triangulo-Trirhenium(III) Alkyl Compounds. The *X*-Ray Crystal Structures of $Re_3(\mu\text{-}Cl)_{1.5}(\mu\text{-}Me)_{1.5}(CH_2Ph)_6$ and $Re_3(\mu\text{-}Me)_3(CH_2Ph)_6$†

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A new large scale synthesis of $Re_3(\mu\text{-}Cl)_3(CH_2Ph)_6$, and the previously unknown $Re_3(\mu\text{-}Cl)_3(CH_2C_6H_4Bu^t\text{-}4)_6$ are described. Substitution of the bridging halide with excess LiMe leads to the complexes $Re_3(\mu\text{-}Me)_3R_6$ ($R = CH_2Ph$ or $CH_2C_6H_4Bu^t\text{-}4$). Stoicheiometric reactions with LiMe give mixed halide–methyl products. The *X*-ray crystal structures of $Re_3(\mu\text{-}Cl)_{1.5}(\mu\text{-}Me)_{1.5}(CH_2Ph)_6$ and $Re_3(\mu\text{-}Me)_3(CH_2Ph)_6$ have been determined. PMe_3 displaces tetrahydrofuran (thf) from $Re_3Cl_9(thf)_3$ to give $Re_3(\mu\text{-}Cl)Cl_6(PMe_3)_3$, which in turn with $AlMe_3$ yields the green compound $Re_3(\mu\text{-}Cl)_3Me_6(PMe_3)_3$.

In previous papers we have described the synthesis and characterization of numerous *triangulo*-trirhenium-(III) and -(IV) cluster alkyls of formulations such as $Re_3(\mu\text{-}Cl)_3R_6$ ($R = Me$, CH_2SiMe_3, CH_2Ph, Ph, or $C_6H_4Me\text{-}p$),[1–3] $Re_3(\mu\text{-}Me)_3R_6$ ($R = Me$ or CH_2SiMe_3),[1,3] or Re_3R_{12} ($R = Me$, CH_2SiMe_3, CH_2CMe_3, or CH_2CMe_2Ph),[1] as well as phosphine[2] and pyridine[1,3] adducts of these. Carboxylato and other derivatives[4] of rhenium(III) such as $Re_6(\mu\text{-}Cl)_6(\mu\text{-}CO_2Me)_6Me_6$, as well as reaction products of $Re_3(\mu\text{-}Cl)_3(CH_2SiMe_3)_6$ with H_2, CO, NO, and HCl were also reported.[2,3] The structures of $Re_3(\mu\text{-}Cl)_3(CH_2SiMe_3)_6$,[5] $Re_3(\mu\text{-}Me)_3Me_6(PEt_2Ph)_2$,[2] $Re_3(\mu\text{-}Cl)_3(CH_2SiMe_3)_5[ON(CH_2SiMe_3)NO]$,[2] $Re_6(\mu\text{-}Cl)_6H(CH_2SiMe_3)_9$,[3] $Re_3(\mu\text{-}Cl)_3ClH(CH_2SiMe_3)_4(PPh_3)$,[3] and $Re_3Cl_3(\mu\text{-}CH_2SiMe_3)_3(CH_2SiMe_3)_3$[3] have been confirmed by *X*-ray diffraction studies.

Benzyl and substituted-benzyl derivatives and the PMe_3 adduct of a methyl cluster of rhenium(III) are now described.

Analytical data are given in Table 1 and n.m.r. data in Table 2.

Table 1. Analytical data for the rhenium cluster compounds

		Analysis (%)*			
Compound	Colour	C	H	Cl	P
$Re_3(\mu\text{-}Cl)_3(CH_2Ph)_6$	Brown-black	41.6 (41.7)	3.7 (3.5)	8.7 (8.8)	
$Re_3(\mu\text{-}Me)_3(CH_2Ph)_6$	Black-red	46.7 (47.0)	4.3 (4.4)		
$Re_3(\mu\text{-}Cl)_{1.5}(\mu\text{-}Me)_{1.5}(CH_2Ph)_6$	Black-red	44.0 (44.2)	3.9 (3.9)	4.7 (4.5)	
$Re_3(\mu\text{-}Cl)_3(CH_2C_6H_4Bu^t\text{-}4)_6$	Brown-black	51.4 (51.2)	6.0 (5.8)	6.5 (6.9)	
$Re_3(\mu\text{-}Me)_3(CH_2C_6H_4Bu^t\text{-}4)_6$	Black-red	56.0 (55.7)	6.9 (6.7)		
$Re_3(\mu\text{-}Cl)_3Cl_6(PMe_3)_3$	Red-purple	9.9 (9.8)	2.4 (2.5)	28.9 (28.8)	8.5 (8.4)
$Re_3(\mu\text{-}Cl)_3Me_6(PMe_3)_3$	Green	17.0 (18.3)	4.0 (4.6)	10.5 (10.8)	9.2 (9.5)

* Calculated values in parentheses.

Results and Discussion

Benzyl Cluster Compounds.—The benzyl halide cluster $Re_3(\mu\text{-}Cl)_3(CH_2Ph)_6$[2] (**1**) was first prepared by the interaction of $Re_3Cl_9(H_2O)_n$ ($n \approx 6$) with benzylmagnesium chloride in diethyl ether, but the product obtained from this route proved difficult to purify and crystalline samples could not be readily obtained. When the reaction was carried out in the presence of tertiary phosphines the cluster compound was obtained pure as black, diamagnetic needles which give intense red solutions in organic solvents.

However, the interaction of $Re_3Cl_9(thf)_3$[3] with benzylmagnesium chloride in tetrahydrofuran (thf) enables the isolation of high yields of the pure and highly crystalline compound and this has proved to be the best route for large scale syntheses (*ca.* 10 g). The product has identical physical properties to those previously reported;[2] noteworthy is the ^1H n.m.r. chemical shift of the benzyl methylene protons (δ 2.45 p.p.m.) and the ^{13}C chemical shift of the methylene carbon atoms (δ 48.44 p.p.m.). Unfortunately despite numerous attempts, no crystals suitable for *X*-ray work could be obtained; all samples examined proved to be multiples.

