Relative Reactivity of Triruthenium and Triosmium Dodecacarbonyls

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RECENT studies on the halogenation of triruthenium and triosmium dodecacarbonyls have revealed significant differences in the reactivity of these clusters which may in part reflect the difference in the stability of the metal–metal bonds. We reported the preparation of the trimeric ruthenium carbonyl derivatives $Ru_3(CO)_{12}X_6$, where X = Cl, Br, or I.[1] We find that these compounds are produced in a two-stage process involving (i) the cleavage of the $Ru_3(CO)_{12}$ cluster to give the monomeric *cis*-$Ru(CO)_4X_2$ derivatives followed by (ii) the re-polymerisation of the mononuclear species to give $Ru_3(CO)_{12}X_6$. This latter reaction is unusual in that polymerisations observed in related systems, *e.g.* $2Mn(CO)_5X \rightarrow Mn_2(CO)_8X_2$ involve the loss of CO-groups.[2] The overall reaction has been followed by observing the change in the CO-stretching region in the i.r. spectrum. By this method *cis*-$Ru(CO)_4X_2$ was clearly identified as an intermediate product. Furthermore, gentle heat on *cis*-$Ru(CO)_4X_2$, prepared by an alternative method, led to the formation of $Ru_3(CO)_{12}X_6$.

In contrast, the reaction of $Os_3(CO)_{12}$ with halogens (X_2) gives the linear compounds $Os_3(CO)_{12}X_2$. This difference in behaviour reflects either the increase in stability of the metal–metal bond towards oxidation on descending a transition-metal triad or may be due to a purely kinetic effect, in which case a complex $Ru_3(CO)_{12}X_2$

may be visualised as an intermediate in the production of *cis*-$Ru(CO)_4X_2$. This may reflect the general difference in lability of second and third row transition metals.[3]

The compounds $Os_3(CO)_{12}X_2$ have been fully characterised by analytical and mass-spectral data. Application of the effective atomic-number rule suggests a linear arrangement of metals for these compounds. In the i.r. spectra three strong bonds are observed in the CO-stretching region consistent with a molecular symmetry D_{4d}. Raman data is also consistent with this symmetry.[4] In the mass spectra of the $Os_3(CO)_{12}X_2$ molecules parent molecular-ions $[Os_3(CO)_{12}X_2]^+$ are observed in all cases together with ions of the type $[Os_3(CO)_lX_2]^+$, (l = 0—11), $[Os_2(CO)_mX]^+$ [m = 0—8], and $[Os(CO)_nX]^+$ (n = 0—4). This pattern contrasts with that observed for cyclic systems.[5,6]

We have found that triruthenium dodecacarbonyl readily polymerises to give tetranuclear hydrido-carbonyl compounds,[6] whereas triosmium dodecacarbonyl yields mainly trinuclear derivatives (although tetranuclear derivatives are also produced in very small yields).[6] We report the ruthenium derivatives $HRu_3(CO)_{10}(SR)$ (R = Et or Bu) which are related to the trinuclear osmium compounds $HOs_3(CO)_{10}(OR)$ (R = H or Me).[6] These were prepared together with other thiol derivatives from the reaction of $Ru_3(CO)_{12}$ with the appropriate thiol. The formulation of these compounds is based on analytical and mass-spectral data. The presence of the hydrido-ligand was confirmed by n.m.r. measurements (Ru–H at τ 25·4 for Et and Bu derivatives). The i.r. spectra of these compounds ν(CO) closely resemble that of $HOs_3(CO)_{10}(OMe)$.[6]

This work emphasizes important differences in the chemistry of $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$. We are investigating the chemistry of the mixed clusters $RuOs_2(CO)_{12}$ and $Ru_2Os(CO)_{12}$. These were prepared by heating $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ together in xylene under carbon monoxide pressure (90 hr.) at 175°, and were identified by mass-spectral data, the ions $[Ru_2Os(CO)_{12}]^+$ and $[OsRu_2(CO)_{12}]^+$ being readily identified by their characteristic isotope patterns.

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