Trirhenium(III) Cluster Alkyls. Synthesis of Tertiary Phosphine Adducts; Cleavage to Rhenium-(III) and -(II) Dimers; Reactions with Carbon Monoxide, Nitric Oxide, and Hydrogen Chloride. *X*-Ray Structural Determinations of Hexamethylbis(diethylphenylphosphine)tri-μ-methyl-*triangulo*-trirhenium(III) and Tri-μ-chloro-(*N*-nitroso-*N*-trimethylsilylmethylhydroxylaminato)pentakis(trimethylsilylmethyl)-*triangulo*-trirhenium(III) †

By **Peter Edwards, Konstantinos Mertis, and Geoffrey Wilkinson,*** Chemistry Department, Imperial College of Science and Technology, London SW7 2AY

Michael B. Hursthouse and **K. M. Abdul Malik,** Chemistry Department, Queen Mary College, Mile End Road, London E1 4NS

A new cluster benzyl, $Re_3Cl_3(CH_2Ph)_6$, and tertiary phosphine (L) adducts of the corresponding cyclohexyl, $Re_3Cl_3(C_6H_{11})_6L_3$, and of the permethyl, $Re_3Me_3L_{2,3}$, have been prepared. The structure of the diethylphenylphosphine derivative $Re_3Me_9(PEt_2Ph)_2$ has been confirmed by a single-crystal *X*-ray structure determination. Crystals are monoclinic, space group *C*2/*c*, with dimensions *a* = 27.220(4), *b* = 9.817(1), *c* = 26.051(5) Å, and β = 102.65(2)° and the structure was solved by direct methods and refined by least squares to an *R* of 0.043 using 4 982 unique observed intensities. The Re_3Me_9 unit present in the trinuclear molecule is considerably distorted as a result of steric compression from the two strongly bound phosphines. The trinuclear rhenium(III) phosphine adducts undergo cleavage reactions to give dimeric compounds of rhenium(III) or rhenium(II), examples being $Re_2Me_6(PMe_2Ph)_2$ and $Re_2Cl_2(CH_2SiMe_3)_2(PMe_3)_4$. The reactions of the blue trimethylsilylmethyl cluster $Re_3Cl_3(CH_2SiMe_3)_6$ with CO, NO, and HCl are described. Nitric oxide is shown to give an insertion product with an *N*-(trimethylsilylmethyl)-*N*-nitrosohydroxylaminato-chelate ring, of formula $Re_3Cl_3(CH_2SiMe_3)_5\{ON(CH_2SiMe_3)NO\}$ whose structure has also been confirmed by *X*-ray structure determination. Crystals are monoclinic, space group $P2_1/a$, with *a* = 33.33(4), *b* = 11.733(5), *c* = 11.947(6) Å, and β = 92.93(4)°. The structure was solved by direct methods and refined by least squares to an *R* of 0.067 using 4 360 observed data. The nitrosohydroxylaminato-ligand chelates symmetrically (Re–O 2.10 Å × 2) to one of the metal atoms, using one out-of-plane and the in-plane terminal sites.

THE synthesis and characterisation of the trirhenium(III) cluster alkyls $Re_3Cl_3(CH_2SiMe_3)_6$ and $(Re_3Me_9)_n$ and their pyridine adducts has been described.[1] The structure of $Re_3Cl_3(CH_2SiMe_3)_6$ has been confirmed by an *X*-ray diffraction study.[2]

We now report the synthesis and characterisation of (*i*) the benzyl $Re_3Cl_3(CH_2Ph)_6$; (*ii*) the phosphine adduct of the cyclohexyl, $Re_3Cl_3(C_6H_{11})_6(PMe_2Ph)_3$; (*iii*) some phosphine adducts of stoicheiometry $Re_3Me_9(PR_3)_n$, $n = 2$ or 3; and (*iv*) the rhenium(II) and rhenium(III) dimeric alkyls, $Re_2Cl_2(CH_2SiMe_3)_2(PR_3)_4$ and $Re_2Me_6(PR_2)_2$ formed by cleavage of the trimers. The reactions of $Re_3Cl_3(CH_2SiMe_3)_6$ with CO, NO, and HCl are also reported.

Nuclear magnetic resonance data for the new compounds are given in Table 1 and analytical data in Table 2.

RESULTS AND DISCUSSION

Cluster Alkyls, $Re_3Cl_3R_6$, *and their Tertiary Phosphine Adducts*.—R = *Benzyl*. The complex $Re_3Cl_3(CH_2Ph)_6$ has been synthesised in a manner similar to that used for $Re_3Cl_3(CH_2SiMe_3)_6$, namely the interaction of aged Re_3Cl_9 and $PhCH_2MgCl$. A crystalline product could be obtained consistently only when the reaction was performed in the presence of dimethylphenylphosphine; however, no phosphine complex could be isolated. The alkyl was characterised by analytical, spectroscopic, and molecular weight data. In the ^1H n.m.r. spectrum there are two resonances at $\delta = 7.14$ and 2.54 p.p.m. in the ratio of 5 : 2 respectively, as expected for equivalent alkyl groups. The i.r. spectrum is typical of other benzyls; the ν(Re–Cl) stretch appears at 351 cm^{-1}.

R = *Cyclohexyl*. The reaction of aged Re_3Cl_9 with $C_6H_{11}MgCl$ in the presence of dimethylphenylphosphine gave a brown, hydrocarbon-soluble powder. Spectroscopic and analytical data are consistent with the formulation of the triphosphine adduct, $Re_3Cl_3(C_6H_{11})_6(PMe_2Ph)_3$. The molecular weight measured in solution is low, probably due to phosphine dissociation, as occurs for $Re_3Me_9(PR_3)_3$ (see below).

Phosphine adducts of Re_3Me_9. In order to obtain suitable crystals of adducts of nonamethyl-*triangulo*-trirhenium(III) for *X*-ray crystal-structure determination, the tertiary phosphine complexes $Re_3Me_9(PMe_2Ph)_3$, $Re_3Me_9(PEt_2Ph)_3$, and $Re_3Me_9(PEt_2Ph)_2$ (1) were synthesised, and suitable crystals of the latter were obtained.

The structure of (1) has been confirmed by an *X*-ray diffraction study. A diagram of the molecular structure is shown in Figure 1, along with the atomic numbering scheme used, whilst some of the more important molecular geometry parameters are given in Table 3. A view of the unit-cell contents is given in Figure 2.

The molecule contains an isosceles triangle of rhenium atoms, with the unique side corresponding to the bond between the two phosphine-carrying Re atoms. Although the molecule does not possess any crystallo-

---

† No reprints available.

graphic symmetry, there is an approximate mirror plane passing through the unique Re atom [Re(3)], the methyl carbons attached to it, and the methyl carbon [C(1)] bridging the unique Re–Re edge. The bond lengths in the Re_3 triangle agree very well with the values expected, assuming a simple correlation between Re covalent radius and Re co-ordination number, as discussed for the structure of $Re_3Cl_3(CH_2SiMe_3)_6$.[2] Whether this variation has its origin in steric effects or the electronic influence of in-plane terminal ligands is open to debate, but distortions in other parts of the molecule are clearly due to steric effects, arising from the co-ordination of the phosphine. The most obvious distortion, as can be seen in Figure 1, is in the methyls bridging the rhenium atoms [Re–Me = **1.938(12)—2.447(11) Å**] in the Re_3Me_3 plane, and we can consider this to arise as follows.

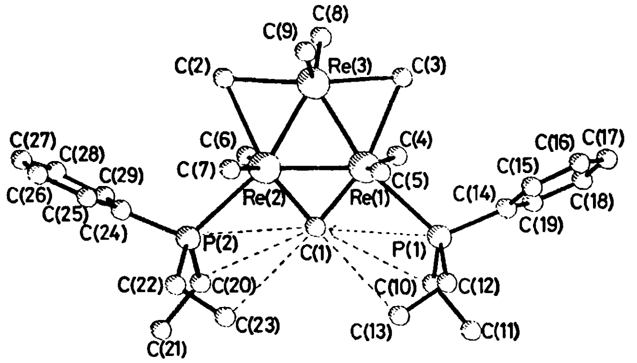


FIGURE 1 The molecular structure of $Re_3Me_9(PEt_2Ph)_2$ (1)