$Re_3(\mu\text{-}Cl)_3(CH_2Ph)_6$ does not react with hydrogen or carbon monoxide (10 atm) in hydrocarbons or ethers. Neither does it react with tertiary phosphines (PMe_3, PMe_2Ph, or $PMePh_2$) at room temperature or in refluxing toluene. This is unexpected in view of the fact that the compound containing the more bulky trimethylsilylmethyl group, $Re_3(\mu\text{-}Cl)_3(CH_2SiMe_3)_6$,[1] reacts with these reagents under much milder conditions to give hydrides,[3] addition and cleavage products.[2]

The bridging halide ligands of (**1**) can however be substituted by methyl groups through reaction with excess methyl-lithium in diethyl ether. The product, $Re_3(\mu\text{-}Me)_3(CH_2Ph)_6$ (**2**), isolated in high yield as black diamagnetic prisms, gives intense red solutions and was characterized by analytical and spectroscopic techniques. Bands of interest in the i.r. spectrum are ν(Re–C) at 427 and 466 cm^{-1}, assigned to the bridging and terminal carbons respectively by comparison with $Re_3(\mu\text{-}Cl)_3(CH_2Ph)_6$, as well as other bands typical of aromatic and aliphatic groups. There are no bands below 427 cm^{-1}, confirming the assignment of the Re–Cl–Re stretching frequency at 351 cm^{-1} in the spectrum of (**1**). The ^1H n.m.r. spectrum has a complex resonance, assigned to the aromatic protons, of at least ten lines in the range δ 7.15—6.74 (10) p.p.m., as well as two singlets [δ 1.78 (4) and 1.39 (3) p.p.m.], assigned on the intensity ratio to the benzylmethylene and bridging methyl protons respectively. The $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum has four resonances (δ 137.45, 131.51, 129.04, and 128.83 p.p.m.), as well as two singlets, which were

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† Sesqui-μ-chloro-sesqui-μ-methyl-*triangulo*-tris[dibenzylrhenium(III)] and tri-μ-methyl-*triangulo*-tris[dibenzylrhenium(III)] respectively.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

Table 2. Hydrogen-1, ^{13}C-{^1H}, and ^{31}P-{^1H} n.m.r. data[a]

Compound	^1H	Assignment	^{13}C-{^1H}	Assignment
$Re_3(\mu\text{-}Cl)_3(CH_2Ph)_6$	6.96 (m, 5)	$\mathrm{CH_2}\mathit{Ph}$	133.15 (s)[b]	$\mathrm{CH_2}\mathit{Ph}$
	2.45 (s, 2)	$\mathit{CH_2}\mathrm{Ph}$	132.54 (s)	
			128.26 (s)	
			127.05 (s)	
			48.44 (s)	$\mathit{CH_2}\mathrm{Ph}$
$Re_3(\mu\text{-}Me)_3(CH_2Ph)_6$	7.15—6.74 (m, 10)	$\mathrm{CH_2}\mathit{Ph}$	137.45 (s)	$\mathrm{CH_2}\mathit{Ph}$
	1.78 (s, 4)	$\mathit{CH_2}\mathrm{Ph}$	131.51 (s)	
	1.39 (s, 3)	Me	129.04 (s)	
			128.83 (s)	
			45.50 (s)	$\mathit{CH_2}\mathrm{Ph}$
			−7.6 (s)	Me
$Re_3(\mu\text{-}Cl)_3(CH_2C_6H_4Bu^t\text{-}4)_6$	7.09 (q, 4)[c]	$-C_6H_4-$	47.05 (s)	$\mathit{CH_2}\mathrm{C_6H_4}$
	2.54 (s, 2)	$\mathit{CH_2}\mathrm{C_6H_4}$	34.73 (s)	$\mathit{C}\mathrm{Me_3}$
	1.20 (s, 9)	Bu^t	31.39 (s)	$\mathrm{C}\mathit{Me_3}$
			150.7 (s)	C_6H_4
			133.7 (s)	
			129.3 (s)	
			125.5 (s)	
$Re_3(\mu\text{-}Me)_3(CH_2C_6H_4Bu^t\text{-}4)_6$	7.05 (q, 8)[d]	$-C_6H_4-$	148.7 (s)	C_6H_4
	1.95 (s, 4)	$\mathit{CH_2}\mathrm{C_6H_4}$	135.1 (s)	
	1.41 (s, 3)	μ-Me	133.6 (s)	
	1.26 (s, 18)	Bu^t	122.3 (s)	
			43.70 (s)	$\mathit{CH_2}\mathrm{C_6H_4}$
			34.60 (s)	$\mathit{C}\mathrm{Me_3}$
			31.50 (s)	$\mathrm{C}\mathit{Me_3}$
			−6.70 (s)	μ-Me
$Re_3(\mu\text{-}Cl)_3Cl_6(PMe_3)_3$	1.50 ('t')[e,f]	PMe_3	*g*	
$Re_3(\mu\text{-}Cl)_3Me_6(PMe_3)_3$	0.83 (d,3)[h]	PMe_3	*i*	
	0.95 (br,2)	Re–Me		

[a] Referenced to $SiMe_4$ at δ 0.00 p.p.m. in C_6D_6 unless otherwise stated, positive shifts downfield of $SiMe_4$; multiplicities and relative intensities are given in parentheses; 85% H_3PO_4 external reference (^{31}P). [b] In $CDCl_3$. [c] Separation of outer lines 27.2 Hz. [d] Separation of outer lines 42.8 Hz. [e] In CD_2Cl_2. [f] J_{P-H} = 8.3 Hz. [g] ^{31}P-{^1H} (CD_2Cl_2): −38.38 (s) (PMe_3). [h] J_{P-H} = 8.1 Hz. [i] ^{31}P-{^1H} (CD_2Cl_2): −48.17 (s) (PMe_3).

