Synthesis of the Carbido Cluster $[Os_{10}(CO)_{24}C]^{2-}$ and the *X*-Ray Structure of $[Os_{10}(CO)_{24}C][(Ph_3P)_2N]_2$

PETER F. JACKSON, BRIAN F. G. JOHNSON, and JACK LEWIS*
(*University Chemical Laboratories, Lensfield Road, Cambridge* CB2 1EW)

and MARY MCPARTLIN and WILLIAM J. H. NELSON
(*Department of Chemistry, The Polytechnic of North London, London* N7 8DB)

Summary The carbido dianion $[Os_{10}(CO)_{24}C]^{2-}$ has been isolated from the pyrolysis of $Os_3(CO)_{11}(py)$ (py = pyridine), and the pyrolysis of $Os_3(CO)_{12}$; an *X*-ray structural analysis of the $[(Ph_3P)_2N]^+$ salt has shown a tetrahedral arrangement of ten metal atoms that is a fragment of a cubic close packed array.

THE pyrolysis of dodecacarbonyl triosmium and its substituted derivatives provides the only means at present of synthesizing high-nuclearity clusters of osmium. Thus $Os_3(CO)_{12}$ itself is known to undergo pyrolysis to form a mixture of cluster carbonyls based on Os_5, Os_6, Os_7, and Os_8 units[1] but pyrolyses of $Os_3(CO)_{11}P(OMe)_3$[2] and $Os_3(CO)_{12-n}(CNR)_n$[3] lead exclusively to the formation of Os_5 and Os_6 clusters respectively. High-temperature pyrolysis of $Os_3(CO)_{12}$ was thought to produce clusters of increased nuclearity since solid state i.r. spectra of the ethyl acetate-insoluble residues revealed carbonyl bands. We now report the synthesis, characterization, and *X*-ray structure of the dianion $[Os_{10}(CO)_{24}C]^{2-}$ (**1**) which is the largest osmium cluster prepared to date and the first polynuclear carbonyl to have ten metal atoms.

Pyrolysis of $Os_3(CO)_{11}(py)$ (py = pyridine) *in vacuo* at 250 °C for 24 h gives a red-brown crystalline solid which may be extracted with ethyl acetate. Addition of diethyl ether causes precipitation of the major product of the reaction (*ca.* 80%), a pink-red solid (**2**), leaving in solution mainly $[HOs_5(CO)_{15}]^-$ but small amounts of $H_4Os_4(CO)_{12}$ and Os_3 clusters have also been identified by i.r. [ν(CO)] and mass spectroscopy. The new compound (**2**) exhibits i.r. vibrational frequencies at 2033 and 1986 cm^{-1} of approximately equal intensity indicative of an anionic species of very high symmetry. Although the cation in (**2**) has yet to be identified, the $[Bu_4N]^+$ salt was prepared by metathesis. The dianion (**1**) has also been isolated from the metallic residues left from the pyrolysis of $Os_3(CO)_{12}$ by the use of acetone rather than ethyl acetate for extraction. The $[(Ph_3P)_2N]^+$ and $[Ph_4As]^+$ salts are formed on addition of $(Ph_3P)_2NCl$ or Ph_4AsCl to this solution and these may be purified by fractional recrystallization. No resonance characteristic of an M–H linkage was detected in the ^{1}H n.m.r. spectrum of (**1**) (τ -40 to $+100$) and no reaction was observed with $[OH]^-$, indicating that (**1**) was not protonated and therefore probably dianionic. Since ionic species are not usually the product of these pyrolysis reactions it is likely that a neutral hydrido carbonyl is originally formed, which then dissociates in the polar solvents used for extraction to give the charged cluster (**1**). This idea is supported by the fact that much higher yields are obtained from the pyrolysis of $Os_3(CO)_{11}(py)$, where the pyridine ligand can function as a hydrogen source, than that of $Os_3(CO)_{12}$ where the H must come from minute quantities of water present on the glass of the Carius tube itself.