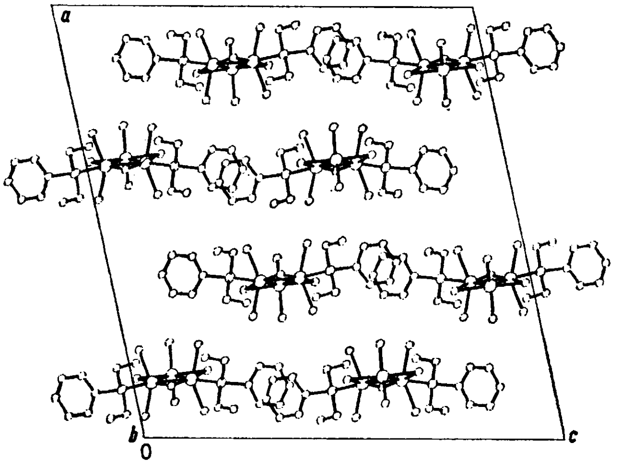


FIGURE 2 View down *b* of the unit-cell contents for $Re_3Me_9(PEt_2Ph)_2$

TABLE 1

Spectroscopic data for rhenium alkyl complexes

Compound	^1H n.m.r., δ/p.p.m.[a]	^{31}P and ^{13}C n.m.r., δ/p.p.m.[b]
$ReCl_3(CH_2Ph)_6$	2.54s, (2), Re–CH_2Ph; 7.14br, (5), Re–CH_2*Ph*	
$Re_3Cl_3(C_6H_{11})_6(PMe_2Ph)_3$	1.82br, (22), Re–$C_6\mathit{H}_{11}$; 1.25br, (6), PMe_2Ph; 7.26br, (5), PMe_2*Ph*	
$Re_3Me_9(PMe_2Ph)_3$	−0.20br, (6), Re–Me; 0.90 br, (3), Re–*Me*–Re; 1.47br, (6), PMe_2Ph; 7.24br, (5), PMe_2*Ph*	
$Re_3Me_9(PEt_2Ph)_3$	−0.15br, (6), Re–*Me*; 0.84br, (3), Re–*Me*–Re; 1.87, 1.11br, (10), PEt_2Ph; 7.24br, (5), PEt_2*Ph*	^{31}P: −24.7 ^{13}C { 9.46, Re–*Me*; −11.83, Re–Me–Re
$Re_3Cl_3(CH_2SiMe_3)_6(CO)_3$	0.34s, Re–CH_2SiMe_3	
$Re_3Cl_3(CH_2SiMe_3)_5[ON(CH_2SiMe_3)NO]$	0.01s, (9), ON(CH_2SiMe_3)NO; 0.35s, (45), Re–CH_2SiMe_3; 0.50s, (2), ON(CH_2SiMe_3)NO; 0.59s, (10), Re–CH_2SiMe_3	
$Re_3Cl_4(CH_2SiMe_3)_5$	0.34s, (27), Re–CH_2SiMe_3; 0.29s, (6), Re–CH_2SiMe_3; 0.24s, (18), Re–CH_2SiMe_3 0.18s, (4), Re–CH_2SiMe_3 [b]	
$Re_3Cl_6(CH_2SiMe_3)_3$	0.17s, Re–CH_2SiMe_3 [c]	
$Re_2Me_6(PMe_3)_2$	−0.05m, br, (1), Re–*Me*; 1.21d, br, (1), PMe_3 [d]	
$Re_2Me_6(PMe_2Ph)_2$	0.34m, br, (9), Re–*Me*; 1.52d, br, (6), PMe_2Ph; 7.29br, (5), PMe_2*Ph*	^{31}P −4.3 [e] ^{13}C { 12.4s, br, Re–*Me*; 28.4d, PMe_2Ph; 129.3m, PMe_2*Ph*
$Re_2Me_6(PEt_2Ph)_2$	0.19s, (6), Re–Me *cis*; 0.48s, br, (3), Re–Me *trans*; 1.05m, br, (6), P($CH_2\mathit{CH}_3)_2$Ph; 1.90m, br, (4), P($\mathit{CH}_2CH_3)_2$Ph; 7.36m, br, (5), $P(CH_2CH_3)_2$*Ph*	^{31}P { −23.21 (35 °C); −27.09 (60 °C)
$Re_2Cl_2(CH_2SiMe_3)_2(PMe_3)_4$	0.16m, br, (11), Re–CH_2SiMe_3; 1.73m, br, (18), PMe_3	^{31}P: −31.7
$Re_2Cl_2(CH_2SiMe_3)_2(PMe_2Ph)_4$	−0.13m, (11), Re–CH_2SiMe_3; 0.16d, br, (12), PMe_2Ph; 7.21br, (10), PMe_2*Ph*	^{31}P: −22.4

[a] C_6H_6 or C_6D_6. [b] C_6H_6 or C_6D_6, ^{31}P relative to 85% aqueous H_3PO_4, ^{13}C relative to $SiMe_4$. [c] [$^2H_6$]Acetone. [d] Pyridine. [e] [^{2}H]-Chloroform.

Starting from a symmetrical Re_3Me_9 unit, the methyl group C(1) is pushed inwards by compression from P(1), P(2), and the phosphine ethyl carbons C(10), C(13), C(20), and C(23). The out-of-plane methyl groups C(4)—C(7) inclusive, are also pushed sideways by the phosphorus atoms, the α carbons of the ethyl groups and some carbons of the phenyl groups. In turn, carbons C(4)—C(7) exert compressions on the two side-bridging methyl groups C(2) and C(3) causing considerable asymmetry in these bridges. The relevant close contacts are indicated on Figure 1 and listed in Table 4. The steric compression also has some effect on the planarity of the Re_3Me_3 nucleus where deviations of the order of 0.1 Å are larger than normally found.

The extent of the distortions present imply fairly strong bonding of the phosphines and the Re–P distances of 2.546(3) and 2.569(3) Å are consistent with this suggestion, especially when compared with the distances of 2.70(2) Å for Re–P bonds in $Re_3Cl_9(PEt_2Ph)_3$.[3] It is also interesting to compare the Re–P bond lengths in the present compound with the two in-plane Re–Cl bond lengths of 2.55(6) and 2.58(3) Å in the anion [4] $[Re_3Cl_{11}]^{2-}$. Since M–Cl bonds are invariably shorter than M–P bonds, this comparison again suggests strong phosphine bonding here. This latter structure is also very useful for a general comparison with our compound since the two are structurally equivalent with one six- and two seven-co-ordinate Re atoms. In fact, the Re_3 triangle geometries are very similar indeed, but the distortions in the chlorine-atom configuration in the halide cluster, especially in the bridges, are smaller. This is not too surprising since the steric crowding is much less.

TABLE 2

Analytical and physical data of rhenium alkyl complexes

Compound	M.p.[a] (θ_c/°C)	Colour	Analysis (%) [b] C	H	Cl	P	Other	M [c]
$Re_3Cl_3(CH_2Ph)_6$	−110 (decomp.)	Brown-black	41.5 (41.7)	3.8 (3.5)	8.6 (8.8)			1 182 (1 211)
$Re_3Cl_3(C_6H_{11})_6(PMe_2Ph)_3$	96—100	Brown-black	44.7 (45.6)	6.4 (6.3)	5.5 (6.7)	7.6 (5.9)		632 (1 515)
$Re_3Me_9(PMe_2Ph)_3$	Sublimes 100 [d]	Mauve	35.5 (35.7)	5.4 (5.4)		7.9 (8.4)		585 (1 110)
$Re_3Me_9(PEt_2Ph)_3$	Sublimes 90 [d]	Mauve	39.5 (39.3)	5.2 (6.0)		7.6 (7.8)		550 (1 179)
$Re_3Cl_3(CH_2SiMe_3)_6(CO)_3$	−120 (decomp.)	Green	25.5 (27.3)	5.5 (5.6)	8.8 (9.0)		41.6 [e] (43.8)	1 188 (1 272)
$Re_3Cl_3(CH_2SiMe_3)_5[ON(CH_2SiMe_3)NO]$	Sublimes 105 [d]	Green	22.3 (22.6)	5.1 (5.2)	8.7 (9.1)		44.4 [e] (44.8) 2.2 [f] (2.2)	1 234 (1 278)
$Re_3Cl_4(CH_2SiMe_3)_5$	100—101	Green	21.2 (21.2)	5.0 (4.9)	13.7 (12.5)			1 151 (1 135)
$Re_3Cl_6(CH_2SiMe_3)_3$	>360	Red	13.0 (13.9)	3.0 (3.2)	22.4 (20.6)		53.9 [e] (54.1)	1 132 (1 035)
$Re_2Me_6(PMe_3)_2$	−150 (decomp.)	Grey-green	23.3 (23.4)	5.7 (5.8)		9.0 (10.0)		(616)
$Re_2Me_6(PMe_2Ph)_2$	−130 (decomp.)	Grey-green	35.8 (35.8)	4.7 (5.4)		8.3 (8.4)		690 (738)
$Re_2Me_6(PEt_2Ph)_2$	−135 (decomp.)	Green	39.5 (39.2)	6.0 (6.0)		7.8 (7.8)		666 (796)
$Re_2Cl_2(CH_2SiMe_3)_2(PMe_3)_4$	−90 (decomp.)	Green-brown	26.5 (26.1)	6.4 (6.3)	8.5 (7.7)	14.2 (13.5)	4.7 [g] (6.1)	837 [h] (921)
$Re_2Cl_2(CH_2SiMe_3)_2(PMe_2Ph)_4$	−160 (decomp.)	Brown	41.0 (41.0)	5.3 (5.6)	6.1 (6.1)	11.2 (10.6)		1 070 (1 171)

[a] Many compounds decompose over a large range of temperature. [b] Calculated values are given in parentheses. [c] Osmometrically in benzene or dichloromethane. [d] At 10^{-3} Torr. [e] Re. [f] N. [g] Si. [h] Cryoscopically in benzene.