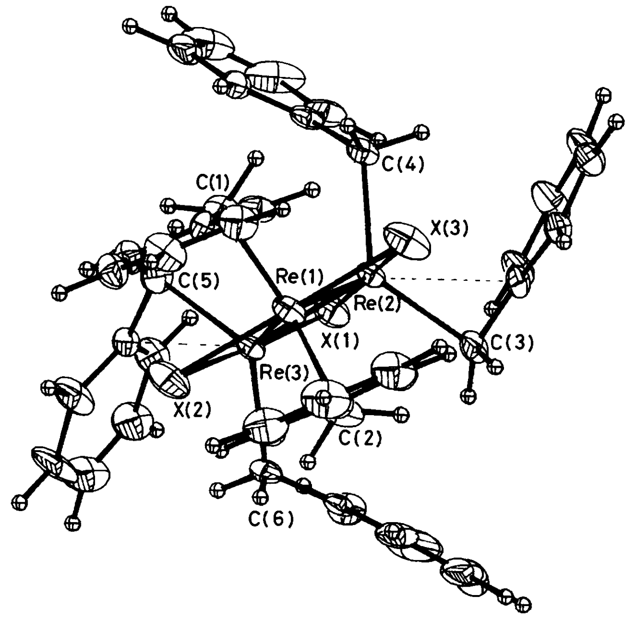


Figure 1. The molecular structure of $Re_3(\mu\text{-}Cl)_{1.5}(\mu\text{-}Me)_{1.5}(CH_2Ph)_6$ (3). The mixed bridge sites are labelled X

assigned, on the basis of the gated ^{13}C n.m.r. spectrum, to the methylene (δ 45.50 p.p.m., triplet, J_{C-H} 132 Hz) and bridging methyl (δ −7.6 p.p.m., quartet, J_{C-H} 122 Hz) carbons.

If stoicheiometric rather than excess quantities of LiMe are used the substitution of the bridging halides is incomplete, even under prolonged (24 h) reaction, as shown by the presence of chloride in the product, and by an *X*-ray structure determination on what proved, in this case, to be crystals of high quality. The molecular structure of $Re_3(\mu\text{-}Cl)_{1.5}(\mu\text{-}Me)_{1.5}(CH_2Ph)_6$ (**3**) is shown in Figure 1, and is similar to that found for $Re_3(\mu\text{-}Cl)_3(CH_2SiMe_3)_6$.[5] The bridging sites seem to have a uniform mix of Me and Cl (see Experimental section) and this is consistent with analytical data. However, this result is rather surprising since on close examination of the molecular geometry data, the structure is seen to have two-fold symmetry, not three. Thus the $Re_3(\mu\text{-}X)_3$ unit is isosceles and this is conveniently seen in Figure 2, which gives selected bond lengths and angles (others are given in Table 3), and also identifies the uniqueness of Re(1) and equivalence of Re(2) and Re(3).

The origin of this symmetry is easy to identify. In the case of Re(2) and Re(3), one of the bound benzyl groups on each shows a much smaller than expected methylene angle (*ca.* 90°) and close contacts of *ca.* 2.60 Å between the metal atoms and the first carbon of the attached phenyl ring. This type of interaction is also found in the structure of $Zr(CH_2Ph)_4(dmpe)$ [dmpe = 1,2-bis(dimethylphosphino)ethane][6] and indeed in $Zr(CH_2Ph)_4$ itself.[7] As a result of the steric effects of the 'pulled-in' benzyls the other benzyl at each of Re(2) and Re(3) shows a larger than expected methylene angle.

The distribution of the methyl and chlorine ligands about all three bridging sites, and indeed the formation of a 1:1 mixture, rather than say 1:2 or 2:1, is difficult to understand. The Re_3X_9 cluster is electron deficient irrespective of whether X is an alkyl or halide, but since the electron providing capabilities of alkyl and halide bridge atoms are formally different (one-electron and three-electron donors respectively) we might have expected to see more obvious localisation of Me and Cl in this mixed complex. In view of the result obtained, it is clear that we may need to revise our ideas on the formal differences between bridging Me and Cl, and consider the two groups to act similarly, certainly in this complex. One possible explanation may be that the methyl groups are bonding not in the 'traditional' electron deficient manner (**Ia**) but as one- + two-electron ligands *via* agostic interactions (**Ib**). Unfortunately, the overlapping of the CH$_3$ and Cl groups precludes a detailed analysis of this point.

Following the intriguing result obtained for the above compound, it became very desirable to obtain crystals of the pure compounds Re$_3$Cl$_3$R$_6$ or Re$_3$Me$_3$R$_6$. Although all attempts to obtain acceptable crystals of the chloride failed, we were eventually successful in obtaining usable crystals of the μ-methyl, and although these were not of a very high quality, we were able to determine the structure.

A diagram of the molecule of Re$_3$(μ-Me)$_3$(CH$_2$Ph)$_6$ (**2**) is shown in Figure 3, whilst selected bond lengths and angles are given in Figure 4 and Table 4. The structure is different to that of the mixed Me/Cl compound (**3**). In this case we find a structure with three-fold chemical symmetry, with one benzyl on each rhenium involved in an additional bonding interaction, see Figure 3. Whilst the occurrence of this structure is not too surprising since the electron deficiency on each rhenium atom

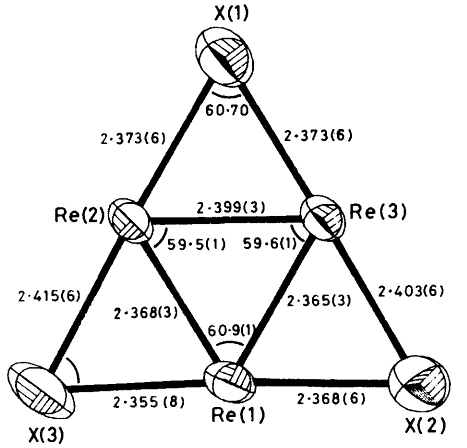
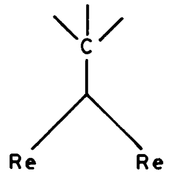


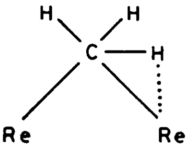
Figure 2. The Re$_3$(μ-X)$_3$ unit in (**3**) with selected bond lengths (Å) and angles (°)

Table 3. Selected bond lengths (Å), bond angles (°) and intramolecular distances (Å) for Re$_3$(μ-Cl)$_{1.5}$(μ-Me)$_{1.5}$(CH$_2$Ph)$_6$ (**3**)

