The Synthesis of the Cluster Dianion $[Os_{10}C(CO)_{24}]^{2-}$ by Pyrolysis. *X*-Ray Structure Analysis of $[N(PPh_3)_2]_2[Os_{10}C(CO)_{24}]$ † and $[Os_5C(CO)_{14}H(NC_5H_4)]$ ‡

Peter F. Jackson, Brian F. G. Johnson, Jack Lewis,* and William J. H. Nelson
University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW
Mary McPartlin *
School of Chemistry, The Polytechnic of North London, London N7 8DB

The cluster species $[Os_{10}C(CO)_{24}]^{2-}$ (1) and $[Os_5C(CO)_{14}H(NC_5H_4)]$ (2) have been obtained for the first time by pyrolysis of $[Os_3(CO)_{11}(py)]$. *X*-Ray analysis of the $[N(PPh_3)_2]^+$ salt of (1) shows a tetracapped octahedral metal arrangement of the $Os_{10}C$ unit which is the first example of a carbido-atom encapsulated in an octahedral Os_6 cavity. In the formation of $[Os_5C(CO)_{14}H(NC_5H_4)]$ orthometallation of the pyridine ligand occurs which bridges two equatorially located osmium atoms of an *arachno*-bipyramidal Os_5 arrangement which surrounds a semi-interstitial carbido-atom. Crystals of $[N(PPh_3)_2]_2[Os_{10}C(CO)_{24}]$ are triclinic, space group $P\bar{1}$, $a = 27.157(5)$, $b = 17.535(4)$, $c = 10.470(2)$ Å, $\alpha = 96.37(2)$, $\beta = 100.71(2)$, $\gamma = 85.92(2)°$, $Z = 2$. Refinement of atomic parameters using 8 942 absorption corrected data converged at R 0.0553. Crystals of $[Os_5C(CO)_{14}H(NC_5H_4)]$ are monoclinic, space group $P2_1/c$, $a = 8.869(2)$, $b = 17.870(3)$, $c = 17.208(3)$ Å, $\beta = 95.30(2)°$, and $Z = 4$. Refinement of atomic parameters using 3 518 absorption corrected data converged at R 0.0604.

Many binary osmium carbonyl species, together with their hydrido- and carbido-derivatives, may conveniently be divided into two structural types using skeletal electron counting procedures such as Wade[1] theory. The first group contains compounds with six skeletal electron pairs ($S = 6$) available for cluster bonding and metal geometries derived from a trigonal bipyramidal (t.b.p.) osmium arrangement such as that found in $[Os_5(CO)_{16}]$.[2,3] This group includes the capped-t.b.p. cluster molecule $[Os_6(CO)_{18}]$ and the *arachno*-t.b.p. species $[Os_3(CO)_{12}]$. The second group is larger and contains species with seven skeletal electron pairs ($S = 7$) and metal arrangements derived from an octahedral osmium arrangement as found in $[Os_6(CO)_{18}]^{2-}$.[4] It includes the carbido-cluster $[Os_5C(CO)_{15}]$ which has a *nido*-octahedral metal core,[5] and the high nuclearity species $[Os_7(CO)_{21}]$ and $[Os_8(CO)_{22}]^{2-}$ which both have capped octahedral osmium arrangements.[6,7] We now report the discovery of a new member of this series, $[Os_{10}C(CO)_{24}]^{2-}$ (1), which is the largest osmium cluster compound so far obtained. This cluster can conveniently be prepared in high yield by pyrolysis of the trinuclear pyridine (py) cluster derivative $[Os_3(CO)_{11}(py)]$. A new pentanuclear osmium carbido-species $[Os_5C(CO)_{14}H(NC_5H_4)]$ (2), in which orthometallation of the pyridine ligand has occurred, is also obtained in low yield from this reaction.

Results and Discussion

The dianion (1) was first isolated when the pyrolysis of $[Os_3(CO)_{11}(py)]$ was investigated for the first time. A red-brown crystalline solid was obtained after heating at 250 °C *in vacuo* for 24 h. Extraction of the solid with ethyl acetate followed by evaporation and precipitation with diethyl ether gave a pink-red solid as the major product of the reaction. This solid, which was purified by t.l.c. using cyclohexane–acetone (1 : 1) as eluant, exhibited i.r. vibrational frequencies at 2 033 and 1 986 cm^{-1} of approximately equal intensity indicative of an anionic species of very high symmetry. The cation present at this stage was not identified but the $[NBu^n_4]^+$ salt was prepared by metathesis. *X*-Ray analysis of this salt was attempted but abandoned due to the very rapid decomposition of the crystals; the unit-cell dimensions appeared to indicate the presence of a very large cluster unit.

At this time a re-investigation of the long established pyrolysis reactions of $[Os_3(CO)_{12}]$ was also in progress and unexpectedly acetone extraction of the residues previously thought to be ' metallic ' in nature gave a solution which displayed an i.r. spectrum identical to that of the anion from the pyrolysis of $[Os_3(CO)_{11}(py)]$. Addition of $[N(PPh_3)_2]Cl$ in MeOH gave the $[N(PPh_3)_2]^+$ salt and *X*-ray analysis showed[8] that (1) was a new dianionic cluster species $[Os_{10}C(CO)_{24}]^{2-}$ which was larger than any osmium cluster previously obtained and had the structure shown in Figure 1.

Detailed investigation of the pyrolysis of $[Os_3(CO)_{11}(py)]$ shows that the distribution of products varies with time. Typical reaction sequences are shown in the Scheme. A second new cluster species $[Os_5C(CO)_{14}H(NC_5H_4)]$ (2), with an *ortho*-metallated pyridine ligand, has been identified together with several known cluster species, namely $[Os_4(CO)_{12}H_4]$,[9] $[Os_3(CO)_{10}H(NC_5H_4)]$,[10] $[Os_5(CO)_{15}H]^-$,[11] and $[Os_2(CO)_6(NC_5H_4)_2]$.[10] The anions were characterised as the $[N(PPh_3)_2]^+$ or $[PMePh_3]^+$ salts (see Experimental section). The mechanism by which these cluster compounds are produced is not clear; a number of reaction pathways are available and the product distribution is almost certainly controlled by kinetic rather than thermodynamic factors. Nevertheless we suspect that the formation of the $Os_{10}C$ cluster involves the previous formation of Os_5 species and there appears to be some correlation between reaction time and the relative yields of deca- and penta-nuclear clusters. Thus the amount of $[Os_{10}C(CO)_{24}]^{2-}$ increases at the expense of $[Os_5(CO)_{15}H]^-$ over longer reaction times (see Scheme).

The dianion $[Os_{10}C(CO)_{24}]^{2-}$ has an overall structure of virtual T_d symmetry which is illustrated in Figure 1. The two

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† μ_6-Carbido-dodecacarbonyl-tetrakis(μ_3-tricarbonylosmio)-*octahedro*-hexaosmate(2−).

‡ μ_5-Carbido-1,1,1,2,2,2,3,3,3,4,4,4,5,5-tetradecacarbonyl-3,5-μ-hydrido-1,5-[μ-2′-pyridyl-C^2(Os^5)N(Os^1)]-*cyclo*-pentaosmium(7 *Os–Os*).

Supplementary data available (No. SUP 23375; 85 pp.): observed and calculated structure factors, thermal parameters, bond lengths and angles, full list of atomic co-ordinates for both (1) and (2). See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

