Synthesis and *X*-Ray Analysis of $[PMePh_3][Os_8H(CO)_{22}]$ and $[Os_8H(CO)_{22}I]$ †

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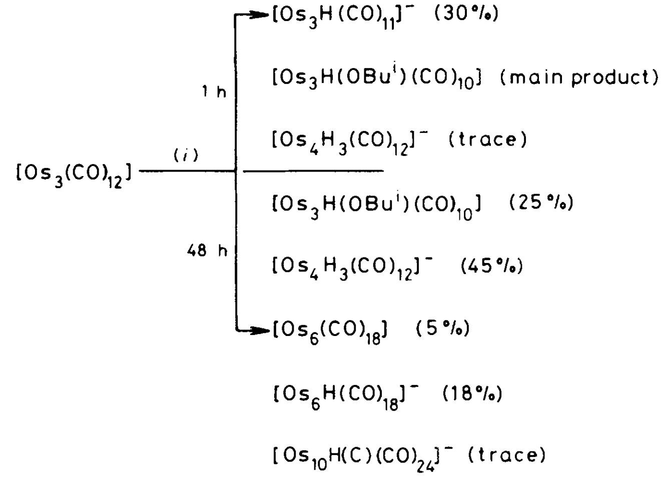
The cluster anion $[Os_8H(CO)_{22}]^-$ (1) has been obtained from the reaction of $[Os_3(CO)_{12}]$ in Bu^{t}OH and *X*-ray analysis of its $[PMePh_3]^+$ salt shows that the anion has an unusual fused tetrahedral metal-core geometry related to that of $[Os_6(CO)_{18}]$. Reaction of (1) with iodine gives $[Os_8H(CO)_{22}I]$ (2) in which an overall change in cluster geometry has occurred; the reaction is reversible and heating (2) with iodide regenerates (1). Reaction of (1) with concentrated H_2SO_4 gives $[Os_8H_2(CO)_{22}]$ which reacts with $P(OMe)_3$ to give $[Os_8H_2(CO)_{22}\{P(OMe)_3\}]$ and with halide ions to give eventually $[Os_8(CO)_{22}]^{2-}$. Crystals of $[PMePh_3][Os_8H(CO)_{22}]$ are triclinic, space group $P\bar{1}$, with a = 16.775(3), b = 13.509(2), c = 11.267(2) Å, α = 89.88(1), β = 103.97(1), γ = 96.99(1)°, and Z = 2. Refinement of atomic parameters using 5 615 absorption-corrected data converged at R = 0.0359. Crystals of $[Os_8H(CO)_{22}I]\cdot H_2O$ are monoclinic, space group $P2_1/c$, with a = 14.386(2), b = 11.037(1), c = 24.629(3) Å, β = 94.30(2)°, and Z = 4. Refinement of atomic parameters using 4 644 absorption-corrected reflections converged at R = 0.0569.

The usual route to the higher clusters of osmium has been *via* the pyrolysis of $[Os_3(CO)_{12}]$ and its derivatives *in vacuo*.[1] However, the reaction conditions employed, and the complex mixture of products obtained, make an understanding of the mechanism of cluster growth difficult. The recently reported[2] synthesis of $[Rh_{22}(CO)_{37}]^{4-}$ from the reaction of $[Rh_4(CO)_{12}]$ with NaOH in Pr^{i}OH prompted us to investigate the corresponding reaction of $[Os_3(CO)_{12}]$. Under similar conditions, which allow the building-up sequence to be more conveniently investigated, we have synthesized a range of cluster species with up to 10 osmium atoms including the new hydrido-monoanion $[Os_8H(CO)_{22}]^-$ (1).[3] This species has an unexpected metal-core geometry which cannot be explained by conventional skeletal electron-counting procedures.

The anion (1) reacts reversibly with iodine to give the neutral derivative $[Os_8H(CO)_{22}I]$ (2); this reaction is accompanied by major structural change involving not only cleavage of Os–Os bonds, but also rearrangement of the carbonyl ligands.[4] This behaviour contrasts to that observed for the carbido-dianion $[Os_{10}C(CO)_{24}]^{2-}$ which was previously shown to react reversibly with I_2 *via* the sequential opening up at capping $Os(CO)_3$ groups without CO migration.[5]

Results and Discussion

The complex $[Os_3(CO)_{12}]$ was heated in Bu^{t}OH under reflux with KOH (Os : $[OH]^-$ = 5 : 1) for varying lengths of time, the products separated by t.l.c. or fractional crystallization (anions as their $[N(PPh_3)_2]^+$ salts), and characterized by spectroscopic methods (Table 1). After 1 h the trinuclear species $[Os_3H(CO)_{11}]^-$ and $[Os_3H(OBu^t)(CO)_{10}]$ were the major products of the reaction (Scheme 1) together with a trace of $[Os_4H_3(CO)_{12}]^-$. However after longer reaction times (12—48 h) larger clusters were also isolated whose concentration became fairly constant (Scheme 1). Thus, a typical product distribution was, after 48 h, $[Os_3H(OBu^t)(CO)_{10}]$ (25%), $[Os_4H_3(CO)_{12}]^-$ (45%), $[Os_6H(CO)_{18}]^-$ (5%), $[Os_6(CO)_{18}]$ (5%), and $[Os_{10}H(C)(CO)_{24}]^-$ (trace). More $[Os_{10}H(C)(CO)_{24}]^-$ was obtained on extending the reaction time but the maximum yield obtained was only *ca.* 10% (after 144 h).



Scheme 1. (*i*) KOH, Bu^{t}OH, $\{[Os_3(CO)_{12}] : [OH^-] = 5 : 1\}$. Reactions of $[Os_3(CO)_{12}]$ with KOH heated under N_2 reflux in Bu^{t}OH. With increasing time the relative concentrations of products became fairly constant; typical approximate distributions are shown. Separation was by t.l.c., characterisation was by i.r. and mass spectroscopy with the anions as their $[N(PPh_3)_2]^+$ salts. Owing to decomposition on t.l.c. plates the anion $[Os_3H(CO)_{11}]^-$ was separated by fractional crystallisation as its $[N(PPh_3)_2]^+$ salt

In order to investigate the building-up sequence the individual stability of the above products was first examined by refluxing them in turn in Bu^{t}OH without base. The anions were found to be stable on heating (48 h) with the exception of $[Os_3H(CO)_{11}]^-$ which gave, after 4 h, $[Os_3H(OBu^t)(CO)_{10}]$ (20%), $[Os_4H_3(CO)_{12}]^-$ (70%), $[Os_6H(CO)_{18}]^-$ (trace), and

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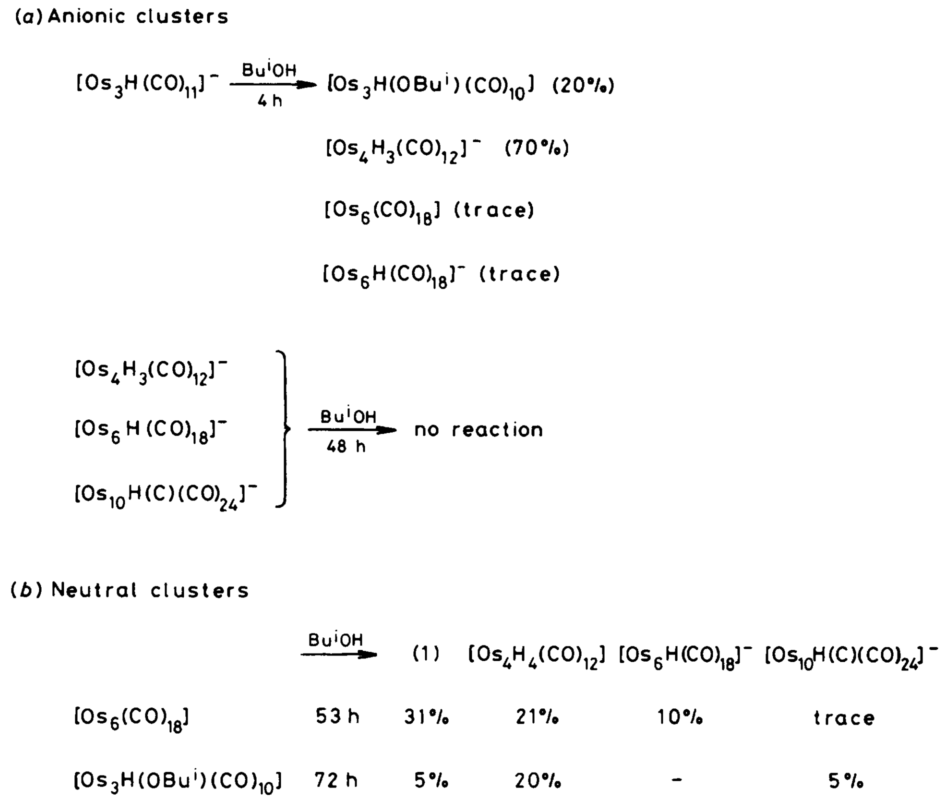
† Methyltriphenylphosphonium 1,1,1,2,2,2,3,3,4,4-decacarbonyl-3,4-μ-{[μ-hydrido-bis(tricarbonylosmio)-*Os*(Os^{3,4})*Os'*(Os^{3,4})]}-1,2,3;1,2,4-di-μ$_3$-tricarbonylosmio-*tetrahedro*-tetraosmate(1 −) and 1,1,1,2,2,2,3,3,4,4,5,5,5,6,6,6,7,7-octadecacarbonyl-3,4,7-μ$_3$-hydrido-1,4-μ-iodo-3,7-μ-tetracarbonylosmio-*cyclo*-heptaosmium (14*Os*–*Os*) respectively.

Supplementary data available (No. SUP 23959, 69 pp.): Bond lengths and angles and H-atom co-ordinates for the $[PMePh_3]^+$ cation, thermal parameters, structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.



