm^3) at −20 °C. The dark green *needles* were washed with cold light petroleum (−78 °C) and dried *in vacuo*. Yield, 3.1 g, 82% based on $Re_3Cl_3R_6$. The product is very soluble in hydrocarbons and most polar solvents; i.r. (CS_2), 2 940s, 2 880m, 2 840m, 2 030w (Re–H), 1 930, 1 850w, 1 260s, 1 245s, 1 010w,br, 915w,br, 800vs,br, 750m, 700m,br, 520w,br, 470w,br, and 340w,br cm^{-1}.

Reaction of the hydrido-alkyl complex (2) *with chlorine*. To the hydrido-complex (0.1 g) in benzene (5 cm^3) cooled to −196 °C was added a large excess (5 cm^3) of a saturated solution of chlorine in carbon tetrachloride. The frozen solutions were evacuated in a closed system attached to a sample vessel suitable for introducing gases into the mass spectrometer, and a suitable pressure measuring device. The solutions were warmed slowly to room temperature and a sample of the volatile products was collected in the sample vessel by cooling it in liquid nitrogen and then isolating it from the vacuum line.

Tri-μ-chloro-chlorohydridotetrakis(trimethylsilylmethyl)-(triphenylphosphine)-triangulo-*trirhenium*(III), $Re_3(\mu\text{-}Cl)_3ClH(CH_2SiMe_3)_4(PPh_3)$, (3). $Re_3(\mu\text{-}Cl)_3ClR_5$ [2] was hydrogenated in benzene (10 cm^3) in the presence of PPh_3 (0.23 g, 0.9 mmol) under the same conditions as above, but for only 5 min. After removal of benzene, the green product was crystallised from light petroleum (3 cm^3) at −20 °C. Yield, 0.84 g, 73% based on $Re_3(\mu\text{-}Cl)_3ClR_5$. The compound is very soluble in hydrocarbons, CH_2Cl_2, CS_2, *etc.*; i.r. (CS_2), 3 125w, 3 045m, 2 884m, 2 020w, 1 645w, 1 329m, 1 290m, 1 250s, 1 150m, 1 080m, 1 005w, 910s, 815s, 750s, 675s, 605w, 540s, 495s, 395m, and 351m cm^{-1}.

Dicarbonyldichlorobis(trimethylsilylmethyl)dirhenium(II) (Re–Re), $Re_2Cl_2(CH_2SiMe_3)_2(CO)_2$, (4). A benzene (10 cm^3) solution of $Re_3Cl_3R_6(CO)_3$ [1] (1 g) was hydrogenated as above and the solvent removed. The brown-green residue was dissolved in light petroleum (10 cm^3), the solution filtered and concentrated to *ca.* 3 cm^3 and cooled to −78 °C to give a brown powder. Yield, 0.27 g, 34%. The complex is soluble in hydrocarbons and other non-polar solvents; i.r. (CS_2), 2 940s, 2 890m, 1 890s, 1 245s, 1 150m, 1 030w, 910m, 830s, 750m, 690m, 470w, and 375 cm^{-1}.

Dichlorobis(trimethylsilylmethyl)bis(triphenylphosphine)-dirhenium(II) (Re–Re), $Re_2Cl_2(CH_2SiMe_3)_2(PPh_3)_2$, (5). A similar hydrogenation of $Re_3Cl_3R_6$ (1 g, 0.8 mmol) in light petroleum containing PPh_3 (0.66 g, 2.4 mmol) produced a green-brown precipitate which was collected, dissolved in toluene, and reprecipitated at low temperature by addition of light petroleum. Yield 0.7 g, 42%. The compound is sparingly soluble in light petroleum but soluble in aromatic hydrocarbons, ether, and acetone; i.r. (CS_2), 3 120w, 3 050s, 2 940s, 2 890m, 1 650w,br, 1 320m, 1 300m, 1 240s, 1 200m, 1 180m, 1 150w, 1 080m,br, 1 020w, 990vw, 910s,br, 830s,br, 740s,br, 690s,br, 615w, 585s, 500s,br, and 400m,br cm^{-1}.

