The Synthesis of the First Undeca-osmium Cluster Species, $[PPh_3Me]_2[Os_{11}C(CO)_{27}]$, and the *X*-Ray Structure Analysis of its $[Cu(NCMe)]^+$ Derivative $[PPh_3Me][Os_{11}C(CO)_{27}Cu(NCMe)]\cdot CH_2Cl_2$

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The first undeca-osmium cluster, $[Os_{11}C(CO)_{27}]^{2-}$ (1), has been isolated as a low-yield product of the vacuum pyrolysis of $Os_3(CO)_{12}$; the dianion (1) reacts with 1 equivalent of $[Cu(NCMe)_4][BF_4]$ to give the monoanion $[Os_{11}C(CO)_{27}Cu(NCMe)]^-$ (2) which has been shown by *X*-ray analysis to have an unusual Os_{11} core geometry with the carbido atom occupying a trigonal prismatic cavity.

Although the vacuum pyrolysis of $Os_3(CO)_{12}$ was first reported in 1972 as giving a series of osmium clusters based on up to eight metal atoms,[1] it is only fairly recently that we isolated the deca-osmium species $[Os_{10}C(CO)_{24}]^{2-}$ as a low-yield product of this reaction.[2] We now report that a new undeca-osmium dianion, $[Os_{11}C(CO)_{27}]^{2-}$ (1), may also be obtained as a low-yield product of the pyrolysis. The dianion (1) was isolated as its $[PPh_3Me]^+$ salt by dissolving the pyrolysis residues, remaining after extraction with ethyl acetate, in acetone–ethanol and adding an excess of $[PPh_3Me]Br$. Fractional crystallisation gave first dark red crystals of $[PPh_3Me]_2[Os_{10}C(CO)_{24}]$ followed by dark brown crystals of $[PPh_3Me]_2[Os_{11}C(CO)_{27}]$ as two crystalline modifications.

The dianion (1), which is a rare example of an M_{11} carbonyl cluster, was characterised by i.r.,† n.m.r. (no hydride signals), and fast-atom bombardment (FAB) mass spectroscopy [m/z 2880 for (1) based on ^{192}Os].

Preliminary *X*-ray analyses of the two crystalline modifications‡ of the $[PPh_3Me]^+$ salt of $[Os_{11}C(CO)_{27}]^{2-}$ established the unusual metal core geometry but disorder of the dianion in both crystalline modifications made satisfactory location of the light atoms impossible.

Attempts to grow suitable crystals of other salts of (1) were unsuccessful but the reaction with $[Cu(NCMe)_4][BF_4]$ gave good crystals of the $[Cu(NCMe)]^+$ derivative (2).† *X*-Ray analysis‡ of the $[PPh_3Me]^+$ salt of $[Os_{11}C(CO)_{27}$-

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† I.r. spectra in CH_2Cl_2, $\nu(CO)/cm^{-1}$: $[PPh_3Me]^+$ salt of (1), 2079w, 2052vs, 2042vs, 2011m, 1989s, 1983m sh, 1960w sh, 1903w, and 1761w br [a trace amount of a compound displaying this i.r. spectrum was previously noted as one of the products of the pyrolysis of $Os_3(CO)_{12}$, after separation by medium-pressure column chromatography, but insufficient was obtained for characterisation; P. F. Jackson, personal communication]; $[PPh_3Me]^+$ salt of (2), 2087w, 2061s, 2054vs, 2023m, 2007s, 1998m sh, 1982m w, 1902w, and 1785w br; $[PPh_3Me][Os_{11}C(CO)_{27}AuPPh_3]$, 2086w, 2065vs, 2053s, 2025s, 2004s, 1995m sh, 1972w sh, and 1781w br; $[PPh_3Me][Os_{11}C(CO)_{27}I]$, 2096w, 2071s, 2030m, and 2009m.

‡ *Crystal data for* (1), $C_{66}H_{36}O_{27}Os_{11}P$, M = 3 414.15; crystalline modification (A): monoclinic, space group $P2_1/c$, a = 24.831(4), b = 13.107(2), c = 25.463(4) Å, β = 109.38(1)°, U = 7 817.4 Å^3, Z = 4; crystalline modification (B): monoclinic, space group $C2/c$, a = 19.866(3), b = 16.705(3), c = 23.233(4) Å, β = 100.85°, U = 7 572.3 Å^3, Z = 4. Full details and a discussion of the problems in this determination will be given in the full paper.

Crystal data for (2), $C_{50}H_{23}Cl_2CuNO_{27}Os_{11}P$, M = 3 327.34, monoclinic, space group $P2_1/c$, a = 16.114(3), b = 13.748(2), c = 29.382(5) Å, β = 97.15(1)°, U = 6 458.5 Å^3, Z = 4, $I/\sigma(I) \geqslant 3.0$, present R factor 0.048 for 5717 reflections corrected for absorption [$\mu(Mo\text{-}K_\alpha)$ = 212.0 cm^{-1}]. The atomic co-ordinates for the structure of (2) 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.

