Crystal and Molecular Structure of Tri-μ-chloro-hexakis(trimethylsilylmethyl)-*triangulo*-trirhenium(III)

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The crystal and molecular structure of the title complex has been determined by single-crystal X-ray analysis. Crystals are monoclinic with $a = 12.021(3)$, $b = 20.489(5)$, $c = 18.194(5)$ Å, $\beta = 91.03(3)°$, space group $P2_{1/n}$, and $Z = 4$. The structure has been solved by direct methods and refined by least squares to R 0.062 for 4 170 observed diffractometer data. The molecular structure is based on an equilateral Re_3 triangle with three in-plane bridging chlorine atoms. To each metal atom are also bonded two out-of-plane terminal trimethylsilylmethyl groups, the bulk of which presumably precludes the additional binding of any in-plane terminal ligands. The Re–Re distances [2.384—2.389(1) Å] are the shortest so far observed in Re_3 cluster compounds. The Re–C and Re–Cl distances are respectively 2.07—2.13(2) and 2.412—2.440(5) Å, whilst the C–Re–C and Re–Cl–Re angles are 122—130(1) and 59.0(1)°.

TRINUCLEAR rhenium halide complexes are well known and a number have been studied by X-ray methods.[1-9] Their structures are based on the Re_3X_9 unit which comprises a triangle of metal atoms with three in-plane bridging halogen atoms and, on each metal atom, two terminal out-of-plane halogen atoms. In most cases, however, some or all of the three metal atoms also possess an in-plane terminal ligand which may also be a halogen atom (alone or part of a neighbouring Re_3X_9 unit) or a donor ligand such as a phosphine. Recently, Wilkinson and his co-workers [10,11] have described the preparation of alkyl derivatives based on the Re_3 cluster. These complexes represent the first examples of cluster alkyls containing metal–metal bonds. As part of our general study of complexes containing bulky ligands we have determined the structure of the complex $[Re_3Cl_3(CH_2SiMe_3)_6]$ by single-crystal X-ray analysis.

EXPERIMENTAL

Crystals, prepared as described in ref. 11, were kindly provided by Professor G. Wilkinson. They were dark blue air-sensitive tablets, and samples used for X-ray study were sealed under nitrogen in Lindemann capillaries.

Crystal Data.—$C_{24}H_{66}Cl_3Re_3Si_6$, $M = 1\,188.27$, Monoclinic, $a = 12.021(3)$, $b = 20.489(5)$, $c = 18.194(5)$ Å, $\beta = 91.03(3)°$, $U = 4\,480.4$ Å^3, space group $P2_{1/n}$ (C^5_2, no. 14), $Z = 4$, $D_c = 1.761$ g cm^{-3}, $F(000) = 2\,280$, μ(Mo-K_α) = 85.12 cm^{-1}, λ(Mo-K_α) = 0.710 69 Å.

The crystal used for intensity measurement had overall dimensions of $0.413 \times 0.215 \times 0.086$ mm, and was bounded by the six intersecting planes [$(\bar{2}11)$, $(2\bar{1}\bar{1})$, (010), $(0\bar{1}0)$, (101), and $(\bar{1}0\bar{1})$]. The unit-cell constants were determined from least-squares refinement of the setting angles for 15 reflections automatically centered on a Nonius CAD4 diffractometer. The space group $P2_{1/n}$ was uniquely determined from systematic absences, $0k0$ for k odd and $h0l$ for $h + l$ odd. Three-dimensional X-ray intensities of 6 383 reflections ($\pm h, k, l$; $1.5 < \theta < 25°$) were measured using monochromated Mo-K_α radiation and an ω—2θ scan technique. A periodic check of two standard reflections showed that the diffracting power of the crystal decreased linearly by *ca.* 37% during data collection. All the intensities were corrected for Lorentz and polarisation factors and brought to a common scale by allowing for crystal deterioration. The data were also corrected for absorption effects and merged to obtain 5 797 unique intensities (internal consistency, R 0.024). The complete data set was used in the initial structure analysis but only 4 170 reflections with $F_o^2 > 2\sigma(F_o^2)$ were used in the refinement.