Tri-μ-chloro-tris(pyridine)tris(trimethylsilylmethyl)-triangulo-*trirhenium*(II), $Re_3(\mu\text{-}Cl)_3(CH_2SiMe_3)_3(py)_3$, (6). $Re_3Cl_3R_6(py)_3$ [1] was hydrogenated in benzene as above (*ca.* 1.5 h). The solvent was removed, the residues were washed with light petroleum, and the green-brown product purified by precipitation from concentrated solutions in thf by addition of light petroleum at low temperature. Yield 56%, based on $Re_3Cl_3R_6(py)_3$; i.r. (Nujol), 2 940s, 2 850s, 1 600m, 1 570w, 1 460s, 1 440s, 1 375m, 1 240m, 1 215m, 1 156w, 1 060w, 1 010w, 900w, 840s, 750s, and 690s cm^{-1}.

Hexakis[triaquo-tri-μ-chloro-tris(trimethylsilylmethyl)-triangulo-*trirhenium*(II)], $[Re_3(\mu\text{-}Cl)_3R_3(OH_2)_3]_6$, (7). $Re_3Cl_3R_6(OH_2)_3$ [1] was hydrogenated in benzene as above (*ca.* 1 h). The solvent was removed and the residues extracted with light petroleum to give a green solution. The compound was purified by low-temperature chromatography on silica with diethyl ether as eluant. Yield, 80%, based on $Re_3Cl_3R_6(OH_2)_3$; i.r. (CS_2), 3 620m, 3 510w, 2 950s, 2 895m, 2 860w, 1 255s, 1 245s, 1 010w, 920w, 840s, 750w, 680m, 615w, 470m, 400s, and 345m cm^{-1}.

Reaction of $Re_3Cl_3(CH_2SiMe_3)_6$ *and* $Re_6Cl_6H_6(CH_2SiMe_3)_6$ *with hydrogen and alkenes*. Reactions were carried out in pressure bottles (30 cm^3) using *ca.* 50 mg $Re_3Cl_3R_6$ in benzene (2 cm^3) and substrate (1 cm^3) under hydrogen (2 atm), for 2 h. The bottle was flushed with hydrogen before pressurisation. The products were analysed by g.l.c. using a Perkin-Elmer 8% Carbowax 20 M + 2% KOH on Chromosorb W 80—100 mesh (serial no. 22657) column on a Perkin-Elmer F33 instrument.

For the hydrido-complex $Re_6Cl_6H_6R_6$ the reaction times were as follows: styrene, 30 min; hex-1-ene, 15 min.

Hexakis(trimethylsilylmethyl)bis[tri-μ-chloro-triangulo-*trirhenium*(II)], $Re_6(\mu\text{-}Cl)_6(CH_2SiMe_3)_6$, (8). To a frozen solution of $Re_6Cl_6H_6R_6$ (1 g) in benzene (5 cm^3) in a Carius tube was condensed tetrafluoroethylene (5 cm^3, from the thermal decomposition of polytetrafluoroethylene). The tube was sealed *in vacuo*, allowed to stand at ambient temperature for 24 h, when it was cooled to −196 °C, opened and the contents allowed to warm to ambient temperature under nitrogen. The green solution was filtered, the solvent removed *in vacuo*, and the green residue chromatographed on silica at −78 °C using diethyl ether. Yield 0.47 g, 47% based on $Re_6Cl_6H_6R_6$; i.r. (CS_2), 2 945s, 2 890m, 1 465s, 1 380s, 1 255s, 1 005w, 940w, 820s, 710m, 485w, and 350m cm^{-1}.

Hexakis(trimethylsilylmethyl)bis[tri-μ-chloro-triangulo-*trirhenium*(II)]*bis[tri-μ-chloro*-triangulo-*trirhenium*(I)], $Re_{12}(\mu\text{-}Cl)_{12}(CH_2SiMe_3)_6$, (9). A solution of $Re_6Cl_6H_6R_6$ (1 g) in benzene (20 cm^3) was stirred for about 3 d, filtered, and evaporated *in vacuo*. The green residue was chromatographed on silica at −78 °C, using diethyl ether. Yield 0.75 g, 85% based on $Re_6Cl_6H_6R_6$. The compound is soluble in hydrocarbons and other non-polar solvents; i.r. (CS_2), 2 945m, 2 895m, 2 850w, 1 460m, 1 385m, 1 250s, 1 010w, 945w, 810s, 710w, 480m, and 350m cm^{-1}.