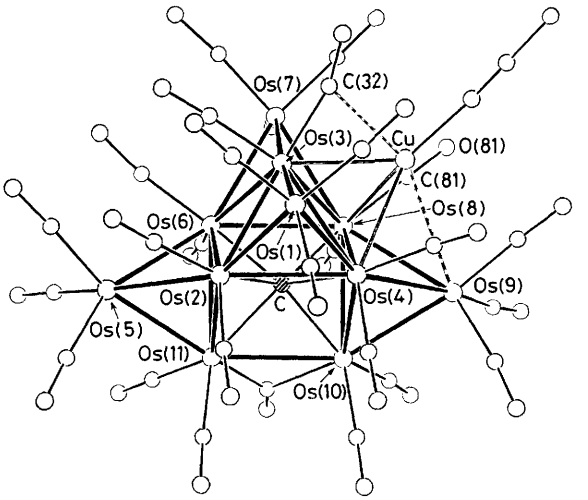


Figure 1. The structure of the monoanion $[Os_{11}C(CO)_{27}Cu(NCMe)]^-$ (**2**). Important bond lengths (Å) are: Os–Os, (1)–(2) 2.798, (1)–(3) 2.733, (1)–(4) 2.824, (2)–(3) 2.755, (2)–(4) 2.848, (2)–(5) 2.813, (2)–(6) 2.810, (2)–(11) 2.868, (3)–(4) 2.822, (3)–(6) 2.735, (3)–(7) 2.738, (3)–(8) 2.827, (4)–(8) 2.826, (4)–(9) 2.815, (4)–(10) 2.904, (5)–(6) 2.801, (5)–(11) 2.739, (6)–(7) 2.794, (6)–(8) 2.847, (6)–(11) 2.809, (7)–(8) 2.790, (8)–(9) 2.820, (8)–(10) 2.824, (9)–(10) 2.754, (10)–(11) 2.809, maximum e.s.d. 0.002 Å; Os(3)–Cu 2.598(4), Os(4)–Cu 2.709(4), Os(8)–Cu 2.627(4), Os(9) · · ·Cu 3.156(4), Cu · · · C(32) 2.34(3), Cu · · · C(81) 2.45(3), Cu–N 1.90(3).

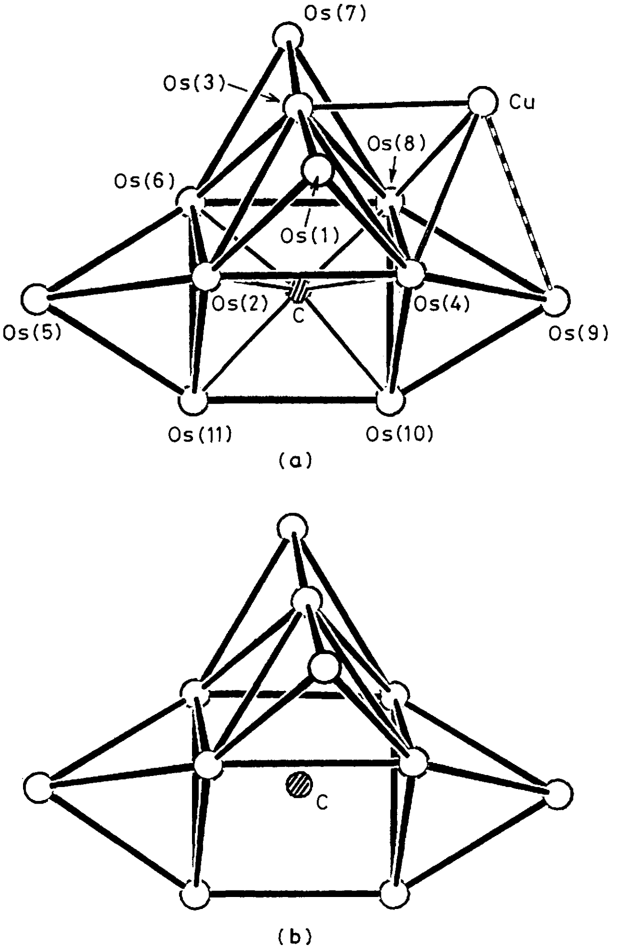
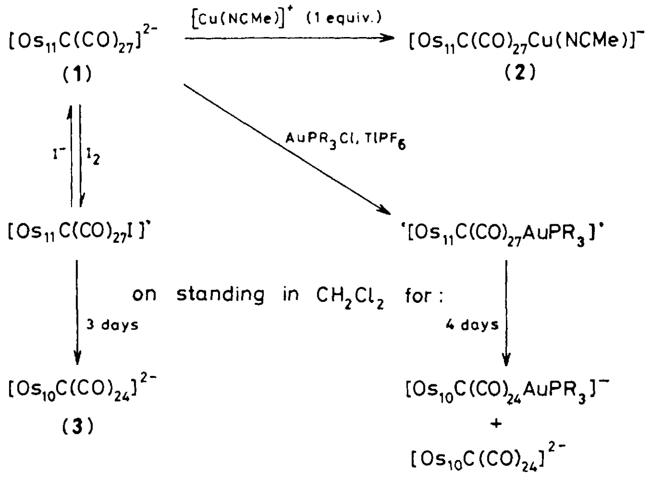


Figure 2. (a) The structure of the core $Os_{11}CCu$ in the monoanion $[Os_{11}C(CO)_{27}Cu(NCMe)]^-$ (**2**). (b) The structure of the Os_{11} core in the dianion $[Os_{11}C(CO)_{27}]^{2-}$ (**1**), showing the probable carbido carbon atom site.