Structure Analysis and Refinement.—The positions of the rhenium and chlorine atoms were obtained from the 'best' E map computed with the automatic direct-methods routine in the SHELX [12] program. The parameters of these atoms were subjected to four cycles of least-squares refinement after which an R value of 0.18 was obtained. The refined parameters of these atoms were used for calculating a difference electron-density synthesis from which the positions of the silicon and carbon atoms were obtained. Isotropic refinement of all the non-hydrogen atoms gave an R of 0.099; introduction of anisotropic thermal parameters reduced R further to 0.065. The positions of the hydrogen atoms were calculated on the basis of an idealised geometry (C–H 1.08 Å, H–C–H 109.5°, H $\cdots$ H 1.764 Å) and included in the calculation of F_c. The methyl groups were refined as rigid bodies, being allowed to pivot on the relevant carbon atom. One common U_{iso} was refined for all the hydrogen atoms [final value 0.08(2) Å^2]. Owing to the large number of parameters, the final stages of refinement were carried out in two blocks with Re(1), Cl(2), and the overall scale factor being refined in each cycle. The weighting scheme $w = 1/[\sigma^2(F_o) + 0.001\,8F_o^2]$

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was applied and gave satisfactory analyses of variance. Final values of R and R' are 0.062 and 0.064. Neutral-atom scattering factors were taken from refs. 13 (Re), 14 (Cl, Si, and C), and 15 (H), with those for the heavier elements being modified for anomalous dispersion.[16]

All the computations are performed on the Queen Mary College ICL1904S and University of London CDC7600 computers.

RESULTS AND DISCUSSION

The fractional co-ordinates of the non-hydrogen atoms are given in Table 1 and the derived interatomic distances and interbond angles in Table 2. The fractional co-ordinates for the hydrogen atoms, anisotropic thermal parameters for the heavier atoms, and lists of observed and calculated structure factors have been deposited in Supplementary Publication No. SUP 22295 (31 pp.).*

TABLE 1

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

Atom			
Re(1)	42 271(6)	17 973(3)	1 949(5)
Re(2)	40 756(6)	18 769(3)	14 974(5)
Re(3)	43 969(6)	28 340(3)	7 819(5)
Cl(1)	3 874(4)	821(2)	923(3)
Cl(2)	4 294(5)	2 923(2)	2 102(3)
Cl(3)	4 557(5)	2 752(2)	−547(3)
Si(1)	7 080(5)	1 535(3)	−417(4)
Si(2)	2 491(6)	1 200(4)	−1 117(4)
Si(3)	5 652(5)	1 174(3)	2 860(4)
Si(4)	1 418(5)	1 163(3)	2 043(4)
Si(5)	6 421(5)	3 980(3)	742(4)
Si(6)	1 671(5)	3 616(3)	926(4)
C(11)	5 634(16)	1 307(10)	−239(12)
C(12)	7 871(21)	1 634(13)	496(18)
C(13)	7 260(23)	2 269(13)	−953(14)
C(14)	7 636(23)	812(12)	−948(15)
C(21)	2 654(16)	1 721(9)	−289(12)
C(22)	3 283(25)	1 571(14)	−1 883(14)
C(23)	2 917(27)	358(13)	−993(17)
C(24)	1 004(25)	1 188(18)	−1 358(20)
C(31)	5 631(15)	1 604(10)	1 950(11)
C(32)	5 269(28)	296(12)	2 721(18)
C(33)	7 065(21)	1 217(18)	3 281(19)
C(34)	4 651(28)	1 507(17)	3 540(16)
C(41)	2 477(14)	1 830(9)	1 961(11)
C(42)	836(18)	864(12)	1 138(15)
C(43)	223(22)	1 527(17)	2 531(19)
C(44)	1 949(23)	458(11)	2 534(18)
C(51)	6 081(15)	3 088(8)	902(11)
C(52)	5 996(20)	4 266(11)	−213(12)
C(53)	5 800(23)	4 496(10)	1 449(15)
C(54)	7 998(19)	4 043(13)	821(18)
C(61)	3 136(15)	3 508(10)	612(11)
C(62)	1 578(23)	3 686(11)	1 944(12)
C(63)	1 196(19)	4 398(10)	512(14)
C(64)	777(19)	2 953(11)	583(16)