syn-, syn-, anti-*Trichloro-tris(μ-trimethylsilylmethyl)-tris(trimethylsilylmethyl)*-triangulo-*trirhenium*(III), $Re_3Cl_3(\mu\text{-}CH_2SiMe_3)_3(CH_2SiMe_3)_3$, (10). The red supernatant obtained in the synthesis of $Re_3Cl_3R_6$ from 10 g $Re_3Cl_9(thf)_3$ was evaporated and the residue dissolved in thf (20 cm^3). The solution was pressurised to 2 atm with hydrogen and stirred for 10 min. The brown solution was filtered, evaporated *in vacuo*, and the residue extracted into light petroleum (2 × 10 cm^3). The solution was filtered, concentrated to *ca.* 3 cm^3, and held at −20 °C for *ca.* 12 h. The red prisms of the complex were collected and dried *in vacuo*. Yield *ca.* 2% based on $Re_3Cl_9(thf)_3$.

TABLE 4

Fractional atomic co-ordinates (Re × 10^5; others × 10^4) for $Re_6(\mu\text{-}Cl)_6H(CH_2SiMe_3)_9$, (1) *

	x	*y*	*z*
Re(1)	19 413(5)	29 740(6)	77 625(5)
Re(2)	33 426(4)	36 512(6)	71 391(5)
Re(3)	22 312(4)	46 132(5)	67 045(5)
Re(4)	24 677(4)	78 289(5)	64 841(5)
Re(5)	11 095(4)	70 923(6)	72 162(5)
Re(6)	21 117(4)	61 559(5)	71 705(5)
Cl(1)	3 064(3)	2 024(4)	8 272(3)
Cl(2)	3 646(3)	5 259(4)	6 039(4)
Cl(3)	799(3)	3 879(4)	7 252(3)
Cl(4)	1 469(3)	8 781(4)	6 508(4)
Cl(5)	746(3)	5 428(4)	7 924(4)
Cl(6)	3 476(3)	6 931(4)	6 434(4)
Si(1)	2 306(5)	2 649(6)	10 131(5)
Si(2)	529(5)	1 143(5)	7 784(6)
Si(3)	4 009(3)	2 245(4)	6 241(4)
Si(4)	5 380(4)	4 301(5)	7 733(5)
Si(5)	1 660(3)	5 811(4)	4 394(4)
Si(6)	3 034(4)	9 486(4)	4 316 4)
Si(7)	4 307(3)	7 980(5)	7 860(5)
Si(8)	1 311(4)	6 835(6)	9 537(4)
Si(9)	−873(3)	7 447(5)	6 406(4)
C(11)	1 641(14)	2 591(18)	9 148(14)
C(12)	3 223(17)	1 991(22)	10 470(19)
C(13)	2 751(21)	3 962(26)	9 869(26)
C(14)	1 507(19)	2 123(22)	11 123(17)
C(21)	1 331(12)	2 190(14)	7 108(14)
C(22)	1 085(21)	209(22)	8 739(26)
C(23)	−377(17)	1 476(22)	8 207(22)
C(24)	90(22)	675(24)	6 988(27)
C(31)	3 508(12)	3 297(16)	6 099(14)
C(32)	4 346(14)	2 606(17)	5 017(16)
C(33)	3 209(14)	1 118(17)	6 653(18)
C(34)	4 973(14)	2 045(19)	7 014(18)
C(41)	4 208(11)	3 905(19)	8 062(15)
C(42)	5 963(21)	3 246(29)	8 541(19)
C(43)	5 667(14)	4 639(19)	6 480(16)
C(44)	5 710(21)	5 374(24)	7 927(33)
C(51)	1 842(11)	4 678(14)	5 377(13)
C(52)	2 634(12)	6 741(16)	4 045(17)
C(53)	764(13)	6 302(18)	4 624(17)
C(54)	1 380(15)	5 570(17)	3 341(14)
C(61)	2 239(12)	8 437(14)	5 066(14)
C(62)	2 999(13)	10 479(14)	4 591(18)
C(63)	4 159(13)	9 232(17)	4 409(17)
C(64)	2 671(17)	9 859(21)	3 094(18)
C(71)	3 364(11)	8 452(13)	7 103(15)
C(72)	4 093(13)	6 762(18)	8 813(16)
C(73)	4 667(15)	8 830(23)	8 351(11)
C(74)	5 221(12)	8 036(19)	7 142(17)
C(81)	781(12)	7 092(12)	8 409(13)
C(82)	2 286(18)	7 759(25)	9 327(23)
C(83)	534(18)	6 922(23)	10 316(18)
C(84)	1 638(21)	5 657(23)	10 085(19)
C(91)	217(10)	7 272(15)	6 173(12)
C(92)	−1 542(14)	7 514(22)	5 388(17)
C(93)	−786(13)	8 573(17)	6 460(17)
C(94)	−1 392(14)	6 429(20)	7 512(20)