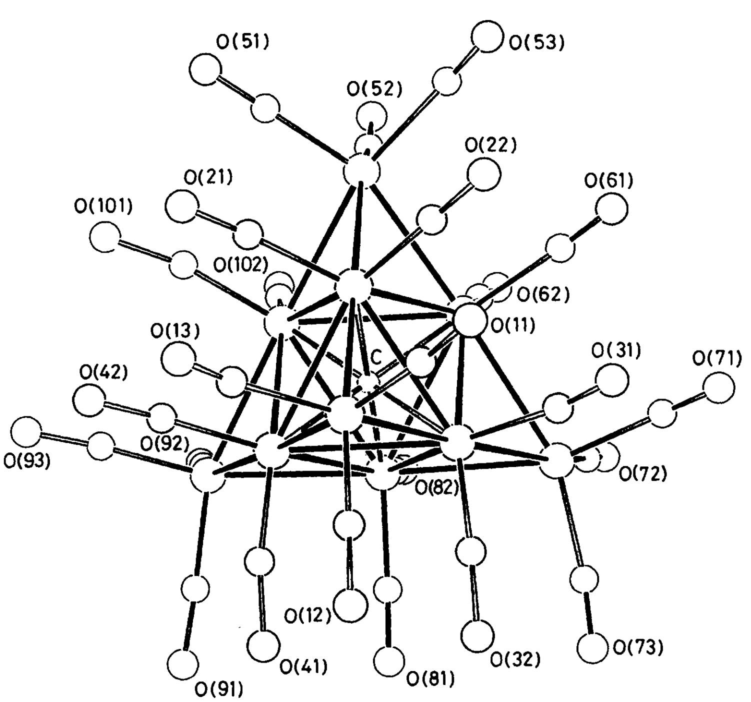
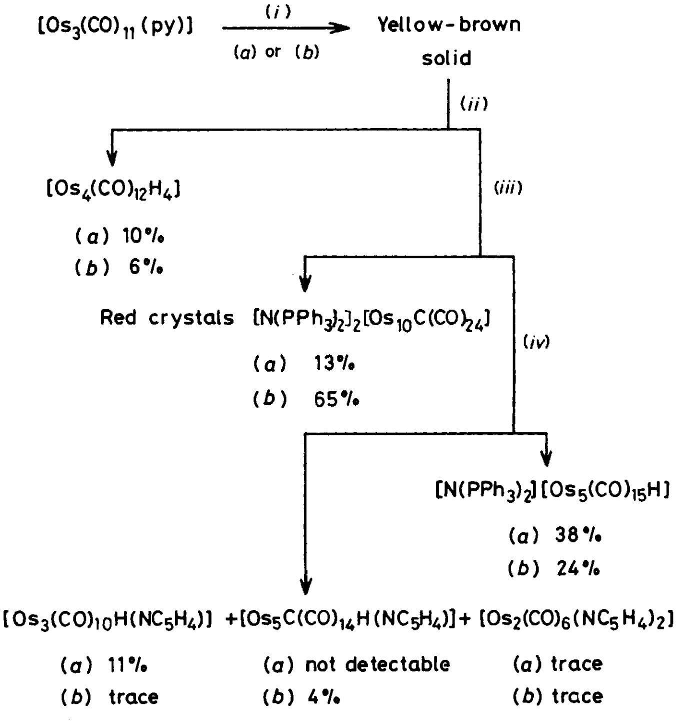


Figure 1. The structure of the $[Os_{10}C(CO)_{24}]^{2-}$ dianion, with the numbering of the oxygen atoms corresponding to that of the relevant carbonyl carbon atoms. The first digit of each oxygen number is the number of the osmium atom to which the carbonyl is attached



Scheme. Pyrolysis of $[Os_3(CO)_{11}(py)]$. Reaction times are (*a*) 15 h and (*b*) 64 h; yields are approximate. (*i*) 250 °C; (*ii*) hot acetone; (*iii*) $[N(PPh_3)_2]Cl$ in MeOH (evaporation); (*iv*) chromatography on silica

cations have the usual bent configuration with P–N–P angles of 144(1) and 137(1)° and mean P–N bond lengths of 1.59 Å. The dianion (1) may be described as a carbido-centred Os_6 octahedron, with two terminal carbonyl ligands *per* osmium atom, 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 explains the very simple i.r. spectrum observed for this species [ν(CO) 2 033s and 1 986s cm^{-1}]. A related tetra-capped octahedral Pd_{10} geometry has recently been reported for the cluster $[Pd_{10}(CO)_{12}(PBu^n_3)_6]$.[12,13] In this structure, however, the capping Pd atoms bridge asymmetrically, each being within bonding distances of two Pd atoms of the central octahedron (2.694—2.722 Å) and at a longer, non-bonding distance (3.301—3.421 Å) from a third. The heteronuclear species $[Hg_6Rh_4(PMe_3)_{12}]$ has also been shown by *X*-ray analysis to have a similar structure to (1); in this cluster the metal core also has virtual T_d symmetry consisting of a regular octahedron of Hg atoms capped on four faces by $Rh(PMe_3)_3$ groups. It is interesting that the structure of (1) is also closely related to that found for $[Rh_6(CO)_{16}]$ in which an $M_6(CO)_{12}$ unit is similarly capped on four tetrahedrally related faces but in this case by triply bridging CO ligands.[14]

Many carbido-centred octahedral Ru_6 clusters are known [15] but $[Os_{10}C(CO)_{24}]^{2-}$ is the first osmium cluster to be shown by *X*-ray analysis to have a completely encapsulated atom although the stability of $[Os_nC]^+$ fragments has been noted in the mass spectrum of several carbido-osmium clusters.[16]

A sample of ^{13}CO enriched $[N(PPh_3)_2]_2[Os_{10}C(CO)_{24}]$ * was prepared from enriched $[Os_3(CO)_{11}(py)]$ (^{13}CO *ca.* 37%) in order to examine the ^{13}C n.m.r. spectrum. In a few cases the resonance due to an encapsulated carbon atom has been detected in carbido-clusters, but no such signal could be found for $[Os_{10}C(CO)_{24}]^{2-}$ despite the use of various pulse delays, pulse angles, and relaxation times. In CD_2Cl_2, two signals of equal intensity appeared due to the CO ligands at 189.9 and

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* The actual degree of enrichment of the carbido-atom was estimated to be 21 atomic % from solid-state i.r. studies (I. A. Oxton, S. F. A. Kettle, P. F. Jackson, B. F. G. Johnson, and J. Lewis, *J. Mol. Struct.*, 1981, **71**, 117).

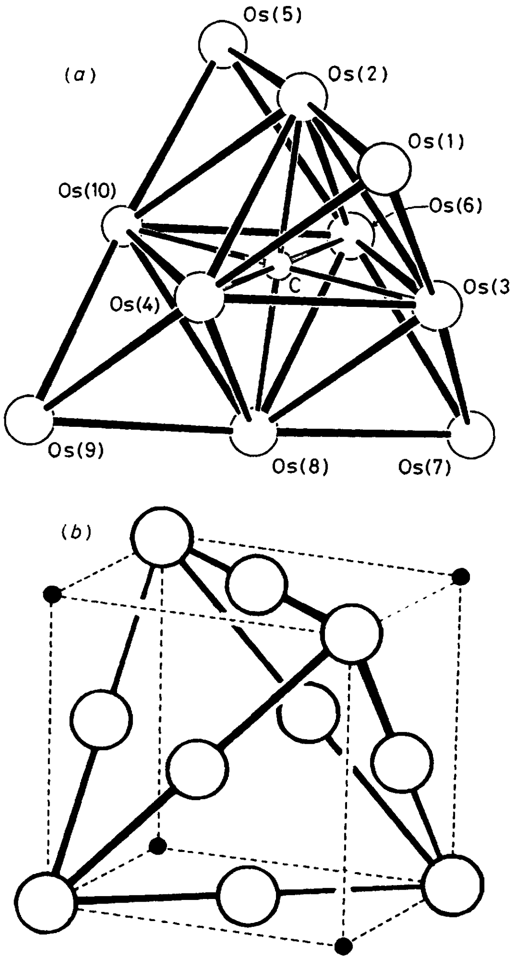

Figure 2. (*a*) The metal core of the $[\mathrm{Os_{10}C(CO)_{24}}]^{2-}$ dianion. (*b*) The relationship between the $\mathrm{Os_{10}}$ core and a f.c.c. unit cell

178.2 p.p.m. relative to $\mathrm{SiMe_4}$; these signals remained unchanged on cooling the solution from 30 °C to −60 °C. This spectrum is consistent with the solid-state structure and indicates that the molecule is not fluxional in solution.

The structure of the $\mathrm{Os_{10}C}$ core of (1) is shown in Figure 2(*a*). There is a marked difference between the Os–Os bond lengths of the central octahedron [2.88(1) Å, mean] and those from the four capping osmium atoms [2.79(1) Å, mean]. In the bicapped octahedral osmium unit of $[\mathrm{Os_8(CO)_{22}}]^{2-}$, which does not contain an interstitial carbon atom, this trend is not observed.[7] Therefore the expansion of the octahedral cavity in $\mathrm{Os_{10}C}$ dianion (1) may be attributed to the interstitial carbon atom. The mean metal–carbido distance of 2.04(2) Å is similar to that observed in hexaruthenium carbido-species.[15]

The metal skeleton in the $[\mathrm{Os_{10}C(CO)_{24}}]^{2-}$ dianion may be regarded as a fragment of a cubic close packed (c.c.p.) array of osmium atoms and corresponds to a face-centred unit cell of metal atoms with four tetrahedrally related faces, corners removed, as illustrated in Figure 2(*b*). Although large rhodium[17] and nickel[18] clusters that contain hexagonally close packed metal arrays are well known, this is the first cluster in which a c.c.p. metal arrangement has been found. Several examples have been reported which indicate that cluster geometries frequently differ from those of the bulk metal; for example, rhodium metal has a c.c.p. structure rather than the hexagonal close packed (h.c.p.) geometry that many of the large clusters display.[17] Interestingly, osmium metal has a h.c.p. metal array in contrast to the c.c.p. arrangement observed in (1).