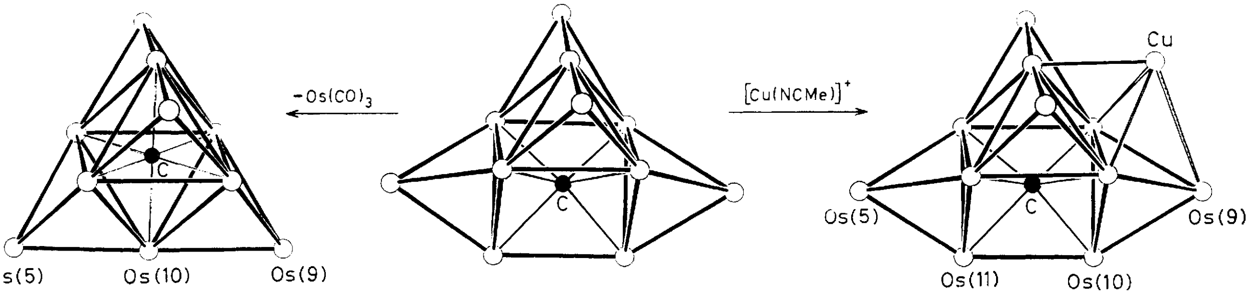
$Cu(NCMe)]^-$ (**2**) showed the overall anionic structure illustrated in Figure 1. The $Os_{11}CCu$ core geometry is shown in Figure 2(a) and has an Os_{11} arrangement very similar to that found in the preliminary *X*-ray analysis of (**1**). The Cu atom caps the face of Os(3), Os(4), Os(8), with a long bond to a fourth Os atom, Os(9) · · · Cu 3.156 Å. In this analysis the carbido carbon atom was readily located in the centre of the prismatic cavity with a mean Os–C bond length of 2.17 Å. Although clusters of the cobalt triad appear to favour prismatic sites for interstitial carbido atoms,[3,4] this is the first example in the iron triad. By analogy with (**2**) it is reasonable to conclude that the carbido C atom in $[Os_{11}C(CO)_{27}]^{2-}$ is also in the prismatic cavity, Figure 2(b).

The highest nuclearity osmium clusters previously isolated have contained ten osmium atoms, and until the recent structural characterisation[5] of the fused tetrahedral cluster anion $[HOs_8(CO)_{22}]^-$ all the high nuclearity osmium clusters reported had the capped octahedral geometries consistent with extended Wade theory.[6] The structure of the Os_{11} core in (**1**) and (**2**) may be described as a bicapped square pyramid sharing its square face with a trigonal prism which is also bicapped on its triangular faces; this novel metal core geometry is not readily explained by the Wade skeletal electron counting method, although overall it obeys the effective atomic number (E.A.N.) rule. However Mingos has recently extended skeletal electron counting procedures to include polyhedral structures fused through triangular faces or edges.[7] Assuming the 64e should be subtracted for the fused square face in (**1**) in applying the Mingos approach, the correct total electron count of 148e for the dianion (**1**) is obtained. This type of metal skeleton has not been observed previously but it shows some resemblance to that of $Rh_8C(CO)_{19}$ which also contains a fused square pyramid and trigonal prism.[3]

The $[Os_{11}C(CO)_{27}]^{2-}$ dianion reacts with one equivalent of iodine to give '$[Os_{11}C(CO)_{27}I]^-$'† and with $AuPR_3Cl$ to give '$[Os_{11}C(CO)_{27}AuPR_3]^-$'.† These undeca-osmium derivatives decompose on standing in CH_2Cl_2 losing '$Os(CO)_3$' and giving ultimately the well known deca-osmium dianion $[Os_{10}C(CO)_{24}]^{2-}$ (**3**) (Scheme 1). The two prismatic capping groups on the prism of (**1**) swing down to generate the tetracapped octahedral structure of (**3**), the carbido atom moving up into the centre of the octahedron. The structurally characterised reactions of the dianion (**1**) are illustrated in Figure 3. It seems likely that the $[Os_{11}C(CO)_{27}]^{2-}$ dianion represents a step in the sequence of cluster growth immediately before the formation of the extremely stable dianion $[Os_{10}C(CO)_{24}]^{2-}$.



Scheme 1. Some reactions of the dianion (**1**).



$[Os_{10}C(CO)_{24}]^{2-}$ (3)

$[Os_{11}C(CO)_{27}]^{2-}$ (1)

$[Os_{11}C(CO)_{27}Cu(NCMe)]^-$ (2)

Figure 3. The metal core structures of clusters produced on reaction of $[Os_{11}C(CO)_{27}]^{2-}$ (**1**).

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