

Cluster Alkyls of Rhenium

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Summary The trinuclear rhenium alkyls, $\text{Re}_3\text{R}_6\text{Cl}_3$ ($\text{R} = \text{Me}_3\text{SiCH}_2$ or Me_3CCH_2), have been made by interaction of trirhenium nonachloride, Re_3Cl_9 , with the appropriate Grignard reagent and the adducts $\text{Re}_3\text{R}_6\text{Cl}_3\text{L}_3$ [$\text{L} = \text{H}_2\text{O}$ or $\text{C}_5\text{H}_5\text{N}$ (py)] and the pyridine adduct, $\text{Re}_3\text{Me}_6\text{Cl}_3\text{py}_3$, of the unstable methyl compound have been characterised; interaction of rhenium pentachloride or the tetrahydrofuranate, $\text{ReCl}_4(\text{thf})_2$, with the Grignard reagents gives what may be a transient species ReR_4 , which gives Re_3R_{12} under argon, the first known dinitrogen peralkyl $\text{Re}_2\text{R}_8\text{N}_2$ under nitrogen, and ReOR_4 in the presence of oxygen.

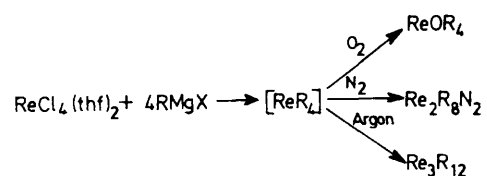
OLIGOMERISATION of co-ordinatively unsaturated transition metal units, MX_n , may account for the formation of dimers or clusters in which the metal atoms attain co-ordinative saturation and commonly the 18e configuration through formation of metal-metal bonds. An example is the formation of $(\text{Me}_3\text{SiCH}_2)_3\text{Mo} \equiv \text{Mo}(\text{CH}_2\text{SiMe}_3)_3$ in the reaction of MoCl_5 and $\text{Me}_3\text{SiCH}_2\text{MgCl}$, possibly *via* the reactive intermediate $(\text{Me}_3\text{SiCH}_2)_3\text{Mo}$.¹

We have synthesised novel alkyl clusters containing the Re_3 unit, either from Re_3Cl_9 or *via* cyclotrimerisation of a presumed highly reactive tetra-alkyl. The various compounds are satisfactorily characterised by elemental analysis, molecular weight determination, mass spectrometry, and by i.r., e.s.r., and n.m.r. spectra.

Interaction of Re_3Cl_9 in ether with RMgCl gives $\text{Re}_3\text{R}_6\text{Cl}_3$ [$\text{R} = \text{CH}_2\text{SiMe}_3$ (**1**), CH_2CMe_3 (**2**), or Me (**3**)]. Compounds (**1**) (blue) and (**2**) (green) are diamagnetic and air-sensitive and crystallise from light petroleum and sublime (110–130 °C at 10^{-3} mmHg). Compound (**3**) is unstable, decomposing above -15 °C, but its stable adduct with pyridine,

$\text{Re}_3\text{Me}_6\text{Cl}_3\text{py}_3$, can be isolated. The structure of these compounds is doubtless similar to the chloride² and based on the Re_3X_9 species in which an equilateral triangle of Re atoms is held together by strong metal-metal bonds and by three halide bridges. Each Re atom bears one alkyl group above and one below the Re_3Cl_3 plane. The third terminal position can be vacant, or occupied by a donor molecule like pyridine. Thus interaction of (**1**) or (**2**) with water or pyridine gives the corresponding adducts $\text{Re}_3\text{Cl}_3\text{R}_6\text{L}_3$, that are green, crystalline, air-stable, light petroleum soluble, volatile (150–180 °C at 10^{-3} mmHg), and diamagnetic.

Interaction of ReCl_5 or $\text{ReCl}_4(\text{thf})_2$ (thf = tetrahydrofuran) with $\text{Me}_2\text{SiCH}_2\text{MgX}$ in carefully deoxygenated solvents under nitrogen produces a crystalline, red-purple, paramagnetic and moderately air-stable complex which is soluble in hydrocarbons. The complex is $(\text{Me}_3\text{SiCH}_2)_8\text{Re}_2\text{N}_2$ according to analysis and molecular weight determination in benzene; the highest discernible ion with the correct isotopic distribution in the mass spectrum corresponds to m/e 532 ($\text{ReR}_4 = 535$). Although a formulation with a dinitrogen bridge seems certain, no bands involving nitrogen can be detected in the i.r. spectrum and decomposition occurs in the beam of a laser Raman spectrometer. A crystal structure determination is in progress. When some oxygen is present in the nitrogen, a mixture of $\text{Re}_2\text{R}_8\text{N}_2$ and ReOR_4^3 is obtained, but under argon, what presumably is the transient ReR_4 intermediate trimerizes to give the cluster alkyl $\text{Re}_3(\text{CH}_2\text{SiMe}_3)_{12}$. This red-brown compound is readily crystallised from light petroleum and is volatile (135 °C at 10^{-3} mmHg). Similar compounds are formed with methyl and neopentyl groups. We thus appear to have the reactions shown in the Scheme. E.s.r. studies of frozen solutions show that the first para-



SCHEME

magnetic mononuclear intermediate is the same under either argon or nitrogen.

We thank the S.R.C. for support.

(Received, 5th August 1976; Com. 912.)

¹ W. Mowat, A. Shortland, G. Yagupsky, N. J. Hill, M. Yagupsky, and G. Wilkinson, *J.C.S. Dalton*, 1972, 533.

² F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' 2nd edn., Wiley, New York, 1972, p. 978.

³ K. Mertis, D. H. Williamson, and G. Wilkinson, *J.C.S. Dalton*, 1975, 607.