The crystal structure is built up from discrete trimeric molecules of $[Re_3Cl_3(CH_2SiMe_3)_6]$ held together only by van der Waals forces. The structure of a single molecule is shown in Figure 1,[17] together with the atom-labelling

TABLE 2

Interatomic distances (Å) and angles (°) with estimated standard deviations * in parentheses

(*a*) Bond distances

Re(1)–Re(2)	2.386(1)	Si(1)–C(11)	1.835(20)
Re(1)–Re(3)	2.384(1)	Si(1)–C(12)	1.909(31)
Re(2)–Re(3)	2.389(1)	Si(1)–C(13)	1.807(26)
Mean Re–Re	2.386	Si(1)–C(14)	1.897(27)
		Si(2)–C(21)	1.855(22)
		Si(2)–C(22)	1.864(28)
		Si(2)–C(23)	1.812(27)
Re(1)–Cl(1)	2.440(5)	Si(2)–C(24)	1.834(31)
Re(1)–Cl(3)	2.413(5)	Si(3)–C(31)	1.875(21)
Re(2)–Cl(1)	2.412(5)	Si(3)–C(32)	1.873(26)
Re(2)–Cl(2)	2.422(5)	Si(3)–C(33)	1.853(28)
Re(3)–Cl(2)	2.415(6)	Si(3)–C(34)	1.870(33)
Re(3)–Cl(3)	2.434(6)	Si(4)–C(41)	1.874(18)
		Si(4)–C(42)	1.881(27)
Mean Re–Cl	2.423	Si(4)–C(43)	1.858(31)
		Si(4)–C(44)	1.809(27)
		Si(5)–C(51)	1.894(18)
		Si(5)–C(52)	1.895(24)
Re(1)–C(11)	2.130(20)	Si(5)–C(53)	1.833(26)
Re(1)–C(21)	2.078(19)	Si(5)–C(54)	1.904(25)
Re(2)–C(31)	2.105(19)	Si(6)–C(61)	1.874(19)
Re(2)–C(41)	2.115(18)	Si(6)–C(62)	1.864(23)
Re(3)–C(51)	2.096(18)	Si(6)–C(63)	1.853(22)
Re(3)–C(61)	2.069(19)	Si(6)–C(64)	1.833(24)
Mean Re–C	2.099	Mean Si–C	1.861