C(1)–Re(1)	2.132(11)	C(2)–Re(1)	2.145(11)
C(3)–Re(2)	2.126(10)	C(4)–Re(2)	2.153(10)
C(5)–Re(3)	2.126(11)	C(6)–Re(3)	2.173(10)
C(11)–C(1)	1.495(12)	C(21)–C(2)	1.487(12)
C(31)–C(3)	1.480(12)	C(41)–C(4)	1.473(10)
C(51)–C(5)	1.480(12)	C(61)–C(6)	1.447(11)
C(1)–Re(1)–Re(2)	108.6(4)	C(1)–Re(1)–Re(3)	108.1(4)
C(1)–Re(1)–Cl(2)	88.1(4)	C(1)–Re(1)–Cl(3)	90.3(4)
C(2)–Re(1)–Re(2)	108.5(4)	C(2)–Re(1)–Re(3)	108.1(4)
C(2)–Re(1)–Cl(2)	90.0(4)	C(2)–Re(1)–Cl(3)	89.1(4)
C(2)–Re(1)–C(1)	137.2(4)	C(3)–Re(2)–Re(1)	111.2(4)
C(3)–Re(2)–Re(3)	112.8(4)	C(3)–Re(2)–Cl(1)	92.2(4)
C(3)–Re(2)–Cl(3)	88.6(4)	C(4)–Re(2)–Re(1)	109.4(4)
C(4)–Re(2)–Re(3)	115.2(3)	C(4)–Re(2)–Cl(1)	95.2(4)
C(4)–Re(2)–Cl(3)	85.7(4)	C(4)–Re(2)–C(3)	128.1(4)
C(5)–Re(3)–Re(1)	111.4(4)	C(5)–Re(3)–Re(2)	112.6(4)
C(5)–Re(3)–Cl(1)	90.9(4)	C(5)–Re(3)–Cl(2)	88.3(4)
C(6)–Re(3)–Re(1)	110.3(4)	C(6)–Re(3)–Re(2)	115.1(3)
C(6)–Re(3)–Cl(1)	95.2(4)	C(6)–Re(3)–Cl(2)	86.7(4)
C(6)–Re(3)–C(5)	127.7(5)		
C(11)–C(1)–Re(1)	103.3(6)	C(21)–C(2)–Re(1)	111.3(7)
C(31)–C(3)–Re(2)	90.4(6)	C(41)–C(4)–Re(2)	121.8(6)
C(51)–C(5)–Re(3)	90.6(6)	C(61)–C(6)–Re(3)	121.4(6)
C(11) ··· Re(1)	2.871(8)	C(31) ··· Re(2)	2.598(8)
C(51) ··· Re(3)	2.603(8)		



(**Ia**)



(**Ib**)

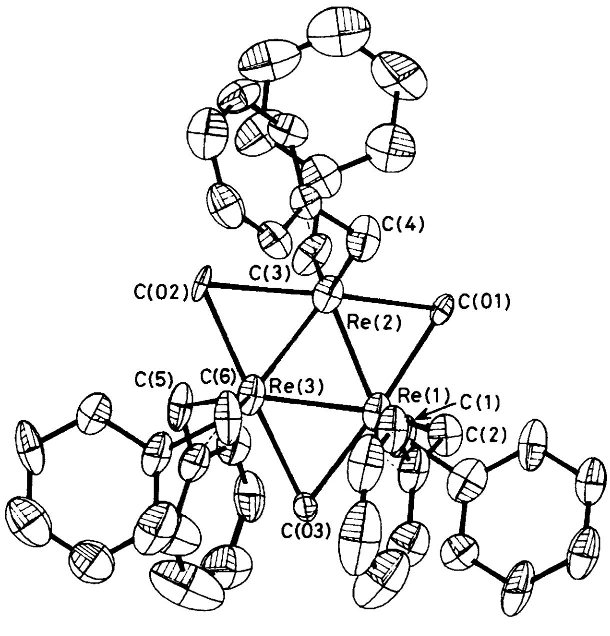


Figure 3. The molecular structure of Re$_3$(μ-Me)$_3$(CH$_2$Ph)$_6$ (**2**)

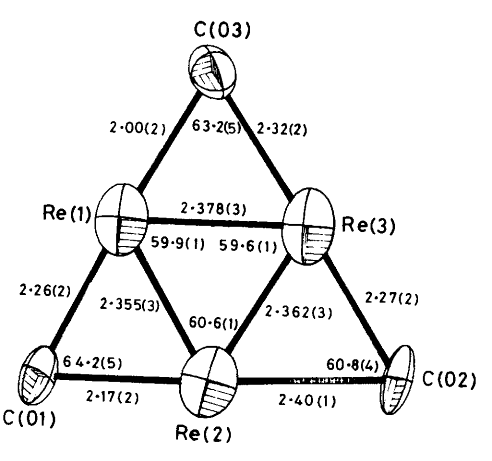


Figure 4. The Re$_3$Me$_3$ unit in (**2**) with selected bond lengths (Å) and angles (°)

Table 4. Selected bond lengths (Å), bond angles (°) and intramolecular distances (Å) for $Re_3(\mu\text{-}Me)_3(CH_2Ph)_6$ (**2**)

C(1)–Re(1)	2.170(18)	C(2)–Re(1)	2.174(18)
C(3)–Re(2)	2.118(20)	C(4)–Re(2)	2.148(23)
C(5)–Re(3)	2.145(19)	C(6)–Re(3)	2.197(17)
C(11)–C(1)	1.535(22)	C(21)–C(2)	1.534(22)
C(21)–C(2)	1.534(22)	C(31)–C(3)	1.511(27)
C(42)–C(4)	1.551(23)	C(51)–C(5)	1.484(22)
C(61)–C(6)	1.477(23)		
C(1)–Re(1)–Re(2)	109.4(6)	C(1)–Re(1)–Re(3)	113.6(5)
C(1)–Re(1)–C(01)	87.7(7)	C(1)–Re(1)–C(03)	92.1(8)
C(2)–Re(1)–Re(2)	110.4(6)	C(2)–Re(1)–Re(3)	117.2(5)
C(2)–Re(1)–C(01)	85.9(7)	C(2)–Re(1)–C(03)	97.5(8)
C(3)–Re(2)–Re(1)	107.6(6)	C(2)–Re(1)–C(1)	126.2(7)
C(3)–Re(2)–Re(3)	106.4(7)	C(3)–Re(2)–C(01)	90.8(7)
C(3)–Re(2)–C(02)	91.2(7)	C(4)–Re(2)–Re(1)	112.5(7)
C(4)–Re(2)–Re(3)	118.1(8)	C(4)–Re(2)–C(01)	85.2(7)
C(4)–Re(2)–C(02)	95.2(7)	C(4)–Re(2)–C(3)	130.4(9)
C(5)–Re(3)–Re(1)	109.5(5)	C(5)–Re(3)–Re(2)	112.6(7)
C(5)–Re(3)–C(02)	90.6(8)	C(5)–Re(3)–C(03)	90.2(8)
C(6)–Re(3)–Re(1)	115.8(5)	C(6)–Re(3)–Re(2)	111.1(7)
C(6)–Re(3)–C(02)	86.1(8)	C(6)–Re(3)–C(03)	94.6(8)
C(6)–Re(3)–C(5)	128.2(8)		
C(11)–C(1)–Re(1)	89.2(9)	C(21)–C(2)–Re(1)	120.1(11)
C(31)–C(3)–Re(2)	95.4(12)	C(41)–C(4)–Re(2)	118.8(12)
C(51)–C(5)–Re(3)	93.0(10)	C(61)–C(6)–Re(3)	121.4(12)
C(11) ··· Re(1)	2.641(14)	C(31) ··· Re(2)	2.716(17)
C(51) ··· Re(3)	2.670(15)		