Crystals of the $[(Ph_3P)_2N]^+$ salt suitable for *X*-ray diffraction were grown from Me_2CO–MeOH and the data were recorded on a Philips PW1100 four-circle diffractometer using the $\omega/2\theta$ technique and graphite-monochromated Mo-K_α radiation. The positions of six osmium atoms (defining an octahedron) were obtained from a Patterson map, and four more Os atoms and the remaining non-hydrogen atoms were located from subsequent difference-Fourier syntheses establishing the molecular formula to be $[Os_{10}(CO)_{24}C]^{2-}$ $[(Ph_3P)_2N]_2{}^+$.† The dianion (**1**) has approximate overall T_d symmetry (Figure) and the structure may be described as a carbido-centred Os_6 octahedron, with two terminal carbonyls per osmium, capped on four tetrahedrally related faces by $Os(CO)_3$ groups. There are thus only two different environments for the 24 carbonyl ligands (12 of each type) which is completely consistent with the i.r. pattern of this species.

Although many carbido-centred octahedral Ru_6 clusters are known,[4] this is the first osmium cluster to be shown by *X*-ray analysis to have a completely encapsulated carbon atom. There is a striking difference between the Os–Os bond lengths of the octahedron [2·88(1) Å, mean] and those from the capping groups [2·79(1) Å, mean]. In the $[Os_8(CO)_{22}]^{2-}$ dianion[5] this trend is not observed and the mean Os–Os bond length is 2·816 Å so therefore the expansion of the octahedron in (**1**) must be attributed to the presence of the central carbon atom.

The metal skeleton in (**1**) is a fragment of a cubic close packed (c.c.p) array and corresponds to a face-centred cubic unit cell with four tetrahedrally related corners removed. Although large Rh[6a] and Ni[6b] clusters are known with a hexagonal close packed (h.c.p.) arrangement of metals, a c.c.p. array has not previously been observed in a metal carbonyl cluster. Several examples have been reported which indicate that cluster geometries differ from those of the bulk metal,[7] and indeed osmium metal has an h.c.p. rather than a c.c.p. lattice. Interestingly, rhodium metal has a c.c.p. lattice rather than the h c.p. geometry that some of the large clusters display. The metal core in the dianion (**1**) has the largest planar surfaces observed to date in a carbonyl cluster and the arrangement of CO ligands perpendicular to each face (Figure) may provide the best analogy so far of a monolayer of carbon monoxide chemisorbed on a metal surface.