Table 1. Selected interatomic distances (Å) in (1) with estimated standard deviations in parentheses

(*a*) Metal–metal			
(*i*) Within octahedron			
Os(2)–Os(3)	2.875(1)	Os(3)–Os(8)	2.883(1)
Os(2)–Os(4)	2.868(1)	Os(4)–Os(8)	2.889(1)
Os(2)–Os(6)	2.877(1)	Os(4)–Os(10)	2.900(1)
Os(2)–Os(10)	2.861(1)	Os(6)–Os(8)	2.890(1)
Os(3)–Os(4)	2.863(1)	Os(6)–Os(10)	2.886(1)
Os(3)–Os(6)	2.902(1)	Os(8)–Os(10)	2.903(1)
	Mean Os–Os	2.883	
(*ii*) Involving capping Os atoms			
Os(1)–Os(2)	2.782(1)	Os(7)–Os(3)	2.785(1)
Os(1)–Os(3)	2.799(1)	Os(7)–Os(6)	2.782(1)
Os(1)–Os(4)	2.781(1)	Os(7)–Os(8)	2.787(1)
Os(5)–Os(2)	2.789(1)	Os(9)–Os(4)	2.783(1)
Os(5)–Os(6)	2.798(1)	Os(9)–Os(8)	2.814(1)
Os(5)–Os(10)	2.776(1)	Os(9)–Os(10)	2.761(1)
	Mean Os–Os	2.786	
(*b*) Metal–ligand			
Os(2)–C	2.032(18)	Os(6)–C	2.045(16)
Os(3)–C	2.018(15)	Os(8)–C	2.033(18)
Os(4)–C	2.040(16)	Os(10)–C	2.065(15)
Mean Os–CO	1.845	Mean C–O	1.181

The metal core in $[\mathrm{Os_{10}C(CO)_{24}}]^{2-}$ has four large planar surfaces, each of which consists of six osmium atoms with six carbonyl ligands approximately perpendicular to each face. The only larger planar cluster surfaces known (seven atoms) are found in $[\mathrm{Pt_{38}(CO)_{44}H}]^-$ which is a more recently discovered[19] example of a cluster with a c.c.p. metal core. In this connection it has been pointed out that carbonyl–carbonyl repulsions are at a maximum on planar surfaces and that these interactions are probably an important factor in

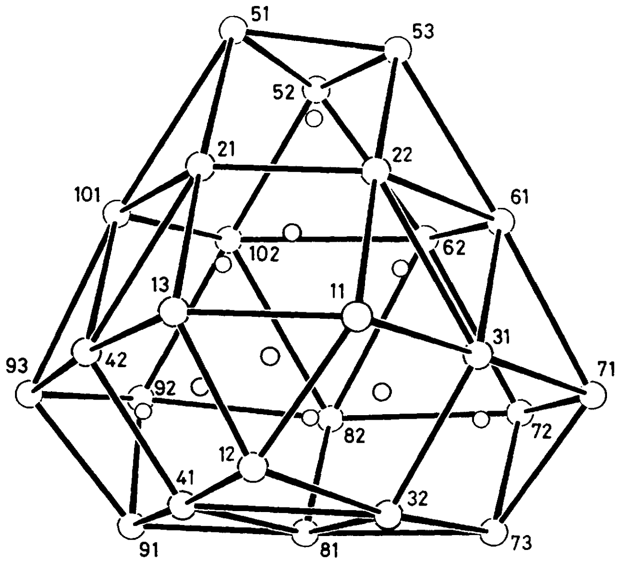

Figure 3. The truncated tetrahedral geometry of the polyhedron formed by the carbonyl oxygen atoms (large circles) in (1). The osmium atoms are shown as small circles

Table 2. Interbond angles (°) for (1) with estimated standard deviations in parentheses

(*a*) Angles between metal atoms

Os(3)–Os(1)–Os(2)	62.0(1)	Os(3)–Os(6)–Os(2)	59.7(1)
Os(4)–Os(1)–Os(2)	62.1(1)	Os(5)–Os(6)–Os(2)	58.8(1)
Os(4)–Os(1)–Os(3)	61.7(1)	Os(5)–Os(6)–Os(3)	118.5(1)
Os(3)–Os(2)–Os(1)	59.3(1)	Os(7)–Os(6)–Os(2)	118.3(1)
Os(4)–Os(2)–Os(1)	58.9(1)	Os(7)–Os(6)–Os(3)	58.6(1)
Os(4)–Os(2)–Os(3)	59.8(1)	Os(7)–Os(6)–Os(5)	176.7(1)
Os(5)–Os(2)–Os(1)	178.5(1)	Os(8)–Os(6)–Os(2)	89.6(1)
Os(5)–Os(2)–Os(3)	119.8(1)	Os(8)–Os(6)–Os(3)	59.7(1)
Os(5)–Os(2)–Os(4)	119.7(1)	Os(8)–Os(6)–Os(5)	118.8(1)
Os(6)–Os(2)–Os(1)	119.9(1)	Os(8)–Os(6)–Os(7)	58.8(1)
Os(6)–Os(2)–Os(3)	60.6(1)	Os(10)–Os(6)–Os(2)	59.5(1)
Os(6)–Os(2)–Os(4)	90.6(1)	Os(10)–Os(6)–Os(3)	89.7(1)
Os(6)–Os(2)–Os(5)	59.2(1)	Os(10)–Os(6)–Os(5)	58.5(1)
Os(10)–Os(2)–Os(1)	119.8(1)	Os(10)–Os(6)–Os(7)	119.2(1)
Os(10)–Os(2)–Os(3)	90.8(1)	Os(10)–Os(6)–Os(8)	60.3(1)
Os(10)–Os(2)–Os(4)	60.8(1)	Os(6)–Os(7)–Os(3)	62.8(1)
Os(10)–Os(2)–Os(5)	58.9(1)	Os(8)–Os(7)–Os(3)	62.3(1)
Os(10)–Os(2)–Os(6)	60.4(1)	Os(8)–Os(7)–Os(6)	62.5(1)
Os(2)–Os(3)–Os(1)	58.7(1)	Os(4)–Os(8)–Os(3)	59.5(1)
Os(4)–Os(3)–Os(1)	58.8(1)	Os(6)–Os(8)–Os(3)	60.3(1)
Os(4)–Os(3)–Os(2)	60.0(1)	Os(6)–Os(8)–Os(4)	90.0(1)
Os(6)–Os(3)–Os(1)	118.5(1)	Os(7)–Os(8)–Os(3)	58.8(1)
Os(6)–Os(3)–Os(2)	59.7(1)	Os(7)–Os(8)–Os(4)	118.2(1)
Os(6)–Os(3)–Os(4)	90.2(1)	Os(7)–Os(8)–Os(6)	58.6(1)
Os(7)–Os(3)–Os(1)	176.8(1)	Os(9)–Os(8)–Os(3)	117.8(1)
Os(7)–Os(3)–Os(2)	118.3(1)	Os(9)–Os(8)–Os(4)	58.4(1)
Os(7)–Os(3)–Os(4)	119.2(1)	Os(9)–Os(8)–Os(6)	117.5(1)
Os(7)–Os(3)–Os(6)	58.5(1)	Os(9)–Os(8)–Os(7)	175.5(1)
Os(8)–Os(3)–Os(1)	119.2(1)	Os(10)–Os(8)–Os(3)	89.7(1)
Os(8)–Os(3)–Os(2)	89.8(1)	Os(10)–Os(8)–Os(4)	60.1(1)
Os(8)–Os(3)–Os(4)	60.4(1)	Os(10)–Os(8)–Os(6)	59.8(1)
Os(8)–Os(3)–Os(6)	59.9(1)	Os(10)–Os(8)–Os(7)	118.4(1)
Os(8)–Os(3)–Os(7)	58.9(1)	Os(10)–Os(8)–Os(9)	57.7(1)
Os(2)–Os(4)–Os(1)	59.0(1)	Os(8)–Os(9)–Os(4)	62.2(1)
Os(3)–Os(4)–Os(1)	59.4(1)	Os(10)–Os(9)–Os(4)	63.1(1)
Os(3)–Os(4)–Os(2)	60.2(1)	Os(10)–Os(9)–Os(8)	62.8(1)
Os(8)–Os(4)–Os(1)	119.6(1)	Os(4)–Os(10)–Os(2)	59.7(1)
Os(8)–Os(4)–Os(2)	89.8(1)	Os(5)–Os(10)–Os(2)	59.3(1)
Os(8)–Os(4)–Os(3)	60.2(1)	Os(5)–Os(10)–Os(4)	119.0(1)
Os(9)–Os(4)–Os(1)	176.5(1)	Os(6)–Os(10)–Os(2)	60.1(1)
Os(9)–Os(4)–Os(2)	117.5(1)	Os(6)–Os(10)–Os(4)	89.8(1)
Os(9)–Os(4)–Os(3)	119.6(1)	Os(6)–Os(10)–Os(5)	59.2(1)
Os(9)–Os(4)–Os(8)	59.5(1)	Os(8)–Os(10)–Os(2)	89.7(1)
Os(10)–Os(4)–Os(1)	118.4(1)	Os(8)–Os(10)–Os(4)	59.7(1)
Os(10)–Os(4)–Os(2)	59.5(1)	Os(8)–Os(10)–Os(5)	119.1(1)
Os(10)–Os(4)–Os(3)	90.2(1)	Os(8)–Os(10)–Os(6)	59.9(1)
Os(10)–Os(4)–Os(8)	60.2(1)	Os(9)–Os(10)–Os(2)	118.5(1)
Os(10)–Os(4)–Os(9)	58.1(1)	Os(9)–Os(10)–Os(4)	58.8(1)
Os(6)–Os(5)–Os(2)	62.0(1)	Os(9)–Os(10)–Os(5)	177.7(1)
Os(10)–Os(5)–Os(2)	61.9(1)	Os(9)–Os(10)–Os(6)	119.4(1)
Os(10)–Os(5)–Os(6)	62.3(1)	Os(9)–Os(10)–Os(8)	59.5(1)