The Re–C distances in the methyl cluster also show some interesting variations. The distances involving two of the Re–Me–Re bridges are unequal, as mentioned previously, but their average values are still greater than those involving terminal bonds. This feature parallels a similar variation in the halide clusters. The distances to the unique bridging methyl group C(1) are much shorter however, and again probably result in part from the steric compression. The out-of-plane terminal bond lengths also fall into two groups with values of 2.11(1) Å for methyls attached to Re(3), the six-co-ordinate metal atom, and 2.16(1)—2.20(1) Å for those attached to Re(1) and Re(2). Here again we are probably seeing the effect of variation in metal radii. The geometry at the phosphorus atoms also reflects the steric crowding since the Re–P–C angles [112.7—118.1(5)°] are greater than tetrahedral and the C–P–C angles [102.5—105.1(6)°] are less. A possible explanation for the apparent strength of the terminal Re–P bonds in our complex is an increase in electron density on the rhenium atom by electron release from the methyl groups, resulting perhaps in some Re–P π back-bonding.

The ease of dissociation of phosphine is reminiscent of the lability of phosphine adducts of Re_3Cl_9 postulated on the basis of their electronic spectra.[3] The dissociation is, however, less than that of pyridine (py) from $Re_3Me_9(py)_3$ [1] in solution or upon warming *in vacuo*, since the phosphine adducts will actually sublime as mixtures at 60 °C and 10^{-3} Torr.* However, the highest peak in the mass spectrum corresponds to the ion $Re_3Me_9^+$ (m/e = 696). Except for those peaks attributable to the phosphine, the fragmentation pattern observed is identical to that of the ion, $Re_3Me_9^+$, generated from $Re_3Me_9(py)_3$.[1]

The ^1H n.m.r. spectrum of $Re_3Me_9(PMe_2Ph)_3$ shows the methyl resonances at δ −0.20 and 0.90 p.p.m. The former may be assigned to the terminal methyls on the basis of their relative areas. The peaks are broadened due to coupling with phosphorus, but are not well resolved because of non-rigid behaviour. The methyls on phosphorus appear at δ = 1.67 p.p.m. as a broad peak, again not well resolved. The solubility of the dimethylphenylphosphine adduct was too low for low-temperature studies, and reproducible $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ spectra could not be obtained as the complex decomposes in the polar solvents required to produce solutions of adequate concentration. However, the diethylphenylphosphine complex was considerably more soluble in apolar solvents. The ^1H n.m.r. spectrum of this compound also shows broad resonances, the terminal methyls appearing at δ = −0.15 p.p.m. and the bridging methyls at δ = 0.84 p.p.m. The multiplet due to ethyl groups of the phosphine occurs at δ = 1.09 p.p.m.; the phenyl resonance is at δ = 7.24 p.p.m. In the $^{13}C\{^1H\}$ spectrum, in addition to resonances due to the carbons of the phosphine, there were two broad peaks at δ = 9.46 and −11.83 p.p.m. (relative to external tetramethylsilane), the high-field signal being assigned to the bridging carbons. This is the converse of the positions in the ^1H n.m.r. spectra and may be due to the de-shielding effect of the paramagnetic ring current in the rhenium triangle. The $^{31}P\{^1H\}$ n.m.r. spectrum at 35 °C shows a broad singlet at δ = −24.20 p.p.m. (relative to 85% aqueous H_3PO_4). At low temperature, −80 °C, several peaks are seen indicating the existence of various dissociated species in solution.

TABLE 3

Some important bond lengths (Å) and angles (°) for (1) with estimated standard deviations in parentheses

(*a*) Lengths

Re(1)–Re(2)	2.474(1)		
Re(1)–Re(3)	2.435(1)	Re(1)–C(4)	2.163(13)
Re(2)–Re(3)	2.433(1)	Re(1)–C(5)	2.203(10)
		Re(1)–P(1)	2.546(3)
Re(1)–C(1)	1.938(12)	Re(2)–C(6)	2.179(10)
Re(1)–C(3)	2.447(11)	Re(2)–C(7)	2.185(13)
Re(2)–C(1)	1.930(12)	Re(2)–P(2)	2.569(3)
Re(2)–C(2)	2.443(12)	Re(3)–C(8)	2.105(13)
Re(3)–C(2)	2.215(11)	Re(3)–C(9)	2.107(13)
Re(3)–C(3)	2.232(9)		

(*b*) Angles

Re(2)–Re(1)–Re(3)	59.4(1)	P(1)–Re(1)–C(1)	86.5(4)
Re(1)–Re(2)–Re(3)	59.5(1)	P(1)–Re(1)–C(3)	109.6(2)
Re(1)–Re(3)–Re(2)	61.1(1)	P(1)–Re(1)–C(4)	77.9(3)
		P(1)–Re(1)–C(5)	81.7(4)
C(1)–Re(1)–C(3)	163.9(4)	C(1)–Re(1)–C(4)	101.0(5)
C(1)–Re(2)–C(2)	163.6(4)	C(1)–Re(1)–C(5)	103.2(5)
C(2)–Re(3)–C(3)	172.5(4)	C(3)–Re(1)–C(4)	82.1(5)
		C(3)–Re(1)–C(5)	80.9(5)
Re(1)–C(1)–Re(2)	79.5(5)	P(2)–Re(2)–C(1)	87.1(3)
Re(2)–C(2)–Re(3)	62.8(3)	P(2)–Re(2)–C(2)	109.1(3)
Re(1)–C(3)–Re(3)	62.5(3)	P(2)–Re(2)–C(6)	80.6(3)
		P(2)–Re(2)–C(7)	79.4(3)
C(4)–Re(1)–C(5)	147.2(4)	C(1)–Re(2)–C(6)	101.1(5)
C(6)–Re(2)–C(7)	145.4(4)	C(1)–Re(2)–C(7)	105.8(5)
C(8)–Re(3)–C(9)	125.5(5)	C(2)–Re(2)–C(6)	79.6(4)
		C(2)–Re(2)–C(7)	80.6(5)
		C(2)–Re(3)–C(8)	88.4(5)
		C(2)–Re(3)–C(9)	88.9(5)
		C(3)–Re(3)–C(8)	89.2(5)
		C(3)–Re(3)–C(9)	86.8(5)

The Cleavage of Cluster Alkyls by Tertiary Phosphines.—The reductive cleavage of *triangulo*-rhenium(III) halides to give dimeric metal–metal bonded rhenium(II) species is well known and there are complexes of the type $Re_2X_4(PR_3)_4$ and $Re_2X_6(PR_3)_2$ (X = halogen).[5] Similar cleavage of the cluster alkyls occurs to give both Re^{III} and sometimes by reduction, Re^{II} dimeric alkyls. It may be noted that our attempts to directly alkylate metal–metal bonded halides, $Re_2Cl_4(PR_3)_4$ and $Re_2Cl_6(PR_3)_2$, were unsuccessful. The only previously known alkyl of this type, with a metal–metal quadruple bond, is $Mo_2Me_4(PMe_3)_4$.[6]

Reactions of $Re_3Cl_3(CH_2SiMe_3)_6$. This cluster reacts at low temperatures with trimethylphosphine in light petroleum or diethyl ether to give a bright green solution which darkens at room temperature. From this dark green solution, the dimeric rhenium(II) complex, $Re_2Cl_2(CH_2SiMe_3)_2(PMe_3)_4$ was isolated and characterised by analysis and molecular weight. In the ^1H n.m.r. spectrum, there is a multiplet at δ = 1.33 p.p.m. (P*Me*$_3$). Neither of these complex multiplets may be interpreted easily, doubtless due to the occurrence of two or more of the several potential isomers of the quadruply metal–metal bonded dimeric structure (I). Attempts to separate isomers by chromatography or fractional crystallisation were unsuccessful. The $^{31}P\{^1H\}$ n.m.r. also shows a complex multiplet at δ = −31.7 p.p.m. The i.r. spectrum shows the expected bands for the alkyl groups as well as bands attributable to tri-

TABLE 4

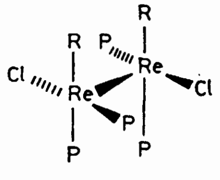
Short intramolecular contacts in molecule (1)

C(1) ··· P(1)	3.105	C(1) ··· P(2)	3.133
C(1) ··· C(4)	3.167	C(1) ··· C(6)	3.177
C(1) ··· C(5)	3.249	C(1) ··· C(7)	3.285
C(1) ··· C(10)	3.455	C(1) ··· C(20)	3.561
C(1) ··· C(13)	3.613	C(1) ··· C(23)	3.529
C(2) ··· P(2)	4.082	C(3) ··· P(1)	4.082
C(2) ··· C(6)	2.964	C(3) ··· C(4)	3.034
C(2) ··· C(7)	3.001	C(3) ··· C(5)	3.022
C(2) ··· C(8)	3.010	C(3) ··· C(8)	3.047
C(2) ··· C(9)	3.027	C(3) ··· C(9)	2.982
C(4) ··· P(1)	2.977	C(6) ··· P(2)	3.085
C(4) ··· C(6)	3.719	C(6) ··· C(8)	3.522
C(4) ··· C(8)	3.504	C(6) ··· C(20)	3.379
C(4) ··· C(10)	3.354	C(6) ··· C(24)	3.702
C(4) ··· C(14)	3.432	C(6) ··· C(29)	3.659
C(4) ··· C(19)	3.604		
C(5) ··· P(1)	3.117	C(7) ··· P(2)	3.051
C(5) ··· C(7)	3.722	C(7) ··· C(9)	3.453
C(5) ··· C(9)	3.504	C(7) ··· C(22)	3.285
C(5) ··· C(12)	3.303	C(7) ··· C(23)	3.708
C(5) ··· C(17)	3.640	C(7) ··· C(24)	3.880