is now satisfied in a uniform manner, this result does little to explain any further what is happening in the mixed-bridge structure. We are undertaking further low-temperature *X*-ray studies in this area, in the hope of obtaining some clarification.

The reactivity of the cluster methyl compound $Re_3(\mu\text{-}Me)_3(CH_2Ph)_6$ (**2**) is similar to that of $Re_3(\mu\text{-}Cl)_3(CH_2Ph)_6$ (**1**), there being no evident reaction with hydrogen or carbon monoxide (10 atm) and tertiary phosphines (PMe_3, PMe_2Ph, or $PMePh_2$); the starting material was reclaimed essentially quantitatively in all cases. The unreactivity may be due in part to intramolecular interaction of the aromatic ring of the benzyl groups with the vacant site on the rhenium together with the general steric crowding by the benzyls. In order further to investigate the Re–CH_2Ph π interaction, variable-temperature (−90 to +100 °C) ^1H n.m.r. studies were made on both compounds but were not definitive. The methylene resonance remains a singlet with slight broadening at low temperatures, probably due to viscosity effects. The phenyl resonance also broadens at very low temperatures with no other discernible change and, although it should be more sensitive to this sort of interaction, minor changes may be difficult to observe in this broad complex pattern. Even for analogous 4-substituted benzyl compounds that give rise to a simple AA′BB′ quartet, changes in this pattern were not easier to determine.

The 4-t-butylbenzyl analogues were prepared similarly to the parent compounds. For $Re_3(\mu\text{-}Cl)_3(CH_2C_6H_4Bu^t\text{-}4)_6$, the compound was isolated from ethers or hydrocarbons as black needles. The i.r. spectrum was similar to that of $Re_3(\mu\text{-}Cl)_3(CH_2Ph)_6$, with ν(Re–Cl) at 354 cm^{-1} and ν(Re–C) at 410 cm^{-1}, as well as other bands characteristic of aromatic and aliphatic hydrocarbon units. The ^1H n.m.r. spectrum has an AA′BB′ quartet due to the phenyl protons [δ 7.09 p.p.m. (4), separation of outer lines 27.2 Hz]. as well as two singlets due to the methyl protons [δ 2.54 p.p.m. (2)] and butyl protons [δ 1.20 p.p.m. (9)]. The $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum has three resonances (δ 31.39, 34.73, and 47.05 p.p.m.), which were assigned, by virtue of the gated ^{13}C spectrum, to the butyl methyl (quartet, J_{C-H} 126 Hz), butyl quaternary (singlet), and methylene (triplet, J_{C-H} 136.5 Hz) carbons respectively. There are also four resonances (δ 150.7, 133.7, 129.3, and 125.5 p.p.m.) attributable to the aromatic carbons.

From the reaction of the chloride with methyl-lithium $Re_3(\mu\text{-}Me)_3(CH_2C_6H_4Bu^t\text{-}4)_6$ can be isolated from ether or hydrocarbons as black needles. The i.r. spectrum has two bands at 415 and 460 cm^{-1} assigned to ν(Re–μ-C) and ν(Re–C) respectively, again by comparison to $Re_3(\mu\text{-}Cl)_3(CH_2C_6H_4Bu^t\text{-}4)_6$. The ^1H n.m.r. spectrum has an AA′BB′ quartet [δ 7.05 p.p.m. (8), separation of outer lines 42.8 Hz] due to the phenyl protons as well as three singlets [δ 1.95(4), 1.41(3), and 1.26 p.p.m. (18)] assigned to the methylene, bridging methyl, and butyl protons respectively. The gated ^{13}C spectrum was again used to aid the assignment of the $^{13}C\text{-}\{^1H\}$ spectrum; thus the bridging methyl carbons (δ −6.7, quartet, J_{C-H} 121 Hz), butyl methyl carbons (δ 31.5, quartet J_{C-H} 128 Hz), butyl quaternary carbons (δ 34.6, singlet) and methylene carbons (δ 43.7, triplet, J_{C-H} 133 Hz) were observed, as well as four resonances (δ 148.7, 135.1, 133.6, and 122.3 p.p.m.) due to the aromatic carbons.

Chloro(methyl)(trimethylphosphine)trirhenium Clusters.—The unstable green $Re_3Cl_3Me_6$ was previously prepared by the interaction of aged Re_3Cl_9 and MgMeCl, and its pyridine (py) adduct, $Re_3Cl_3Me_6(py)_3$, was also obtained as a thermally stable, crystalline complex.[1] PMe_2Ph and PEt_2Ph adducts were obtained only with the cyclohexyl ligand[2] or with Re_3Me_9.[2] However, excess PMe_2Ph, PEt_2Ph, or stoicheiometric amounts of PMe_3 cleave the *triangulo* unit to give dimeric compounds of rhenium-(III) or -(II).[2]

