Synthesis in Solution of High Nuclearity Osmium Cluster Species: *X*-Ray Analysis of $[HOs_8(CO)_{22}]^-$

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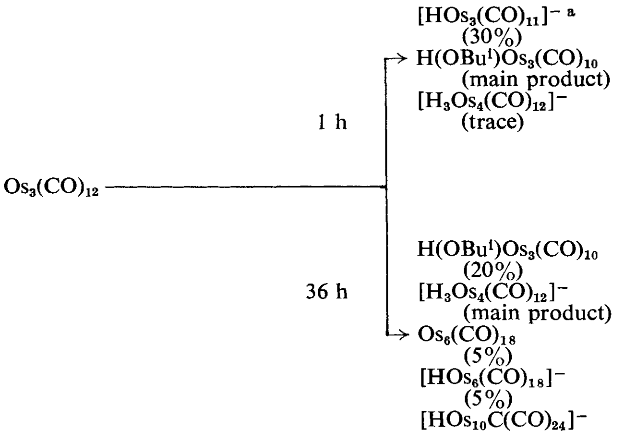
Reaction of $Os_3(CO)_{12}$ with KOH in isobutanol has given a range of high nuclearity cluster species based on up to ten osmium atoms; in the absence of base a new cluster hydrido-monoanion $[HOs_8(CO)_{22}]^-$ is produced which, on the basis of an *X*-ray analysis, has been shown to possess an unusual metal core geometry that cannot be explained by conventional skeletal electron counting procedures.

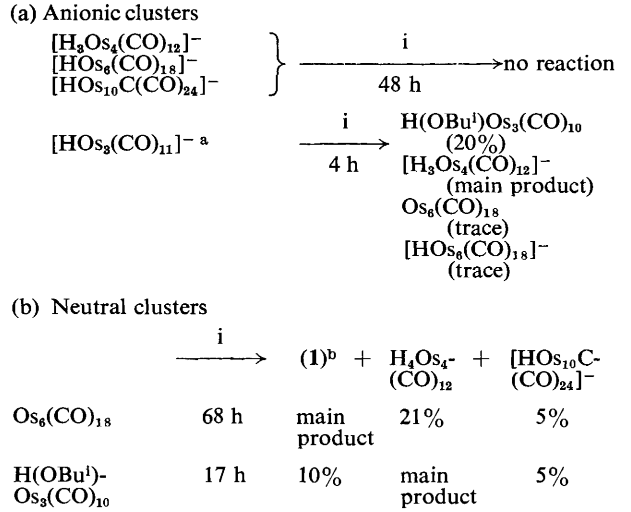
Until now the only route to the higher clusters of osmium has been *via* the pyrolysis of $Os_3(CO)_{12}$ and its derivatives.[1] However, the reaction conditions employed and the complex mixture of products obtained make an understanding of the mechanisms by which cluster growth occurs very difficult. We report that reactions carried out in alcohols of high boiling point give not only a range of known cluster species with up to ten osmium atoms, but also the new hydrido-anion $[HOs_8(CO)_{22}]^-$ (**1**) which has an unexpected metal core geometry which cannot be explained by conventional skeletal electron-counting procedures.

The recently reported[2] synthesis of $[Rh_{22}(CO)_{37}]^{4-}$ by the reaction of $Rh_4(CO)_{12}$ with NaOH in isopropanol prompted us to reinvestigate the reaction of $Os_3(CO)_{12}$ with base which,



[a] Owing to decomposition on t.l.c. plates this anion was separated by fractional crystallisation as its $[PPN]^+$ salt.

Scheme 1. *Reagents:* i, KOH–isobutanol, $\{[Os] : [OH^-] = 5:1\}$. Reactions of $Os_3(CO)_{12}$ on heating in KOH–isobutanol under N_2 reflux. With increasing time the relative concentrations of products became fairly constant; typical approximate distributions are shown. Separation was by t.l.c. (1 : 1 acetone–hexane eluant), characterisation was by i.r. and mass spectroscopy with the anions as their $[(PPh_3)_2N]^+$ (PPN) salts.



