Synthesis and *X*-Ray Analysis of the Tetrahydrido-dianion $[H_4Os_{10}(CO)_{24}]^{2-}$, the First Non-carbido Decaosmium Cluster

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The non-carbido decaosmium cluster dianion $[H_4Os_{10}(CO)_{24}]^{2-}$ (**1**) has been prepared in low yield by heating several trinuclear osmium clusters in isobutyl alcohol; *X*-ray analysis of the $[(Ph_3P)_2N]^+$ salt shows that the tetrahydrido-dianion (**1**) is very similar in structure to the carbido-dianion $[Os_{10}C(CO)_{24}]^{2-}$ (**2**) indicating that the four hydrido-ligands in (**1**) may possibly be interstitial in the solid state.

The tetrahydrido-dianion $[H_4Os_{10}(CO)_{24}]^{2-}$ (**1**), which has been obtained in low yield by heating $Os_3(CO)_{12}$, $Os_3(CO)_{10}(OEt)_2$,[1] $HOs_3(CO)_{10}Cl$, or $Os_3(CO)_{12}$/sodium benzoate in isobutyl alcohol is the first example of a new type of decaosmium cluster which does not contain a central carbido-atom. The first Os_{10} cluster species to be isolated was the dianion $[Os_{10}C(CO)_{24}]^{2-}$ (**2**) in which, for the first time, a carbon atom was located in an octahedral Os_6 cavity.[2] Since then several derivatives of this species have been isolated[3,4] and until now all have been found to contain the same basic carbido-centred octahedral Os_6 unit.

We recently reported that a range of high nuclearity cluster compounds is obtained when $Os_3(CO)_{12}$ is heated in KOH/Bu^{i}OH.[5] We now find that, when the reaction is carried out in Bu^{i}OH under reflux (108 °C) in the absence of base,† among the products obtained are two new high nuclearity clusters, an Os_9 monoanion and the new decaosmium species $[H_4Os_{10}(CO)_{24}]^{2-}$ (**1**). The dianion (**1**) was isolated from the reaction products by t.l.c. (1 : 1 acetone/hexane), crystallised as the $[(Ph_3P)_2N]^+$ salt and characterised by i.r. (Figure 1), *X*-ray analysis, and ^1H n.m.r. spectroscopy.

X-Ray analysis‡ showed that the dianion (**1**) has a tetra-capped octahedral structure (Figure 2) which is very similar

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† At 130 °C in 2-methylbutan-1-ol or on prolonged reflux in Bu^{i}OH the carbido-dianion is formed showing that the reaction may be very sensitive to small changes in reaction conditions.

‡ *Crystal data:* $[H_4Os_{10}(CO)_{24}][(Ph_3P)_2N]_2$, $C_{96}H_{64}N_2O_{24}P_4Os_{10}$, M = 3 655.5, triclinic, space group $P\bar{1}$, a = 26.940(3), b = 17.421(2), c = 10.601(2) Å, α = 96.17(1), β = 100.68(1), γ = 86.47(1)°, Z = 2, U = 4 855.6 Å^3, D_c = 2.5 g cm^{-3}, $I/\sigma(I) \geqslant 3.0$, present R-factor = 0.0605 for 7121 reflections corrected for absorption [μ(Mo-K_α) = 126.37 cm^{-1}]. Data were collected on a Philips PW1100 diffractometer in the θ-range 3—25°.

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.