$Re_3(\mu\text{-}Cl)_3Me_6(PMe_3)_3$ has now been synthesized by the interaction of the trimethylphosphine adduct, $Re_3(\mu\text{-}Cl)_3Cl_6(PMe_3)_3$ (see below), with three equivalents of $AlMe_3$ per rhenium, in dichloromethane or toluene. Excess $AlMe_3$ is not detrimental since it is not powerful enough to remove the bridging halides under the reaction conditions. The compound can be obtained quantitatively and crystallized from diethyl ether as bright green needles. Prolonged evacuation removes co-ordinated PMe_3 leaving an insoluble, probably polymeric, product. Bands of interest in the i.r. spectrum are ν(Re–C) at 490 cm^{-1} and ν(Re–Cl) at 340 cm^{-1}, by comparison to previous assignments.[1] The ^1H n.m.r. spectrum shows the co-ordinated PMe_3 as a doublet at δ 0.83 p.p.m. (J_{P-H} 8.1 Hz), whereas the terminal methyls appear as a band at δ 0.95 p.p.m., significantly broadened due to long distance coupling with the ^{31}P nucleus. The $^{31}P\text{-}\{^1H\}$ spectrum has only a single sharp peak at δ −48.17 p.p.m.

The starting material, $Re_3(\mu\text{-}Cl)_3Cl_6(PMe_3)_3$, is readily prepared by displacing tetrahydrofuran from $Re_3Cl_9(thf)_3$ in dichloromethane. The red-purple microcrystalline complex can be crystallized from CH_2Cl_2–light petroleum; again excessive evacuation removes co-ordinated PMe_3. The ^1H n.m.r. spectrum shows the co-ordinated PMe_3 as a pseudo-triplet at δ 1.50 p.p.m. (J_{P-H} 8.3 Hz), whereas the $^{31}P\text{-}\{^1H\}$ spectrum consists of a single peak at δ −38.38 p.p.m.

Experimental

Microanalyses were by Pascher, Laboratories (Remagen). The following spectrometers were used: i.r., Perkin-Elmer 683 (spectra in Nujol mulls or KBr discs, in cm^{-1}) calibrated with polystyrene; n.m.r., Bruker WM-250 and JEOL FX-900 [data in p.p.m. relative to $SiMe_4$, 85% H_3PO_4 external (^{31}P)]. $Re_3Cl_9(thf)_3$[3] and PMe_3[8] were prepared by literature procedures. Diethyl ether, thf, toluene, and hexane were refluxed over sodium or sodium–benzophenone under nitrogen, and distilled prior to use. Dichloromethane was dried by refluxing over calcium hydride under nitrogen, and was distilled before use. The light petroleum used had b.p. 40—60 °C. All syntheses and manipulations were carried out under oxygen-free nitrogen or argon when necessary; solvents were degassed by nitrogen purge.

*Hexabenzyl-tri-μ-chloro-*triangulo*-trirhenium*(III), (**1**).—To a suspension of $Re_3Cl_9(thf)_3$ (4.6 g, 4.2 mmol) in thf (100 cm^3) cooled to −78 °C, was added with stirring a solution of $Mg(CH_2Ph)Cl$ (26.5 cm^3 of a 1.0 mol dm^{-3} solution in Et_2O, 26.5 mmol). The suspension was allowed to warm slowly to ambient temperature until all the $Re_3Cl_9(thf)_3$ had dissolved (*ca.* 2 h). The deep purple-brown solution was evaporated to dryness and the dark brown residue extracted with warm toluene (4 × 100 cm^3). The extracts were separated from the residues by centrifugation, then combined and concentrated until the solution was saturated when warm (solid that appears is redissolved by warming, followed by evaporation and warming cycles until the hot solution contains some crystals). By cooling slowly, first to room temperature and then at −20 °C, large brown-black crystals were obtained. These were collected, washed with light petroleum, and dried *in vacuo*. The supernatant liquor provides a second crop of crystals. Yield: 4 g, 80% based on $Re_3Cl_9(thf)_3$.

I.r.: 3 050m, 3 010m, 2 910m, 1 587m, 1 481s, 1 445s, 1 208m, 1 198m, 1 175w, 1 023m, 839w, 805m, 752s, 742m, 735m, 725w, 695s, 688m, 565m, 555w, 535m, 525w, 514m, 452m, 413w, and 351s cm^{-1}.

*Hexabenzyl-tri-μ-methyl-*triangulo*-trirhenium*(III), (**2**).—To a solution of $Re_3Cl_3(CH_2Ph)_6$ (1 g, 0.83 mmol) in diethyl ether (60 cm^3) at −78 °C was added, with stirring, a solution of LiMe (4.9 cm^3 or a 1.0 mol dm^{-3} solution in Et_2O, 4.9 mmol). The solution was allowed to warm to room temperature, stirred for 1—2 h, then recooled to −78 °C. Degassed, distilled water (*ca.* 10 cm^3) was added with stirring, the mixture allowed to warm up until the water melted, and then allowed to settle. The mixture was then recooled to *ca.* −20 °C to freeze the water, the suspension filtered, and the filtrate evaporated to dryness. The red-brown residue was extracted into toluene (3 × 30 cm^3), the extracts concentrated until saturated, and then cooled at −20 °C. The red prisms obtained were collected, washed with cold light petroleum (5 cm^3), and dried *in vacuo*. Yield: 0.66 g, 70% based on $Re_3Cl_3(CH_2Ph)_6$.

I.r.: 3 040w, 3 030w, 3 010m, 2 900w, 2 880w, 1 592m, 1 490s, 1 450s, 1 209m, 1 180m, 1 150w, 1 120w, 1 029m, 820w, 805w, 752s, 700s, 580m, 570w, 550m, 466s, and 427m cm^{-1}.

$Re_3(\mu\text{-}Cl)_{1.5}(\mu\text{-}Me)_{1.5}(CH_2Ph)_6$ (**3**).—This compound was prepared as above, but using a stoicheiometric amount of LiMe with respect to $Re_3Cl_3(CH_2Ph)_6$.

Tri-μ-chloro-hexa(*4-t-butylphenylmethyl*)-triangulo-*trirhenium*(III) *and Tri-μ-methyl-hexa*(*4-t-butylphenylmethyl*)-triangulo-*trirhenium*(III).—Both compounds were prepared similarly to $Re_3(\mu\text{-}Cl)_3(CH_2Ph)_6$ and $Re_3(\mu\text{-}Me)_3(CH_2Ph)_6$ respectively, except that they were extracted into and recrystallised from light petroleum instead of toluene. A white impurity sometimes appears in the preparation of $Re_3(\mu\text{-}Cl)_3(CH_2C_6H_4Bu^t)_6$; this can be removed by vacuum sublimation (80 °C, 10^{-1} Torr) before recrystallisation of the product. Yield: *ca.* 70% based on $Re_3Cl_9(thf)_3$ and $Re_3(\mu\text{-}Cl)_3(CH_2C_6H_4Bu^t)_6$ respectively.