---

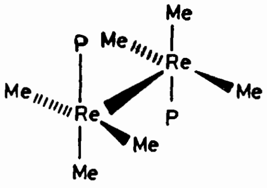
* Throughout this paper: 1 Torr = (101 325/760) Pa; 1 atm = 101 325 Pa.

methylphosphine; a rhenium–chlorine stretch appears at 340 cm^{-1}. In the mass spectrum, although the molecular ion was not observed, there is a peak at $m/e = 896$, corresponding to the loss of phosphine, and methyl groups from the molecular ion. A strong fragmentation pattern is observed, showing the successive loss of phosphine, and methyl groups. The isotope patterns of the observed peaks are consistent with the dimeric formulation. A peak at $m/e = 460$ showing the rhenium isotope pattern may be due to the monomeric species $ReClR(PMe_3)_2$ formed by dissociation of the Re–Re bond. Other tertiary phosphines reduce $Re_3Cl_3(CH_2SiMe_3)_6$ but the compounds were not crystalline and the n.m.r. spectra are complex, presumably due to the existence of isomers.



(I)

Reactions of Re_3Me_9. When Re_3Me_9 or $Re_3Me_9(PR_3)_3$ is treated with a large excess of tertiary phosphine, green-red dichroic solutions are obtained from which the dimeric complexes $Re_2Me_6(PR_3)_2$ may be crystallised. The compounds have been characterised by analysis, molecular weight, and spectroscopic data. The structure is evidently of the type (II). The ^{1}H n.m.r. spectrum of the diethylphenylphosphine complex shows two rhenium methyl resonances at $\delta = 0.19$ and 0.48 p.p.m. in an intensity ratio of 2 : 1. These may be assigned from intensities to the methyls *cis* and *trans* to phosphorus respectively. The peak due to the *trans* methyls is broadened due to a small coupling with phosphorus, but that of the *cis* methyls is quite sharp showing no effective coupling. The $^{31}P\{^1H\}$ n.m.r. spectrum shows a broad singlet at $\delta = -23.2$ p.p.m. which remains a singlet at −60 °C. The $^{13}C\{^1H\}$ n.m.r. spectrum of the dimethylphenylphosphine complex shows a broad singlet attributable to the rhenium alkyls; here again there is essentially no coupling to phosphorus. There is also no appreciable coupling with phosphorus in the ^{1}H n.m.r. of this compound where the methyl resonances appear slightly broadened, as they do for the diethylphenyl analogue. However, for the trimethylphosphine compound, a broad multiplet is seen at $\delta = -0.06$ p.p.m. (Re–CH_3) and has not been fully interpreted.



(II)

The mass spectra of the dimethylphenyl- and trimethyl-phosphine complexes show a peak due to the ion $(Re_2Me_6)^+$ at $m/e = 464$. For the trimethylphosphine complex a peak 31 mass units above this was observed. The diethylphenylphosphine complex shows in addition to a peak at $m/e = 464$, peaks up to 767 ($M^+ - C_2H_5$). The isotopic patterns of these peaks are consistent with the dimeric formulation. In each case there is a large peak due to corresponding phosphine.

The dimeric methyls have also been obtained from the interaction of dilithium octamethyldirhenate(III), $Li_2Re_2Me_8$, with stoicheiometric quantities of phenol in the presence of an excess of tertiary phosphine. The products are isolated as green crystalline solids in higher yields than those obtained by the cleavage of the trinuclear alkyls. The complexes from both routes are identical (confirmed by i.r. and n.m.r. spectra), and this is taken as further evidence of their assigned formulation.

Other Reactions of $Re_3Cl_3(CH_2SiMe_3)_6$.—*With carbon monoxide.* On treating $Re_3Cl_3(CH_2SiMe_3)_6$ either in the solid state or in light petroleum solution at −78 °C with CO at 1 atm, the blue compound turns green due to the formation of $Re_3Cl_3(CH_2SiMe_3)_6(CO)_3$. This carbonyl readily loses CO on warming *in vacuo* or upon recrystallisation in the absence of CO. The CO is also readily replaced by water to give $Re_3Cl_3(CH_2SiMe_3)_6(H_2O)_3$ [1] on recrystallisation from wet acetone. As for the H_2O and py adducts [1] the ^{1}H resonances of CH_2 and CH_3 in the alkyl group are coincident. Apart from the strong, broad CO stretch at 1 895—2 050 cm^{-1}, the rest of the i.r. spectrum resembles that of $Re_3Cl_3(CH_2SiMe_3)_6$. On prolonged interaction (15 min) with CO, a brown solution is obtained from which we have been unable to isolate any pure complexes.

With nitric oxide. On addition of NO to blue light petroleum solutions of $Re_3Cl_3(CH_2SiMe_3)_6$ at −78 °C, emerald green solutions are formed. The crystalline solid isolated has analytical data, in excellent agreement with the NO insertion product, $Re_3Cl_3(CH_2SiMe_3)_5[ON(CH_2SiMe_3)NO]$. In addition to bands attributable to CH_2SiMe_3 groups, as in $Re_3Cl_3(CH_2SiMe_3)_6$, the i.r. spectrum shows several bands due to the $ON(CH_2SiMe_3)NO$ group similar to those observed in the compound, $WMe_4[ON(Me)NO]_2$.[7] The ^{1}H n.m.r. spectrum shows four resonances attributable to two non-equivalent types of alkyl group in the ratio of 5 : 1, the alkyls bonded to rhenium appearing to be equivalent. The structure proposed for this compound is similar to that of the thenoyltrifluoroacetylacetonate, $Re_3Cl_3(CH_2SiMe_3)_5(CF_3COCHCOC_4H_5S)$, previously reported,[8] and has been confirmed by a single-crystal *X*-ray study, as shown in Figure 3, along with the atom-numbering scheme used. A diagram of the unit-cell contents is given in Figure 4. Although the accuracy of the bond lengths and angles (Table 5) have been reduced by the effect on the data of the crystal decomposition (see Experimental section), a number of interesting features emerge.

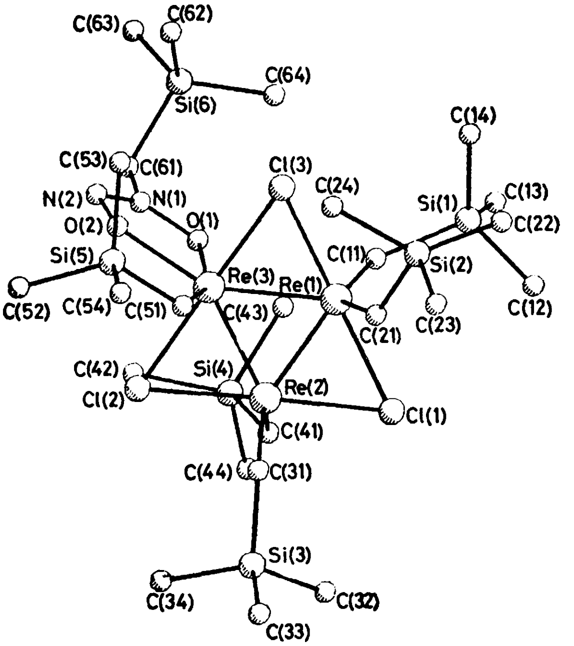


FIGURE 3 The molecular structure of $\mathrm{Re_3Cl_3(CH_2SiMe_3)_5\{ON(CH_2SiMe_3)NO\}}$ (2)

The $\mathrm{Re_3}$ triangle, comprising two six- and one seven-co-ordinate metal atoms, has an isosceles geometry, but whilst the bond between the two six-co-ordinate atoms [Re(1) and Re(2)] is, at 2.383(1) Å, equal to the Re–Re bonds in $\mathrm{Re_3Cl_3(CH_2SiMe_3)_6}$,[2] the bonds between the six- and seven-co-ordinate atoms Re(1)–Re(3) and Re(2)–Re(3) are, at 2.405(1) and 2.406(1) Å, shorter than expected [*cf.* 2.435 Å in (1)]. It is also somewhat surprising to find that the *N*-alkyl-*N*-nitrosohydroxylaminato-ligand chelates *symmetrically* to Re(3), in spite of the fact that one of the oxygen atoms occupies the terminal in-plane site, and that both Re–O bonds are quite short. From past experience, the in-plane bond would be expected to be longer than the out-of-plane bonds. However, since the oxygen and methylene carbon atoms which make up most of the immediate environment around the Re atoms are relatively small, this structure contains what is probably the least sterically crowded, but co-ordinatively saturated Re atom for this type of system. If, therefore, the Re–Re bonds are flexible enough to be affected by the steric interactions of the ligands, then the longer bonds found in the polyhalides may well have resulted from such effects.

