Some New Hydrido-carbonyl Complexes of Osmium

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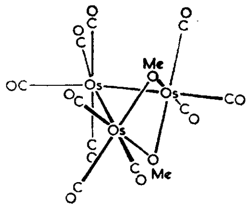
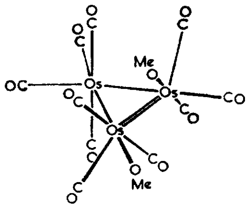
BRADFORD and NYHOLM[1] have shown that tri-osmium dodecacarbonyl $Os_3(CO)_{12}$ may be obtained in good yields by the reaction of osmium tetroxide in xylene with carbon monoxide under conditions of high pressure (128 atm.) and moderate temperature (175°). We have investigated the reaction of osmium tetroxide in methyl alcohol with carbon monoxide under a variety of conditions of pressures and temperatures. By this method we have been able to isolate $Os_3(CO)_{12}$ in yields of up to 85%, furthermore we have also isolated the trinuclear derivatives $HOs_2(CO)_{10}(OH)$, $HOs_3(CO)_{10}(OMe)$, and $Os_3(CO)_{10}(OMe)_2$ which form a family of closely related compounds. Good analytical data has been obtained for all the compounds and molecular weights have been determined by the mass-spectrometric method when parent molecular-ions were observed in all cases. The infrared spectra of the compounds in the CO stretching region are closely related and complicated indicating that the molecules are of low symmetry. No bands due to bridging CO groups were observed. On the basis of the effective atomic number rule we may formulate the compounds as having a cyclic structure related to that found for the parent carbonyl[2] and in agreement with this suggestion over 90% of all ions produced by electron impact in the mass spectrometer are trinuclear.[3] At least two structures† may be considered for these compounds, one involving bridging methoxy-groups with two metal–metal bonds (a) and the other involving terminal methoxy-groups with an additional metal–metal double bond (b). In both cases the effective atomic number rule is obeyed for the osmium atoms. For the hydrido-hydroxy- and dihydrido-compounds structure (b) appears to be the more attractive. Preliminary measurements of the Raman spectra[4a] of these metal clusters indicate that for the dimethoxy-compound the presence of three metal–metal vibrations[4b] which may be readily correlated with structure (b).



(a)



(b)

Triruthenium dodecacarbonyl, $Ru_3(CO)_{12}$, has been shown to react with base or sodium amalgam to produce uncharacterised anionic species which on acidification yield the tetranuclear hydrido-compounds α-$H_4Ru_4(CO)_{12}$,[5] β-$H_4Ru_4(CO)_{12}$[5,6] and $H_2Ru_4(CO)_{13}$.[6] All of these compounds are thought to have structures involving a tetrahedral distribution of four ruthenium atoms. Triosmium dodecacarbonyl has now been shown to behave similarly and the tetranuclear osmium derivatives $H_4Os_4(CO)_{12}$[6] and $H_2Os_4(CO)_{13}$ have been isolated together with the trinuclear hydrido-compounds $H_2Os_3(CO)_{10}$ and $HOs_3(CO)_{10}(OMe)$. The trinuclear dihydrido-compound appears to belong to the series of osmium derivatives discussed above.

For iron, the only neutral trinuclear hydridocarbonyl known is $H_2Fe_3(CO)_{11}$[7] which appears to contain two electrons in excess of the osmium compounds discussed here. In systems of this type it is very difficult to assess the hydrogen content of the compound accurately and we have checked the hydrogen content by both n.m.r. and mass-spectroscopic methods. Thus in the n.m.r. spectra of $H_2Os_3(CO)_{10}$ and $Os_3(CO)_{10}(OMe)_2$ single signals attributable respectively to the hydrido- and methoxy- hydrogens have been observed. For corresponding solutions of CHI_3, $H_2Os_3(CO)_{10}$ and $Os_3(CO)_{10}(OMe)_2$ the intensity of the hydrogen signals were in the ratio 1:2:6. In the mass spectrum no ions corresponding to the compound $H_4Os_3(CO)_{10}$ were observed. It would thus appear that the osmium derivative is not related to this trinuclear carbonyl hydride of iron and this may be associated with the higher affinity for metal bonding shown by the third-row transition elements.

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† A single-crystal *X*-ray structure determination is being carried out by Professor R. Mason, Dept. of Chemistry, University of Sheffield.

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[2] E. R. Corey and L. F. Dahl, *Inorg. Chem.*, 1962, **1**, 531.
[3] B. F. G. Johnson, J. Lewis, I. H. Williams, and J. M. Wilson, *J. Chem. Soc.* (*A*), 1967, 341.
[4] (a) M. J. Ware, private communication; (b) C. D. Quicksall and T. G. Spiro, *Chem. Comm.*, 1967, 839.
[5] The hydrido-compound $H_4Ru_4(CO)_{12}$ first reported by J. W. S. Jamieson, J. V. Kingston, and B. Wilkinson, *Chem. Comm.*, 1966, 569 is designated α-$H_4Ru_4(CO)_{12}$: the compound $H_4Ru_4(CO_{12}$ reported by B. F. G. Johnson, R. D. Johnston, J. Lewis, and B. M. Robinson (ref. 6) is designated β-$H_4Ru_4(CO)_{12}$.
[6] B. F. G. Johnson, R. D. Johnston, J. Lewis, and B. H. Robinson, *Chem. Comm.*, 1966, 851.
[7] M. L. Green and G. Wilkinson, unpublished observations.