I.r.: 1 600m, 1 510(sh), 1 500m, 1 410w, 1 360m, 1 268s, 1 212w, 1 200w, 1 190m, 1 128m, 1 108m, 1 015m, 830(sh), 828s, 810w, 800w, 740w, 580m, 570m, 540w, 410m, and 354m cm^{-1}.

Tri-μ-chloro-hexakis(*chloro*)*tris*(*trimethylphosphine*)-tri-angulo-*trirhenium*(III).—To a stirred suspension of $Re_3Cl_9(thf)_3$ (4.4 g, 4.0 mmol) in CH_2Cl_2 (50 cm^3) was added PMe_3 (1.4 cm^3, 14 mmol), whereupon the solid rapidly dissolved to give an intense red-purple solution. If the solution is concentrated until saturated, and then cooled, good quality crystals may be obtained. However, if the solution is filtered and light petroleum (150 cm^3) added, followed by cooling (−78 °C), a higher yield of microcrystalline product is obtained, which is pure enough for further reactions. The product was collected, washed with Et_2O (10 cm^3), and dried *in vacuo* for a few minutes. Excessive evacuation will remove co-ordinated PMe_3. Yield: 3.56 g, 80% based on $Re_3Cl_9(thf)_3$.

I.r.: 2 990w, 2 980m, 2 908m, 1 430m, 1 415s, 1 408(sh), 1 283m, 1 280s, 955s br, 850m, 750m, 738s, 675m, 345s, 338(sh), and 322m cm^{-1}.

Tri-μ-chloro-hexamethyltris(*trimethylphosphine*)-tri-angulo-*trirhenium*(III).—To a solution of $Re_3(\mu\text{-}Cl)_3Cl_6(PMe_3)_3$ (0.7 g, 0.63 mmol) in CH_2Cl_2 or toluene (90 cm^3) was added dropwise with stirring, a solution of $AlMe_3$ (0.83 cm^3 of a 2.3 mol dm^{-3} solution in hexane, 1.91 mmol). The red solution becomes clear and bright green before all the $AlMe_3$ solution is added; after stirring for 1 h, the solution was evaporated to dryness, the green residue washed with light petroleum (5 cm^3) and crystallized from diethyl ether (*ca.* 15 cm^3).

X-*Ray Crystallography*.—Crystallographic measurements were made on crystals sealed under argon in thin-walled glass capillaries using a CAD4 diffractomer, graphite monochromated Mo-K_α radiation (λ = 0.710 69 Å) and, for intensity measurement, the ω–2θ scan method, following previously detailed procedures.[9] The structures were solved by application

Table 5. Crystallographic data for $Re_3(\mu\text{-}Cl)_{1.5}(\mu\text{-}Me)_{1.5}(CH_2Ph)_6$ (**3**) and $Re_3(\mu\text{-}Me)_3(CH_2Ph)_6$ (**2**)

Complex	(**3**)	(**2**)
(*a*) Crystal data:		
Formula	$C_{43.5}H_{46.5}Cl_{1.5}Re_3$	$C_{46}H_{51}Re_3$
M	1 181.12	1 150.49
Crystal system	Triclinic	Monoclinic
a/Å	12.659(2)	25.455(4)
b/Å	16.301(6)	13.177(2)
c/Å	10.263(2)	24.964(4)
α/°	105.77(2)	90
β/°	109.18(1)	110.99(2)
γ/°	89.20(2)	90
U/Å^3	1 918.35(89)	7 817.80
Space group	$P\bar{1}$	*Ia*
D_c/g cm^{-3}	2.04	1.95
Z	2	8
F(000)	1 116	4 368
μ(Mo-K_α)/cm^{-1}	97.64	94.25
(*b*) Data collection:		
$\theta_{min.}$; $\theta_{max.}$	1.5,25	1.5,25
Total data measured	7 076	7 619
Total data unique	6 733	6 866
Total data observed	4 948	3 250
Significance test	$F_o > 3\sigma(F_o)$	$F_o > 4\sigma(F_o)$
(*c*) Refinement:		
No. of parameters	415	367
Weighting scheme parameter *g*[a]	0.0022	0.000 65
Final *R*[b]	0.0374	0.0442
Final *R′*[c]	0.0408	0.0515

[a] $w = 1/[\sigma^2(F_o) + gF_o^2]$. [b] $R = \Sigma|\Delta F|/\Sigma|F_o|$. [c] $R' = [\Sigma w(\Delta F)^2/\Sigma w|F_o^2|]^{\frac{1}{2}}$.