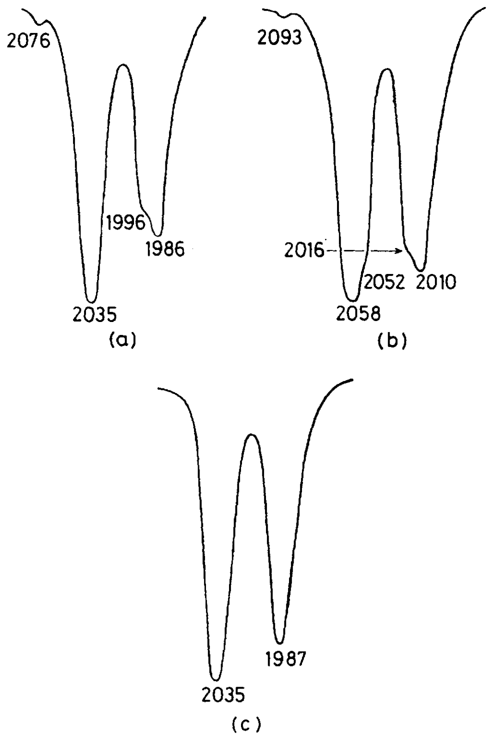

Figure 1. Comparison of the i.r. spectra {ν(CO)/cm^{-1}, $[(Ph_3P)_2N]^+$ salts in CH_2Cl_2} of (a) $[H_4Os_{10}(CO)_{24}]^{2-}$ (**1**), (b) $[H_5Os_{10}(CO)_{24}]^-$, and (c) $[Os_{10}C(CO)_{24}]^{2-}$ (**2**).

to that found previously[2] (Figure 3) for the carbido-dianion (**2**) but with the important difference that in (**1**) there is no central carbido-atom.§ The mean Os–Os bond distance for the octahedral Os_6 unit in (**1**) [2.857(1) Å] is significantly shorter than that in the carbido-dianion (**2**) [2.883(1) Å][2] as expected from the known tendency of interstitial C atoms to produce polyhedral expansion.[6]

Although it was not possible to locate any hydrogen atoms directly in the *X*-ray analysis, the presence of four hydrido-ligands (contributing a total of 4e) was deduced from the observed Os_{10} geometry for which skeletal electron counting theories[7] require the same total number of electrons as in the carbido-cluster (**2**). The presence of H-ligands was confirmed by the ^1H n.m.r. spectrum of the residual crystals (CD_2Cl_2, room temp.) which showed a broad singlet at 26.48 τ implying that the protons are fluxional in solution at this temperature. At 198 K two sharper signals of equal intensity at 24.70 and 29.08 τ were observed. However the signals were still too broad to detect $^{187}Os-^1H$ satellites.

From a comparison of Figure 2 and Figure 3 it can be seen that the carbonyl distribution in the tetrahydrido-dianion (**1**) and the carbido-dianion (**2**) is very similar. There is no sign of the characteristic displacement of the CO ligands normally observed when a hydrogen ligand is attached

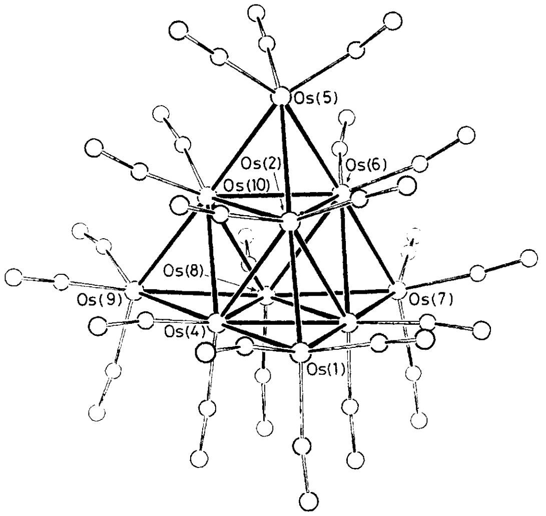

Figure 2. The structure of the $[H_4Os_{10}(CO)_{24}]^{2-}$ dianion (**1**) in the $[(Ph_3P)_2N]^+$ salt. Os–Os bond length (Å) are: (within the octahedron) (2)–(3) 2.881, (2)–(4) 2.831, (2)–(6) 2.903, (2)–(10) 2.823, (3)–(4) 2.768, (3)–(6) 2.903, (3)–(8) 2.817, (4)–(8) 2.810, (4)–(10) 2.826, (6)–(8) 2.924, (6)–(10) 2.881, (8)–(10) 2.917; (within the tetrahedra) (1)–(2) 2.804, (1)–(3) 2.776, (1)–(4) 2.795, (5)–(2) 2.853, (5)–(6), 2.796, (5)–(10) 2.776, (7)–(3) 2.750, (7)–(6) 2.780, (7)–(8) 2.863, (9)–(4) 2.775, (9)–(8) 2.888, (9)–(10) 2.754; maximum e.s.d. 0.002 Å.