(*b*) Metal–carbido–metal

Os(3)–C–Os(2)	90.4(7)	Os(8)–C–Os(4)	90.4(6)
Os(4)–C–Os(2)	89.6(7)	Os(8)–C–Os(6)	90.3(7)
Os(4)–C–Os(3)	89.7(6)	Os(10)–C–Os(2)	88.6(6)
Os(6)–C–Os(2)	89.8(6)	Os(10)–C–Os(3)	178.9(10)
Os(6)–C–Os(3)	91.1(6)	Os(10)–C–Os(4)	89.9(6)
Os(6)–C–Os(4)	178.9(8)	Os(10)–C–Os(6)	89.2(6)
Os(8)–C–Os(2)	178.8(8)	Os(10)–C–Os(8)	90.2(7)
Os(8)–C–Os(3)	90.8(6)		

(*c*) Carbon–metal–metal

(*i*) At the capping Os atoms

C(11)–Os(1)–Os(2)	98.7(8)	C(71)–Os(7)–Os(3)	97.3(9)
C(11)–Os(1)–Os(3)	102.4(9)	C(71)–Os(7)–Os(6)	95.6(7)
C(11)–Os(1)–Os(4)	158.8(9)	C(71)–Os(7)–Os(8)	154.7(8)
C(12)–Os(1)–Os(2)	159.3(9)	C(72)–Os(7)–Os(3)	160.8(7)

(*c*) Carbon–metal–metal

(*i*) At the capping Os atoms—*continued*

C(12)–Os(1)–Os(3)	99.5(8)	C(72)–Os(7)–Os(6)	101.3(7)
C(12)–Os(1)–Os(4)	101.9(9)	C(72)–Os(7)–Os(8)	101.5(7)
C(13)–Os(1)–Os(2)	101.9(9)	C(73)–Os(7)–Os(3)	98.6(7)
C(13)–Os(1)–Os(3)	160.4(10)	C(73)–Os(7)–Os(6)	158.3(6)
C(13)–Os(1)–Os(4)	101.7(11)	C(73)–Os(7)–Os(8)	99.6(6)
C(51)–Os(5)–Os(2)	101.1(8)	C(91)–Os(9)–Os(4)	100.6(9)
C(51)–Os(5)–Os(6)	158.8(7)	C(91)–Os(9)–Os(8)	98.9(8)
C(51)–Os(5)–Os(10)	99.1(8)	C(91)–Os(9)–Os(10)	159.2(8)
C(52)–Os(5)–Os(2)	155.7(8)	C(92)–Os(9)–Os(4)	159.9(7)
C(52)–Os(5)–Os(6)	99.2(8)	C(92)–Os(9)–Os(8)	101.3(7)
C(52)–Os(5)–Os(10)	96.5(8)	C(92)–Os(9)–Os(10)	100.0(7)
C(53)–Os(5)–Os(2)	105.2(7)	C(93)–Os(9)–Os(4)	94.4(10)
C(53)–Os(5)–Os(6)	102.7(6)	C(93)–Os(9)–Os(8)	153.3(10)
C(53)–Os(5)–Os(10)	163.1(6)	C(93)–Os(9)–Os(10)	96.3(10)

(*ii*) At the Os atoms of the octahedron

C(21)–Os(2)–Os(1)	87.3(8)	C(61)–Os(6)–Os(2)	98.1(8)
C(21)–Os(2)–Os(3)	143.3(8)	C(61)–Os(6)–Os(3)	99.4(7)
C(21)–Os(2)–Os(4)	91.1(8)	C(61)–Os(6)–Os(5)	89.7(7)
C(21)–Os(2)–Os(5)	93.3(8)	C(61)–Os(6)–Os(7)	92.3(7)
C(21)–Os(2)–Os(6)	148.7(9)	C(61)–Os(6)–Os(8)	149.8(6)
C(21)–Os(2)–Os(10)	93.7(10)	C(61)–Os(6)–Os(10)	147.0(7)
C(22)–Os(2)–Os(1)	91.1(7)	C(62)–Os(6)–Os(2)	149.1(7)
C(22)–Os(2)–Os(3)	100.0(6)	C(62)–Os(6)–Os(3)	147.0(7)
C(22)–Os(2)–Os(4)	149.1(6)	C(62)–Os(6)–Os(5)	92.2(7)
C(22)–Os(2)–Os(5)	90.2(7)	C(62)–Os(6)–Os(7)	90.3(7)
C(22)–Os(2)–Os(6)	99.3(7)	C(62)–Os(6)–Os(8)	96.3(8)
C(22)–Os(2)–Os(10)	148.3(7)	C(62)–Os(6)–Os(10)	97.5(8)
C(31)–Os(3)–Os(1)	89.4(8)	C(82)–Os(8)–Os(3)	149.8(9)
C(31)–Os(3)–Os(2)	97.8(6)	C(82)–Os(8)–Os(4)	148.2(8)
C(31)–Os(3)–Os(4)	147.1(7)	C(82)–Os(8)–Os(6)	99.1(9)
C(31)–Os(3)–Os(6)	98.9(7)	C(82)–Os(8)–Os(7)	92.1(9)
C(31)–Os(3)–Os(7)	92.1(8)	C(82)–Os(8)–Os(9)	90.7(9)
C(31)–Os(3)–Os(8)	149.7(8)	C(82)–Os(8)–Os(10)	98.5(8)
C(32)–Os(3)–Os(1)	90.2(8)	C(81)–Os(8)–Os(3)	95.7(8)
C(32)–Os(3)–Os(2)	147.2(7)	C(81)–Os(8)–Os(4)	97.3(8)
C(32)–Os(3)–Os(4)	96.6(7)	C(81)–Os(8)–Os(6)	146.6(7)
C(32)–Os(3)–Os(6)	149.4(8)	C(81)–Os(8)–Os(7)	89.7(7)
C(32)–Os(3)–Os(7)	92.6(8)	C(81)–Os(8)–Os(9)	93.7(7)
C(32)–Os(3)–Os(8)	97.9(9)	C(81)–Os(8)–Os(10)	149.5(7)
C(41)–Os(4)–Os(1)	90.9(8)	C(101)–Os(10)–Os(2)	98.5(9)
C(41)–Os(4)–Os(2)	148.3(8)	C(101)–Os(10)–Os(4)	101.0(7)
C(41)–Os(4)–Os(3)	97.3(7)	C(101)–Os(10)–Os(5)	88.3(7)
C(41)–Os(4)–Os(8)	97.9(8)	C(101)–Os(10)–Os(6)	146.7(8)
C(41)–Os(4)–Os(9)	92.5(8)	C(101)–Os(10)–Os(8)	151.3(7)
C(41)–Os(4)–Os(10)	149.0(9)	C(101)–Os(10)–Os(9)	92.8(7)
C(42)–Os(4)–Os(1)	89.5(12)	C(102)–Os(10)–Os(2)	148.9(6)
C(42)–Os(4)–Os(2)	97.7(10)	C(102)–Os(10)–Os(4)	149.1(6)
C(42)–Os(4)–Os(3)	147.7(12)	C(102)–Os(10)–Os(5)	90.7(6)
C(42)–Os(4)–Os(8)	149.1(12)	C(102)–Os(10)–Os(6)	99.3(6)
C(42)–Os(4)–Os(9)	90.9(12)	C(102)–Os(10)–Os(8)	99.7(6)
C(42)–Os(4)–Os(10)	98.2(10)	C(102)–Os(10)–Os(9)	91.4(6)

