Interaction of Hydrogen with Hexakis(trimethylsilylmethyl)-μ-trichloro-triangulo-trirhenium(III); the *X*-Ray Crystal Structure of Nonakis-(trimethylsilylmethyl)hydrido-μ-hexachloro-hexarhenium. New types of Rhenium(II) Alkyls

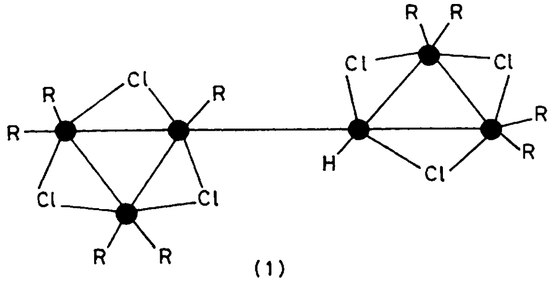
By KONSTANTINOS MERTIS, PETER G. EDWARDS, and GEOFFREY WILKINSON,*
(*Chemistry Department, Imperial College, London* SW7 2AY)

and K. M. ABDUL MALIK and MICHAEL B. HURSTHOUSE*
(*Chemistry Department, Queen Mary College, London* E1 4NS)

Summary The interaction of hydrogen with the *triangulo*-trirhenium complex, $Re_3(\mu\text{-}Cl)_3(CH_2SiMe_3)_6$, leads to new types of cluster alkyls: $Re_6(\mu\text{-}Cl)_6H(CH_2SiMe_3)_9$ (whose structure is determined by *X*-ray diffraction), $Re_6(\mu\text{-}Cl)_6H_6(CH_2SiMe_3)_6$, and $Re_6(\mu\text{-}Cl)_6(CH_2SiMe_3)_6$.

The *triangulo*-trirhenium(III) alkyl,[1] $Re_3(\mu\text{-}Cl)_3(CH_2SiMe_3)_6$, in tetrahydrofuran undergoes hydrogenolysis (20 °C, 2 atm) to give tetramethylsilane and green $Re_6(\mu\text{-}Cl)_6H(CH_2SiMe_3)_9$ (**1**) according to equation (1). The structure of (**1**) has been determined by *X*-ray diffraction.

$$2Re_3(\mu\text{-}Cl)_3(CH_2SiMe_3)_6 + 2H_2 = Re_6(\mu\text{-}Cl)_6H(CH_2SiMe_3)_9 + 3Me_4Si \qquad (1)$$



(1)

● = Re; R = Me_3SiCH_2

Crystal data: $C_{36}H_{100}Cl_6Re_6Si_9$, F.W. 2115·89, triclinic, a = 15·950(5), b = 16·351(6), c = 16·386(6) Å, α = 62·31(2), β = 94·23(5), γ = 99·77(3)°, U = 3729·1 Å^3, space group $P\bar{1}$, Z = 2, D_c = 1·88 g cm^{-3}, μ(Mo-K_α) = 101·8 cm^{-1}. The determination of the unit-cell parameters and intensity data collection were done at 270 K on a Nonius CAD4 diffractometer using Mo-K_α radiation (λ = 0·71069 Å). The six independent rhenium atoms were located from an *E*-map and other atoms from successive electron density syntheses. Anisotropic least-squares refinement of the non-hydrogen atoms has given R = 0·055 for 6796 reflections with $F_0 > 4\sigma(F_0)$. Hydrogen atoms have been ignored.†