(*b*) Bond angles

Re(2)–Re(1)–Re(3)	60.1(1)	Cl(1)–Re(1)–C(11)	87.8(6)
Re(1)–Re(2)–Re(3)	59.9(1)	Cl(1)–Re(1)–C(21)	90.1(6)
Re(1)–Re(3)–Re(2)	60.0(1)	Cl(3)–Re(1)–C(11)	92.0(6)
		Cl(3)–Re(1)–C(21)	88.9(6)
Cl(1)–Re(1)–Cl(3)	178.8(2)	Cl(1)–Re(2)–C(31)	90.7(6)
Cl(1)–Re(2)–Cl(2)	178.6(2)	Cl(1)–Re(2)–C(41)	92.7(5)
Cl(2)–Re(3)–Cl(3)	178.4(2)	Cl(2)–Re(2)–C(31)	88.2(6)
		Cl(2)–Re(2)–C(41)	87.2(5)
C(11)–Re(1)–C(21)	122.0(8)	Cl(2)–Re(3)–C(51)	87.3(6)
C(31)–Re(2)–C(41)	129.7(7)	Cl(2)–Re(3)–C(61)	92.7(6)
C(51)–Re(3)–C(61)	123.5(7)	Cl(3)–Re(3)–C(51)	91.1(6)
		Cl(3)–Re(3)–C(61)	88.2(6)
Re(1)–Cl(1)–Re(2)	58.9(1)		
Re(2)–Cl(2)–Re(3)	59.2(1)		
Re(1)–Cl(3)–Re(3)	58.9(1)		
Re(1)–C(11)–Si(1)	134.9(1.1)	Re(1)–C(21)–Si(2)	118.0(1.0)
Re(2)–C(31)–Si(3)	117.9(1.0)	Re(2)–C(41)–Si(4)	133.5(1.0)
Re(3)–C(51)–Si(5)	115.9(0.9)	Re(3)–C(61)–Si(6)	136.3(1.1)
C(11)–Si(1)–C(12)	109.4(1.1)	C(21)–Si(2)–C(22)	108.9(1.1)
C(11)–Si(1)–C(13)	115.5(1.1)	C(21)–Si(2)–C(23)	114.9(1.2)
C(11)–Si(1)–C(14)	103.6(1.1)	C(21)–Si(2)–C(24)	106.8(1.3)
C(12)–Si(1)–C(13)	108.6(1.2)	C(22)–Si(2)–C(23)	109.6(1.4)
C(12)–Si(1)–C(14)	110.6(1.2)	C(22)–Si(2)–C(24)	109.6(1.5)
C(13)–Si(1)–C(14)	109.1(1.2)	C(23)–Si(2)–C(24)	106.8(1.6)
C(31)–Si(3)–C(32)	109.5(1.2)	C(41)–Si(4)–C(42)	114.2(1.0)
C(31)–Si(3)–C(33)	109.9(1.2)	C(41)–Si(4)–C(43)	106.1(1.2)
C(31)–Si(3)–C(34)	114.5(1.2)	C(41)–Si(4)–C(44)	112.8(1.1)
C(32)–Si(3)–C(33)	108.8(1.5)	C(42)–Si(4)–C(43)	105.7(1.2)
C(32)–Si(3)–C(34)	106.2(1.5)	C(42)–Si(4)–C(44)	107.1(1.2)
C(33)–Si(3)–C(34)	107.7(1.5)	C(43)–Si(4)–C(44)	110.7(1.5)
C(51)–Si(5)–C(52)	112.0(1.0)	C(61)–Si(6)–C(62)	112.7(1.1)
C(51)–Si(5)–C(53)	111.3(1.0)	C(61)–Si(6)–C(63)	105.2(1.0)
C(51)–Si(5)–C(54)	105.7(1.0)	C(61)–Si(6)–C(64)	111.0(1.0)
C(52)–Si(5)–C(53)	111.0(1.1)	C(62)–Si(6)–C(63)	108.2(1.1)
C(52)–Si(5)–C(54)	107.4(1.3)	C(62)–Si(6)–C(63)	110.4(1.2)
C(53)–Si(5)–C(54)	109.0(1.3)	C(63)–Si(6)–C(64)	109.1(1.1)

* These standard deviations do not include errors in the cell dimensions.

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

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

scheme used. The molecule contains an equilateral Re_3 triangle with three symmetrically bridging coplanar chlorine atoms and to each metal atom are also bonded two out-of-plane alkyl groups. The rhenium atoms are thus considered to be six-co-ordinate if the Re–Re interactions are included. The structure is basically the same as that found for the previously mentioned halide complexes, but belongs to the small class of structures in which there are no in-plane terminal ligands. The molecule does not possess any crystallographic symmetry but the $Re_3Cl_3C_6$ nucleus approximates very closely to D_{3h}. The root-mean-square deviation from their least-squares plane of atoms in the Re_3Cl_3 unit is 0.012 Å.