* Estimated standard deviations (e.s.d.s) are in parentheses in this and other tables.

TABLE 5

Fractional atomic co-ordinates (× 10^4) for $Re_3(\mu\text{-}Cl)_3ClH(CH_2SiMe_3)_4(PPh_3)$, (3)

	x	*y*	*z*
Re(1)	3 266(1)	2 570(1)	687(1)
Re(2)	3 056(1)	828(1)	438(1)
Re(3)	2 130(1)	1 983(1)	1 311(1)
Cl(1)	4 191(5)	1 434(6)	−259(6)
Cl(2)	1 939(5)	208(4)	1 052(6)
Cl(3)	2 352(4)	3 762(4)	1 562(6)
Cl(4)	1 165(4)	2 416(4)	−254(5)
P(1)	972(4)	2 267(4)	2 561(5)
Si(1)	3 522(6)	4 393(7)	−1 213(8)
Si(2)	4 209(7)	3 414(9)	3 337(8)
Si(3)	3 816(8)	−842(9)	2 747(11)
Si(4)	2 830(7)	−689(7)	−1 904(9)
C(11)	3 005(16)	3 269(19)	−889(20)
C(12)	4 584(19)	3 975(31)	−1 125(37)
C(13)	3 221(22)	5 541(21)	−177(30)
C(14)	3 121(28)	4 817(27)	−2 782(28)
C(21)	4 200(15)	2 939(25)	1 822(26)
C(22)	3 773(30)	4 792(35)	3 268(47)
C(23)	5 238(21)	3 503(28)	3 908(34)
C(24)	3 516(38)	3 168(68)	4 340(34)
C(31)	3 781(22)	−212(29)	1 425(28)
C(32)	3 133(38)	−547(30)	3 693(43)
C(33)	4 509(47)	−1 991(44)	3 057(55)
C(34)	3 525(48)	−2 065(45)	1 811(83)
C(41)	2 607(18)	611(17)	−1 241(20)
C(42)	2 368(25)	−1 665(27)	−1 170(35)
C(43)	2 424(32)	−653(29)	−3 375(30)
C(44)	3 820(27)	−981(42)	−2 011(60)
C(111)	510(15)	1 113(16)	2 554(19)
C(112)	125(17)	787(21)	1 552(23)
C(113)	−197(19)	−139(23)	1 527(31)
C(114)	−262(22)	−698(26)	2 471(36)
C(115)	103(30)	−421(26)	3 472(38)
C(116)	524(20)	511(27)	3 564(26)
C(121)	1 214(15)	2 541(18)	4 074(20)
C(122)	729(20)	3 191(28)	4 644(28)
C(123)	911(25)	3 420(32)	5 851(25)
C(124)	1 461(23)	2 926(27)	6 442(24)
C(125)	1 965(21)	2 250(26)	5 852(27)
C(126)	1 844(18)	2 055(19)	4 666(24)
C(131)	163(16)	3 258(17)	2 121(19)
C(132)	352(17)	4 196(18)	1 724(23)
C(133)	−156(19)	4 938)22)	1 415(28)
C(134)	−924(22)	4 758(27)	1 497(25)
C(135)	−1 138(22)	3 821(25)	1 919(42)
C(136)	−566(17)	3 031(21)	2 301(35)