[a] Earlier observations showed that pyrolysis of $[HOs_3(CO)_{11}]^-$ in a range of donor solvents (*e.g.* tetrahydrofuran, diglyme, or dioxan) gives a similar mixture of species with up to six metal atoms (P. A. Dawson, personal communication). [b] ν(CO) $[PPN]^+$ salt (CH_2Cl_2) 2092w, 2065ssh, 2059vs, 2043vs, 2015s, 1997m, 1980w, and 1966w cm^{-1}.

Scheme 2. *Reagent:* i, isobutanol. The reactions of the individual clusters under N_2 reflux in isobutanol.

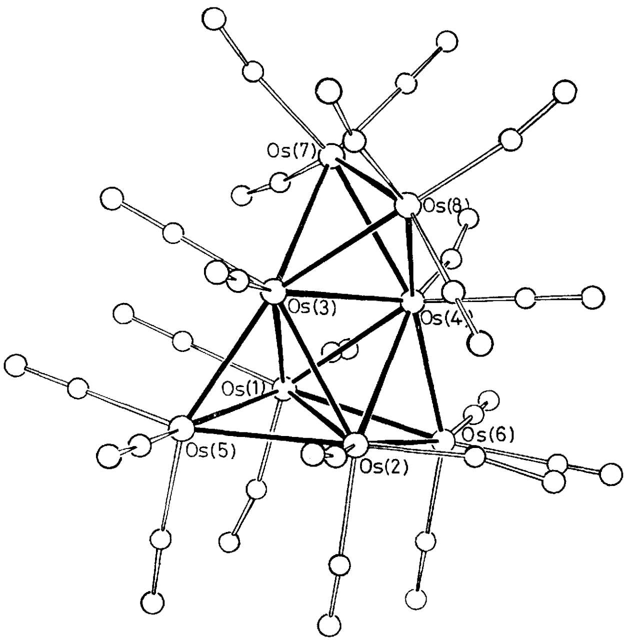


Figure 1. The structure of the anion $[HOs_8(CO)_{22}]^-$ (**1**). Os–Os bond lengths (those for the $[Ph_3PMe]^+$ salt are given first and those for the $[PPN]^+$ salt are in parentheses): (1)–(2) 2.740, (2.758); (1)–(3) 2.842, (2.823); (1)–(4) 2.829, (2.825); (1)–(5) 2.866, (2.842); (1)–(6) 2.854, (2.850); (2)–(3) 2.837, (2.842); (2)–(4) 2.839, (2.840); (2)–(5) 2.861, (2.845); (2)–(6) 2.868, (2.872); (3)–(4) 2.600, (2.606); (3)–(5) 2.723, (2.702); (3)–(7) 2.783, (2.801); (3)–(8) 2.805, (2.805); (4)–(6) 2.710, (2.711); (4)–(7) 2.803, (2.735); (4)–(8) 2.734, (2.800); (7)–(8) 2.848, (2.842). Maximum e.s.d.'s are 0.001 Å for the $[Ph_3PMe]^+$ salt and 0.004 Å for the $[PPN]^+$ salt.

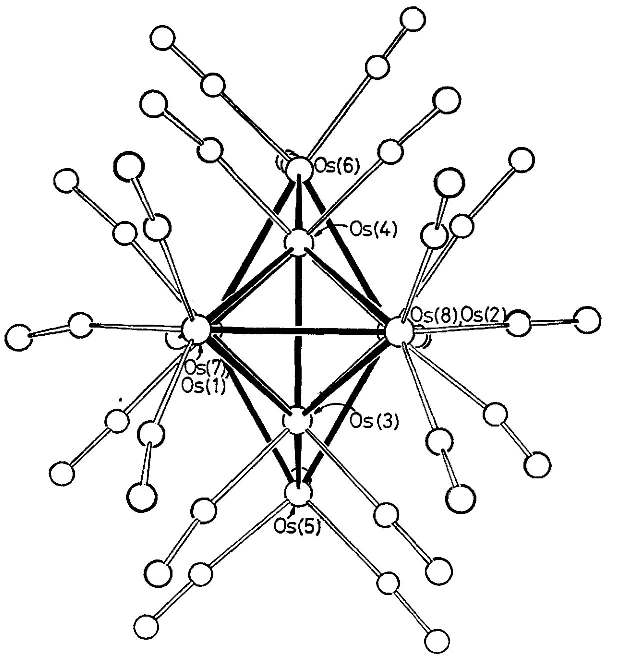


Figure 2. The anion $[HOs_8(CO)_{22}]^-$ viewed down the virtual C_2 axis. The H-ligand bridges Os(7)–Os(8).

under certain conditions had been shown to yield tetranuclear clusters as the largest species produced.[3] By using more forcing conditions we have now shown that $Os_3(CO)_{12}$, when heated with KOH in isobutanol under nitrogen reflux, on prolonged reaction gives a range of known higher nuclearity clusters containing from four to ten osmium atoms (Scheme 1).