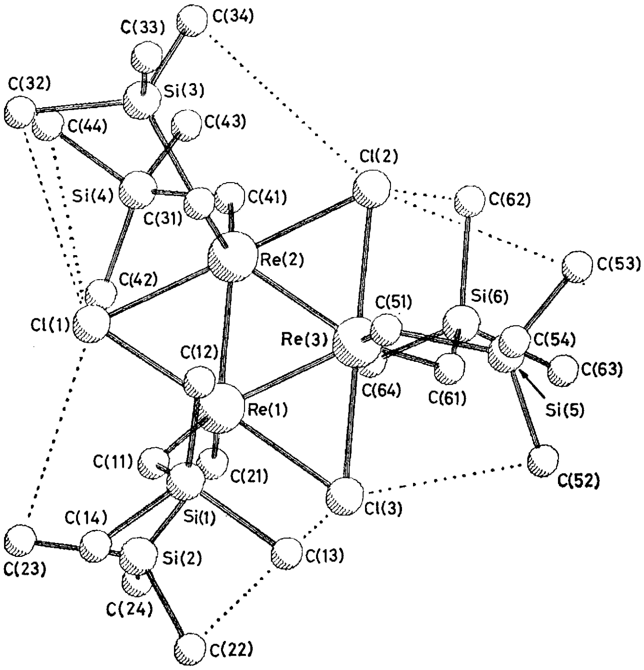

FIGURE 1 View of one molecule of $[Re_3Cl_3(CH_2SiMe_3)_6]$ showing the atom-labelling system used. The broken lines represent short intramolecular Me · · · Cl contacts

The average Re–Re distance (2.386 Å) is 0.05—0.11 Å shorter than in other rhenium(III) clusters, *e.g.* 2.465 Å in Re_3Br_9,[1] 2.48 Å in $[Re_3Cl_{12}]^{3-}$,[2] 2.48 Å in Re_3Cl_9[3] and $[Re_3Cl_9(PEt_2Ph)_3]$,[4] and 2.50 Å in $[Re_3Br_{12}]^{3-}$.[5] The nature of the metal–metal bonding in all cases is expected to be the same, with a net Re–Re bond order of 2 and variations in bond lengths are therefore most likely to arise from interligand steric repulsions and/or variations in metal co-ordination numbers. In the species $[Re_3Cl_{11}]^{2-}$ (ref. 6) two of the metal atoms are seven-co-ordinate and one six-co-ordinate. The distances between two seven-co-ordinate atoms and one seven- and one six-co-ordinate atom are 2.483 and 3.413 Å respectively. By simple interpolation, the distance between two six-co-ordinate atoms would then be 2.381 Å, which is very close to the value in our complex. From the data currently available, therefore, it does seem that in these triangular clusters there is a fairly simple correlation between Re–Re bond length and Re co-ordination number[6,7,18] with a smaller (0.01—0.02 Å) perturbation possibly attributable to ligand steric effects. Of course, it is also possible to argue that the Re–Re bonds are weakened, and thus lengthened, by the bonding of in-plane terminal ligands *via* a mechanism similar to that suggested for the effect of axial ligands in binuclear M≡M systems.[19]

TABLE 3

Selected non-bonded intramolecular (*a*) and intermolecular distances (*b*) (≤ 4.0 Å)

(*a*)		(*b*)	
Cl(1) · · · C(23)	3.77	Cl(1) · · · C(14)	3.81
Cl(1) · · · C(32)	3.80	Cl(2) · · · C(24)	3.90
Cl(1) · · · C(42)	3.68	Cl(3) · · · C(43)	3.89
Cl(1) · · · C(44)	3.84	C(13) · · · C(34)	3.94
Cl(2) · · · C(34)	3.93	C(14) · · · C(42)	3.91
Cl(2) · · · C(53)	3.89	C(14) · · · C(44)	3.92
Cl(2) · · · C(62)	3.63	C(52) · · · C(52)	3.93
Cl(3) · · · C(13)	3.49	C(52) · · · C(53)	4.00
Cl(3) · · · C(22)	3.74	C(54) · · · C(63)	3.96
Cl(3) · · · C(52)	3.60		