Table 6. Fractional atomic co-ordinates (× 10^4) for (**1**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Re(1)	5 463(0.5)	2 552(0.5)	10 052(0.5)	C(31)	2 116(5)	2 819(3)	6 610(5)
Re(2)	3 597(0.5)	2 901(0.5)	9 103(0.5)	C(32)	2 572(5)	3 432(3)	6 139(5)
Re(3)	4 071(0.5)	2 111(0.5)	10 849(0.5)	C(33)	1 955(5)	4 159(3)	6 005(5)
X(1)	2 203(4)	2 471(3)	9 920(4)	C(34)	972(5)	4 273(3)	6 342(5)
X(2)	5 984(4)	1 796(3)	11 808(5)	C(35)	560(5)	3 660(3)	6 814(5)
X(3)	5 060(4)	3 315(3)	8 322(5)	C(36)	1 132(5)	2 933(3)	6 948(5)
C(1)	6 420(8)	3 651(6)	11 663(11)	C(41)	3 180(5)	4 599(3)	11 235(5)
C(2)	5 756(9)	1 470(6)	8 511(11)	C(42)	2 050(5)	4 617(3)	11 110(5)
C(3)	2 788(9)	2 112(6)	6 972(9)	C(43)	1 746(5)	5 007(3)	12 309(5)
C(4)	3 506(8)	4 252(5)	9 951(9)	C(44)	2 573(5)	5 381(3)	13 633(5)
C(5)	4 218(9)	2 883(6)	12 945(9)	C(45)	3 703(5)	5 363(3)	13 758(5)
C(6)	3 665(8)	737(5)	9 973(10)	C(46)	4 007(5)	4 973(3)	12 559(5)
C(11)	7 594(5)	3 507(3)	11 689(5)	C(51)	3 795(5)	2 145(3)	13 266(5)
C(12)	8 318(5)	3 176(3)	12 738(5)	C(52)	2 637(5)	1 984(3)	12 877(5)
C(13)	9 419(5)	3 053(3)	12 775(5)	C(53)	2 198(5)	1 239(3)	12 998(5)
C(14)	9 796(5)	3 262(3)	11 763(5)	C(54)	2 917(5)	654(3)	13 508(5)
C(15)	9 072(5)	3 593(3)	10 713(5)	C(55)	4 075(5)	815(3)	13 898(5)
C(16)	7 971(5)	3 716(3)	10 676(5)	C(56)	4 514(5)	1 560(2)	13 777(5)
C(21)	6 884(5)	1 575(3)	8 394(6)	C(61)	2 733(5)	376(3)	8 662(6)
C(22)	7 798(5)	1 292(3)	9 314(6)	C(62)	1 648(5)	297(3)	8 697(6)
C(23)	8 857(5)	1 350(3)	9 189(6)	C(62)	773(5)	−116(3)	7 446(6)
C(24)	9 002(5)	1 691(3)	8 145(6)	C(64)	983(5)	−451(3)	6 160(6)
C(25)	8 088(5)	1 974(3)	7 226(6)	C(65)	2 068(5)	−373(3)	6 125(6)
C(26)	7 029(5)	1 916(3)	7 351(6)	C(66)	2 944(5)	41(3)	7 376(6)

* The sites represented by atoms X have the composition 0.5 Cl + 0.5 C.

Table 7. Fractional atomic co-ordinates (× 10^4) for (**2**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Re(1)	992(0.5)	6 811(1)	2 027(0.5)	C(31)	901(7)	5 827(10)	3 801(7)
Re(2)	1 193(0.5)	5 804(1)	2 856(0.5)	C(32)	1 249(7)	6 591(10)	4 128(7)
Re(3)	767(0.5)	5 052(1)	1 943(0.5)	C(33)	1 588(7)	6 404(10)	4 697(7)
C(01)	1 394(6)	7 410(9)	2 932(6)	C(34)	1 578(7)	5 454(10)	4 940(7)
C(02)	972(7)	4 030(9)	2 721(8)	C(35)	1 230(7)	4 690(10)	4 613(7)
C(03)	567(7)	6 139(11)	1 164(7)	C(36)	892(7)	4 877(10)	4 043(7)
C(1)	277(7)	7 783(12)	1 938(9)	C(41)	2 305(5)	4 489(7)	3 462(6)
C(2)	1 766(7)	7 264(13)	1 911(9)	C(42)	2 358(5)	4 103(7)	3 999(6)
C(3)	542(9)	6 042(13)	3 183(9)	C(43)	2 584(5)	3 138(7)	4 162(6)
C(4)	2 080(9)	5 583(15)	3 295(11)	C(44)	2 758(5)	2 560(7)	3 788(6)
C(5)	1 358(8)	4 249(13)	1 666(10)	C(45)	2 705(5)	2 946(7)	3 250(6)
C(6)	−118(7)	4 675(12)	1 779(10)	C(46)	2 478(5)	3 911(7)	3 088(6)
C(11)	545(5)	8 618(9)	1 691(5)	C(51)	919(5)	3 565(8)	1 287(5)
C(12)	915(5)	9 302(9)	2 067(5)	C(52)	756(5)	2 682(8)	1 493(5)
C(13)	1 215(5)	9 990(9)	1 863(5)	C(53)	319(5)	2 089(8)	1 131(5)
C(14)	1 146(5)	9 994(9)	1 283(5)	C(54)	44(5)	2 380(8)	561(5)
C(15)	776(5)	9 310(9)	907(5)	C(55)	207(5)	3 264(8)	354(5)
C(16)	476(5)	8 621(9)	1 111(5)	C(56)	644(5)	3 856(8)	717(5)
C(21)	2 009(5)	6 611(9)	1 547(5)	C(61)	−581(5)	5 307(10)	1 398(5)
C(22)	2 439(5)	5 915(9)	1 801(5)	C(62)	−811(5)	6 073(10)	1 631(5)
C(23)	2 668(5)	5 359(9)	1 462(5)	C(63)	−1 236(5)	6 692(10)	1 272(5)
C(24)	2 466(5)	5 499(9)	869(5)	C(64)	−1 430(5)	6 546(10)	679(5)
C(25)	2 035(5)	6 195(9)	615(5)	C(65)	−1 199(5)	5 781(10()	446(5)
C(26)	1 807(5)	6 751(9)	954(5)	C(66)	−775(5)	5 161(10)	806(5)

of direct methods (Re positions) and developed *via* routine heavy-atom phasing procedures. Refinement was by full-matrix least squares, with Re and C atoms assigned anisotropic, and H atoms isotropic, displacement factor coefficients. In both cases, H atoms on the phenyl rings were included in idealised positions. In the case of the mixed-bridge complex CH_2 hydrogens were freely refined. Details of crystallographic data and experimental features are summarised in Table 5. For the mixed Cl/Me complex (**3**), detailed investigations were made to assess the most realistic composition of the three bridging sites. Refinements were made with occupancies varying and displacement factor coefficients fixed, with the sites occupied by carbon only or chlorine only. In all cases, the U_{ij} values indicated no serious spread of electron density and the occupancies always gave a strong indication of equal densities at all three sites. With $U_{iso.}$ values fixed at equal values, corresponding to those adopted by the Re atoms +5%, the occupancies all refined to *ca.* 0.66—0.7 when the site was assigned as Cl. Accordingly we have used a fixed occupancy of 0.7 which corresponds closely to 0.5 Cl + 0.5 C. This value is consistent with analytical results, but of course the latter do not necessarily relate to single-crystal specimens; the sample could contain pure methyl and chloride species also. Final fractional atomic co-ordinates are given in Tables 6 and 7.

Acknowledgements

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