A new polynuclear carbonyl of rhenium

Finely divided rhenium heptasulphide, intimately mixed with copper powder, has been carbonylated to yield a mixture of decacarbonyldirhenium and a new polynuclear tetracarbonyl. A typical experiment may be summarised as follows:

$$\begin{array}{lllcll} Re_2S_7 + & Cu & + CO & \xrightarrow[7\ h]{200^\circ} & Re_2(CO)_{10} + & [Re(CO)_4]_n \\ (4.0\ g) & (12.0\ g) & (85\ atm) & & (0.02\ g) & (0.3\ g) \end{array}$$

A pentane extraction separated the compound $Re_2(CO)_{10}$ and sublimation of the residue (100°/0.1 mm) yielded the pure, white, crystalline tetracarbonyl, which is virtually insoluble in organic solvents, but is sufficiently soluble in chloroform for its infrared spectrum in the C–O stretching region to be obtained [2055 (s), 1995 (m) cm^{-1}]. This spectrum indicates the absence of bridging carbonyl groups. Magnetic measurements show no evidence for unpaired electrons (μ_{eff} = 0.6 B.M. independent of temperature), but unfortunately, a molecular weight determination was not possible. The simplest structure, which must consist of an even number of $Re(CO)_4$ units, would be a tetramer, in which the rhenium atoms are located at the corners of a tetrahedron. We have little evidence, however, in favour of the tetramer, although the volatility of the compound suggests the minimum degree of polymerisation. The simple infrared spectrum implies that the local symmetry of each $Re(CO)_4$ unit is identical. Kaesz *et al.*[1] have described recently a different polymeric carbonyl of rhenium, which they now formulate as a trimeric hydride. We see no reason to formulate our compound as a hydride (no analytical evidence for hydrogen has been found, but this is a poor criterion); it is insufficiently soluble for NMR study.

A suspension of the carbonyl in cyclohexane reacts with the tertiary phosphines Ph_3P and $(PhO)_3P$ under ultraviolet irradiation to yield complexes of the empirical formula $Re(CO)_3L_2$. Magnetic measurements in the solid state indicate that the triphenylphosphine complex is paramagnetic (μ_{eff} = 1.1 B.M.) and that the triphenylphosphite complex is diamagnetic. These complexes may thus be formulated as a monomer and a dimer respectively. Both are monomeric in benzene, however, and dissociation of the complex $\{Re(CO)_3[(PhO)_3P]_2\}_2$ has been checked by measuring its magnetic moment in this solvent. It was found to be paramagnetic with μ_{eff} = 1.0 B.M. The complex $[Re(CO)_3(Ph_3P)_2]$ has been formulated previously as a dimer[2].

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