Scheme 2. The reactions of the individual anionic or neutral clusters under N_2 reflux in Bu^tOH

$[Os_6(CO)_{18}]$ (trace) (Scheme 2). This is in accord with earlier observations that have shown that the pyrolysis of $[Os_3H(CO)_{11}]^-$ in a range of donor solvents [*e.g.* bis(2-methoxyethyl) ether, dioxane, or tetrahydrofuran] gives a similar mixture of species with up to six metal atoms.[6]

Heating the neutral cluster $[Os_6(CO)_{18}]$ in Bu^tOH under reflux (53 h) gave not only the known species $[Os_4H_4(CO)_{12}]$ (21%), $[Os_6H(CO)_{18}]^-$ (10%), and $[Os_{10}H(C)(CO)_{24}]^-$ (trace), but also the new hydrido-monoanion $[Os_8H(CO)_{22}]^-$ (1) (Scheme 2) which was separated in 31% yield as its $[N(PPh_3)_2]^+$, $[PMePh_3]^+$, or $[NMe_4]^+$ salts. Reflux of $[Os_3H(OBu^t)(CO)_{10}]$ in Bu^tOH (72 h) also gave (1) in low yield (5%) together with $[Os_4H_4(CO)_{12}]$ (20%) and $[Os_{10}H(C)(CO)_{24}]^-$ (5%) (Scheme 2). However most of the starting material remained unreacted in this case.

X-Ray analysis has shown that the monoanion $[Os_8H(CO)_{22}]^-$ (1) has the same overall structure, of virtual C_{2v} symmetry, in the $[N(PPh_3)_2]^+$ and $[PMePh_3]^+$ salts (Figure 1). The bond lengths and angles of the anion (1) in the two salts are equal within experimental error. Full details of the analysis of the $[PMePh_3]^+$ salt, which gave much better data than the $[N(PPh_3)_2]^+$ salt, are reported here.* The bond lengths and angles for the anion are given in Tables 2 and 3 respectively. Bond length and angle data for the $[PMePh_3]^+$ cation have been deposited (SUP No. 23959). The carbonyl ligands are terminal with Os–C–O angles in the range 172—180° (see Table 3).

The dianion $[Os_8(CO)_{22}]^{2-}$, from which the hydride (1) is formally derived, has the bicapped octahedral geometry[7] expected for an Os_8 species with seven skeletal electron pairs ($S = 7$).[8,9] Unexpectedly the Os_8 core in the $[Os_8H(CO)_{22}]^-$ monoanion (1) has an unrelated structure consisting of fused tetrahedra (Figure 1). Three of the tetrahedra are linked by sharing faces [Os(1),Os(2),Os(3) and Os(1),Os(2),Os(4)] giving a bicapped tetrahedral unit similar to the Os_6 core observed in $[Os_6(CO)_{18}]$.[9] The fourth tetrahedron shares an edge with the basic Os_6 unit forming a remarkably short bond Os(3)–Os(4) of length 2.600(1) Å in the $[PMePh_3]^+$ salt. The previous shortest Os–Os bonds reported are those of 2.601 and 2.606 Å in $[Os_5H(CO)_{13}(PhNC_6H_4N\text{-}o)]$, which were attributed to some multiple-bond character.[10]

Hydrogen ligands are known to produce unusual metal rearrangements in osmium cluster compounds; for example $[Os_6H_2(CO)_{18}]$ and $[Os_5H_2(CO)_{16}]$ have been shown to have capped square-pyramidal[11] and edge-bridged tetrahedral[12] metal arrangements whereas the expected geometries were octahedral and square pyramidal respectively. Up until the structure of the monoanion (1) was initially reported[3] it had been possible to rationalize all cluster structures of this type by extended skeletal electron-counting procedures.[11-13] The monoanion (1) was the first example of a high nuclearity osmium cluster whose metal geometry could not readily be explained by these procedures, although overall the cluster obeys the effective atomic number (e.a.n.) rule. Recently Mingos[14] has extended skeletal accounting procedures to include clusters with condensed polyhedral metal frames. Basically he states that, for clusters of this type, the same total number of skeletal electrons would be required as the constituent polyhedra minus the electron count characteristic of any edge or face shared by two polyhedra. Therefore the total electron count expected for (1) would be that due to four tetrahedra (4 × 60 e), minus those equivalent to the two shared faces (−2 × 48 e), and minus those for the shared edge (−34 e). This gives a required total of 110 e for this type of Os_8 geom-

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* The *X*-ray data for the $[N(PPh_3)_2]^+$ salt of (1) are given in the preliminary account of this work,[3] and the atomic co-ordinates are available from the Cambridge Data Centre.

Table 1. I.r.[a] and mass spectra of the clusters synthesised

Cluster	ν(CO)/cm^{-1}	*m/z* [b]
$[Os_3H(CO)_{11}]^-$	2 080w, 2 017s, 1 988s, 1 945m	—
$[Os_3H(OBu^t)(CO)_{10}]$	2 109w, 2 067s, 2 058m, 2 020s, 1 997m, 1 981w	930
$[Os_4H_3(CO)_{12}]^-$	2 046s, 2 039(sh), 2 020s, 1 997s, 1 975m	—
$[Os_4H_4(CO)_{12}]$	2 083s, 2 065vs, 2 017s, 1 994w	1 108
$[Os_6H(CO)_{18}]$	2 032s br, 2 020s, 2 005w, 1 956w	—
$[Os_6(CO)_{18}]$	2 104w, 2 075s, 2 061s, 2 037s, 2 029(sh), 1 999w	1 656
$[Os_8(CO)_{22}]^{2-}$	2 070w, 2 036s, 2 014vs, 2 006vs, 1 980s, 1 968m(sh), 1 943w, 1 720w br	—
(1) $[Os_8H(CO)_{22}]^-$	2 091w, 2 065s, 2 058s, 2 044s, 2 014m, 1 996mw, 1 978w, 1 967w	—
(3) $[Os_8H_2(CO)_{22}]$	2 086(sh), 2 082s, 2 066s, 2 039w br	2 154
(2) $[Os_8H(CO)_{22}I]$	2 117w, 2 093m, 2 077s, 2 054vs, 2 042m(sh), 2 020m	2 280
(4) $[Os_8H_2(CO)_{22}\{P(OMe)_3\}]$	2 099w, 2 087w, 2 072s, 2 067m, 2 051vs, 2 038m, 2 030w(sh), 2 013w, 2 002w, 1 993w	2 278
$[Os_{10}H(C)(CO)_{24}]^-$	2 062(sh), 2 057s, 2 019m, 2 009s, 2 002m(sh)	—

[a] In CH_2Cl_2, all anions as their $[N(PPh_3)_2]^+$ salts. [b] Based on ^{192}Os.

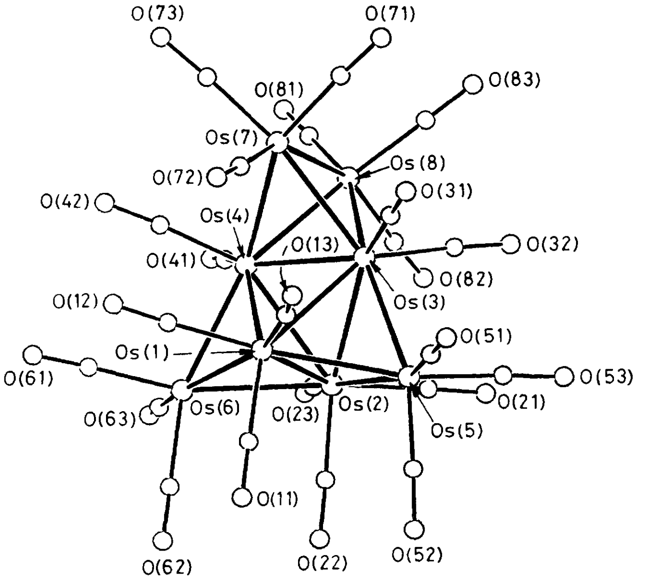


Figure 1. The structure of the monohydride anion $[Os_8H(CO)_{22}]^-$ (1) in the $[PMePh_3]^+$ salt. The carbonyl carbon atoms have the same numbers as the oxygen atoms to which they are attached

Table 2. Bond lengths (Å) for the $[PMePh_3]^+$ salt of $[Os_8H(CO)_{22}]^-$ (1)

Os(1)–Os(2)	2.740(1)	Os(1)–Os(3)	2.842(1)
Os(1)–Os(4)	2.829(1)	Os(1)–Os(5)	2.866(1)
Os(1)–Os(6)	2.854(1)	Os(1)–C(11)	1.897(18)
Os(1)–C(12)	1.913(17)	Os(1)–C(13)	1.920(16)
Os(2)–Os(3)	2.837(1)	Os(2)–Os(4)	2.839(1)
Os(2)–Os(5)	2.861(1)	Os(2)–Os(6)	2.868(1)
Os(2)–C(21)	1.900(17)	Os(2)–C(22)	1.874(22)
Os(2)–C(23)	1.870(21)	Os(3)–Os(4)	2.600(1)
Os(3)–Os(5)	2.723(1)	Os(3)–Os(7)	2.783(1)
Os(3)–Os(8)	2.805(1)	Os(3)–C(31)	1.896(15)
Os(3)–C(32)	1.867(15)	Os(4)–Os(6)	2.710(1)
Os(4)–Os(7)	2.803(1)	Os(4)–Os(8)	2.794(1)
Os(4)–C(41)	1.871(20)	Os(4)–C(42)	1.863(18)
Os(5)–C(51)	1.824(18)	Os(5)–C(52)	1.848(23)
Os(5)–C(53)	1.838(17)	Os(6)–C(61)	1.880(21)
Os(6)–C(62)	1.941(17)	Os(6)–C(63)	1.879(23)
Os(7)–Os(8)	2.848(1)	Os(7)–C(71)	1.913(18)
Os(7)–C(72)	1.911(14)	Os(7)–C(73)	1.864(21)
Os(8)–C(81)	1.863(20)	Os(8)–C(82)	1.893(19)
Os(8)–C(83)	1.861(18)	C–O range 1.10(2)—1.21(2)	

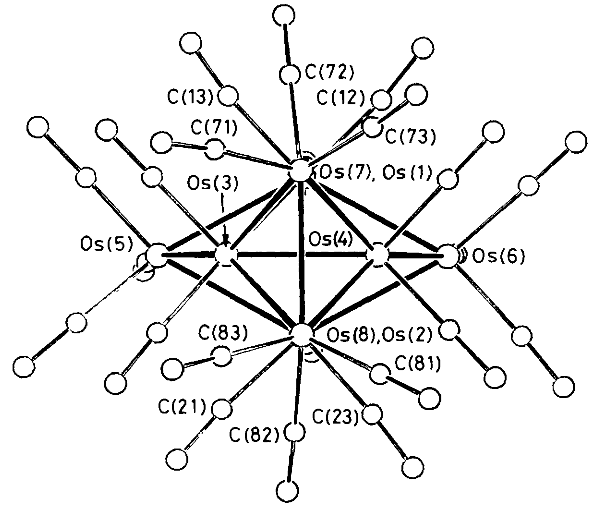


Figure 2. The anion $[Os_8H(CO)_{22}]^-$ (1) viewed down the virtual C_2 axis to show the displacement of the CO ligands caused by the H ligand bridging Os(7)–Os(8)

etry which is the number observed in the monoanion $[Os_8H(CO)_{22}]^-$ (1). An alternative approach, which reflects the possible sequence of cluster growth, is to regard the monoanion as a diosmium derivative of $[Os_6(CO)_{18}]$ (see later).