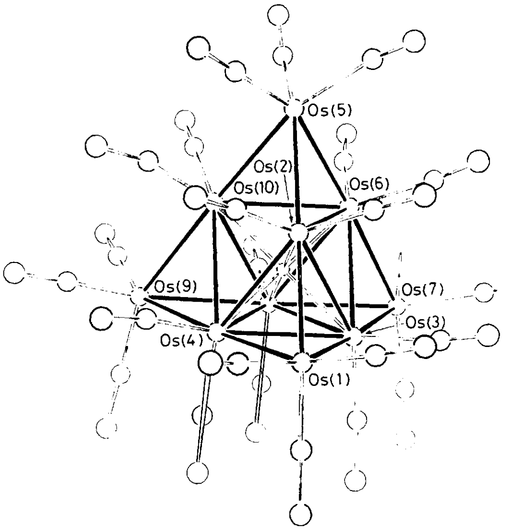

Figure 3. The structure of the carbido-dianion $[Os_{10}C(CO)_{24}]^{2-}$ (**2**) (ref. 2) showing the similarity of the carbonyl distribution to that of the tetrahydride $[H_4Os_{10}(CO)_{24}]^{2-}$.

to the surface of a cluster.[8,9] From the same type of observations in the *X*-ray analysis of $[HRu_6(CO)_{18}]^-$ the presence of the first interstitial H-ligand in a carbonyl cluster was deduced,[10] and the assignment was later confirmed by neutron diffraction.[11] More recently it was inferred, from the very close similarity of the carbonyl distribution in the mono-hydride $[HOs_{10}C(CO)_{24}]^-$ (**3**) to that in the dianion (**2**), that the H-ligand in (**3**) is also interstitial and is located in one of the tetrahedral Os_4 capping groups.[12] It may also be possible that in the tetrahydride (**1**) the H-ligands are not on the surface but are interstitial, although the n.m.r. data are more consistent with the presence of surface hydride ligands in solution.

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§ The $[(Ph_3P)_2N]^+$ salts of the dianion (**1**) and the well characterized carbido-dianion $[Os_{10}C(CO)_{24}]^{2-}$ (**2**) are isomorphous crystallising in the triclinic space group $P\bar{1}$ with unit cell dimensions so similar that had it not been for small but significant differences in their i.r. spectra [which persisted even after the careful purification of (**1**) by t.l.c. and crystallisation], the *X*-ray analysis would have been discontinued on the assumption that it was the carbido-dianion (**2**) that had been isolated. Remarkably the same problem arose in the characterisation of $[(Ph_3P)_2N]_2$-$[Os_{10}C(CO)_{22}(NO)I]$ which is also isomorphous with the $[(Ph_3P)_2N]^+$ salt of (**2**) (unpublished results).

$[HOs_{10}C(CO)_{24}]^-$ **(3)** $[Os_8(CO)_{22}]^{2-}$ **(4)**

In the *X*-ray analysis of the monohydride anion **(3)**[12] a small expansion of one capping tetrahedron was noticed with a mean Os–Os bond length of 2.856 Å compared to 2.837 Å for the other three capping groups and the corresponding value of 2.835 Å in the parent dianion **(2)**. It was concluded[12] that the slightly enlarged capping group in **(3)** was the site of the interstitial H-atom by analogy with previous observations[10,11] that such atoms cause a similar expansion of octahedral cavities. This interpretation is consistent with the solution n.m.r. data which reveal ^{187}Os–^1H satellites in accord with the solid state structure.[13] It would not be valid to compare the size of the capping tetrahedra in **(1)** with those in the carbido-dianion **(2)** because in each tetrahedron three of the Os–Os bonds are in common with the central octahedron and the bond length changes due to the carbido atom would mask any other effect. The largest non-carbido osmium cluster previously reported is the dianion $[Os_8(CO)_{22}]^{2-}$ **(4)** which has a bi-capped octahedral metal geometry.[14] The mean Os–Os distance for the capping tetrahedra in the tetrahydrido-dianion **(1)** is 2.829(1) Å, significantly longer than the corresponding distance in **(4)** of 2.793(1) Å. This would be consistent with the hydrogen ligands in **(1)** being located in the capping tetrahedra. However on closer inspection one capping tetrahedron in **(1)**, from Os(1), has a mean bond length of only 2.809 Å, close to the value observed in **(4)**,[14] and significantly shorter than the individual mean values for the other three tetrahedra in **(1)** (2.839, 2.839, and 2.829 Å). Therefore it seems probable that in **(1)**, if the hydrogen atoms are interstitial, three of them are in the three larger tetrahedral caps and one of them is in the central Os_6 cavity. It is consistent with this idea that the mean octahedral Os–Os bond length of 2.857(1) Å in **(1)** is also larger than the corresponding value for the empty Os_6 cavity in **(4)** of 2.831(1) Å.[14]