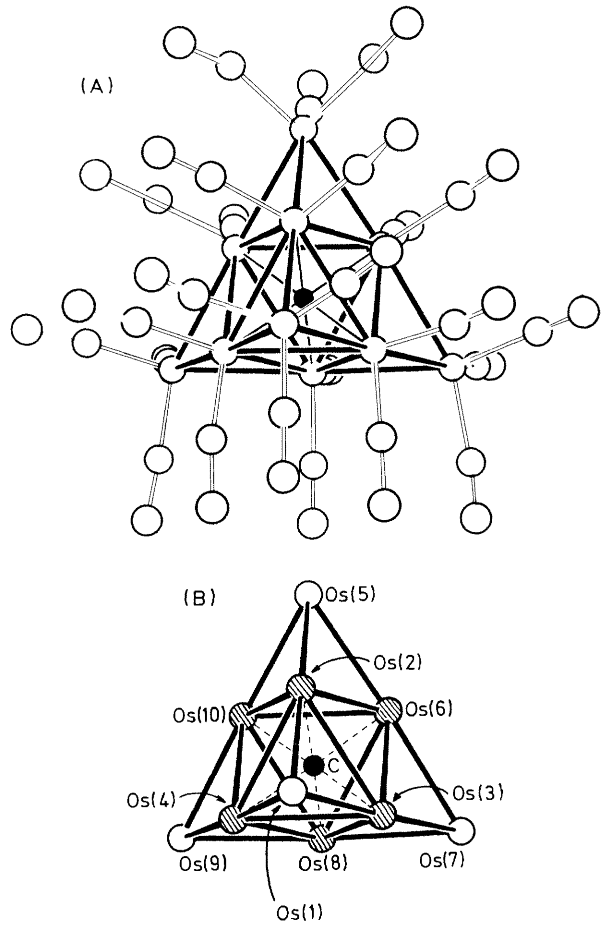

FIGURE The structure of (**1**). (A) The $[Os_{10}C(CO)_{24}]^{2-}$ dianion (B) The $Os_{10}C$ unit without the carbonyl ligands. Important bond lengths are Os–Os: (1)–(2) 2·782, (1)–(3) 2·801, (1)–(4) 2·779, (2)–(3) 2·874, (2)–(4) 2·866, (2)–(5) 2·788, (2)–(6) 2·875, (2)–(10) 2·857, (3)–(4) 2·865, (3)–(6) 2·902, (3)–(7) 2·782, (3)–(8) 2·882, (4)–(8) 2·889, (4)–(9) 2·786, (4)–(10) 2·904, (5)–(6) 2·796, (5)–(10) 2·775, (6)–(7) 2·782, (6)–(8) 2·887, (6)–(10) 2·885, (7)–(8) 2·787, (8)–(9) 2·809, (8)–(10) 2·903, and (9)–(10) 2·759 Å; maximum Os–Os e.s.d. 0·004 Å; mean Os–C (carbido) 2·04(3) Å.

The dianion (**1**) has 134 valence electrons, so using Wade's electron counting scheme[8] (12 electrons allocated to each Os for M–C bonds and essentially non-bonding orbitals, the remainder are used for cluster bonding), seven electron pairs are available for cluster bonding indicating that the fundamental polyhedron should be an octahedron. Since capped and uncapped versions of the same polyhedron require the same number of skeletal electron pairs the remaining four osmium atoms may be accommodated in face-capping positions, thus giving the observed structure. Other approaches are less successful in rationalizing the structure. For example, although Lauher[9] envisaged a

† *Crystal data*: triclinic, space group $P\bar{1}$, $a = 27{\cdot}157$, $b = 17{\cdot}535$, $c = 10{\cdot}470$ Å, $\alpha = 96{\cdot}37$, $\beta = 100{\cdot}71$, $\gamma = 85{\cdot}92°$, $Z = 2$, $I/\sigma(I) \geqslant 3{\cdot}0$, θ-range 3—25°, present R value $= 0{\cdot}1113$ for 9069 reflections. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

tetrahedral arrangement for 10 metal atoms his calculations indicate that it would require 140 valence electrons, which would correspond to the incorrect formulation $[Os_{10}(CO)_{27}C]^{2-}$ for (**1**).

We thank the S.R.C. for the award of Research Studentships (to P.F.J. and W.J.H.N.).

(*Received, 4th December* 1979; *Com.* 1269.)

[1] C. R. Eady, B. F. G. Johnson, and J. Lewis, *J.C.S. Dalton*, 1975, 2606.

[2] J. M. Fernandez, B. F. G. Johnson, and J. Lewis, unpublished results.

[3] M. J. Mays and P. D. Gavens, *J. Organometallic Chem.*, 1979, **177**, 443.

[4] B. F. G. Johnson, R. D. Johnston, and J. Lewis, *J. Chem. Soc. (A)*, 1968, 2865; R. Mason and W. R. Robinson, *Chem. Comm.*, 1968, 468; A. Sirigu, M. Bianchi, and E. Benedetti, *ibid.*, 1969, 596.

[5] P. F. Jackson, B. F. G. Johnson, J. Lewis, and P. R. Raithby, *J.C.S. Chem. Comm.*, 1980, 60.

[6] (a) S. Martinengo, G. Ciani, A. Sironi, and P. Chini, *J. Amer. Chem. Soc.*, 1978, **100**, 7096 and references therein: (b) R. W. Broach, L. F. Dahl, G. Longoni, P. Chini, A. J. Schultz, and J. M. Williams, *Adv. Chem. Series*, 1978, **167**, 93.

[7] M. Moskovits, *Accounts Chem. Res.*, 1979, **12**, 229 and references therein.

[8] K. Wade, *Adv. Inorg. Chem. Radiochem.*, 1976, **18**, 1.

[9] J. W. Lauher, *J. Amer. Chem. Soc.*, 1978, **100**, 5305.