Synthesis and Carbon-13 Nuclear Magnetic Resonance Studies of the Hexanuclear Osmium Clusters $[H_2Os_6(CO)_{18}]$, $[HOs_6(CO)_{18}]^-$, and $[Os_6(CO)_{18}]^{2-}$ †

By Colin R. Eady, Brian F. G. Johnson, and Jack Lewis*
(*University Chemical Laboratory, Lensfield Road, Cambridge* CB2 1EW)

Summary The bicapped tetrahedral osmium carbonyl, $[Os_6(CO)_{18}]$ undergoes a reversible structural transformation when treated with reducing agents to give $[Os_6(CO)_{18}]^{2-}$, the spectroscopic properties of which are consistent with a regular octahedral O_h osmium geometry; the compounds $[H_2Os_6(CO)_{18}]$ and $[HOs_6(CO)_{18}]^-$ are produced upon acidification of this dianion.

Implicit in Wade's Theory[1] is the view that when transition-metal clusters gain or lose two electrons the structure of the cluster unit (M_n) will change shape in a systematic and predetermined manner. The inherent interest lies in the possible cyclic, catalytic nature of these structural transformations particularly since there is evidence to suggest that small molecules, such as CO, C_2H_4, or H_2, on reaction with a metal can induce structural change within this metal surface.[2] Metal carbonyls have often been postulated as models for catalysis but almost all those known, under two-electron reduction, do not undergo simple rearrangement of the metal unit but lead either to breakdown of the cluster or loss of a carbonyl group and replacement by two electrons.

We report here our studies of $[Os_6(CO)_{18}]$[3] which has been shown readily to undergo, under mild conditions, reversible reduction to produce $[Os_6(CO)_{18}]^{2-}$. In so doing the Os_6 unit changes from a bicapped tetrahedral geometry (C_{2v}) to the more familiar regular octahedral (O_h) arrangement. This transformation is in accordance with the predictions of Wade.[1]

Treatment of $[Os_6(CO)_{18}]$ with activated zinc, sodium-mercury amalgam or tetra-n-butylammonium iodide provides an efficient route to $[Os_6(CO)_{18}]^{2-}$. The dianionic cluster was isolated as the $[Me_4N]^+$, $[(Bu^t)_4N]^+$ and $[(Ph_3P)_2N]^+$ salts (orange-red crystals) and characterized by microanalysis, conductivity, i.r., and n.m.r. spectroscopy. The i.r. spectrum (ν_{CO}) exhibits just one broad band[3c] whilst ^{13}C n.m.r. (^{13}CO, *ca.* 40%) reveals just one resonance which remains unaltered on cooling from 0 °C [δ (CD_2Cl_2) 195·0 p.p.m., 25·2MHz; relative to Me_4Si; δ (Me_4Si) = δ(CH_2Cl_2) −54·2 p.p.m.] to −113 °C. These data are consistent with a regular octahedral (O_h) arrangement of osmium atoms with three terminal carbonyl groups bonded to each metal atom (Figure).

Although microanalysis is consistent with a formulation of $[Os_6(CO)_{18}]^{2-}$ this technique cannnot accurately determine the number of carbonyl groups and/or the presence of *e.g.* carbides. However, the presence of six osmium atoms and eighteen carbonyl groups is confirmed by our observation that $[Os_6(CO)_{18}]^{2-}$, upon treatment with iodine is converted into $[Os_6(CO)_{18}]$ which itself reacts further with iodine over a period of three hours. Thus we have effected a reversible structural transformation [equation (1)].

$$[Os_6(CO)_{18}] \underset{I_2}{\overset{I^-}{\rightleftharpoons}} [Os_6(CO)_{18}]^{2-} \qquad (1)$$

Treatment of $[Os_6(CO)_{18}]$ with other common nucleophilic reagents also leads to $[Os_6(CO)_{18}]^{2-}$ but yields are considerably reduced as a result of the formation of smaller clusters. However, reaction of $[Os_6(CO)_{18}]$ with sodium borohydride (1 mole) in tetrahydrofuran leads smoothly to the formation of $[HOs_6(CO)_{18}]^-$. This ion has been isolated as the $[(Bu^t)_4N]^+$ and $[(Ph_3P)_2N]^+$ salts (deep red crystals) and characterized by i.r. and n.m.r. spectroscopy together with microanalysis and conductivity measurements. Whereas the ^1H n.m.r. spectrum shows a sharp singlet [τ (CD_2Cl_2, + 40 °C) 21·26], variable temperature ^{13}C (*ca.* 40% ^{13}CO) n.m.r. studies reveal a singlet at 0°C [δ (CD_2Cl_2) 187·6 p.p.m.] which broadens at −85 °C and at −112 °C splits into two sharp singlets of equal intensity [δ (CD_2Cl_2–$CHFCl_2$) 191·5, 184·6 p.p.m.]. These data are consistent with a face- rather than edge-bridging hydride (C_{3v}) which above −85 °C moves over the eight faces of the octahedron thus leading to averaging of the eighteen carbonyl groups.‡ Below −85 °C, the hydride becomes localized on one face but even at −112 °C the expected carbonyl orientations associated with the hydride face are not frozen out. The ^{13}C n.m.r. spectrum of an edge-bridging hydride (C_{2v}) would be expected to give rise to four signals of intensity 2:2:1:1. The presence at −85 °C of an edge-bridging hydride scrambling over three edges of a triangular face can be discounted because such a hydride has an equal probability of scrambling over all the edges of the octahedron. As far as we can judge, this is the first example in which direct evidence is provided for the existence of a face-bridging hydride (Figure).