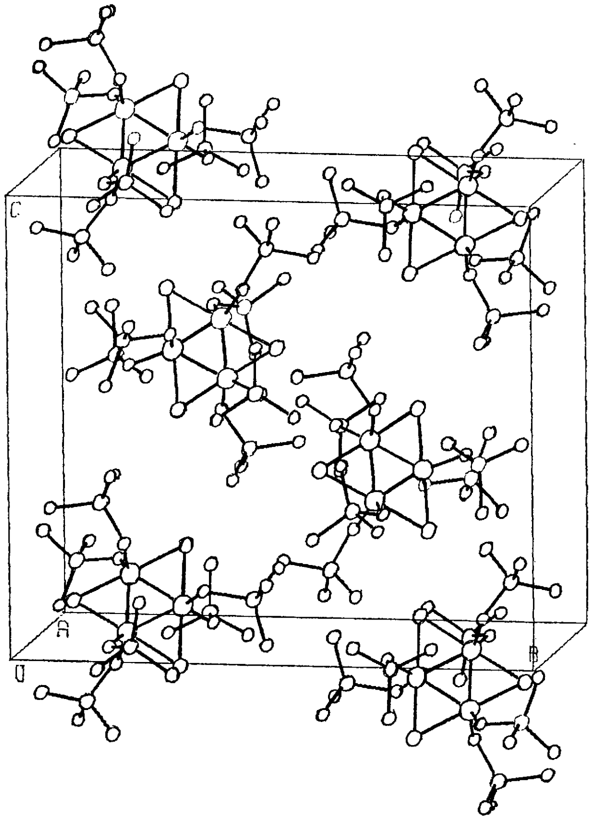

FIGURE 2 The packing of molecules in the unit cell

The six independent Re–Cl distances are equal, within the limits of experimental error, and the average value (2.423 Å) is generally longer than values found in

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[18] J. E. Fergusson, B. R. Penfold, M. Elder, and W. T. Robinson, *J. Chem. Soc.*, 1965, 5500.

[19] F. A. Cotton and W. T. Hall, *Inorg. Chem.*, 1977, **16**, 1867 and refs. therein.

the other chloride derivatives, 2.35—2.39 Å (but 2.46 Å in Re_3Cl_9). The lengthening, and possible weakening, of the Re–Cl bonds may be a consequence of the strengthening of the Re–Re bonding; certainly it is in the opposite direction to that expected to follow from the reduction in metal co-ordination number. Steric repulsions between the chlorines and methylene carbon atoms of the alkyl group may also be a contributory factor. The crowding in the molecule in general is also evident from the C–Re–C angles which lie between 122 and 130° (all less than the 134° found [7] for the Br–Re–Br angle at the six-co-ordinate Re atom in $[Re_3Br_{11}]^{2-}$) and a number of short (<4.0 Å) Me · · · Cl contacts (Table 3 and Figure 1). These also affect the geometry of the CH_2SiMe_3 groups. The CH_2–Si–Me angles fall into two ranges (111.3—115.5 and 103.6—111.0°) and in all cases values in the former group are attributable to short Me · · · Cl contacts. The variations in Re–CH_2–Si and Cl–Re–CH_2 angles (115.9—136.3 and 87.3—92.7° respectively) are probably also due to the way in which the alkyl groups pack within the molecule.

The Re–C distances [2.07—2.13(2), mean 2.10 Å] do not seem to be affected by crowding and are in fact a little shorter than those in the $[Re_2Me_8]^{2-}$ ion [2.19(1) Å].[20] The Si–C bond lengths (mean 1.861 Å) are very close to expected values.

The molecular packing for the structure is shown in Figure 2. The shortest intermolecular contact (Table 3) is a chlorine–carbon contact of 3.81 Å, and the intermolecular contacts in general indicate fairly loose packing.

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[8/017 *Received, 5th January*, 1978]

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