Although the hydrogen ligand was not located directly in the *X*-ray analyses of $[Os_8H(CO)_{22}]^-$, its site was readily deduced from the characteristic displacement of the close-packed carbonyl ligands produced by the steric requirements of the 'invisible' H atom. The CO ligands are apparently 'pushed back' from the Os(7)–Os(8) bond (mean *cis* C–Os–Os angle 106.9°, Table 3) as can be seen in the view of (1) onto this bond shown in Figure 2.

The ^1H n.m.r. spectra of the $[PMePh_3]^+$ and $[NMe_4]^+$ salts of (1) exhibit only a single resonance at τ 20.8; further the satellite peaks due to $^{187}Os-^1H$ coupling [doublet, $^1J(^{187}Os-^1H) = 34$ Hz] are fully consistent with the solid-state structure.[15]

We previously reported that variable-temperature ^1H n.m.r. spectra of the $[N(PPh_3)_2]^+$ salt of (1) revealed signals at τ 20.79, 26.47, and 30.42 whose relative intensities were consistent with a number of monohydrido isomers being present in solution. Although we cannot rule out the possibility that isomers exist in solution for the $[N(PPh_3)_2]^+$ salt of (1), we believe that the extra signals in the ^1H n.m.r. spec-

Table 3. Bond angles (°) for the $[PMePh_3]^+$ salt of $[Os_8H(CO)_{22}]^-$ (1)

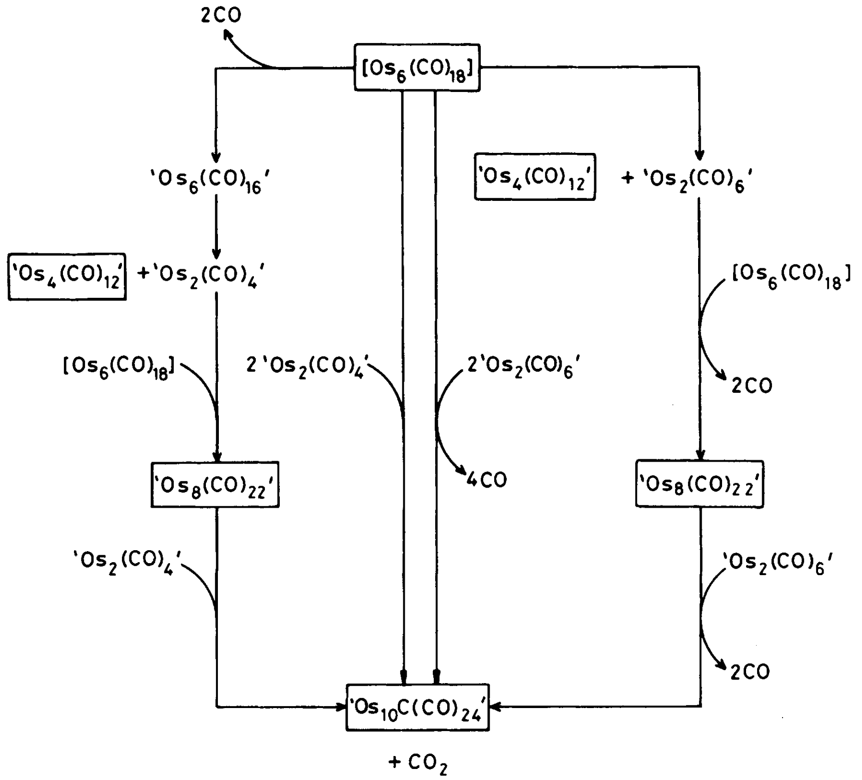
Os(3)–Os(1)–Os(2)	61.1(1)	Os(4)–Os(1)–Os(2)	61.3(1)	Os(2)–Os(4)–Os(1)	57.8(1)	Os(3)–Os(4)–Os(1)	63.0(1)
Os(4)–Os(1)–Os(3)	54.6(1)	Os(5)–Os(1)–Os(2)	61.3(1)	Os(3)–Os(4)–Os(2)	62.7(1)	Os(6)–Os(4)–Os(1)	62.0(1)
Os(5)–Os(1)–Os(3)	57.0(1)	Os(5)–Os(1)–Os(4)	104.7(1)	Os(6)–Os(4)–Os(2)	62.2(1)	Os(6)–Os(4)–Os(3)	116.3(1)
Os(6)–Os(1)–Os(2)	61.6(1)	Os(6)–Os(1)–Os(3)	104.7(1)	Os(7)–Os(4)–Os(1)	94.3(1)	Os(7)–Os(4)–Os(2)	124.5(1)
Os(6)–Os(1)–Os(4)	56.9(1)	Os(6)–Os(1)–Os(5)	121.2(1)	Os(7)–Os(4)–Os(3)	61.9(1)	Os(7)–Os(4)–Os(6)	148.5(1)
C(11)–Os(1)–Os(2)	95.9(5)	C(11)–Os(1)–Os(3)	142.7(5)	Os(8)–Os(4)–Os(1)	125.5(1)	Os(8)–Os(4)–Os(2)	95.1(1)
C(11)–Os(1)–Os(4)	142.1(5)	C(11)–Os(1)–Os(5)	86.7(5)	Os(8)–Os(4)–Os(3)	62.5(1)	Os(8)–Os(4)–Os(6)	149.1(1)
C(11)–Os(1)–Os(6)	86.0(5)	C(12)–Os(1)–Os(2)	134.4(5)	Os(8)–Os(4)–Os(7)	61.2(1)	C(41)–Os(4)–Os(1)	147.5(6)
C(12)–Os(1)–Os(3)	123.6(5)	C(12)–Os(1)–Os(4)	84.8(5)	C(41)–Os(4)–Os(2)	99.9(7)	C(41)–Os(4)–Os(3)	131.5(6)
C(12)–Os(1)–Os(5)	164.0(5)	C(12)–Os(1)–Os(6)	74.7(5)	C(41)–Os(4)–Os(6)	87.2(6)	C(41)–Os(4)–Os(7)	118.2(6)
C(12)–Os(1)–C(11)	93.6(7)	C(13)–Os(1)–Os(2)	136.3(4)	C(41)–Os(4)–Os(8)	75.8(5)	C(42)–Os(4)–Os(1)	100.0(5)
C(13)–Os(1)–Os(3)	86.3(4)	C(13)–Os(1)–Os(4)	123.6(5)	C(42)–Os(4)–Os(2)	148.6(5)	C(42)–Os(4)–Os(3)	130.7(5)
C(13)–Os(1)–Os(5)	77.0(5)	C(13)–Os(1)–Os(6)	161.7(5)	C(42)–Os(4)–Os(6)	88.4(5)	C(42)–Os(4)–Os(7)	75.0(5)
C(13)–Os(1)–C(11)	94.0(7)	C(13)–Os(1)–C(12)	87.0(7)	C(42)–Os(4)–Os(8)	116.3(5)	C(42)–Os(4)–C(41)	88.6(8)
Os(3)–Os(2)–Os(1)	61.2(1)	Os(4)–Os(2)–Os(1)	60.9(1)	Os(2)–Os(5)–Os(1)	57.2(1)	Os(3)–Os(5)–Os(1)	61.1(1)
Os(4)–Os(2)–Os(3)	54.5(1)	Os(5)–Os(2)–Os(1)	61.5(1)	Os(3)–Os(5)–Os(2)	61.0(1)	C(51)–Os(5)–Os(1)	103.6(6)
Os(5)–Os(2)–Os(3)	57.1(1)	Os(5)–Os(2)–Os(4)	104.6(1)	C(51)–Os(5)–Os(2)	160.0(6)	C(51)–Os(5)–Os(3)	106.3(6)
Os(6)–Os(2)–Os(1)	61.1(1)	Os(6)–Os(2)–Os(3)	104.4(1)	C(52)–Os(5)–Os(1)	103.6(6)	C(52)–Os(5)–Os(2)	100.5(6)
Os(6)–Os(2)–Os(4)	56.7(1)	Os(6)–Os(2)–Os(5)	120.9(1)	C(52)–Os(5)–Os(3)	160.0(6)	C(52)–Os(5)–C(51)	89.1(9)
C(21)–Os(2)–Os(1)	133.1(5)	C(21)–Os(2)–Os(3)	85.9(5)	C(53)–Os(5)–Os(1)	161.6(6)	C(53)–Os(5)–Os(2)	109.5(6)
C(21)–Os(2)–Os(4)	126.5(6)	C(21)–Os(2)–Os(5)	72.9(5)	C(53)–Os(5)–Os(3)	102.1(6)	C(53)–Os(5)–C(51)	87.6(8)
C(21)–Os(2)–Os(6)	165.7(5)	C(22)–Os(2)–Os(1)	94.3(6)	C(53)–Os(5)–C(52)	91.0(9)	Os(2)–Os(6)–Os(1)	57.2(1)
C(22)–Os(2)–Os(3)	142.8(6)	C(22)–Os(2)–Os(4)	139.6(6)	Os(4)–Os(6)–Os(1)	61.1(1)	Os(4)–Os(6)–Os(2)	61.1(1)
C(22)–Os(2)–Os(5)	87.3(6)	C(22)–Os(2)–Os(6)	83.9(6)	C(61)–Os(6)–Os(1)	108.6(6)	C(61)–Os(6)–Os(2)	161.7(6)
C(22)–Os(2)–C(21)	93.9(8)	C(23)–Os(2)–Os(1)	137.0(6)	C(61)–Os(6)–Os(4)	102.8(6)	C(62)–Os(6)–Os(1)	98.6(5)
C(23)–Os(2)–Os(3)	119.7(7)	C(23)–Os(2)–Os(4)	84.5(7)	C(62)–Os(6)–Os(2)	99.3(5)	C(62)–Os(6)–Os(4)	156.8(5)
C(23)–Os(2)–Os(5)	159.9(6)	C(23)–Os(2)–Os(6)	79.1(6)	C(62)–Os(6)–C(61)	94.0(8)	C(63)–Os(6)–Os(1)	159.8(6)
C(23)–Os(2)–C(21)	87.2(8)	C(23)–Os(2)–C(22)	97.4(9)	C(63)–Os(6)–Os(2)	103.9(7)	C(63)–Os(6)–Os(4)	105.1(7)
Os(2)–Os(3)–Os(1)	57.7(1)	Os(4)–Os(3)–Os(1)	62.5(1)	C(63)–Os(6)–C(61)	88.1(9)	C(63)–Os(6)–C(62)	91.2(9)
Os(4)–Os(3)–Os(2)	62.8(1)	Os(5)–Os(3)–Os(1)	62.0(1)	Os(4)–Os(7)–Os(3)	55.5(1)	Os(8)–Os(7)–Os(3)	59.7(1)
Os(5)–Os(3)–Os(2)	61.9(1)	Os(5)–Os(3)–Os(4)	115.8(1)	Os(8)–Os(7)–Os(4)	59.3(1)	C(71)–Os(7)–Os(3)	100.3(6)
Os(7)–Os(3)–Os(1)	94.5(1)	Os(7)–Os(3)–Os(2)	125.4(1)	C(71)–Os(7)–Os(4)	153.5(6)	C(71)–Os(7)–Os(8)	100.8(5)
Os(7)–Os(3)–Os(4)	62.7(1)	Os(7)–Os(3)–Os(5)	148.2(1)	C(72)–Os(7)–Os(3)	93.3(5)	C(72)–Os(7)–Os(4)	98.5(5)
Os(8)–Os(3)–Os(1)	124.6(1)	Os(8)–Os(3)–Os(2)	94.9(1)	C(72)–Os(7)–Os(8)	151.3(5)	C(72)–Os(7)–C(71)	93.2(7)
Os(8)–Os(3)–Os(4)	62.1(1)	Os(8)–Os(3)–Os(5)	149.2(1)	C(73)–Os(7)–Os(3)	165.6(6)	C(73)–Os(7)–Os(4)	110.3(6)
Os(8)–Os(3)–Os(7)	61.3(1)	C(31)–Os(3)–Os(1)	98.0(4)	C(73)–Os(7)–Os(8)	112.8(5)	C(73)–Os(7)–C(71)	93.2(8)
C(31)–Os(3)–Os(2)	144.8(5)	C(31)–Os(3)–Os(4)	132.2(5)	C(73)–Os(7)–C(72)	91.1(7)	Os(4)–Os(8)–Os(3)	55.3(1)
C(31)–Os(3)–Os(5)	84.8(5)	C(31)–Os(3)–Os(7)	77.4(5)	Os(7)–Os(8)–Os(3)	59.0(1)	Os(7)–Os(8)–Os(4)	59.6(1)
C(31)–Os(3)–Os(8)	120.4(5)	C(32)–Os(3)–Os(1)	146.9(6)	C(81)–Os(8)–Os(3)	161.5(5)	C(81)–Os(8)–Os(4)	106.3(5)
C(32)–Os(3)–Os(2)	97.5(5)	C(32)–Os(3)–Os(4)	129.3(5)	C(81)–Os(8)–Os(7)	112.3(6)	C(82)–Os(8)–Os(3)	94.5(6)
C(32)–Os(3)–Os(5)	87.7(6)	C(32)–Os(3)–Os(7)	118.6(6)	C(82)–Os(8)–Os(4)	98.4(5)	C(82)–Os(8)–Os(7)	151.7(6)
C(32)–Os(3)–Os(8)	74.9(6)	C(32)–Os(3)–C(31)	91.8(6)	C(82)–Os(8)–C(81)	89.9(8)	C(83)–Os(8)–Os(3)	102.7(6)
Os–C–O range 172(9)—180(9)				C(83)–Os(8)–Os(4)	155.7(6)	C(83)–Os(8)–Os(7)	101.8(6)
				C(83)–Os(8)–C(81)	95.0(8)	C(83)–Os(8)–C(82)	93.1(8)