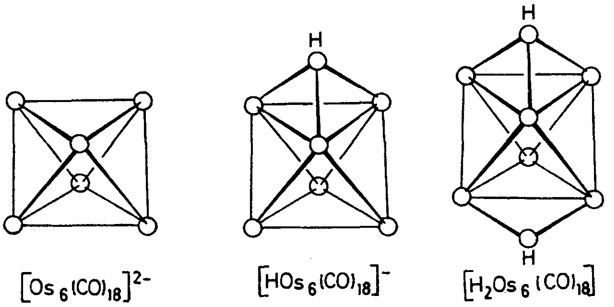

Figure. Proposed structures for $[Os_6(CO)_{18}]^{2-}$, $[HOs_6(CO)_{18}]^-$, and $[H_2Os_6(CO)_{18}]$ (three terminal carbonyl groups per osmium atom).

Acidification of anions to form their neutral analogues is a notoriously unpredictable and inefficient process.[4] We

---

† No reprints available.

‡ Alternatively the face-bridged H could remain fixed to three osmium atoms and the eighteen CO groups scramble over the Os_6 unit. This is regarded as less likely since the activation energies for CO scrambling in Os systems are greater than those for H-migration.

believe that this is the result of the acid nature of the neutral clusters [*e.g.* equation (2)]. Thus $[H_2Os_6(CO)_{18}]$,

$$[H_2Os_6(CO)_{18}] \rightleftharpoons [HOs_6(CO)_{18}]^- + H^+ \rightleftharpoons [Os_6(CO)_{18}]^{2-} + 2H^+ \quad (2)$$

which was isolated as a minor product from the pyrolysis of $[Os_3(CO)_{12}]$ with water,[5] does not dissociate in cyclohexane or dichloromethane whereas in basic solvents, *e.g.* tetrahydrofuran, it behaves as an acid with the resultant formation of $[HOs_6(CO)_{18}]^-$. Acidification of $[Os_6(CO)_{18}]^{2-}$ with excess H_2SO_4 in *e.g.* tetrahydrofuran or methanol, gave mainly $[HOs_6(CO)_{18}]^-$ with only trace amounts of $[H_2Os_6(CO)_{18}]$. A conventional technique for displacement of the equilibrium either to the left or right hand side is by precipitation of the necessary product. We have found that by stirring $[Os_6(CO)_{18}]^{2-}$ in acetonitrile with excess sulphuric acid, $[H_2Os_6(CO)_{18}]$ is quantitatively precipitated. The composition of this neutral cluster was confirmed by analysis, mass, n.m.r., and i.r. (ν_{CO}) spectroscopy. The analogous $[H_2Ru_6(CO)_{18}]$,[6] which, on the basis of single crystal *X*-ray diffraction studies, is thought to contain two symmetrically placed face-bridging hydrides, has an i.r. spectrum (ν_{CO}, CH_2Cl_2) related to that of $[H_2Os_6(CO)_{18}]$. However, the ^1H n.m.r. spectrum of $[H_2Os_6(CO)_{18}]$ reveals at +40 °C a doublet of doublets [τ (CD_2Cl_2) 22·15/22·17, 31·69/31·71, 80 MHz, *J* 1·7 Hz] which remains unaltered on warming to +100 °C (C_7D_8) or cooling to −85 °C (CD_2Cl_2). The proposed structure of $[H_2Os_6(CO)_{18}]$ contrasts with that reported for $[H_2Ru_6(CO)_{18}]$§ and we are presently investigating the ^1H n.m.r. spectrum of this ruthenium cluster. Single crystal *X*-ray diffraction studies are in progress on the three clusters shown in the Figure.

We thank Johnson Matthey and Co. Ltd. for their loan of OsO_4 and Trinity Hall (Cambridge) and the Salters' Company for Fellowships (to C.R.E.).

(*Received, 29th December* 1975; *Com.* 1427.)

---

§ *Added in proof.* Preliminary *X*-ray studies indicate that, unlike Ru_6 in $[H_2Ru_6(CO)_{18}]$, the Os_6 unit does not possess D_{3d} symmetry.

[1] K. Wade, *Chemistry in Britain*, 1975, **11**, 177.

[2] *e.g.* R. F. Baddour, M. Modell, and R. L. Goldsmith, *J. Phys. Chem.*, 1970, **74**, 1787.

[3] C. R. Eady, B. F. G. Johnson, and J. Lewis, (a) *J. Organometallic Chem.*, 1972, **37**, C39; (b) *J.C.S. Dalton*, 1975, 2606; (c) C. R. Eady, W. G. Jackson, B. F. G. Johnson, J. Lewis, and T. W. Matheson, *J.C.S. Chem. Comm.*, 1975, 958.

[4] R. P. Stewart, U. Anders, and W. A. G. Graham, *J. Organometallic Chem.*, 1971, **32**, C49; B. F. G. Johnson, R. D. Johnston, J. Lewis, B. H. Robinson, and G. Wilkinson, *J. Chem. Soc. (A)*, 1968, 2856; J. Knight and M. J. Mays, *J.C.S. Dalton*, 1972, 1022.

[5] C. R. Eady, B. F. G. Johnson, and J. Lewis, *J. Organometallic Chem.*, 1973, **57**, C84.

[6] M. R. Churchill and J. Wormald, *J. Amer. Chem. Soc.*, 1971, **93**, 5670.