TABLE 5

Some important bond lengths (Å) and angles (°) for (2) with estimated standard deviations in parentheses

(*a*) Lengths

Re(1)–Re(2)	2.383(1)	Re(1)–C(11)	2.054(24)
Re(1)–Re(3)	2.405(1)	Re(1)–C(21)	2.108(21)
Re(2)–Re(3)	2.406(1)	Re(2)–C(31)	2.103(18)
		Re(2)–C(41)	2.081(19)
Re(1)–Cl(1)	2.443(5)	Re(3)–C(51)	2.172(19)
Re(1)–Cl(3)	2.413(5)	Re(3)–O(1)	2.104(11)
Re(2)–Cl(1)	2.422(6)	Re(3)–O(2)	2.101(14)
Re(2)–Cl(2)	2.414(6)		
Re(3)–Cl(2)	2.415(5)	N(1)–O(1)	1.316(24)
Re(3)–Cl(3)	2.414(5)	N(2)–O(2)	1.288(22)
		N(1)–N(2)	1.293(27)
		N(1)–C(61)	1.453(25)

(*b*) Angles

Re(2)–Re(1)–Re(3)	60.3(1)	Cl(1)–Re(1)–C(11)	88.2(7)
Re(1)–Re(2)–Re(3)	60.3(1)	Cl(1)–Re(1)–C(21)	86.6(6)
Re(1)–Re(3)–Re(2)	59.4(1)	Cl(3)–Re(1)–C(11)	90.1(7)
		Cl(3)–Re(1)–C(21)	94.4(5)
Cl(1)–Re(1)–Cl(3)	178.3(2)	Cl(1)–Re(2)–C(31)	89.0(7)
Cl(1)–Re(2)–Cl(2)	178.4(2)	Cl(1)–Re(2)–C(41)	88.0(7)
Cl(2)–Re(3)–Cl(3)	179.4(2)	Cl(2)–Re(2)–C(31)	89.7(7)
		Cl(2)–Re(2)–C(41)	91.7(7)
Re(1)–Cl(1)–Re(2)	58.7(1)	Cl(2)–Re(3)–C(51)	89.1(5)
Re(2)–Cl(2)–Re(3)	59.8(1)	Cl(2)–Re(3)–O(1)	93.7(4)
Re(1)–Cl(3)–Re(3)	59.8(1)	Cl(2)–Re(3)–O(2)	88.4(4)
		Cl(3)–Re(3)–C(51)	90.6(5)
C(11)–Re(1)–C(21)	134.6(9)	Cl(3)–Re(3)–O(1)	86.8(4)
C(31)–Re(2)–C(41)	120.8(7)	Cl(3)–Re(3)–O(2)	92.1(4)
C(51)–Re(3)–O(1)	−55.4(4)		
C(51)–Re(3)–O(2)	84.3(7)	Re(3)–O(1)–N(1)	115(1)
O(1)–Re(3)–O(2)	71.4(5)	Re(3)–O(2)–N(2)	121(1)
		O(1)–N(1)–N(2)	121(2)
		O(1)–N(1)–C(61)	119(2)
		N(2)–N(1)–C(61)	120(2)
		O(2)–N(2)–N(1)	112(2)

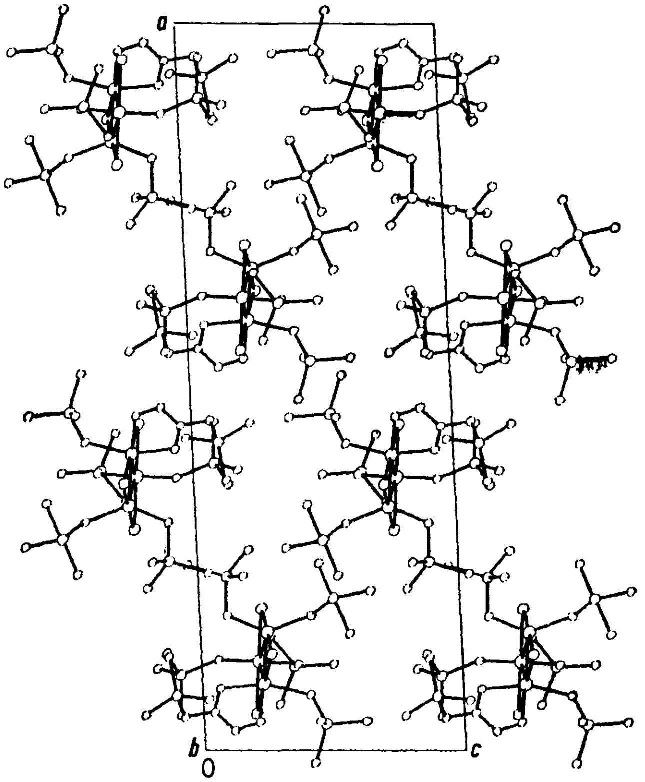


FIGURE 4 View down *b* of the unit-cell contents for $\mathrm{Re_3Cl_3(CH_2SiMe_3)_5\{ON(CH_2SiMe_3)NO\}}$

The geometry of the *N*-alkyl-*N*-nitrosohydroxylaminato-ligand is also very interesting. Within the limits of experimental error, the O–N and N–N bonds are equal in length and all show some degree of multiple bonding, suggesting the presence of delocalisation. The high degree of planarity of the ONNO grouping (Table 6) is also indicative of such a system. The rhenium atom to which this ligand is attached is less than 0.1 Å out of the ONNO plane and it is tempting to suggest that this atom is also incorporated into the delocalised system.

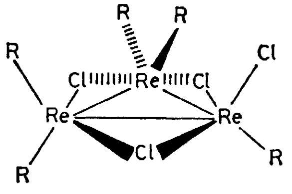
This would explain the short and equal Re–O bonds but the inferred partial multiple O=Re bonding would not fit in with generally accepted ideas on the bonding in these clusters, since for a seven-co-ordinate Re atom, all available orbitals are in use. The green *N*-alkyl-*N*-nitrosohydroxylaminato-complex readily reacts further with NO at low temperatures to give a brown, diamagnetic powder, insoluble in light petroleum. The i.r. of this product shows a broad ν(N–O) stretch at 1 725 cm^{-1} and the ^{1}H n.m.r. shows a single resonance at $\delta = 0.20$ p.p.m. Although analytical data for this compound, which cannot be recrystallised, are poor, it seems reasonable to assume that the structure is similar to the above complex, but with a terminal NO on the other two rhenium atoms. This could account for the diamagnetism through pairing of the unpaired electrons on the NO groups *via* the Re–Re bond. The reason that only one insertion reaction occurs is not understood, but is presumably due to electronic factors (see below).

TABLE 6

Least-squares planes in the form $Ax + By + Cz = D$, where x, y, z are fractional co-ordinates. Deviations (Å × 10^3) of relevant atoms are given in square brackets

Compound (1): plane: Re(1), Re(2), Re(3)
$26.6476x + 1.5940y - 2.4455z = 3.5751$
[C(1) −76, C(2) −28, C(3) 76, P(1) −103, P(2) 13]
Compound (2): plane (*i*): Re(1), Re(2), Re(3)
$-3.8458x - 1.6678y + 11.8002z = 2.2072$
[Cl(1) −26, Cl(2) 55, Cl(3) −39, O(2) −211]
plane (*ii*): O(1), O(2), N(1), N(2)
$16.2511x + 9.9661y + 2.1133z = 3.4344$
[Re(3) −80, O(1) −3, O(2) 3, N(1) 6, N(2) −6]

With hydrogen chloride. Light petroleum solutions of $Re_3Cl_3(CH_2SiMe_3)_6$ react with HCl at low temperatures turning green, and a crystalline alkyl, with a terminal chlorine atom, $Re_3Cl_3(CH_2SiMe_3)_5Cl$ can be isolated. The ^{1}H n.m.r. spectrum of the compound shows peaks consistent with two types of non-equivalent alkyl groups, with an intensity ratio of 2 : 3. This suggests that the alkyl groups below the plane of the rhenium triangle [see structure (III)], with respect to the terminal chlorine ligand, are all magnetically equivalent but are inequivalent to those above the plane. The methylene protons of all the alkyls are shifted considerably up field from the position at which they occur in $Re_3Cl_3(CH_2SiMe_3)_6$, showing that variations in the electronic environment of only one rhenium in the triangle significantly effect the electronic behaviour at the other two rhenium atoms. This is probably the most important factor limiting the above nitric oxide insertion reaction to one rhenium atom in the triangle. The i.r. spectrum of this compound is essentially the same as that for $Re_3Cl_3(CH_2SiMe_3)_6$, showing a strong band at 350 cm^{-1} assigned as ν(Re–Cl).



