A New Cluster Ruthenium Carbonyl

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UP to now $Ru(CO)_5$ and $[Ru(CO)_4]_3$ were the only known unsubstituted ruthenium carbonyls. The ruthenium carbonyl hydride $H_3Ru_4(CO)_{12}$,[1] recently detected by mass spectrometry, suggested the existence of cluster ruthenium carbonyls of higher complexity.

We now report that a new cluster ruthenium carbonyl may be obtained by heating $[Ru(CO)_4]_3$ in benzene or cyclohexane solution at 150° under nitrogen. A deep red compound is thus formed which crystallizes in needles from cyclohexane, and analyzes as $[Ru(CO)_3]_x$. The compound is diamagnetic, and on heating under vacuum decomposes above 235°; heated in benzene solution at 150°, under 100 atm. CO pressure, it may be reconverted into $[Ru(CO)_4]_3$.

According to differential vapour-pressure measurements (Mechrolab osmometer, dichloroethane solution, *c* 2·21 g./l.) the molecular weight is 1050, not very far from the value corresponding to $Ru_6(CO)_{18}$ (*M* calc. for $Ru_6C_{18}O_{18}$: 1110·61); an *X*-ray investigation is in progress.

The i.r. spectrum of a cyclohexane solution of this compound in the 2200—1600 cm.$^{-1}$ region shows two strong bands at 2066 and 2047 cm.$^{-1}$ and two very weak bands at 2002 and 1850 cm.$^{-1}$.

The extremely low relative intensity of the absorption in the 1800 cm.$^{-1}$ region strongly suggest that the 1850 cm.$^{-1}$ band is not fundamental, and hence that there are no bridging carbon monoxide groups of the type previously suggested for $Co_2(CO)_8$,[2] $Co_4(CO)_{12}$,[3] $Rh_4(CO)_{12}$,[3] and $Rh_6(CO)_{16}$.[3,4]

On the other hand, the very low intensity of the bands appearing at 1858 and 1866 cm.$^{-1}$ in the i.r. spectrum of $Fe_3(CO)_{12}$,[5] for which a structure having at least two bridging CO groups has recently been suggested,[6] leads us to consider the question as still open.

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