In CH_2Cl_2 **(1)** reacts with conc. H_2SO_4 to give a product tentatively formulated as the monoanion $[H_5Os_{10}(CO)_{24}]^-$ on the basis of the i.r. spectrum (Figure 1). Although the carbido-monohydride $[HOs_{10}C(CO)_{24}]^-$ deprotonates readily, attempts to deprotonate **(1)** have so far proved unsuccessful. Preliminary i.r. results indicate that, unlike the carbido-dianion **(2)**, the dianion **(1)** reacts irreversibly with 1 equiv. of iodine to give a monoanionic product.¶ It may be anticipated that, unlike the carbido-centred decaosmium clusters, the derivatives of **(1)** will exhibit a flexibility of metal core similar to that observed for other high nuclearity osmium cluster compounds.[5,15]

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References

1 M.-A. Pearsall, personal communication.

2 P. F. Jackson, B. F. G. Johnson, J. Lewis, M. McPartlin, and W. J. H. Nelson, *J. Chem. Soc., Chem. Commun.*, 1980, 224.

3 D. H. Farrar, P. F. Jackson, B. F. G. Johnson, J. Lewis, W. J. H. Nelson, M. D. Vargas, and M. McPartlin, *J. Chem. Soc., Chem. Commun.*, 1981, 1009.

4 D. Braga, K. Henrick, B. F. G. Johnson, J. Lewis, M. McPartlin, W. J. H. Nelson, and J. Puga, *J. Chem. Soc., Chem. Commun.*, 1982, 1083.

5 D. Braga, K. Henrick, B. F. G. Johnson, J. Lewis, M. McPartlin, W. J. H. Nelson, and M. D. Vargas, *J. Chem. Soc., Chem. Commun.*, 1982, 419.

6 B. F. G. Johnson, J. Lewis, S. W. Sankey, K. Wong, M. McPartlin, and W. J. H. Nelson, *J. Organomet. Chem.*, 1980, **191**, C3.

7 K. Wade, *Adv. Inorg. Chem. Radiochem.*, 1976, **18**, 1; R. Mason, K. M. Thomas, and D. M. P. Mingos, *J. Am. Chem. Soc.*, 1973, **95**, 3802.

8 M. McPartlin, C. R. Eady, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc., Chem. Commun.*, 1976, 883.

9 M. R. Churchill and J. Wormald, *J. Am. Chem. Soc.*, 1971, **93**, 5670; R. G. Teller and R. Bau, *Struct. Bonding (Berlin)*, 1981, **44**, 1.

10 C. R. Eady, B. F. G. Johnson, J. Lewis, M. C. Malesta, P. Machin, and M. McPartlin, *J. Chem. Soc., Chem. Commun.*, 1976, 945.

11 P. F. Jackson, B. F. G. Johnson, J. Lewis, P. R. Raithby, M. McPartlin, W. J. H. Nelson, K. D. Rouse, J. Allibon, and S. A. Mason, *J. Chem. Soc., Chem. Commun.*, 1980, 295.

12 P. F. Jackson, B. F. G. Johnson, J. Lewis, M. McPartlin, and W. J. H. Nelson, *J. Chem. Soc., Chem. Commun.*, 1982, 49.

13 E. C. Constable, B. F. G. Johnson, J. Lewis, G. N. Pain, and M. J. Taylor, *J. Chem. Soc., Chem. Commun.*, 1982, 754.

14 P. F. Jackson, B. F. G. Johnson, J. Lewis, and P. R. Raithby, *J. Chem. Soc., Chem. Commun.*, 1980, 60.

15 D. Braga, B. F. G. Johnson, J. Lewis, M. McPartlin, W. J. H. Nelson, and M. D. Vargas, unpublished work.

¶ ν(CO), CH_2Cl_2, 2095w, 2073m, 2061s, 2053s, and 2018s cm^{-1}.