Tri-μ-chloro-hexaphenyl-triangulo-*trirhenium*(III), $Re_3(\mu\text{-}Cl)_3Ph_6$, (11). To $Re_3Cl_9(thf)_3$ (1 g, 0.9 mmol) suspended in thf (30 cm^3) at −78 °C was added with vigorous stirring a solution of phenylmagnesium bromide (0.98 mol dm^{-3} in diethyl ether; 8.5 cm^3, 2.7 mmol). The solution was allowed to warm to ambient temperature with stirring when the solution changed colour from green through brown to deep red. After all the halide had dissolved (*ca.* 30 min at 20 °C), the solvent was removed and the brown residue extracted into toluene (3 × 20 cm^3). This solution was shaken with water (10 cm^3) until the toluene was green, after which it was separated, cooled to −78 °C, filtered, and evaporated in vacuum. The green residue was washed with light petroleum (2 × 20 cm^3) leaving a green powder. The compound could be further purified by low-temperature (−78 °C) elution from silica gel by toluene. Yield, 0.88 g, 85% based on $Re_3Cl_9(thf)_3$; i.r. (KBr disc), 3 050, 2 965, 1 570, 1 557, 1 472, 1 417, 1 198, 1 155, 1 027, 992, 920, 728, 692, and 350 cm^{-1}.

Tri-μ-chloro-hexakis(p-*tolyl*)-triangulo-*trirhenium*(III), $Re_3(\mu\text{-}Cl)_3(C_6H_4Me\text{-}p)_6$, (12). The procedure was as for the phenyl derivative but using 4-methylphenylmagnesium chloride. The product can be purified by crystallisation from diethyl ether at −20 °C. Yield 75% based on Re_3Cl_9-

(thf)$_3$; i.r. (KBr disc), 3 045, 2 970, 2 925, 2 850, 1 565, 1 555, 1 460, 1 380, 1 210, 1 170, 1 013, 995, 910, 820, 540, and 351 cm^{-1}.

Tris(μ-methyl)-hexakis(trimethylsilylmethyl)-triangulo-*trirhenium*(III), $Re_3(\mu\text{-}CH_3)_3(CH_2SiMe_3)_6$, (13). To a solution of $Re_3(\mu\text{-}Cl)_3R_6$ (1.18 g, 1 mmol) and PPh_3 (1.56 g, 6 mmol) in diethyl ether (50 cm^3) was added at −78 °C with vigorous stirring a solution of methyl-lithium (3 mmol, 3.93 cm^3, 0.97 mol dm^{-3} in diethyl ether). The solution was allowed to warm slowly to ambient temperature during which time it changed from the initial blue to red. The solution was cooled to −20 °C, water (5 cm^3) added slowly, and after warming to ambient temperature the organic layer was separated, the solvent removed *in vacuo*, and the residues extracted with light petroleum. The solution was evaporated, the residue washed twice with methanol, and the compound crystallised from light petroleum at −20 °C. Yield 0.52 g, 47%; i.r. (CS_2), 2 945s, 2 890m, 2 820m, 1 260s, 1 250s, 1 010w, 960w, 940w, 840s,br, 740m,br, 690m, 670m, 610w, 500w,br, and 390w,br cm^{-1}.

TABLE 6

Fractional atomic co-ordinates (Re × 10^5; others × 10^4) for $Re_3Cl_3(\mu\text{-}CH_2SiMe_3)_3(CH_2SiMe_3)_3$, (10)