trum are due to several so far unidentified species present in solution.

Careful acidification of $[Os_8H(CO)_{22}]^-$ (1) with concentrated H_2SO_4 in MeCN, or with HCl(g) in CH_2Cl_2, gives the known dihydride $[Os_8H_2(CO)_{22}]$ (3) [16] which was characterized by i.r. and mass spectroscopy (Table 1). The reaction of this neutral derivative with $P(OMe)_3$ in CH_2Cl_2 gives a single product which appears to be the adduct $[Os_8H_2(CO)_{22}\{P(OMe)_3\}]$ (4) from i.r. and mass spectral data (Table 1).

Addition of X^- (X = Cl, Br, or I) or proton sponge [1,8-bis(dimethylamino)naphthalene] to solutions of (3), in CH_2Cl_2 at room temperature, deprotonates the cluster to give first $[Os_8H(CO)_{22}]^-$ (1) (hours), then $[Os_8(CO)_{22}]^{2-}$ (days); this behaviour is common for large hydrido-osmium clusters. For example addition of X^- to suspensions of $[Os_{10}H_2(C)(CO)_{24}]$ or $[Os_7H_2(CO)_{20}]$ in CH_2Cl_2 ultimately yields the dianions $[Os_{10}C(CO)_{24}]^{2-}$ and $[Os_7(CO)_{20}]^{2-}$.[17] The dianion $[Os_8(CO)_{22}]^{2-}$ is, however, more conveniently prepared by addition of a methanolic solution of KOH to a solution of (1) in CH_2Cl_2. It should be noted that the deprotonation of (1) to give $[Os_8(CO)_{22}]^{2-}$ involves a rearrangement of the metal core (see later) from fused tetrahedral to bicapped octahedral.

It is interesting that the products derived from heating $[Os_6(CO)_{18}]$ in Bu^{t}OH contain an even number of osmium atoms. Significantly neither $[Os_4H_4(CO)_{12}]$ nor $[Os_8H(CO)_{22}]^-$ gave rise to other species under the same conditions. This suggests that an unsaturated Os_2 fragment, generated from the breakdown of $[Os_6(CO)_{18}]$, may be involved as the building block in this reaction (Scheme 3). It is interesting in this connection that dinuclear osmium carbonyl clusters containing multiple Os–Os bonds have recently been prepared.[18] However we have not ruled out the possibility that di- or mono-nuclear cations are involved in cluster growth, as has been found for other metal cluster systems.[19] It seems reasonable to conclude that the metal geometry in (1) is a function of the building sequence and in this connection it is interesting to note the work of Hayward and Shapley [20] who have shown that high anionic clusters of osmium based only on octahedrally derived close-packed metal geometries are produced from the reaction of $[Os_3(CO)_{12}]$ with sodium in ether solvents at various higher temperatures. At present is is not clear at which stage in the reaction sequence the carbido-atom in $[Os_{10}H(C)(CO)_{24}]^-$ is generated, but we have established that the solvent, loss of CO from $[Os_6(CO)_{18}]$, and temperature are



Scheme 3. Possible building-up sequences in the reaction of $[Os_6(CO)_{18}]$ with Bu^{t}OH

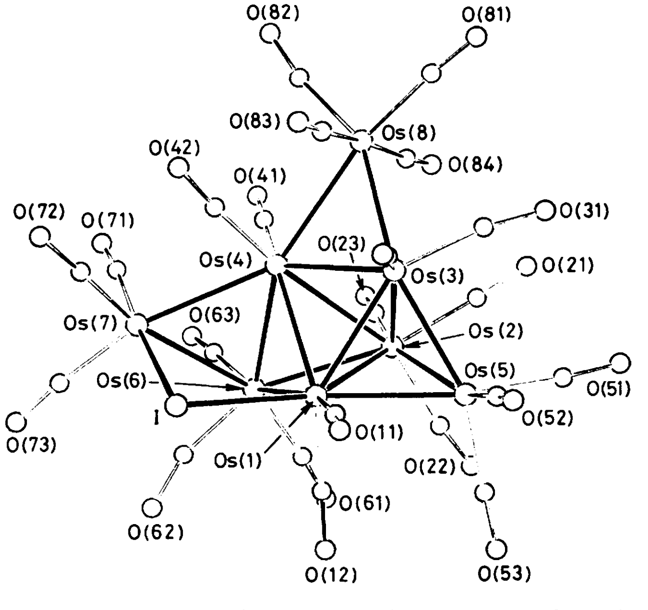


Figure 3. The structure of the neutral iodide $[Os_8H(CO)_{22}I]$ (2). The carbonyl carbon atoms have the same numbers as the oxygen atoms to which they are attached

crucial factors which influence the course of the reaction. Thus, although no cluster build up is observed on heating $[Os_6(CO)_{18}]$ in octane (b.p. 126 °C), or in Bu^{t}OH (b.p. 108 °C) with CO passing through the solution, preliminary results indicate that heating $[Os_6(CO)_{18}]$ in n-hexanol (b.p. 157 °C) under reflux gives $[Os_4H_4(CO)_{12}]$ and the carbido-cluster $[Os_{10}H(C)(CO)_{24}]^-$ as the only products.