An investigation of the stability of the individual clusters on heating under reflux in isobutanol, in the absence of base, was undertaken as a first step in the study of the building-up sequence (Scheme 2). The new monoanion (**1**) was separated as the major product of the reaction of $Os_6(CO)_{18}$ as its $[(Ph_3P)_2N]^+$ (PPN) or $[Ph_3MeP]^+$ salt.

The variable temperature ^1H n.m.r. spectra of the $[PPN]^+$ salt of (**1**) in CD_2Cl_2 revealed signals at 20.79, 26.47, and 30.42 τ whose relative intensities were consistent with a number of mono-hydrido isomers being present in solution. *X*-Ray analysis† of both this and the $[Ph_3PMe]^+$ salt (Figure 1) shows the anion (**1**) to have twenty-two terminal carbonyl ligands and a new type of metal core geometry. This may be derived from the bicapped tetrahedral metal arrangement[4] of $Os_6(CO)_{18}$ by the addition of two osmium atoms, Os(7) and Os(8), to form an extra tetrahedron linked to the original Os_6 core through a common edge, Os(3)–Os(4).

The mass spectrum of (**1**)‡ showed a parent peak at *m/e* 2154 (^{192}Os) followed by the stepwise loss of 22 CO ligands and this, together with the *X*-ray and variable temperature ^1H n.m.r. evidence, is consistent with the formulation of (**1**) as $[HOs_8(CO)_{22}]^-$. Hydrogen ligands are well known to produce a marked distortion of the close packed CO ligands in cluster species,[5] and, in the structure of (**1**), the carbonyl ligands bonded to Os(7) and Os(8) are pushed back from the Os(7)–Os(8) bond (Figure 2) which is consistent with a μ_2-H ligand being located in this position.

The cluster anion $[HOs_8(CO)_{22}]^-$ (**1**) has the same number of valence electrons as the dianion $[Os_8(CO)_{22}]^{2-}$ which has the bi-capped octahedral metal arrangement[6] predicted by skeletal electron counting procedures.[4,7] The presence of hydrogen ligands has been shown to produce unusual metal rearrangements in osmium cluster compounds; for example $H_2Os_6(CO)_{18}$ and $H_2Os_5(CO)_{16}$ were shown to have unexpected capped square-pyramidal[8] and edge-bridged tetrahedral[9] metal arrangements, respectively. Until now it has always proved possible to rationalise such geometries by extended skeletal electron counting procedures;[8,10] the anion (**1**) is thus the first example of a high nuclearity osmium cluster, with only CO and H ligands whose structure may not be readily explained in this way. Interestingly, if localised electron pairs are assigned to all the metal–metal bonds in (**1**) a mean of 18 electrons *per* Os atom may be allocated so that overall the cluster appears to obey the effective atomic number rule. However, there is evidence that two very short Os–Os bonds (2.601 and 2.606 Å) in $HOs_5(CO)_{13}(PhNC_6H_4N)$ have multiple bond character,[11] so that it is probable that the Os(3)–Os(4) bond in (**1**), which is the shortest so far reported {2.600(1) Å in the $[Ph_3PMe]^+$ salt}, should be regarded as a double bond.

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† *Crystal data:* $[C_{19}H_{18}P][C_{22}HO_{22}Os_8]$, triclinic, space group $P\bar{1}$, $a = 16.775(3)$, $b = 13.509(2)$, $c = 11.267(2)$ Å, $\alpha = 89.88$, $\beta = 103.97$, $\gamma = 96.99°$, $Z = 2$, $I/\sigma(I) > 3.0$, present *R*-value 0.0362, for 5615 absorption-corrected reflections. $[C_{36}H_{30}NP_2][C_{22}HO_{22}Os_8]$, monoclinic, space group $C2/c$, $a = 32.670$, $b = 22.918$, $c = 18.125$ Å, $\beta = 90.09°$, $Z = 8$, $I/\sigma(I) > 3.0$, present *R*-value = 0.0967, for 3529 absorption-corrected reflections. Data were collected using Mo-K_α radiation with a Philips PW1100 diffractometer in the θ-ranges 3—25° for the $[Ph_3PMe]^+$ salt and 3—20° for the $[PPN]^+$ salt which showed 20% decomposition during data collection. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

‡ Disproportion of anions to neutral species on the mass spectrometric probe has been noted before, for example good spectra may be obtained from the anion $[HOs_5(CO)_{15}]^-$.