(*d*) Carbonyl–metal–carbonyl

(*i*) At the capping osmium atoms

C(12)–Os(1)–C(11)	94.4(12)	C(72)–Os(7)–C(71)	95.0(11)
C(13)–Os(1)–C(11)	90.5(14)	C(73)–Os(7)–C(71)	98.2(9)
C(13)–Os(1)–C(12)	94.0(12)	C(73)–Os(7)–C(72)	94.1(10)
C(52)–Os(5)–C(51)	92.9(11)	C(92)–Os(9)–C(91)	93.0(11)
C(53)–Os(5)–C(51)	93.9(10)	C(93)–Os(9)–C(91)	97.7(11)
C(53)–Os(5)–C(52)	93.5(11)	C(93)–Os(9)–C(92)	98.5(12)

(*ii*) At the Os atoms of the octahedron

C(22)–Os(2)–C(21)	95.1(11)	C(62)–Os(6)–C(61)	91.9(12)
C(32)–Os(3)–C(31)	91.4(10)	C(82)–Os(8)–C(81)	91.8(12)
C(42)–Os(4)–C(41)	91.3(12)	C(102)–Os(10)–C(101)	87.4(10)

determining the size of cluster faces.[20] These large cluster faces may provide the best analogy so far of a monolayer of carbon monoxide chemisorbed onto a metal surface. However the analogy may be limited by the fact that the density of CO molecules on the surface of (1) is 1.0 per metal atom whereas for chemisorbed CO it does not exceed *ca.* 0.66 per surface metal atom.

The carbonyl ligands on the surface of (1) are closely packed and the largest OC–Os–CO angle in the structure (Table 2) is only 98.5°, with the mean value being 94(3)°. The carbonyl array has a truncated tetrahedral geometry as illustrated in Figure 3. With such close packing of carbonyls it might therefore be expected that reaction with incoming ligands will necessitate an opening out of the metal core and preliminary results with halogen ligands appear to confirm this. For example, when the cluster dianion reacts with iodine there is successive opening up of the capping tetrahedra.[21]

Wade theory [1] extended to include capped *closo*-polyhedra [3] and capped *nido*- and *arachno*-polyhedra [4] has had remarkable success in predicting and rationalising the geometries of osmium cluster species. The dianion (1) has 134 valence electrons, so using Wade's skeletal electron counting procedures the fundamental polyhedron should be an octahedron to accommodate the seven skeletal electron pairs. Since capped and uncapped versions of the same polyhedron require the same number of skeletal electron pairs, location of the four remaining osmium atoms in capping positions, as observed (Figure 2), would have been predicted by Wade theory. The largest multicapped octahedral cluster so far reported is the heteronuclear trianion $[Fe_6Pd_6(CO)_{24}H]^{3-}$.[22] This has a central Pd core capped by Fe atoms on all but two *trans* faces. It is interesting to speculate that if the capping principle holds for larger clusters with $S = 7$ the limit would be an octacapped M_{14} species with a structure corresponding to the complete face-centred cubic (f.c.c.) unit cell shown in Figure 2(*b*).

For (1), other approaches to cluster bonding have been less successful in rationalising the Os_{10} geometry. For example, before the discovery of (1) Lauher [23] concluded from extended Hückel molecular orbital calculations that a cluster with an overall tetrahedral arrangement of 10 metal atoms would require 140 valence electrons not the 134 actually observed here. In more recent work Lauher [24] suggests that the structure of (1) may be consistent with the results of these calculations if it is regarded as a member of an electron deficient class of cluster compound usually limited to the earlier transition metals.

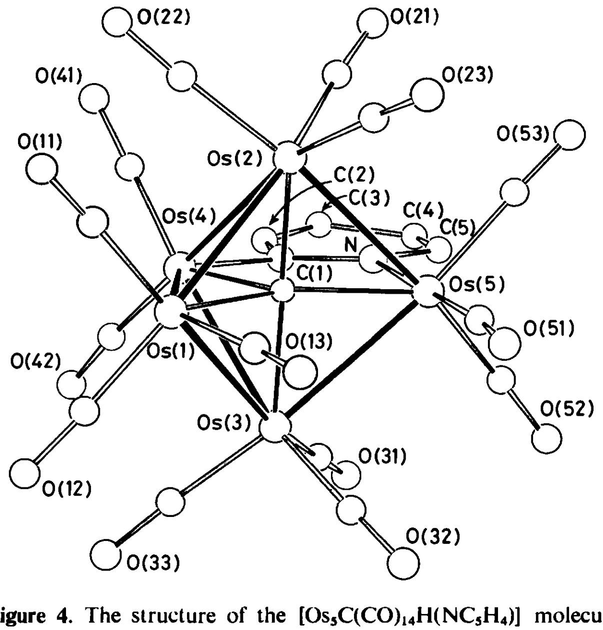

Figure 4. The structure of the $[Os_5C(CO)_{14}H(NC_5H_4)]$ molecule. The carbonyl carbon atoms have the same numbers as the relevant oxygen atoms

X-Ray analysis has established that the pentanuclear carbido-species obtained from the pyrolysis of $[Os_3(CO)_{11}(py)]$, *i.e.* $[Os_5C(CO)_{14}H(NC_5H_4)]$ (2), has the structure shown in Figure 4. Four osmium atoms form a 'butterfly' arrangement

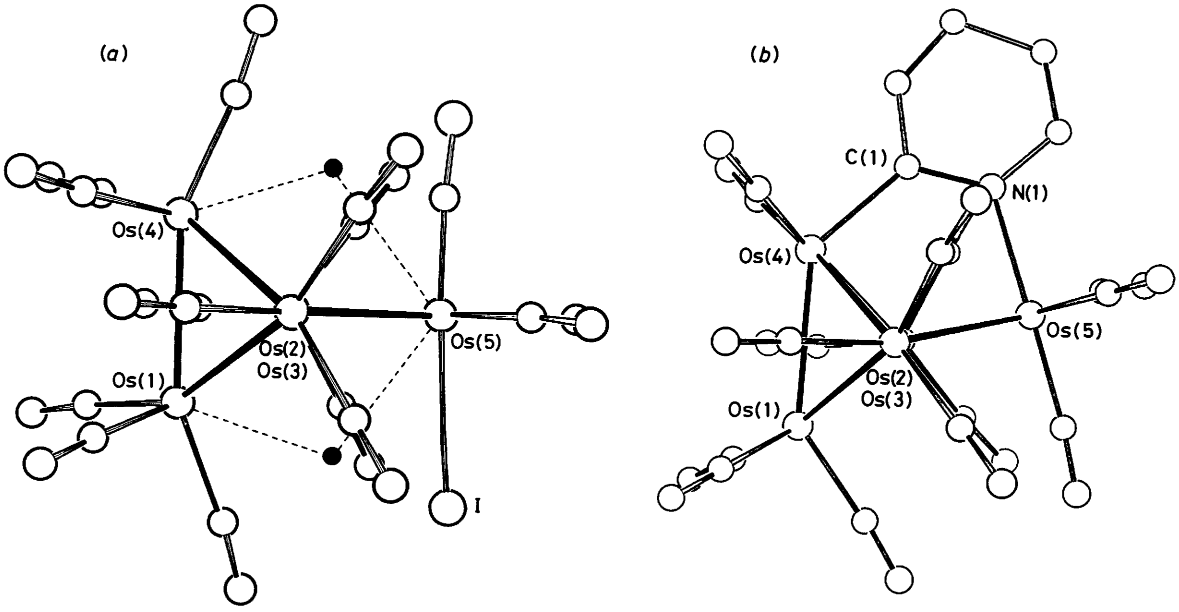

Figure 5. (*a*) The *arachno*-pentagonal bipyramidal structure of the anion $[Os_5C(CO)_{15}HI]^-$ (*ref.* 5). (*b*) A view of the $[Os_5C(CO)_{14}H(NC_5H_4)]$ molecule viewed along the Os(2) ··· Os(3) axis

Table 3. Selected interatomic distances (Å) for (2) with estimated standard deviations in parentheses