(III)

At ambient temperatures, in the solid state or in solution, $Re_3Cl_3(CH_2SiMe_3)_6$ reacts with HCl gas to give a rust coloured powder which is soluble only in polar organic solvents, and which is clearly $Re_3Cl_3(CH_2SiMe_3)_3Cl_3$. The ^{1}H n.m.r. consists of a singlet at $\delta = 0.18$ p.p.m. On following the reaction by n.m.r. in benzene, the peak due to the methylene protons in $Re_3Cl_3(CH_2SiMe_3)_6$ gradually disappears and a peak due to $SiMe_4$ appears. The i.r. shows a broad ν(Re–Cl) band at 350 cm^{-1}, as well as bands due to the CH_2SiMe_3 group.

EXPERIMENTAL

Microanalyses were by the Imperial College, Butterworth Microanalytical Consultancy Limited, and Pascher, Bonn Laboratories.

Instruments.—Perkin-Elmer 325, 457, and 597 spectrometers calibrated with polystyrene were used to record i.r. spectra. Perkin-Elmer R12A (60 MHz) and R32 (90 MHz) and Varian Associates XL–100–12 (F.T. mode with noise-proton decoupling) were used for the n.m.r. spectroscopy. Molecular weights were determined cryoscopically, or osmometrically using a Hitachi–Perkin-Elmer osmometer.

All syntheses and manipulations were carried out under oxygen-free nitrogen or argon. Tetrahydrofuran, diethyl ether, light petroleum (b.p. 40—60 °C, unless otherwise stated), 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. Trirhenium nonachloride was prepared from rhenium metal (99.9%) *via* rhenium pentachloride, and was aged in air to the more reactive hydrated chloride ($Re_3Cl_9 \cdot ca. 6H_2O$). The compounds $Re_3Cl_3(CH_2SiMe_3)_6$ and $(Re_3Me_9)_n$ were prepared as before.[1]

*Hexabenzyltri-μ-chloro-*triangulo*-trirhenium*(III).—To trirhenium nonachloride (1 g, 1 mmol) suspended in diethyl ether (30 cm^3) at −78 °C, was added a solution of benzylmagnesium chloride (0.99 mol dm^{-3} in ether, 15.4 cm^3, 15 mmol), with vigorous stirring, followed by dimethylphenylphosphine (1 cm^3, 7 mmol). The suspension was allowed to warm to ambient temperature maintaining stirring. The solvent was removed *in vacuo* and the residue extracted into toluene (40 cm^3). After filtration the red-brown solution was reduced in volume to *ca.* 15 cm^3 and held at −78 °C overnight, giving brown-black needles which were collected, washed with light petroleum (2 × 5 cm^3), and dried *in vacuo*; yield 0.62 g, 50% based on $Re_3Cl_9 \cdot 6H_2O$. The product is readily soluble in light petroleum, toluene, and similar hydrocarbons, and in diethyl ether, dichloromethane, acetone, *etc.*

Infrared (KBr disc) bands at: 3 050, 3 010, 2 910, 1 587, 1 481s, 1 445s, 1 208, 1 198, 1 175, 1 023, 839, 805, 752, 742, 735, 725, 694s, 688, 565, 555, 535, 525, 514, 452, 413, and 351 cm^{-1}.

Tri-μ-chloro-hexacyclohexyltris(dimethylphenylphosphine)-triangulo-*trirhenium*(III).—To trirhenium nonachloride (1 g, 1 mmol) suspended in diethyl ether (20 cm^3) at −78 °C, was added with vigorous stirring, a solution of cyclohexylmagnesium chloride (1.94 mol dm^{-3} in ether, 9.0 cm^3, 6 mmol) followed by dimethylphenylphosphine (0.9 cm^3, 6 mmol). The resulting green-brown suspension was allowed to warm to ambient temperatures whilst maintaining stirring, when it was red-brown. The solvent was removed *in vacuo* and the brown residues extracted into toluene (30 cm^3), filtered, and the solution was concentrated to *ca.* 5 cm^3. Light petroleum was added (3 cm^3) and the solution cooled to −78 °C to give a brown powder; yield 0.35 g, 30% based on $Re_3Cl_9{\cdot}6H_2O$.

Infrared (KBr disc) bands at: 3 040, 2 900, 1 550, 1 477, 1 430s,br, 1 290br, 1 090, 934, 897s, 800w, 740, 693, 484, and 410s,br cm^{-1}.

Tris(dimethylphenylphosphine)tri-μ-methyl-hexamethyl-triangulo-*trirhenium*(III).—To trirhenium nonachloride (1 g, 1 mmol) suspended in diethyl ether (60 cm^3) at −78 °C, was added a solution of methylmagnesium chloride (1.06 mol dm^{-3} in ether, 25 cm^3, 20 mmol), with vigorous stirring, followed by dimethylphenylphosphine (1 cm^3, 7 mmol). The suspension was allowed to warm to 0 °C when it was mauve-red; water was then added (2 cm^3) to destroy excess of Grignard, followed by immediate cooling to −78 °C. The suspension was filtered, reduced in volume to 40 cm^3, and held at −20 °C overnight to give dark mauve hexagonal crystals; yield 0.34 g, 30% based on $Re_3Cl_9{\cdot}6H_2O$. The compound is soluble in polar organic solvents with which it often reacts slowly. It is insoluble in aliphatic hydrocarbons, but sparingly soluble in benzene.

Infrared (KBr disc) bands at: 3 047, 2 960, 2 900, 2 845, 1 483, 1 470, 1 430, 1 418, 1 323, 1 294, 1 275, 1 167, 1 023, 937, 900, 742, 693, 670, 483, and 400 cm^{-1}.

Tris(diethylphenylphosphine)tri-μ-methyl-hexamethyl-triangulo-*trirhenium*(III).—As for the dimethylphenylphosphine complex, but using diethylphenylphosphine (1 cm^3, 6 mmol). After destruction of excess of Grignard with water and filtration, the residues were extracted with toluene to give a second crop of the dark mauve crystals; yield 0.6 g, 50% based on $Re_3Cl_9{\cdot}6H_2O$. The product is soluble in hydrocarbons.

Infrared (KBr disc) bands at: 3 038, 2 957, 2 920, 2 860, 1 582, 1 448, 1 430, 1 374, 1 323, 1 240, 1 183, 1 158, 1 040, 975, 760, 741, 724, 695, 628, 470, and 419 cm^{-1}.

The bis complex (1) studied crystallographically was obtained by crystallisation of the tris complex from toluene at −20 °C.

Triscarbonyltri-μ-chloro-hexakis(trimethylsilylmethyl)-triangulo-*trirhenium*(III).—Carbon monoxide was passed through a cooled (−78 °C) solution of $Re_3Cl_3(CH_2SiMe_3)_6$ (0.2 g) in light petroleum (20 cm^3), until the solution became dark green (*ca.* 5 min). The solution was then evaporated *in vacuo* at −78 °C before being allowed to warm. Further purification was difficult due to loss of CO upon sublimation or extensive drying *in vacuo*, and due to substitution of CO by water unless apparatus and solvents were rigorously dried. However, crystals which collapse on drying may be obtained from light petroleum; yield 0.21 g, *ca.* 100%, based on $Re_3Cl_3(CH_2SiMe_3)_6$.

Infrared (CS_2 or Nujol) bands at: 2 945, 2 887, 1 970, [ν(C–O)], 1 390, 1 300, 1 256, 1 242, 1 177, 1 029, 920, 825, 743, 714, 676, 613, 470, and 337 cm^{-1}.

*Tri-μ-chloro-(*N*-nitroso-*N*-trimethylsilylmethylhydroxylaminato)pentakis(trimethylsilylmethyl)*-triangulo-*trirhenium*(III) (2).—Nitric oxide was passed through a cooled (−78 °C) solution of $Re_3Cl_3(CH_2SiMe_3)_6$ (0.5 g) in diethyl ether (20 cm^3) until the solution had become dark green (*ca.* 5 min). The solution was then evaporated at −78 °C and at room temperature the green solid was extracted into light petroleum (15 cm^3). This was filtered, concentrated to 3 cm^3, and held at −20 °C overnight. The green crystals were collected and dried *in vacuo*. The product could be further purified by sublimation at 105 °C, 10^{-3} Torr; yield 0.45 g, 84% based on $Re_3Cl_3(CH_2SiMe_3)_6$. The compound is soluble in hydrocarbons.

Infrared (CS_2 or Nujol) bands at: 2 950, 2 893, 1 733, 1 427, 1 400, 1 300, 1 249, 1 187, 1 050, 940, 840, 752, 714, 677, 618, 555, and 332 cm^{-1}.

Tri-μ-chloro-chloropentakis(trimethylsilylmethyl)-triangulo-*trirhenium*(III).—Dry hydrogen chloride was passed through a cooled solution of $Re_3Cl_3(CH_2SiMe_3)_6$ (1 g) in light petroleum (30 cm^3) until the solution had turned deep green. Dissolved hydrogen chloride was then removed by evacuating the flask to avoid further reaction. The solution was then filtered, concentrated to *ca.* 3 cm^3, and held at −20 °C overnight. The green *needles* were collected, washed with cold (−78 °C) light petroleum (3 cm^3), and recrystallised from light petroleum; yield before recrystallisation, 0.7 g, 74% based on $Re_3Cl_3(CH_2SiMe_3)_6$. The compound is soluble in hydrocarbons, ethers, dichloromethane, *etc.*

Infrared (KBr disc) bands at: 2 950, 2 890, 1 434, 1 403, 1 315, 1 262, 1 247, 1 093, 1 030, 998, 962, 930, 838, 750, 723, 705, 677, 618, 350, and 270 cm^{-1}.