	x	*y*	*z*
Re(1)	748(3)	−8 262(4)	29 965(2)
Re(2)	7 500(3)	9 041(5)	28 807(2)
Re(3)	−4 481(3)	3 771(4)	21 182(2)
Cl(1)	498(2)	−2 771(3)	3 028(2)
Cl(2)	1 958(2)	928(4)	2 741(2)
Cl(3)	−1 443(2)	1 507(3)	2 241(2)
Si(1)	−837(2)	−1 478(4)	4 028(2)
Si(2)	2 210(3)	−1 151(4)	4 019(2)
Si(3)	1 100(3)	3 466(3)	3 699(2)
Si(4)	−449(2)	3 132(4)	1 440(2)
Si(5)	472(3)	−1 318(6)	1 167(2)
Si(6)	−2 169(2)	−1 315(3)	1 704(2)
C(11)	−596(8)	−271(11)	3 533(6)
C(12)	−1 297(10)	−2 855(14)	3 584(9)
C(13)	57(11)	−1 952(17)	4 687(9)
C(14)	−1 602(11)	−790(16)	4 312(9)
C(21)	1 246(7)	−291(11)	3 758(6)
C(22)	2 518(9)	−1 892(14)	3 418(8)
C(23)	3 013(9)	−69(22)	4 451(10)
C(24)	2 114(13)	−2 312(20)	4 594(9)
C(31)	377(7)	2 171(11)	3 382(6)
C(32)	1 443(10)	4 253(13)	3 098(8)
C(33)	479(13)	4 547(16)	3 974(11)
C(34)	2 010(11)	2 988(16)	4 333(9)
C(41)	242(7)	2 009(14)	1 983(6)
C(42)	−1 298(9)	2 482(14)	802(7)
C(43)	−831(10)	4 239(14)	1 875(8)
C(44)	207(10)	3 911(15)	1 073(9)
C(51)	−250(9)	−390(17)	1 352(6)
C(52)	1 197(18)	−2 190(29)	1 779(12)
C(53)	114(16)	−1 881(33)	426(11)
C(54)	1 262(19)	−105(33)	1 042(19)
C(61)	−1 074(7)	−1 367(11)	2 192(6)
C(62)	−2 780(9)	−756(13)	2 157(8)
C(63)	−2 430(9)	−476(14)	928(7)
C(64)	−2 445(10)	−2 912(13)	1 488(8)

X-*Ray Crystallography*.—All crystallographic measurements were made on crystals sealed under N_2 in Lindemann capillaries and cooled to 270 K in a stream of cold air. The unit-cell and crystal-orientation matrices were obtained using the SEARCH and INDEX routines on a Nonius CAD4 diffractometer and accurate cell parameters by least-squares refinement of the setting angles for 25 high-angle reflections [$16 < \theta(\text{Mo-}K_\alpha) < 18°$]. The Laue groups were confirmed by comparing the symmetry related intensities and the space group $P2_1/n$ was assigned for (10) on the basis of the sytematic absences $h0l$ for $h + l$ odd and $0k0$ for k odd. The structures (1) and (3) were solved and refined successfully in space group $P\bar{1}$. Full crystal data and details of data collection are given in Table 3.

The intensity data were recorded and processed as described in detail.[9] During data collection all three compounds showed signs of systematic decay, as indicated by the fall in the intensities of the standard reflections which were monitored every hour. All data were corrected for the decay, for absorption, and for Lorentz and polarisation effects but not for extinction.

The structures of all three compounds were solved first by locating the rhenium atoms from E maps (SHELX-76) and the remaining atoms from successive difference electron-density synthesis interspersed with cycles of least-squares refinement. In the final stages of refinement, all non-hydrogen atoms were refined anisotropically, and the weighting scheme $w = 1/[\sigma^2(F_o) + g(F_o)^2]$ was used with the parameter g chosen to give approximately flat analyses of variance with $(F_o/F_{\text{max.}})^{\frac{1}{2}}$ and sin θ. The moderate quality of data (rather broad peak widths and crystal decay) did not enable us to locate the hydrogen atoms in any of the structures and these were ignored. For (1) and (3), there were indications in the difference maps that solvent molecules (thf) are present in the open regions of the crystal structures, but these were severely disordered and could not be fitted into any chemically recognisable molecular fragment. Accordingly, no attempts were made to allow for this. The final R values were 0.055 (1), 0.063 (3), and 0.048 (10) for 6 796, 3 704, and 5 293 reflections [$F_o > 4\sigma(F_o)$] respectively.

The atomic fractional co-ordinates are given in Tables 4—6. Anisotropic thermal parameters and observed and calculated structure factors have been deposited in Supplementary Publication No. SUP 22971 (75 pp.).* Sources of scattering factors, programs, and computers are the same as mentioned in reference 2.

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1979, Index issue.