(*a*) Osmium–osmium

Os(1)–Os(2)	2.896(1)	Os(2)–Os(5)	2.912(1)
Os(1)–Os(3)	2.902(1)	Os(3)–Os(4)	2.853(1)
Os(1)–Os(4)	2.927(1)	Os(3)–Os(5)	2.908(1)
Os(2)–Os(4)	2.860(1)	Os(1) · · · Os(5)	4.080(1)
		Os(4) · · · Os(5)	3.626(1)

(*b*) Osmium–ligand

Os(1)–C	2.11(3)	Os(5)–C	2.12(3)
Os(2)–C	1.97(3)	Os(4)–C(1)	2.04(2)
Os(3)–C	2.01(3)	Os(5)–N(1)	2.16(2)
Os(4)–C	2.06(3)	Mean Os–CO	1.88

(*c*) Intraligand

N–C(1)	1.39(3)	C(2)–C(3)	1.41(4)
N–C(5)	1.42(3)	C(3)–C(4)	1.47(5)
C(1)–C(2)	1.42(4)	C(4)–C(5)	1.35(4)
		Mean C–O	1.17

Table 4. Selected interbond angles (°) for (2) with estimated standard deviations in parentheses

(*a*) Angles between osmium atoms

Os(2)–Os(1)–Os(3)	86.8(1)	Os(1)–Os(3)–Os(4)	61.1(1)
Os(2)–Os(1)–Os(4)	58.8(1)	Os(1)–Os(3)–Os(5)	89.2(1)
Os(3)–Os(1)–Os(4)	58.6(1)	Os(4)–Os(3)–Os(5)	78.0(1)
Os(1)–Os(2)–Os(4)	61.1(1)	Os(1)–Os(4)–Os(2)	60.0(1)
Os(1)–Os(2)–Os(5)	89.3(1)	Os(4)–Os(4)–Os(3)	60.2(1)
Os(4)–Os(2)–Os(5)	77.8(1)	Os(2)–Os(4)–Os(3)	88.4(1)
		Os(2)–Os(5)–Os(3)	86.4(1)

(*b*) Angles at the carbido-atom

Os(1)–C–Os(2)	90.5(10)	Os(2)–C–Os(4)	90.5(11)
Os(1)–C–Os(3)	89.5(11)	Os(2)–C–Os(5)	90.8(11)
Os(1)–C–Os(4)	89.4(10)	Os(3)–C–Os(4)	89.0(11)
Os(1)–C–Os(5)	150.2(13)	Os(3)–C–Os(5)	89.4(10)
Os(2)–C–Os(3)	179.5(13)	Os(4)–C–Os(5)	120.6(13)

(*c*) Osmium–osmium–ligand angles

Os(2)–Os(1)–C(11)	89.2(9)	Os(4)–Os(3)–C(32)	162.0(9)
Os(2)–Os(1)–C(12)	170.1(10)	Os(4)–Os(3)–C(33)	96.1(8)
Os(2)–Os(1)–C(13)	98.0(9)	Os(5)–Os(3)–C(31)	85.3(9)
Os(3)–Os(1)–C(11)	171.4(9)	Os(5)–Os(3)–C(32)	92.6(9)
Os(3)–Os(1)–C(12)	89.8(10)	Os(5)–Os(3)–C(33)	173.8(9)
Os(3)–Os(1)–C(13)	94.0(9)	Os(1)–Os(4)–C(1)	136.2(7)
Os(4)–Os(1)–C(11)	112.8(9)	Os(1)–Os(4)–C(41)	119.4(11)
Os(4)–Os(1)–C(12)	111.6(10)	Os(1)–Os(4)–C(42)	116.0(9)
Os(4)–Os(1)–C(13)	142.5(9)	Os(2)–Os(4)–C(1)	91.2(7)
Os(1)–Os(2)–C(21)	160.4(10)	Os(2)–Os(4)–C(41)	88.2(11)
Os(1)–Os(2)–C(22)	88.1(10)	Os(2)–Os(4)–C(42)	175.9(10)
Os(1)–Os(2)–C(23)	104.6(8)	Os(3)–Os(4)–C(1)	89.1(7)
Os(4)–Os(2)–C(21)	99.5(10)	Os(3)–Os(4)–C(41)	176.1(11)
Os(4)–Os(2)–C(22)	91.3(11)	Os(3)–Os(4)–C(42)	90.0(10)
Os(4)–Os(2)–C(23)	162.1(8)	Os(2)–Os(5)–N(1)	86.1(5)
Os(5)–Os(2)–C(21)	89.6(9)	Os(2)–Os(5)–C(51)	92.5(7)
Os(5)–Os(2)–C(22)	168.8(11)	Os(2)–Os(5)–C(52)	173.4(8)
Os(5)–Os(2)–C(23)	91.9(8)	Os(2)–Os(5)–C(53)	87.1(8)
Os(1)–Os(3)–C(31)	156.7(8)	Os(3)–Os(5)–N(1)	86.4(5)
Os(1)–Os(3)–C(32)	104.5(8)	Os(3)–Os(5)–C(51)	94.0(8)
Os(1)–Os(3)–C(33)	89.4(8)	Os(3)–Os(5)–C(52)	88.5(8)
Os(4)–Os(3)–C(31)	95.6(8)	Os(3)–Os(5)–C(53)	172.9(8)

(*d*) Ligand–osmium–ligand angles

C(11)–Os(1)–C(12)	93.0(13)	C(1)–Os(4)–C(41)	89.0(12)
C(11)–Os(1)–C(13)	94.1(13)	C(1)–Os(4)–C(42)	92.6(12)
C(12)–Os(1)–C(13)	91.6(14)	C(41)–Os(4)–C(42)	93.5(15)
C(21)–Os(2)–C(22)	89.2(14)	N(1)–Os(5)–C(51)	178.5(9)
C(21)–Os(2)–C(23)	95.0(13)	N(1)–Os(5)–C(52)	89.4(9)
C(22)–Os(2)–C(23)	99.3(13)	N(1)–Os(5)–C(53)	90.4(10)
C(31)–Os(3)–C(32)	98.3(12)	C(51)–Os(5)–C(52)	92.1(10)
C(31)–Os(3)–C(33)	93.6(12)	C(51)–Os(5)–C(53)	89.1(11)
C(32)–Os(3)–C(33)	94.5(12)	C(52)–Os(5)–C(53)	97.8(11)

with the fifth spanning the ' wing tips '. The carbonyl ligands are all terminal with Os–C–O angles in the range 173—179°. In (2) the unique osmium atom, Os(5), is linked to one of the ' hinge ' atoms, Os(4), *via* a bridging C_5H_4N ligand. This has been formed by orthometallation of the unidentate pyridine group, present in $[Os_3(CO)_{11}(py)]$ before pyrolysis, to give an Os(4)–C(1) bond of length 2.04(2) Å.

The molecule (2) is a member of a small group of pentanuclear osmium species with eight skeletal electron pairs ($S = 8$) which all have similar bridged ' butterfly ' metal core geometries. At first sight these did not appear to be explicable by Wade theory. However, for the anion $[Os_5C(CO)_{15}HI]^-$ (3) the metal core has virtual C_{2v} symmetry and it was shown that the metal arrangement can be derived from a pentagonal bipyramid by removal of two equatorial vertices as shown in Figure 5(*a*).[5] The Os_5 geometry in this class of cluster is therefore also compatible with Wade theory which requires an *arachno*-pentagonal bipyramidal metal arrangement for pentanuclear species with $S = 8$.

In the anion $[Os_5C(CO)_{15}HI]^-$ (3), the two sets of osmium atoms adjacent to the vacant equatorial sites have almost equal separations, Os(1) · · · Os(5) 4.022 Å and Os(4) · · · Os(5) 4.007 Å. In (2) the metal core is distorted from the ideal C_{2v} symmetry by the bonding requirements of the bridging C_5H_4N ligand, Figure 5(*b*). The bridged equatorial osmium atoms are considerably closer [Os(4) · · · Os(5) 3.626 Å] than the two non-bridged osmium atoms adjacent to the second vacant site [Os(1) · · · Os(5) 4.080 Å (Table 3)].

The hydrogen ligand in (2) was not located directly but its position may be inferred by the marked bending back of the carbonyls associated with the ' hinge ' bond Os(1)–Os(4) consistent with the location of a μ-H ligand between these atoms. The distortion of the carbonyl distribution in (2) can be seen by comparison with that of the non-hydrido-cluster (3) shown in Figure 5(*a*). The mean Os–Os–C angle at the ' hinge ' in (2) is 115.0° (Table 4) whereas in (3) it is 99.2°. It is significant that the Os(1)–Os(4) bond of 2.748(1) Å in (3) is the shortest present whereas in (2) this ' hinge ' bond is 2.927(1) Å and is longer than any other metal–metal bond in that structure. It is well known that a bridging hydrogen ligand often produces lengthening of the metal–metal bond so this is further evidence of its location. Bridging H ligands associated with the ' hinge ' Os–Os bond have also been inferred in the similar bridged ' butterfly ' structures of three pentanuclear cluster compounds obtained from pyrolysis of $[Os_3(CO)_{11}\{P(OMe)_3\}]$.[25]

Experimental

Infrared spectra were recorded on a Perkin-Elmer 257 instrument using carbon monoxide gas calibrant (central position 2 143 cm^{-1}), and n.m.r. spectra were obtained on a Varian XL-100 spectrometer. Thin layer chromatography plates were bought from Merck and consisted of 20 × 20 cm glass plates coated with a 0.25 mm layer of silica gel. Silica gel (70—230 mesh) was used for column chromatography.