Hexamethylbis(trimethylphosphine)dirhenium(III) (Re–Re).—To a solution of Re_3Me_9 (1 g, 1.5 mmol) in tetrahydrofuran (20 cm^3) was added trimethylphosphine (3 cm^3, 30 mmol). The solution became green immediately and was stirred for *ca.* 20 h when it was olive green and a grey precipitate had formed. The solution was filtered, concentrated to *ca.* 10 cm^3, and held at −20 °C overnight to give grey-green *needles*. These were collected, washed with diethyl ether (2 × 5 cm^3), and dried *in vacuo*; yield 0.48 g, 36% based on Re_3Me_9. The compound is soluble only in very polar organic solvents in which it decomposes slowly.

Infrared (KBr disc) bands at: 2 955, 2 900, 2 840, 1 417, 1 310, 1 300, 1 282, 1 273, 947, 716, 663, 483, 328, and 270 cm^{-1}.

Bis(dimethylphenylphosphine)hexamethyldirhenium(III) (Re–Re).—To a suspension of Re_3Me_9 (1 g, 1.5 mmol) in toluene (30 cm^3) was added dimethylphenylphosphine (4.2 cm^3, 30 mmol) at ambient temperature.

The resulting green solution was stirred for 2 h when a green precipitate had formed. The precipitate was collected, washed with light petroleum (2 × 5 cm^3), extracted into hot toluene (*ca.* 15 cm^3), and the solution filtered and cooled to −20 °C when grey-green needles separated. A further crop of compound was obtained by precipitating more product from the supernatant liquid from the first filtration, by the addition of an equal volume of light petroleum. The second precipitate was then recrystallised in the same manner as the first; yield, 0.76 g, 54% based on Re_3Me_9. The compound is soluble in aromatic hydrocarbons and more polar organic solvents such as diethyl ether, dichloromethane, chloroform, *etc.*

Infrared (Nujol) bands at: 3 020, 1 600, 1 580, 1 430, 1 294, 1 278, 938, 900, 775, 740, 690, 519, 484, and 400 cm^{-1}.

Bis(diethylphenylphosphine)hexamethyldirhenium(III) (Re–Re).—Re_3Me_9 (1 g, 1.5 mmol) was dissolved in diethylphenylphosphine (10 cm^3, 60 mmol). The red-brown solution was allowed to stand for *ca.* 2 weeks when a green precipitate was formed. The precipitate was decanted, washed with cold light petroleum (3 × 5 cm^3), and recrystallised from toluene (5 cm^3) to give emerald green *crystals*; yield 0.17 g, 10% based on Re_3Me_9.

TABLE 7

Crystal data and details of data collection and structure analyses

	Compound (1)	Compound (2)
(*a*) Crystal data		
Formula	$C_{29}H_{57}P_2Re_3$	$C_{24}H_{66}Cl_3N_2O_2Re_3Si_6$
Formula weight	1 026.3	1 248.3
Crystal system	Monoclinic	Monoclinic
a/Å	27.220(4)	33.334(8)
b/Å	9.817(1)	11.733(5)
c/Å	26.051(5)	11.947(6)
α/°	90	90
β/°	102.65(2)	92.93(4)
γ/°	90	90
U/Å^3	6 792.5	4 666.5
Space group	$C2/c$ (no. 15)	$P2_1/a$ (no. 14)
Z	8	4
D_c/g cm^{-3}	2.01	1.78
F(000)	3 888	2 400
μ(Mo-K_α)/cm^{-1}	109.0	81.8
λ(Mo-K_α)/Å	0.710 69	0.710 69
(*b*) Data collection		
Crystal size/mm	0.575 × 0.187 × 0.0875	(*i*) 0.374 × 0.25 × 0.070 (*ii*) 0.560 × 0.300 × 0.080
Crystal faces	{010}, {001}, {100}	(*i*) {010}, {101}, {100} (*ii*) {001}, {110}, {100}
$\theta_{min.}$, $\theta_{max.}$/°	1.5, 27.5	1.5, 25
w scan width parameters, A, B (°) in width = A + B tan θ	0.8, 0.2	0.8, 0.35
Horizontal aperture (APT) parameters A, B (mm) in APT = A + B tan θ	4.0, 0.3	4.0, 0.0
Total data collected	8 578	(*i*) 5 631 (*ii*) 2 191
Observed unique data, $F_o > 4\sigma(F_o)$	4 982	4 361
Crystal decay	None	(*i*) 37%, linear (*ii*) 10%, linear
(*c*) Refinement		
Number of parameters	307	361
Weighting scheme coefficient, g, in $w = 1/[\sigma^2(F_o) + gF_o^2]$	0.000 68	0.0008
Final $R = \Sigma\Delta F/\Sigma\|F_o\|$	0.043	0.067
$R' = [\Sigma w\Delta F^2/\Sigma wF_o^2]^{\frac{1}{2}}$	0.053	0.074

Infrared (Nujol) bands at: 3 070, 1 585, 1 570, 1 300, 1 157, 1 038, 908, 761, 746, 725, 697, and 487 cm^{-1}.

Dichlorotetrakis(trimethylphosphine)bis(trimethylsilylmethyl)dirhenium(II) (Re–Re).—To a solution of $Re_3Cl_3(CH_2SiMe_3)_6$ (0.5 g, 0.4 mmol) in light petroleum, was added trimethylphosphine (0.75 cm^3, 7.4 mmol) at ambient temperature with vigorous stirring. The solution turned green, then brown after *ca.* 10 min. The solution was stirred for 12 h and the solvent removed *in vacuo*. The brown-green solid was extracted into diethyl ether (2 cm^3) and chromatographed on silica gel with diethyl ether eluant. The first green fraction was collected and the solvent removed. Cooling of concentrated solutions of the product gave a dark green *powder*; yield 0.44 g, 72% based on $Re_3Cl_3(CH_2SiMe_3)_6$. The compound is very soluble in hydrocarbons.

Infrared (CS_2) bands at: 2 945, 2 905, 1 390, 1 298, 1 279, 1 258, 1 242, 1 207, 1 166, 1 060, 1 037, 1 010, 945, 835, 751, 722, 670, 628, and 340 cm^{-1}.

TABLE 8

Fractional co-ordinates (Re × 10^5, others × 10^4) for (1) with estimated standard deviations in parentheses

Atom	x	y	z
Re(1)	13 652(2)	18 222(5)	14 446(2)
Re(2)	12 794(2)	17 759(5)	4 795(2)
Re(3)	14 512(2)	−3 076(5)	4 795(2)
P(1)	1 284(1)	3 594(3)	2 865(1)
P(2)	1 111(1)	3 490(3)	5 284(1)
C(1)	1 203(5)	3 278(12)	4 067(4)
C(2)	1 374(5)	−497(12)	4 868(4)
C(3)	1 565(5)	−395(12)	3 132(4)
C(4)	630(4)	1 369(13)	3 411(5)
C(5)	2 173(4)	2 138(14)	3 218(5)
C(6)	495(4)	1 283(12)	4 862(4)
C(7)	2 035(5)	1 979(13)	4 671(5)
C(8)	830(5)	−1 622(12)	4 070(5)
C(9)	2 208(5)	−922(14)	3 902(5)
C(10)	714(5)	4 666(14)	3 067(5)
C(11)	672(8)	5 857(16)	2 716(6)
C(12)	1 792(5)	4 884(13)	2 684(5)
C(13)	1 867(6)	5 728(14)	3 132(5)
C(14)	1 240(5)	2 873(12)	2 233(4)
C(15)	1 672(5)	2 440(17)	1 888(4)
C(16)	1 661(7)	1 859(17)	1 436(6)
C(17)	1 216(7)	1 661(16)	1 278(5)
C(18)	776(7)	2 081(16)	1 614(6)
C(19)	806(6)	2 635(15)	2 085(5)
C(20)	553(5)	4 503(13)	5 310(4)
C(21)	433(6)	5 659(15)	5 710(5)
C(22)	1 613(5)	4 794(15)	5 296(5)
C(23)	1 726(6)	5 659(15)	4 810(6)
C(24)	1 023(4)	2 723(13)	5 940(4)
C(25)	1 427(5)	2 488(16)	6 171(5)
C(26)	1 357(7)	1 863(16)	6 650(6)
C(27)	911(8)	1 369(17)	6 903(6)
C(28)	487(6)	1 586(14)	6 674(5)
C(29)	560(5)	2 259(15)	6 202(5)

Dichlorotetrakis(dimethylphenylphosphine)bis(trimethylsilylmethyl)dirhenium(II) (Re–Re).—To a solution of $Re_3Cl_9(CH_2SiMe_3)_6$ (0.5 g, 0.4 mmol) in light petroleum (20 cm^3) was added dimethylphenylphosphine (1 cm^3, 7 mmol) with stirring. The solution was refluxed for 2 h when the colour had changed through green to brown and a brown precipitate had formed. The mixture was then cooled to −78 °C, filtered, and the brown powder recrystallised from hot light petroleum; yield, 0.18 g, 30% based on $Re_3Cl_3(CH_2SiMe_3)_6$. The product is soluble in hydrocarbons.