Table 4. Bond lengths (Å) for $[Os_8H(CO)_{22}I]$ (2)

Os(1)–Os(2)	2.764(2)	Os(1)–Os(3)	2.803(2)
Os(1)–Os(4)	2.868(2)	Os(1)–Os(5)	2.795(2)
Os(1)–Os(6)	2.814(2)	Os(1)–I	2.753(2)
Os(1)–C(11)	1.94(3)	Os(1)–C(12)	1.92(4)
Os(2)–Os(3)	2.894(1)	Os(2)–Os(4)	2.868(2)
Os(2)–Os(5)	2.890(2)	Os(2)–Os(6)	2.800(2)
Os(2)–C(21)	1.88(3)	Os(2)–C(22)	1.88(3)
Os(2)–C(23)	1.87(3)	Os(3)–Os(4)	2.699(2)
Os(3)–Os(5)	2.695(2)	Os(3)–Os(8)	2.742(2)
Os(3)–C(31)	1.86(3)	Os(3)–C(32)	1.93(3)
Os(4)–Os(6)	2.782(2)	Os(4)–Os(7)	2.882(2)
Os(4)–Os(8)	2.904(2)	Os(4)–C(41)	1.88(3)
Os(4)–C(42)	1.80(3)	Os(5)–C(51)	1.92(5)
Os(5)–C(52)	1.87(3)	Os(5)–C(53)	1.94(4)
Os(6)–Os(7)	2.870(2)	Os(6)–C(61)	1.89(3)
Os(6)–C(62)	1.88(4)	Os(6)–C(63)	1.92(4)
Os(7)–I	2.736(2)	Os(7)–C(71)	1.82(3)
Os(7)–C(72)	1.74(4)	Os(7)–C(73)	1.89(4)
Os(8)–C(81)	1.91(4)	Os(8)–C(82)	1.88(4)
Os(8)–C(83)	1.90(3)	Os(8)–C(84)	1.97(3)

C–O range 1.09(5)—1.27(5)

As part of our study of the reactions of high osmium clusters with halogens, we examined the reaction of the anion $[Os_8H(CO)_{22}]^-$ (1) with iodine in CH_2Cl_2. A single neutral product was formed by addition of I_2 which was shown to be $[Os_8H(CO)_{22}I]$ (2) on the basis of its ^1H n.m.r. (singlet at δ −8.84 p.p.m.) and i.r. spectra (Table 1), and an *X*-ray single-crystal analysis.

The structure of the neutral molecule $[Os_8H(CO)_{22}I]$ (2), which crystallizes with one molecule of water, is shown in Figure 3, and the bond lengths and angles are given in Tables

Table 5. Bond angles (°) for $[Os_8H(CO)_{22}I]$ (2)

Os(3)–Os(1)–Os(2)	62.6(1)	Os(4)–Os(1)–Os(2)	61.2(1)	Os(7)–Os(4)–Os(6)	60.9(1)	Os(8)–Os(4)–Os(1)	118.8(1)
Os(4)–Os(1)–Os(3)	56.8(1)	Os(5)–Os(1)–Os(2)	62.6(1)	Os(8)–Os(4)–Os(2)	94.8(1)	Os(8)–Os(4)–Os(3)	58.5(1)
Os(5)–Os(1)–Os(3)	57.6(1)	Os(5)–Os(1)–Os(4)	106.8(1)	Os(8)–Os(4)–Os(6)	151.5(1)	Os(8)–Os(4)–Os(7)	146.0(1)
Os(6)–Os(1)–Os(2)	60.3(1)	Os(6)–Os(1)–Os(3)	107.7(1)	C(41)–Os(4)–Os(1)	145.5(9)	C(41)–Os(4)–Os(2)	95.1(9)
Os(6)–Os(1)–Os(4)	58.6(1)	Os(6)–Os(1)–Os(5)	120.0(1)	C(41)–Os(4)–Os(3)	129(1)	C(41)–Os(4)–Os(6)	89.1(9)
I–Os(1)–Os(2)	141.4(1)	I–Os(1)–Os(3)	119.7(1)	C(41)–Os(4)–Os(7)	94(1)	C(41)–Os(4)–Os(8)	81.0(9)
I–Os(1)–Os(4)	87.2(1)	I–Os(1)–Os(5)	154.8(1)	C(42)–Os(4)–Os(1)	120(1)	C(42)–Os(4)–Os(2)	169(1)
I–Os(1)–Os(6)	85.1(1)	C(11)–Os(1)–Os(2)	136(1)	C(42)–Os(4)–Os(3)	106(1)	C(42)–Os(4)–Os(6)	130(1)
C(11)–Os(1)–Os(3)	86(1)	C(11)–Os(1)–Os(4)	127(1)	C(42)–Os(4)–Os(7)	70(1)	C(42)–Os(4)–Os(8)	77(1)
C(11)–Os(1)–Os(5)	75(1)	C(11)–Os(1)–Os(6)	164(1)	C(42)–Os(4)–C(41)	91(1)	Os(2)–Os(5)–Os(1)	58.2(1)
C(11)–Os(1)–I	80(1)	C(12)–Os(1)–Os(2)	93(1)	Os(3)–Os(5)–Os(1)	61.4(1)	Os(3)–Os(5)–Os(2)	62.3(1)
C(12)–Os(1)–Os(3)	144(1)	C(12)–Os(1)–Os(4)	135(1)	C(51)–Os(5)–Os(1)	159(1)	C(51)–Os(5)–Os(2)	101(1)
C(12)–Os(1)–Os(5)	89(1)	C(12)–Os(1)–Os(6)	77(1)	C(51)–Os(5)–Os(3)	110(1)	C(52)–Os(5)–Os(1)	111(1)
C(12)–Os(1)–I	96(1)	C(12)–Os(1)–C(11)	98(1)	C(52)–Os(5)–Os(2)	158(1)	C(52)–Os(5)–Os(3)	96(1)
Os(3)–Os(2)–Os(1)	59.3(1)	Os(4)–Os(2)–Os(1)	61.2(1)	C(52)–Os(5)–C(51)	88(2)	C(53)–Os(5)–Os(1)	99(1)
Os(4)–Os(2)–Os(3)	55.8(1)	Os(5)–Os(2)–Os(1)	59.2(1)	C(53)–Os(5)–Os(2)	101(1)	C(53)–Os(5)–Os(3)	159(1)
Os(5)–Os(2)–Os(3)	55.6(1)	Os(5)–Os(2)–Os(4)	104.2(1)	C(53)–Os(5)–C(51)	86(2)	C(53)–Os(5)–C(52)	99(2)
Os(6)–Os(2)–Os(1)	60.8(1)	Os(6)–Os(2)–Os(3)	105.5(1)	Os(2)–Os(6)–Os(1)	59.0(1)	Os(4)–Os(6)–Os(1)	61.6(1)
Os(6)–Os(2)–Os(4)	58.8(1)	Os(6)–Os(2)–Os(5)	117.2(1)	Os(4)–Os(6)–Os(2)	61.8(1)	Os(7)–Os(6)–Os(1)	84.9(1)
C(21)–Os(2)–Os(1)	129.0(9)	C(21)–Os(2)–Os(3)	75.7(9)	Os(7)–Os(6)–Os(2)	122.1(1)	Os(7)–Os(6)–Os(4)	61.3(1)
C(21)–Os(2)–Os(4)	113(1)	C(21)–Os(2)–Os(5)	76.5(9)	C(61)–Os(6)–Os(1)	103.4(9)	C(61)–Os(6)–Os(2)	80(1)
C(21)–Os(2)–Os(6)	164(1)	C(22)–Os(2)–Os(1)	102(1)	C(61)–Os(6)–Os(4)	141(1)	C(61)–Os(6)–Os(7)	157(1)
C(22)–Os(2)–Os(3)	132(1)	C(22)–Os(2)–Os(4)	157(1)	C(62)–Os(6)–Os(1)	97(1)	C(62)–Os(6)–Os(2)	149(1)
C(22)–Os(2)–Os(5)	77(1)	C(22)–Os(2)–Os(6)	100(1)	C(62)–Os(6)–Os(4)	127(1)	C(62)–Os(6)–Os(7)	70(1)
C(22)–Os(2)–C(21)	89(1)	C(23)–Os(2)–Os(1)	139(1)	C(62)–Os(6)–C(61)	88(1)	C(63)–Os(6)–Os(1)	160(1)
C(23)–Os(2)–Os(3)	128.4(9)	C(23)–Os(2)–Os(4)	89(1)	C(63)–Os(6)–Os(2)	114(1)	C(63)–Os(6)–Os(4)	98(1)
C(23)–Os(2)–Os(5)	162(1)	C(23)–Os(2)–Os(6)	80(1)	C(63)–Os(6)–Os(7)	84(1)	C(63)–Os(6)–C(61)	93(1)
C(23)–Os(2)–C(21)	88(1)	C(23)–Os(2)–C(22)	96(1)	C(63)–Os(6)–C(62)	95(2)	Os(6)–Os(7)–Os(4)	57.9(1)
Os(2)–Os(3)–Os(1)	58.0(1)	Os(4)–Os(3)–Os(1)	62.8(1)	I–Os(7)–Os(4)	87.2(1)	I–Os(7)–Os(6)	84.4(1)
Os(4)–Os(3)–Os(2)	61.6(1)	Os(5)–Os(3)–Os(1)	61.1(1)	C(71)–Os(7)–Os(4)	89(1)	C(71)–Os(7)–Os(6)	95(1)
Os(5)–Os(3)–Os(2)	62.1(1)	Os(5)–Os(3)–Os(4)	114.8(1)	C(71)–Os(7)–I	176(1)	C(72)–Os(7)–Os(4)	108(1)
Os(8)–Os(3)–Os(1)	127.3(1)	Os(8)–Os(3)–Os(2)	97.8(1)	C(72)–Os(7)–Os(6)	166(1)	C(72)–Os(7)–I	93(1)
Os(8)–Os(3)–Os(4)	64.5(1)	Os(8)–Os(3)–Os(5)	151.7(1)	C(72)–Os(7)–C(71)	87(2)	C(73)–Os(7)–Os(4)	163(1)
C(31)–Os(3)–Os(1)	148(1)	C(31)–Os(3)–Os(2)	107(1)	C(73)–Os(7)–Os(6)	105(1)	C(73)–Os(7)–I	93(1)
C(31)–Os(3)–Os(4)	139(1)	C(31)–Os(3)–Os(5)	87(1)	C(73)–Os(7)–C(71)	91(1)	C(73)–Os(7)–C(72)	89(2)
C(31)–Os(3)–Os(8)	80(1)	C(32)–Os(3)–Os(1)	100(1)	Os(4)–Os(8)–Os(3)	57.0(1)	C(81)–Os(8)–Os(3)	110(1)
C(32)–Os(3)–Os(2)	156(1)	C(32)–Os(3)–Os(4)	120(1)	C(81)–Os(8)–Os(4)	167(1)	C(82)–Os(8)–Os(3)	153(1)
C(32)–Os(3)–Os(5)	100(1)	C(32)–Os(3)–Os(8)	104(1)	C(82)–Os(8)–Os(4)	97(1)	C(82)–Os(8)–C(81)	96(2)
C(32)–Os(3)–C(31)	86(1)	Os(2)–Os(4)–Os(1)	57.6(1)	C(83)–Os(8)–Os(3)	79(1)	C(83)–Os(8)–Os(4)	90.4(9)
Os(3)–Os(4)–Os(1)	60.4(1)	Os(3)–Os(4)–Os(2)	62.6(1)	C(83)–Os(8)–C(81)	87(1)	C(83)–Os(8)–C(82)	95(1)
Os(6)–Os(4)–Os(1)	59.7(1)	Os(6)–Os(4)–Os(2)	59.4(1)	C(84)–Os(8)–Os(3)	96.1(8)	C(84)–Os(8)–Os(4)	88.2(8)
Os(6)–Os(4)–Os(3)	111.6(1)	Os(7)–Os(4)–Os(1)	83.7(1)	C(84)–Os(8)–C(81)	94(1)	C(84)–Os(8)–C(82)	90(1)
Os(7)–Os(4)–Os(2)	119.2(1)	Os(7)–Os(4)–Os(3)	136.7(1)	C(84)–Os(8)–C(83)	174(1)	Os(7)–I–Os(1)	88.7(1)