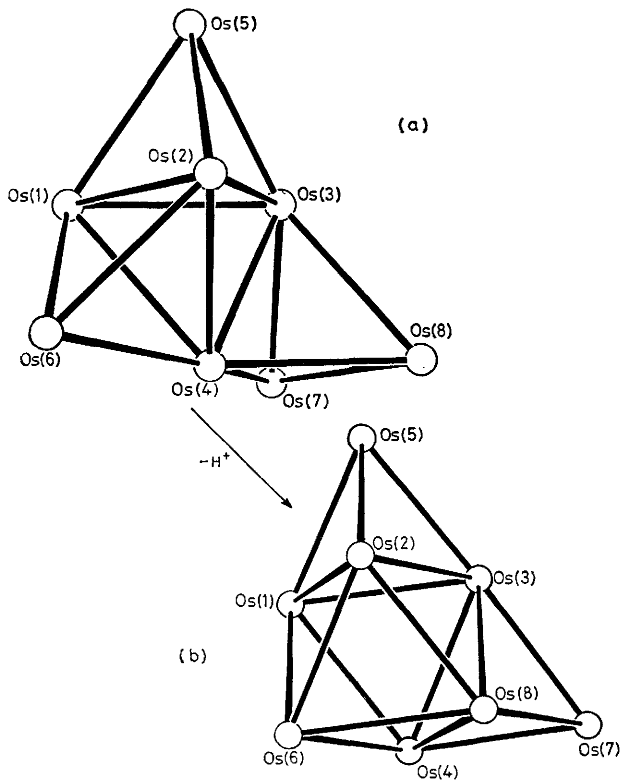

Figure 3. The rearrangement of the Os_8 core from linked tetrahedral (a) to bi-capped octahedral (b) when $[HOs_8(CO)_{22}]^-$ gives $[Os_8(CO)_{22}]^{2-}$ on deprotonation.

Careful protonation of the monoanion (**1**) with conc. H_2SO_4 in MeCN gives a neutral compound (**2**) [ν(CO) (CH_2Cl_2) 2081m, 2070vs, 2048vs, and 2035s cm^{-1}] which may be formulated as $H_2Os_8(CO)_{22}$. Deprotonation of (**1**) gives the known[6] dianion $[Os_8(CO)_{22}]^{2-}$; this reaction is accompanied by a rearrangement of the Os_8 core (Figure 3) from the linked tetrahedral arrangement in (**1**) to the bi-capped octahedron in $[Os_8(CO)_{22}]^{2-}$. This emphasises previous observations that the energy differences between alternative metal geometries are very small, and isoelectronic species often do not contain the same metal core or distribution of ligands.[12] It is particularly relevant that, in boron cluster chemistry, eight-vertex systems as a group are relatively pliable cages whose geometries are unusually sensitive to subtle electronic and steric influences.[13]

It is interesting to note that all the products derived from heating $Os_6(CO)_{18}$ under reflux in isobutanol (Scheme 2) have an even number of Os atoms. This, together with the observation that unlike $Os_6(CO)_{18}$ neither $H_4Os_4(CO)_{12}$ nor $[HOs_8(CO)_{22}]^-$ give rise to higher species on prolonged heating in isobutanol, may indicate that unsaturated Os_2 fragments generated from breakdown of $Os_6(CO)_{18}$ are involved as the building blocks in the reaction. It seems reasonable to conclude that the metal geometry produced is a function of the building sequence and the predominance of octahedrally derived close packed geometries for the higher Os clusters observed until now is related to the fact that they were always derived from pyrolysis reactions *in vacuo*.

We thank C. N. Pq. (Brazil) (M.D.V.), I.C.I. (P.F.J. and W.J.H.N.), and S.R.C. (D.B.) for financial support.

Received, 8th January 1982; Com. 018

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