Infrared (Nujol) bands at: 3 040, 1 592, 1 580, 1 547, 1 292, 1 276, 1 258, 1 242, 1 153, 1 077, 1 015, 937, 903, 834, 737, 719, 690, and 483 cm^{-1}.

Alternative Preparation of the Hexamethylbisphosphinedirhenium(III) (Re–Re) *Dimers from Dilithium Octamethyldirhenate*.—The procedure for the diethylphenylphosphine complex is given, and may be taken as a general method for the other complexes.

To a solution of $Li_2Re_2Me_8{\cdot}2Et_2O$ [9] (0.5 g, 0.75 mmol) in light petroleum (20 cm^3) cooled to −78 °C was added diethylphenylphosphine (0.8 cm^3, 4.5 mmol). This solution was stirred for 5 min then a solution of phenol (0.14 g, 1.5 mmol) in light petroleum (19 cm^3) was added dropwise. The resultant solution was allowed to warm slowly to room temperature when it was green. The solution was then evaporated to *ca.* 10 cm^3, filtered, and cooled to −20 °C overnight to yield emerald green needles which were separated. The supernatant was concentrated further to *ca.* 5 cm^3 to yield another crop of crystals; yield 0.4 g, 68% based upon $Li_2Re_2Me_8{\cdot}2Et_2O$. The product was recrystallised from light petroleum–toluene (1 : 1) mixtures to remove traces of PEt_2Ph.

TABLE 9

Fractional co-ordinates (Re × 10^5, others × 10^4) for (2) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Re(1)	16 349(3)	11 879(5)	25 712(6)
Re(2)	12 324(2)	−4 622(5)	22 068(6)
Re(3)	9 164(3)	13 709(5)	23 629(6)
Cl(1)	1 956(2)	−670(4)	2 391(5)
Cl(2)	510(2)	−311(4)	2 039(4)
Cl(3)	1 327(2)	3 042(3)	2 700(4)
Si(1)	2 396(3)	2 256(7)	1 104(7)
Si(2)	2 101(3)	2 290(7)	5 157(7)
Si(3)	1 157(2)	−2 992(4)	3 562(5)
Si(4)	1 034(2)	−810(5)	−822(6)
Si(5)	363(2)	2 134(4)	4 679(5)
Si(6)	753(3)	4 267(5)	−1 013(6)
O(1)	854(5)	1 906(10)	682(9)
O(2)	391(4)	2 354(10)	2 152(10)
N(1)	528(7)	2 501(12)	424(14)
N(2)	276(6)	2 740(13)	1 179(16)
C(11)	1 863(7)	1 636(22)	1 068(19)
C(12)	2 757(11)	1 316(33)	1 983(37)
C(13)	2 543(13)	2 331(39)	−420(32)
C(14)	2 396(14)	3 764(29)	1 733(37)
C(21)	1 862(7)	1 178(16)	4 251(18)
C(22)	2 573(26)	2 663(84)	4 625(44)
C(23)	2 207(12)	1 670(34)	6 586(27)
C(24)	1 710(34)	3 328(57)	5 484(68)
C(31)	1 187(8)	−1 432(15)	3 676(15)
C(32)	1 571(7)	−3 562(16)	2 664(21)
C(33)	1 196(9)	−3 566(19)	5 058(20)
C(34)	645(9)	−3 324(16)	2 928(23)
C(41)	1 248(7)	−1 250(18)	649(16)
C(42)	484(8)	−484(22)	−885(22)
C(43)	1 335(9)	508(23)	−1 358(23)
C(44)	1 130(10)	−2 178(25)	−1 726(23)
C(51)	770(7)	1 331(15)	4 113(15)
C(52)	−172(9)	1 656(23)	4 165(21)
C(53)	408(9)	3 730(15)	4 467(20)
C(54)	410(8)	1 846(19)	6 244(17)
C(61)	458(8)	2 912(17)	−717(16)
C(62)	701(14)	5 250(22)	240(21)
C(63)	491(12)	4 921(22)	−2 261(24)
C(64)	1 284(12)	3 981(36)	−1 278(41)

Crystallographic Studies.—For both compounds, crystals suitable for *X*-ray work were mounted under nitrogen in Lindemann capillaries. Unit-cell parameters and orientation matrices were determined by least-squares refinement of the setting angles for 15 [compound (1)] and 25 [compound (2)] reflections automatically centred on a Nonius CAD4 diffractometer.

For (1), systematic absences *hkl* with *h* + *k* odd and *h0l* with *l* odd indicated space groups *C2/c* or *Cc*; the former was confirmed by the structure analysis and refinement. For (2), absences *h0l* with *h* odd and *0k0* with *k* odd gave space group $P2_1/a$ uniquely.

Intensity data were recorded on the CAD4 with graphite monochromatised Mo-K_α radiation and an w—2θ scan, using methods described in detail in previous papers from our laboratory.[2,10] Crystals of compound (1) were quite stable but those of (2) deteriorated on *X*-irradiation and so two crystals were needed to obtain the complete data set. All data were corrected for Lorentz and polarization factors, absorption and, in the case of (2), for decay. The two blocks of data for (2) were merged on the basis of 123 common reflections with a merging *R* value of 0.027. Both structures were solved by direct methods and successive difference syntheses and refined by least squares using anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms belonging to the phenyl and ethyl groups in (1) were inserted in calculated positions with C–H distances of 1.00 and 1.08 Å respectively, and their contributions included in the calculation of F_c. A common U_{iso} value for these atoms refined to 0.09(1) $Å^2$. Methyl hydrogens in (1) and all hydrogen atoms in (2) were ignored. Crystal data, intensity data, collection parameters, and details of the refinements are given in Table 7. Lists of final atomic positional parameters are given in Tables 8 and 9. The hydrogen-atom co-ordinates for (1), dimensions of the ligands, lists of anisotropic thermal parameters, and structure factors are given in Supplementary Publication No. SUP 22679 (57 pp.).*

Neutral-atom scattering factors were taken from ref. 11 (for Re), 12 (for Cl, P, Si, O, N, and C), and 13 (for H), with those for the heavier elements being corrected for anomalous dispersion using $\Delta f'$ and $\Delta f''$ values from ref. 14. All calculations were performed on the Queen Mary College ICL 1904S and 2900 and University of London CDC 7600 computers, using the programs CAD4,[15] SHELX,[16] XANADU,[17] and PLUTO.[18]

We thank the S.R.C. for a studentship (to P. E.) and a fellowship (to K. M. A. M. and in part to K. M.) and the S.R.C., together with the Royal Society, for assistance in the purchase of the diffractometer.

[9/402 *Received, 12th March,* 1979]

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

REFERENCES

[1] A. F. Masters, K. Mertis, J. F. Gibson, and G. Wilkinson, *Nouveau J. Chim.*, 1971, **1**, 389.

[2] M. B. Hursthouse and K. M. A. Malik, *J.C.S. Dalton*, 1978, 1334.

[3] F. A. Cotton and J. T. Mague, *Inorg. Chem.*, 1974, **3**, 1094.

[4] B. R. Penfold and W. T. Robinson, *Inorg. Chem.*, 1966, **5**, 1758.

[5] J. A. Bert, J. J. Smith, and R. A. Walton, *Inorg. Chem.*, 1978, **17**, 99, and refs. therein.

[6] R. A. Andersen, R. A. Jones, and G. Wilkinson, *J.C.S. Dalton*, 1978, 446.

[7] A. J. Shortland and G. Wilkinson, *J.C.S. Dalton*, 1973, 872; S. R. Fletcher, A. Shortland, A. C. Skapski, and G. Wilkinson, *J.C.S. Chem. Comm.*, 1972, 922.

[8] P. Edwards, F. Felix, K. Mertis, and G. Wilkinson, *J.C.S. Dalton*, 1979, 361.

[9] F. A. Cotton, K. D. Gage, K. Mertis, L. W. Shive, and G. Wilkinson, *J. Amer. Chem. Soc.*, 1976, **98**, 6922.

[10] M. B. Hursthouse, R. A. Jones, K. M. A. Malik, and G. Wilkinson, *J. Amer. Chem. Soc.*, 1979, **101**, 4128.

[11] D. T. Cromer and J. R. Waber in 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4, p. 101.

[12] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[13] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[14] D. T. Cromer and D. Libermann, *J. Chem. Phys.*, 1970, **53**, 1891.

[15] 'CAD4' Processing Program, J. E. Davies, Queen Mary College, 1975.

[16] 'SHELX' Crystallographic Calculation Program, G. M. Sheldrick, University of Cambridge, 1976.

[17] 'XANADU' Least-squares Plane and Torsion Angle Calculation Program, P. Roberts and G. M. Sheldrick, University of Cambridge.

[18] 'PLUTO' Program for Crystallographic Drawing, N. D. S. Motherwell, University of Cambridge.