Os–C–O range 164(4)—179(4)

4 and 5 respectively. The carbonyl ligands are terminal with Os–C–O angles in the range 164—179°. The iodine atom links the two 'wing-tips' atoms of a 'butterfly' Os_4 unit with bridging bond lengths Os(1)–I = 2.753(2) and Os(7)–I = 2.736(2) Å.

The hydrogen ligand in (2) was not found directly in the *X*-ray analysis and it proved unusually difficult to locate by the normal indirect criteria of M–M bond lengthening and CO ligand displacement.[21] For example the longest bond is Os(4)–Os(8) 2.904 Å but the *cis*-Os–Os–C angles adjacent to it are relatively small and occur in the range 77—97°, much smaller than the *cis* angles for the CO ligands 'pushed back' by the μ-H ligand in (1) which occur in the range 101—113°. The Orpen 'potential energy' minimization program [22] also failed to find a site of suitable energy.

It was decided to attempt location of the H atom by examination of close-packed models of the molecule, derived from the refined atomic co-ordinates, using a program written by Keller [23] which draws each atom as a sphere of van der Waals radius. In the initial diagrams the core metal atoms, which have very large van der Waals radii, 'swamped' the surface ligand atoms making it difficult to judge if they were in contact. Much more useful drawings were obtained by assigning covalent radii to the underlying core osmium atoms

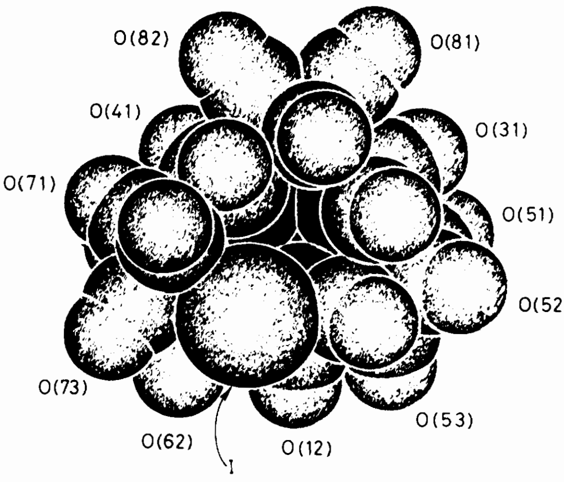


Figure 4. Computer drawings (ref. 23) of space-filling models of the neutral hydride $[Os_8H(CO)_{22}I]$ (2) viewed onto the H-bridged face Os(1), Os(3), Os(4)

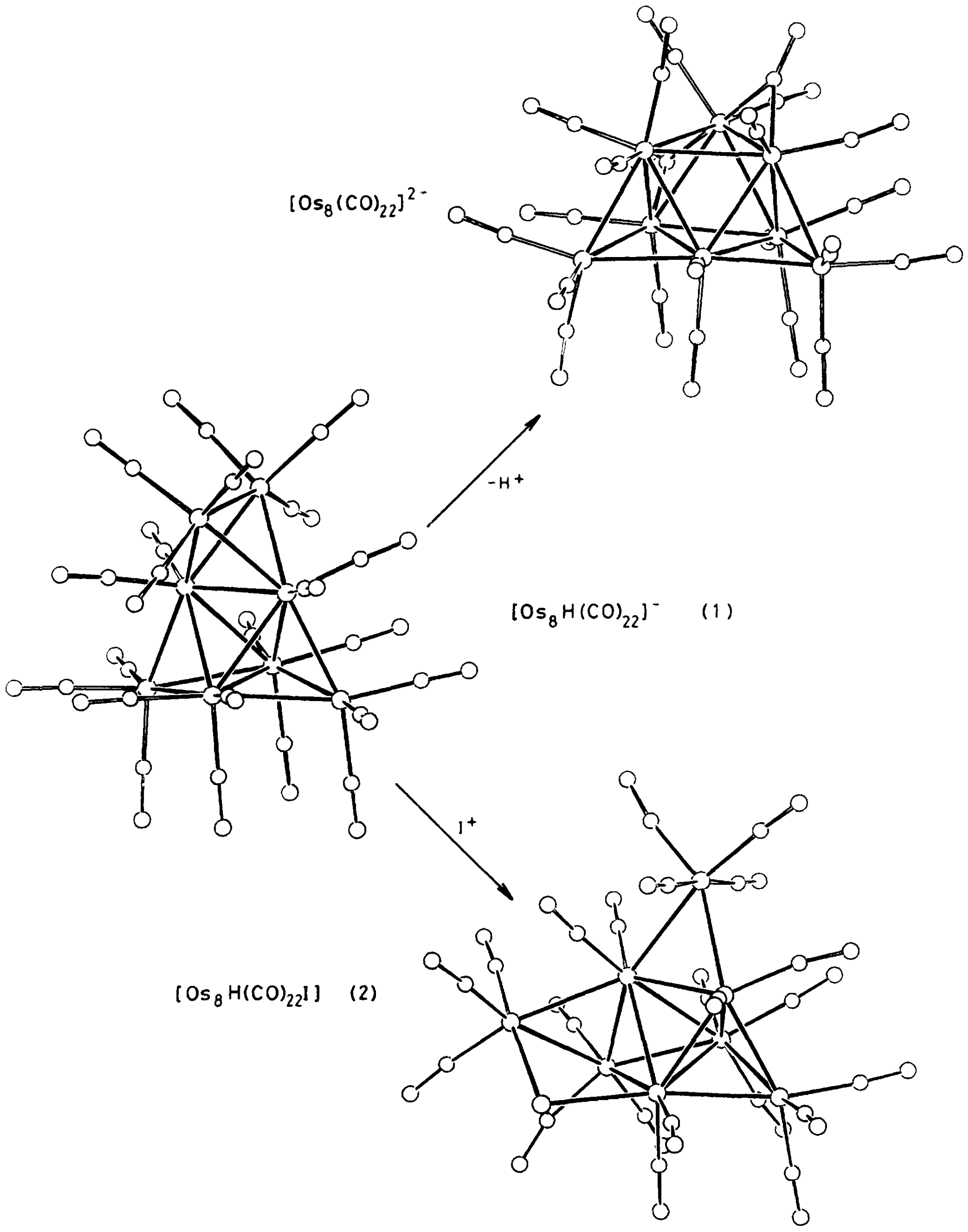


Figure 5. The structural changes observed for reactions of $[Os_8H(CO)_{22}]^-$ (1)

so that the carbonyl ligands can be seen in tangential close-packed contact. Only one gap appears in the surface ligand coverage which can be seen in Figure 4. The 'hole' in the carbonyl ligands is undoubtedly due to the steric requirements of the H atom which is thought to be bonded to the three osmium atoms Os(1), Os(3), and Os(4) visible through the gap in the surface ligand coverage. The area of the metal atoms exposed through the 'hole' in the carbonyl ligands is very asymmetric indicating an unusual asymmetric type of μ_3-H bridging mode. This explains why the site was not identified using the Orpen program which assumes symmetrical bonding for the hydride ligand.[24] The Os–Os distances round the μ_3 site are unusually short for hydrogen-bridged bonds (mean 2.787 Å) which partly accounts for the difficulty in locating this H ligand by the usual indirect criteria.