Pyrolysis of $[Os_3(CO)_{11}(py)]$.—The compound $[Os_3(CO)_{11}(py)]$ (400 mg), whose synthesis has been described pre-

Table 5. Fractional atomic co-ordinates for the dianion * (1) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Os(1)	0.350 49(4)	0.147 15(6)	−0.141 91(8)	C(52)	0.238 8(11)	0.385 0(14)	0.355 7(23)
Os(2)	0.318 02(3)	0.248 30(5)	0.053 22(7)	O(52)	0.210 8(8)	0.414 3(10)	0.419 7(17)
Os(3)	0.249 91(3)	0.201 31(5)	−0.182 55(7)	C(53)	0.300 9(10)	0.447 8(14)	0.221 6(21)
Os(4)	0.286 71(4)	0.093 37(5)	0.003 38(8)	O(53)	0.313 8(8)	0.504 8(11)	0.203 6(17)
Os(5)	0.283 41(4)	0.347 35(5)	0.248 52(8)	C(61)	0.223 2(10)	0.397 9(13)	−0.040 3(21)
Os(6)	0.215 09(4)	0.306 17(5)	0.020 35(7)	O(61)	0.231 2(8)	0.453 8(11)	−0.079 5(17)
Os(7)	0.150 40(4)	0.257 47(5)	−0.208 16(7)	C(62)	0.161 9(11)	0.346 4(14)	0.093 1(23)
Os(8)	0.183 11(4)	0.150 25(5)	−0.028 96(7)	O(62)	0.125 8(8)	0.373 4(11)	0.136 2(17)
Os(9)	0.223 10(4)	0.048 16(5)	0.157 78(8)	C(71)	0.156 7(10)	0.341 8(14)	−0.295 1(22)
Os(10)	0.252 61(4)	0.197 60(5)	0.207 89(7)	O(71)	0.161 6(7)	0.393 1(10)	−0.347 2(15)
C(11)	0.380 8(12)	0.217 1(16)	−0.221 4(25)	C(72)	0.089 4(10)	0.290 7(13)	−0.166 6(21)
O(11)	0.394 0(9)	0.263 9(12)	−0.271 4(19)	O(72)	0.049 1(8)	0.310 6(10)	−0.140 8(16)
C(12)	0.348 0(11)	0.069 3(15)	−0.285 0(24)	C(73)	0.122 9(9)	0.191 4(11)	−0.353 2(18)
O(12)	0.347 0(8)	0.020 3(10)	−0.369 3(17)	O(73)	0.108 7(6)	0.151 1(8)	−0.443 8(14)
C(13)	0.411 7(13)	0.112 7(17)	−0.059 2(27)	C(81)	0.157 2(10)	0.073 7(13)	−0.151 5(21)
O(13)	0.451 8(10)	0.086 4(13)	−0.011 8(22)	O(81)	0.144 2(7)	0.019 0(10)	−0.224 7(16)
C(21)	0.374 7(11)	0.218 4(15)	0.162 1(24)	C(82)	0.126 7(12)	0.163 5(15)	0.034 6(25)
O(21)	0.412 3(7)	0.196 5(10)	0.238 5(16)	O(82)	0.087 2(10)	0.175 0(12)	0.076 7(20)
C(22)	0.345 6(9)	0.327 6(12)	0.000 0(19)	C(91)	0.201 6(11)	−0.044 0(15)	0.062 1(23)
O(22)	0.359 6(7)	0.384 4(10)	−0.037 7(15)	O(91)	0.194 1(8)	−0.101 8(11)	0.004 9(18)
C(31)	0.265 5(10)	0.273 3(13)	−0.285 9(20)	C(92)	0.173 2(10)	0.053 4(13)	0.255 3(21)
O(31)	0.274 9(8)	0.319 4(10)	−0.353 3(17)	O(92)	0.139 3(9)	0.057 9(11)	0.311 5(19)
C(32)	0.236 0(10)	0.130 5(13)	−0.324 8(21)	C(93)	0.275 5(12)	0.005 7(16)	0.278 1(25)
O(32)	0.225 6(8)	0.082 1(10)	−0.415 9(16)	O(93)	0.301 7(9)	−0.035 1(12)	0.352 1(19)
C(41)	0.277 9(10)	0.005 6(13)	−0.110 3(21)	C(101)	0.299 4(10)	0.175 5(13)	0.348 9(20)
O(41)	0.269 3(8)	−0.047 0(11)	−0.184 4(17)	O(101)	0.332 8(8)	0.153 7(10)	0.432 9(17)
C(42)	0.340 4(14)	0.048 6(18)	0.102 3(29)	C(102)	0.207 7(9)	0.221 8(11)	0.321 6(18)
O(42)	0.377 7(12)	0.021 0(15)	0.167 3(25)	O(102)	0.177 9(7)	0.238 1(10)	0.388 2(16)
C(51)	0.335 9(11)	0.336 6(14)	0.388 6(22)	C	0.250 5(7)	0.199 4(9)	0.010 1(14)
O(51)	0.372 6(7)	0.327 4(10)	0.472 5(16)				

* The atomic co-ordinates of the two $[N(PPh_3)_2]^+$ cations have been deposited, see SUP No. 23375.

Table 6. Fractional atomic co-ordinates for (2) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Os(1)	0.497 96(11)	0.217 58(6)	0.320 76(6)	C(22)	0.511 9(38)	0.046 9(19)	0.409 5(20)
Os(2)	0.328 03(11)	0.087 72(6)	0.362 92(6)	O(22)	0.621 9(29)	0.019 5(14)	0.440 0(16)
Os(3)	0.284 52(10)	0.228 61(5)	0.182 92(5)	C(23)	0.239 4(29)	0.116 9(15)	0.454 1(16)
Os(4)	0.443 81(10)	0.091 47(5)	0.213 27(6)	O(23)	0.185 5(26)	0.136 3(13)	0.509 5(15)
Os(5)	0.068 30(10)	0.141 85(5)	0.262 73(6)	C(31)	0.173 3(32)	0.195 6(15)	0.090 0(17)
C	0.306 0(30)	0.157 7(15)	0.274 2(16)	O(31)	0.101 4(26)	0.175 7(13)	0.033 5(14)
N	0.114 6(21)	0.051 2(11)	0.185 1(11)	C(32)	0.176 7(32)	0.318 6(16)	0.197 2(17)
C(1)	0.259 0(26)	0.034 9(13)	0.164 1(14)	O(32)	0.102 6(25)	0.371 2(13)	0.204 3(13)
C(2)	0.271 0(30)	−0.022 6(16)	0.108 2(16)	C(33)	0.433 2(31)	0.274 4(15)	0.130 3(17)
C(3)	0.143 4(38)	−0.061 9(19)	0.074 1(20)	O(33)	0.522 6(27)	0.301 7(13)	0.088 8(14)
C(4)	−0.005 2(32)	−0.042 9(16)	0.099 3(17)	C(41)	0.533 9(37)	0.003 4(20)	0.236 4(20)
C(5)	−0.015 6(29)	0.012 3(15)	0.152 1(16)	O(41)	0.597 7(29)	−0.058 1(16)	0.252 1(16)
C(11)	0.645 6(35)	0.196 1(17)	0.405 0(18)	C(42)	0.525 3(35)	0.099 7(17)	0.120 4(19)
O(11)	0.736 6(29)	0.185 8(14)	0.454 2(16)	O(42)	0.570 3(26)	0.107 5(13)	0.056 4(14)
C(12)	0.616 3(36)	0.289 7(18)	0.280 5(19)	C(51)	0.030 2(27)	0.221 4(14)	0.334 2(15)
O(12)	0.698 0(26)	0.334 2(13)	0.254 9(13)	O(51)	0.016 4(23)	0.271 5(11)	0.372 7(13)
C(13)	0.396 8(33)	0.290 2(16)	0.377 4(17)	C(52)	−0.085 5(28)	0.175 9(14)	0.188 3(15)
O(13)	0.346 1(31)	0.335 7(15)	0.410 8(17)	O(52)	−0.179 4(25)	0.203 8(12)	0.145 1(13)
C(21)	0.243 2(35)	−0.009 1(18)	0.359 0(19)	C(53)	−0.053 6(30)	0.076 6(15)	0.319 4(16)
O(21)	0.184 0(27)	−0.065 3(14)	0.361 0(14)	O(53)	−0.130 0(25)	0.037 3(13)	0.351 3(13)