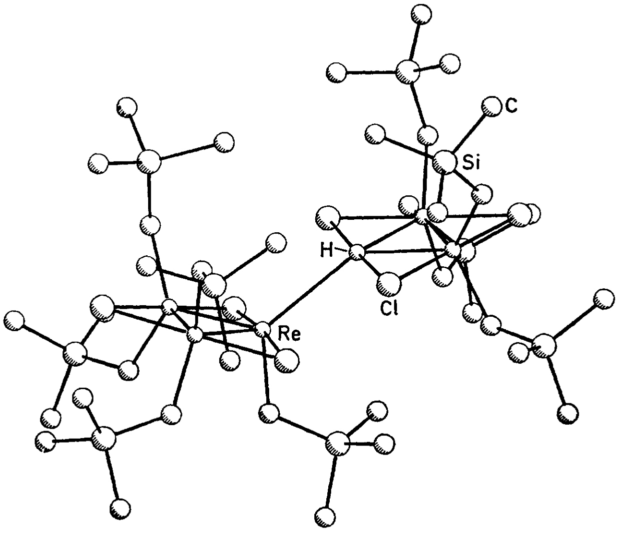


FIGURE. The molecular structure of $Re_6(\mu\text{-}Cl)_6H(CH_2SiMe_3)_9$

The structure (Figure) comprises two Re_3 triangular clusters linked by an Re–Re bond. This has a length of 2·993(1) Å compared with values of 2·390—2·420(1) Å in the triangle. The dihedral angle between the two Re_3 planes is 19·5°. Other bond distances and angles in the clusters are normal, although the Re–Re and Re–Cl distances do reflect, in a small way, chemical differences between the Re atoms. The compound probably arises *via* oxidative addition of hydrogen to one Re^{III} atom in the triangle, followed by intra- then inter-molecular reductive elmination of tetramethylsilane, the last step leading to Re–Re bond formation.

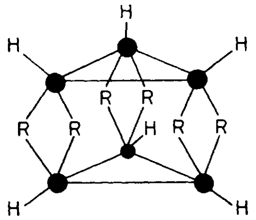
In benzene, hydrogenolysis gives a hexanuclear green cluster, for which we propose structure (**2**), by reaction (2). This compound, which has only CH_2SiMe_3 (δ 0·3) and

$$2Re_3(\mu\text{-}Cl)_3(CH_2SiMe_3)_6 + 6H_2 = \underset{(\mathbf{2})}{Re_6(\mu\text{-}Cl)_6(H)_6(CH_2SiMe_3)_6} + 6Me_4Si \qquad (2)$$

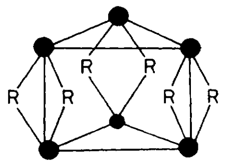
H (δ −5·85, ν 2030 cm^{-1}) ligands, slowly isomerises alk-1-enes under nitrogen and hydrogenates them under hydrogen. The catalytic reaction dies out owing to the formation of $Re_6(\mu\text{-}Cl)_6(CH_2SiMe_3)_6$, which is also obtained by reaction (3). Since removal of hydrogen constitutes reduction to

$$Re_6^{III}(\mu\text{-}Cl)_6H_6(CH_2SiMe_3)_6 + 3C_2F_4 = Re_6^{II}(\mu\text{-}Cl)_6(CH_2SiMe_3)_6 + 3C_2H_2F_4 \qquad (3)$$

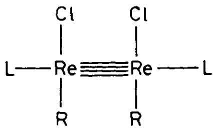
rhenium(II), we suggest that Re–Re bonds are formed between two Re_3 *triangulo* units as in structure (**3**).



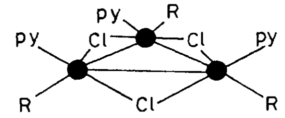
(2) (μ-Cl omitted)



(3) (μ-Cl omitted)



(4) L = CO, PPh_3



(5)

● = Re

Interaction of hydrogen with the tris adducts of $Re_3(\mu\text{-}Cl)_3(CH_2SiMe_3)_6$ with CO and PPh_3, by contrast, leads to the diamagnetic dinuclear rhenium(II) species which, according to analysis and spectroscopic data, have structures of type (**4**), but the pyridine adduct gives a

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

triangulo trirhenium complex whose e.s.r. spectrum is consistent with Re^{II} as in (**5**). Few *triangulo*-rhenium(II) complexes are known and these are polymeric amine halides.[2]

Other Re_6, Re_{12}, and more highly polymeric, but petroleum-soluble, alkyls have been obtained, *inter alia* from reaction of $Re_3(\mu\text{-}Cl)_3(CH_2SiMe_3)_6$ and other similar alkyls and aryls with hydrogen and with methyl-lithium.

Although other *d*-group, especially second and third row, elements should, in principle, give polynuclear cluster alkyls, attempts to synthesise them by alkylation of cluster halides and alkoxides of Nb, Ta, Mo, and W such as Mo_6Cl_{12} have been unsuccessful.

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[1] A. F. Masters, K. Mertis, J. F. Gibson, and G. Wilkinson, *Nouv. J. Chim.*, 1977, **1**, 389; P. G. Edwards, K. Mertis, G. Wilkinson, M. B. Hursthouse, and K. M. A. Malik, *J. Chem. Soc., Dalton Trans.*, 1980, 334.

[2] D. G. Tisley and R. A. Walton, *Inorg. Chem.*, 1973, **12**, 373.