There are several reactions of osmium clusters known which involve opening of a capping tetrahedral Os_4 group to give a bridged 'butterfly' arrangement such as that observed in (2). For example $[Os_{10}C(CO)_{24}]^{2-}$ reacts with iodine to give the monoiodide $[Os_{10}C(CO)_{24}I]^-$ and the neutral di-iodide $[Os_{10}C(CO)_{24}I_2]$ with sequential opening of tetrahedral capping groups to give this type of bridged 'butterfly' unit.[5] However in the octaosmium clusters there is no simple relationship between the structure of the iodide (2) and that of the monoanion (1) from which it was formed. Apparently there is a fundamental rearrangement of the core metal geometry and carbonyl distribution when (1) reacts with I_2 to give (2). It is significant that the deprotonation of (1) to give the dianion $[Os_8(CO)_{22}]^{2-}$ (see above) also involves a rearrangement of the metal core from fused tetrahedral to bicapped octahedral. These unusual rearrangement reactions are summarized in Figure 5.

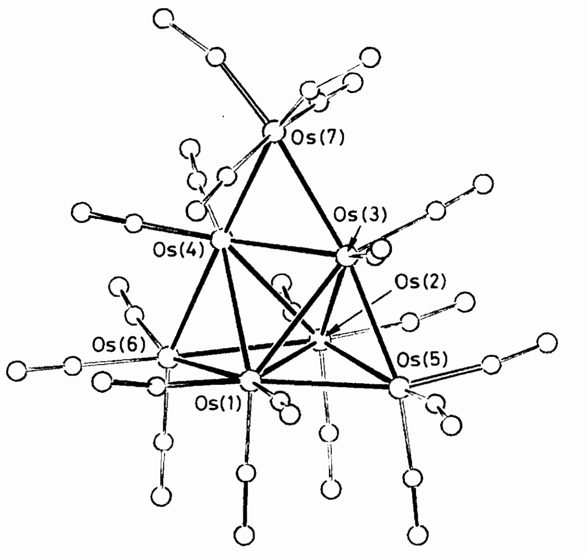
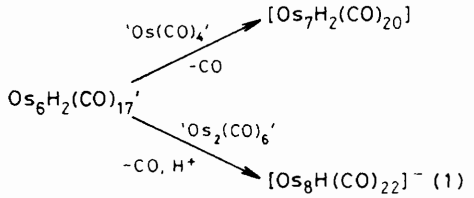


Figure 6. The structure of the dihydride $[Os_7H_2(CO)_{20}]$ (ref. 31) showing the similarity of the Os_7 core geometry to the Os_8 geometry in $[Os_8H(CO)_{22}I]$ (2)

Apart from reversible opening and closing of tetrahedral capping Os_4 units, in the wide range of reactions of the decaosmium carbido-dianion now known, no cluster rearrangement occurs, and the central octahedral $Os_{10}C$ unit is always maintained.[25-27] We attribute the greater flexibility observed in the Os_8 systems compared to the Os_{10} systems to the fact that no interstitial carbide atom is present in the former to 'bind' the metal core together.

This work shows that various Os_8 cluster cages, like their borane counterparts,[28] appear to have relatively similar energies. Consequently their geometries are unusually sensitive to subtle electronic and steric influences. Indeed, it is interesting to note that, to date, for M_8 carbonyl clusters in general, no two species have been reported to contain the same arrangement of metal atoms.[29] The proton in $[Os_8H(CO)_{22}]^-$ (1) obviously has some stabilizing effect on the Os_8 metal core since although (1) reacts reversibly with iodine, the dianion $[Os_8(CO)_{22}]^{2-}$ decomposes on reaction with I_2 and Os_7 species are generated.[30] It may be significant that the only Os_8 or Os_7 halogen containing clusters that have been observed so far are $[Os_8H(CO)_{22}I]$ and $[Os_7H_2(CO)_{19}Br]$ (ref. 30) which both contain H ligands.

It is interesting that the metal core in $[Os_8H(CO)_{22}I]$ closely resembles that of the unusual structure recently reported for the heptaosmium dihydride $[Os_7H_2(CO)_{20}]$ (Figure 6).[31] These two molecules were the first clusters of the iron triad, containing only H or CO ligands, which could not be rationalized by Wade theory as their metal cores are not *closo*- or *nido*-triangulated polyhedra nor capped versions of these. Both structures however obey the e.a.n. rule and may be satisfactorily explained by the procedure recently developed by Mingos to extend polyhedral skeletal counting methods to fused polyhedra (see above). However both $[Os_7H_2(CO)_{20}]$ and (1) contain a similar Os_6 unit to that found in $[Os_6(CO)_{18}]$ so that their core geometries may more simply be explained by regarding them as derivatives of this molecule with mono- and di-osmium substitution respectively. Thus $[Os_7H_2(CO)_{20}]$ may be regarded as formed by replacement of a CO ligand in the hypothetical dihydride '$Os_6H_2(CO)_{17}$' by an '$Os(CO)_4$' ligand, formally a two-electron donor. Similarly $[Os_8H(CO)_{22}]^-$ (1) may be formally regarded as derived from the monoanion '$[Os_6H(CO)_{17}]^-$' by replacing a CO ligand by a bridging '$Os_2(CO)_6$' group, also formally a two-electron donor (see below).



Experimental

Infrared spectra were recorded on a Perkin-Elmer 257 instrument using carbon monoxide gas as calibrant (central position 2 143 cm^{-1}). N.m.r. spectra were obtained on a Varian XL-100 or a Bruker WH400 spectrometer. Thin-layer chromatography plates were purchased 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. Mass spectra were obtained on an A.E.I. M.S. 12 spectrometer using tris(perfluoroheptyl)-*s*-triazine as calibrant and were analysed by comparison with the isotopic patterns. The solvents were of A.R. grade and were distilled and deoxygenated before use.

Reaction of $[Os_3(CO)_{12}]$ + KOH *in* Bu^tOH.—A series of five reactions was investigated; $[Os_3(CO)_{12}]$ (80 mg, 5 mol equiv.) with KOH (2.6 mg, 3 mol equiv.) was heated under reflux in Bu^tOH (50 cm^3) for 1, 4, 16, 48, and 144 h respectively. The solvent was removed under vacuum and the residue was stirred in acetone with $[N(PPh_3)_2]Cl$ until it had dissolved. The mixture was separated by t.l.c. using first acetone (running the compounds until they were *ca.* 2 cm up from the base line) then CH_2Cl_2–hexane (1 : 1) as eluants. For the 48 h reaction this gave five main bands. The band of highest R_f (faint brown) was $[Os_6(CO)_{18}]$ (yield 3.6 mg, 5%). The second was the yellow compound $[Os_3H(OBu^t)(CO)_{10}]$ (20.4 mg, 25%). The third band was the orange salt $[N(PPh_3)_2][Os_4H_3(CO)_{12}]$ (main product, yield 48.8 mg, 45%). The fourth was also an orange salt, $[N(PPh_3)_2]_2[Os_6(CO)_{18}]$ (yield 6.0 mg, 5%) and the band of lowest R_f was the carbido-complex $[N(PPh_3)_2]_2[Os_{10}C(CO)_{24}]$ (trace amounts).*

Reaction of $[N(PPh_3)_2][Os_3H(CO)_{11}]$ *in* Bu^tOH *under Reflux*.—$[N(PPh_3)_2][Os_3H(CO)_{11}]$ was prepared according to the literature method.[32] This salt (30 cm) was heated in Bu^tOH (30 cm^3) under reflux for 4 h. The solvent was evaporated off and the residue dissolved in CH_2Cl_2. The mixture was separated by t.l.c. as before. This gave four bands. The band of highest R_f (faint brown) was $[Os_6(CO)_{18}]$ (trace). The second (yellow) was $[Os_3H(OBu^t)(CO)_{10}]$ (yield 4.1 mg, 20%). The third band was the orange salt $[N(PPh_3)_2][Os_4H_3(CO)_{12}]$, the main product (yield 18.9 mg, 70%). The band of lowest R_f was $[N(PPh_3)_2]_2[Os_6(CO)_{18}]$ (trace amounts).*

Reactions of $[N(PPh_3)_2][Os_4H_3(CO)_{12}]$,[33] $[N(PPh_3)_2][Os_6H(CO)_{18}]$,[34] *and* $[N(PPh_3)_2][Os_{10}H(C)(CO)_{24}]$[35] *in* Bu^tOH *under Reflux*.—Each of the anions in turn (15 mg), prepared

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* All yields quoted are after recrystallization of the products. Although i.r. spectra of the reaction mixtures indicated that the hydrido-monoanions $[Os_6H(CO)_{18}]^-$ and $[Os_{10}H(C)(CO)_{24}]^-$ were formed in the reactions in Bu^tOH these species usually dissociated to their respective dianions $[Os_6(CO)_{18}]^{2-}$ and $[Os_{10}C(CO)_{24}]^{2-}$ during work-up.