viously,[26] was placed in a Carius tube of 100 cm^3 capacity and evacuated at 10^{-3} Torr (0.133 Pa) for 15 min. The tube was then sealed under vacuum, placed in an oven, and heated to 250 °C. The product distribution was dependent on the reaction time. After 15 h a yellow-brown solid was formed; this was extracted with portions of hot acetone and the solution reduced in volume to 5 cm^3 in stages. This led to the precipitation of $[Os_4(CO)_{12}H_4]$ (36 mg, 10% based on Os). An excess of $[N(PPh_3)_2]Cl$ in MeOH was added to the remaining solution and slow evaporation produced dark red crystals of the complex $[N(PPh_3)_2]_2[Os_{10}C(CO)_{24}]$ (60 mg, 13%) (Found: C, 31.40; H, 1.80; N, 0.75. Calc. for $C_{97}H_{60}N_2O_{24}Os_{10}P_4$: C, 31.80; H, 1.65; N, 0.75%). The brown supernatant was then separated by column chromatography (eluant 1 : 90 acetone–hexane) giving first a yellow band, $[Os_3(CO)_{10}H(NC_5H_4)]$ (42 mg, 11%), then $[N(PPh_3)_2][Os_5(CO)_{15}H]$ (180 mg, 38%). Both clusters were characterised by i.r. and mass spectroscopy after protonation by concentrated H_2SO_4 in MeCN in the case of the anion. A small additional amount of $[N(PPh_3)_2]_2[Os_{10}C(CO)_{24}]$ (10 mg, 2%) was then extracted from the column using pure acetone. When the reaction time was extended to 64 h the product was red-brown; work up as above yielded $[Os_4(CO)_{12}H_4]$ (20 mg, 6%), $[N(PPh_3)_2]_2[Os_{10}C(CO)_{24}]$ (300 mg, 65%), and $[N(PPh_3)_2][Os_5(CO)_{15}H]$ (113 mg, 24%) as the major components, but Os metal was also present. However, in this case the yellow fraction obtained from the column was predominantly $[Os_5C(CO)_{14}H(NC_5H_4)]$ (2) (13 mg, 4%) which was separated from traces of $[Os_3(CO)_{10}H(NC_5H_4)]$ by fractional crystallisation. Analysis for (2), Found: C, 16.60; H, 0.25; N, 1.00. Calc. for $C_{20}H_5NO_{14}Os_5$: C, 16.80; H, 0.35; N, 1.00%. I.r., ν(CO) for (2) (hexane) at 2 105w, 2 077s, 2 059vs, 2 054m (sh), 2 025m, 2 010s, 1 998m, 1 994m, 1 981w, and 1 955w cm^{-1}. ^1H N.m.r. for (2) ($CDCl_3$), τ 1.37(d), 1.91(d), 3.17(t), 3.64(t), and 33.96(s).

Pyrolysis of $[Os_3(CO)_{12}]$.—Excess $[N(PPh_3)_2]Cl$ in MeOH was added to a filtered acetone solution of the residues from the vacuum tube pyrolysis of $[Os_3(CO)_{12}]$. Recrystallisation from acetone–methanol yielded crystals of $[N(PPh_3)_2]_2$-$[Os_{10}C(CO)_{24}]$ {yield <5% from a 1 g charge of $[Os_3(CO)_{12}]$}.

X-*Ray Crystallography*.—Crystals of the $[NBu^n{}_4]^+$ salt of (1) were obtained by slow evaporation from tetrahydrofuran–MeOH and mounted in a Lindemann tube with some of the mother-liquor to obtain unit-cell dimensions. Repeated movement of the crystal prevented further data collection. Stable crystals of the $[N(PPh_3)_2]^+$ salt were recrystallised from Me_2CO–MeOH and were used for data collection.

Crystal data for (1), $[NBu^n{}_4]^+$ *salt.* $C_{57}H_{72}N_2O_{24}Os_{10}$, $M =$ 3 071.2, Monoclinic, space group $I2/c$ or Ic, $a = 17.870$, $b = 28.692$, $c = 17.864$ Å, $\beta = 113.05°$.

Crystal data for (1), $[N(PPh_3)_2]^+$ *salt.* $C_{97}H_{60}N_2O_{24}Os_{10}P_4$, $M = 3\,634.2$, Triclinic, space group $P\bar{1}$, $a = 27.157(5)$, $b = 17.535(4)$, $c = 10.470(2)$ Å, $\alpha = 96.37(2)$, $\beta = 100.71(2)$, $\gamma = 85.92(2)°$, $U = 4\,862.2$ Å^3, $F(000) = 3\,336$, $D_m = 2.50$, $Z = 2$, $D_c = 2.49$ g cm^{-3}, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 126.2 cm^{-1}. The space group was assumed and confirmed by satisfactory refinement. Suitable crystals of (2) were obtained from CH_2Cl_2 at −20 °C.

Crystal data for (2). $C_{20}H_5NO_{14}Os_5$, $M = 1\,434.2$, Monoclinic, space group $P2_1/c$, $a = 8.869(2)$, $b = 17.870(3)$, $c = 17.208(3)$ Å, and $\beta = 95.30(2)°$, $U = 2\,715.6$ Å^3, $F(000) = 2\,496$, $Z = 4$, $D_c = 2.56$ g cm^{-3}, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 224.7 cm^{-1}. The space group was unambiguously assigned from systematic absences in the data $h0l$, $l = 2n + 1$, and $0k0$, $k = 2n + 1$.

The methods of data collection, data processing, and absorption correction used for the $[N(PPh_3)_2]^+$ salt of (1) and for (2) have been described previously.[27] The crystals selected for data collection had dimensions 0.26 × 0.21 × 0.07 mm (1) and 0.25 × 0.25 × 0.24 mm (2). A scan width of 0.80° was used to collect data in the θ range 3—25.0° for both crystals. 432 Azimuthal scan data for (1) and 384 for (2) were used in absorption correction and relative transmission factors varied from 1.0 to 0.149 for (1) and from 1.0 to 0.796 for (2). Equivalent reflections were averaged to give 8 942 and 3 518 data with $I/\sigma(I) \geqslant 3.0$ for (1) and (2) respectively.

Structure solution and refinement.[28] The position of six osmium atoms for (1) (defining an octahedron) were found from a Patterson synthesis. The remaining four osmium atoms and the non-hydrogen atoms were found from subsequent difference-Fourier syntheses and established the formulation of (1) as $[Os_{10}C(CO)_{24}]^{2-}$. Blocked full-matrix refinement of the atomic positional and thermal parameters converged at a final R of 0.0553 and R' of 0.0581.[27] The phenyl groups were treated as rigid hexagons [d(C–C) = 1.395 Å] and no allowance was made for the phenyl hydrogen atoms in the structure factor calculations. Anisotropic thermal parameters were assigned to the Os, P, and N atoms in the final cycles of refinement. A final difference-Fourier synthesis showed a few residual peaks of *ca.* 2 e Å^{-3} in the region of the osmium atoms.

For (2) all five osmium atoms were located from a Patterson map and the remaining non-hydrogen atoms were found in subsequent difference-Fourier syntheses. Blocked full-matrix refinement with anisotropic thermal parameters assigned to the osmium atoms converged at R 0.0604 and R' 0.0599. A difference-Fourier synthesis calculated using data with $\sin\theta < 0.35$ failed to reveal the location of the hydrogen atoms. The final atomic co-ordinates for the dianion in the $[N(PPh_3)_2]^+$ salt of (1) and for (2) are given in Tables 5 and 6 respectively. Selected bond lengths for (1) and (2) are in Tables 1 and 3 and the corresponding interbond angles in Tables 2 and 4 respectively.

Note added in proof: We have recently found that $[Os_3(CO)_{11}(py)]$ may be more conveniently prepared by adding one equivalent of NMe_3O, dissolved in MeOH, to a solution of $[Os_3(CO)_{12}]$ in CH_2Cl_2 containing a slight excess of pyridine. Filtration through silica followed by evaporation of the solvent gives $[Os_3(CO)_{11}(py)]$ in > 90% yield.

Acknowledgements

We thank the S.R.C. for financial support (to P. F. J. and W. J. H. N.).

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Received 20th April 1982; *Paper* 2/658