Table 6. Fractional atomic co-ordinates for the $[PMePh_3]^+$ salt of $[Os_8H(CO)_{22}]^-$ (1)

Atom	*x*	*y*	*z*
Os(1)	0.410 58(4)	0.321 58(4)	0.136 49(6)
Os(2)	0.361 71(4)	0.123 18(5)	0.077 56(6)
Os(3)	0.250 60(4)	0.262 68(4)	−0.017 18(6)
Os(4)	0.273 38(4)	0.224 93(4)	0.214 13(6)
Os(5)	0.384 08(4)	0.255 82(5)	−0.113 24(6)
Os(6)	0.426 37(4)	0.183 10(5)	0.329 96(6)
Os(7)	0.169 31(4)	0.368 34(5)	0.119 09(6)
Os(8)	0.117 41(4)	0.161 69(5)	0.062 05(6)
P(1)	0.859 9(3)	0.218 5(3)	0.413 0(4)
C(11)	0.524 9(11)	0.316 6(12)	0.149 7(15)
O(11)	0.594 4(8)	0.311 9(9)	0.156 2(11)
C(12)	0.429 9(10)	0.401 3(12)	0.283 2(15)
O(12)	0.441 7(8)	0.457 8(9)	0.364 8(12)
C(13)	0.408 6(10)	0.444 2(11)	0.049 9(14)
O(13)	0.412 5(7)	0.520 7(9)	0.011 7(11)
C(21)	0.316 4(11)	0.051 3(13)	−0.073 3(17)
O(21)	0.289 2(8)	−0.000 3(9)	−0.160 3(12)
C(22)	0.469 4(12)	0.093 4(14)	0.088 0(18)
O(22)	0.535 8(10)	0.071 9(12)	0.097 7(15)
C(23)	0.325 0(12)	0.010 0(15)	0.154 7(19)
O(23)	0.303 7(9)	−0.065 9(11)	0.197 1(14)
C(31)	0.238 2(9)	0.382 5(11)	−0.104 0(14)
O(31)	0.232 0(8)	0.455 1(9)	−0.157 4(11)
C(32)	0.187 5(10)	0.186 0(12)	−0.152 8(15)
O(32)	0.151 0(8)	0.134 9(9)	−0.236 0(11)
C(41)	0.231 0(12)	0.117 6(14)	0.295 2(18)
O(41)	0.206 9(9)	0.048 8(10)	0.347 0(13)
C(42)	0.275 6(11)	0.307 3(12)	0.347 6(16)
O(42)	0.281 5(8)	0.358 2(9)	0.433 1(12)
C(51)	0.395 5(11)	0.371 6(13)	−0.194 6(17)
O(51)	0.400 3(9)	0.447 6(11)	−0.250 4(13)
C(52)	0.488 2(13)	0.233 1(15)	−0.125 8(19)
O(52)	0.555 2(12)	0.212 2(13)	−0.129 2(17)
C(53)	0.336 6(11)	0.193 3(13)	−0.262 7(17)
O(53)	0.308 0(9)	0.152 5(11)	−0.359 8(14)
C(61)	0.447 5(12)	0.254 7(15)	0.479 5(19)
O(61)	0.462 5(9)	0.298 3(10)	0.567 1(14)
C(62)	0.541 5(10)	0.164 2(11)	0.347 0(15)
O(62)	0.606 8(8)	0.155 3(9)	0.355 3(12)
C(63)	0.408 1(14)	0.065 9(17)	0.414 8(21)
O(63)	0.392 4(10)	−0.007 1(12)	0.459 9(15)
C(71)	0.094 5(12)	0.426 9(13)	−0.009 5(17)
O(71)	0.049 1(9)	0.454 9(10)	−0.089 9(14)
C(72)	0.251 1(9)	0.482 7(11)	0.141 0(14)
O(72)	0.297 2(8)	0.554 4(9)	0.154 8(11)
C(73)	0.124 3(11)	0.416 3(13)	0.240 3(17)
O(73)	0.099 4(9)	0.452 6(11)	0.317 0(14)
C(81)	0.052 9(11)	0.103 7(13)	0.163 2(17)
O(81)	0.012 5(9)	0.066 7(10)	0.227 2(13)
C(82)	0.137 3(11)	0.033 4(13)	0.018 0(17)
O(82)	0.145 4(8)	−0.043 5(10)	−0.012 1(13)
C(83)	0.029 0(12)	0.165 6(13)	−0.073 6(18)
O(83)	−0.024 6(10)	0.168 3(11)	−0.156 1(15)
C(1)	0.843 0(12)	0.082 4(14)	0.426 0(18)
C(111)	0.843 8(7)	0.246 3(8)	0.254 7(8)
C(112)	0.910 2(7)	0.284 6(8)	0.206 8(8)
C(113)	0.897 2(7)	0.303 5(8)	0.082 3(8)
C(114)	0.817 8(7)	0.284 2(8)	0.005 7(8)
C(115)	0.751 5(7)	0.245 9(8)	0.053 6(8)
C(116)	0.764 5(7)	0.226 9(8)	0.178 1(8)
C(121)	0.788 8(7)	0.274 6(8)	0.476 8(10)
C(122)	0.756 6(7)	0.359 5(8)	0.424 6(10)
C(123)	0.699 4(7)	0.402 6(8)	0.473 0(10)
C(124)	0.674 5(7)	0.360 9(8)	0.573 6(10)
C(125)	0.706 6(7)	0.276 0(8)	0.625 7(10)
C(126)	0.763 8(7)	0.232 9(8)	0.577 4(10)
C(131)	0.964 9(7)	0.262 6(9)	0.490 4(11)
C(132)	0.983 5(6)	0.353 1(9)	0.556 5(11)
C(133)	1.065 8(6)	0.392 2(9)	0.605 4(11)
C(134)	1.129 6(6)	0.340 7(9)	0.588 2(11)
C(135)	1.111 0(6)	0.250 2(9)	0.522 1(11)
C(136)	1.028 7(6)	0.211 1(9)	0.473 2(11)

according to literature methods, was heated in Bu^tOH (15 cm^3) under reflux for 48 h. The i.r. spectra of the reaction mixtures were recorded in Bu^tOH or CH_2Cl_2 and did not show any change in the characteristic frequencies of the starting salts.

Reaction of $[Os_6(CO)_{18}]$ *in* Bu^tOH *under Reflux; Synthesis of* $[Os_8H(CO)_{22}]^-$ (1).—$[Os_6(CO)_{18}]$ (200 mg) was heated in Bu^tOH (40 cm^3) under reflux for 53 h, after which time the i.r. spectrum showed no $[Os_6(CO)_{18}]$ remaining. The solvent was removed under vacuum and the residues were taken up in acetone (10 cm^3). This gave a dark red solution plus a dark solid. Following the addition of $[PMePh_3]Br$ in MeOH (32 mg, 10 cm^3), the mixture was left stirring under N_2 for 1 h, then the solvents were evaporated off under vacuum. On addition of a minimum of acetone (5 cm^3), $[Os_4H_4(CO)_{12}]$ separated as a white powder which was filtered off. The acetone mixture was separated by column chromatography using acetone–hexane (1 : 1) as eluant to give four main fractions. The first (faint yellow) was $[Os_4H_4(CO)_{12}]$ (total yield 32.6 mg, 21%). The second (dark red, main product) was $[PMePh_3][Os_8H(CO)_{22}]$; this was crystallized from CH_2Cl_2–Pr^iOH by slow evaporation techniques (total yield 48.1 mg, 31%). The third fraction was $[PMePh_3]_2[Os_6(CO)_{18}]$ (yield 23.9 mg, 10%). Finally the fourth fraction was $[PMePh_3]_2[Os_{10}C(CO)_{24}]$ (trace).

Protonation of $[PMePh_3][Os_8H(CO)_{22}]$.—Addition of one drop of concentrated H_2SO_4 to $[PMePh_3][Os_8H(CO)_{22}]$ (10 mg) in MeCN (1 cm^3) resulted in the formation of $[Os_8H_2(CO)_{22}]$ (3) in quantitative yield which precipitated in the form of a brown powder. This was characterized by i.r. and mass spectroscopy.

Deprotonation of $[Os_8H(CO)_{22}]^-$ (1).—Addition of an excess of KOH (one pellet) in MeOH (4 cm^3) to a methanolic solution of $[PMePh_3][Os_8H(CO)_{22}]$ (20 mg in 4 cm^3) led to the formation of the dianion after 1 h at room temperature. The solvent was removed under vacuum and water (6 cm^3) was added to remove excess KOH. The suspension was filtered through silica; the dark brown solid was first washed with water (3 times) then removed from the silica with CH_2Cl_2 (8 cm^3), and dried over $MgSO_4$. After filtration, the CH_2Cl_2 was reduced in volume to 3 cm^3 and $[PMePh_3]Br$ in MeOH (20 mg in 2 cm^3) was added. Slow evaporation at room temperature gave crystals of $[PMePh_3]_2[Os_8(CO)_{22}]$ which were washed first with cold MeOH then with pentane (yield 14 mg, 62%).

Deprotonation of $[PMePh_3][Os_8H(CO)_{22}]$ (10 mg) in acetone (4 cm^3) is also achieved by addition of a 10-fold excess of $[NBu_4]I$, $[PMePh_3]Br$, $[N(PPh_3)_2]Cl$, or proton sponge [1,8-bis(dimethylamino)naphthalene] in CH_2Cl_2 (*ca.* 1 cm^3). The reaction is complete after 24 h.

Reaction of $[Os_4H_4(CO)_{12}]$ *or* $[PMePh_3][Os_8H(CO)_{22}]$ *in* Bu^tOH *under Reflux*.—Both compounds (15 mg) were heated in turn in Bu^tOH (10 cm^3) under reflux for 48 h. No reaction occurred according to the i.r. spectra and spot t.l.c. of the solutions [using acetone–hexane (1 : 1) as eluant].

Table 7. Fractional atomic co-ordinates for $[Os_8H(CO)_{22}I]$ (2)

Atom	x	y	z	Atom	x	y	z
Os(1)	0.259 36(8)	0.331 83(10)	0.408 09(5)	C(51)	0.153 7(30)	0.142 1(42)	0.560 0(19)
Os(2)	0.114 54(7)	0.167 19(11)	0.407 72(15)	O(51)	0.119 4(19)	0.078 0(27)	0.589 6(12)
Os(3)	0.303 53(7)	0.094 34(10)	0.441 01(4)	C(52)	0.315 5(23)	0.254 9(33)	0.561 1(15)
Os(4)	0.257 32(7)	0.131 14(10)	0.334 06(4)	O(52)	0.379 7(19)	0.272 0(27)	0.592 0(12)
Os(5)	0.214 98(9)	0.239 23(12)	0.508 56(5)	C(53)	0.137 6(27)	0.370 9(38)	0.531 7(17)
Os(6)	0.128 74(8)	0.318 22(12)	0.317 35(5)	O(53)	0.091 5(23)	0.447 6(33)	0.545 7(14)
Os(7)	0.289 10(8)	0.315 60(12)	0.254 71(5)	C(61)	0.018 3(21)	0.378 8(29)	0.344 2(13)
Os(8)	0.310 74(8)	−0.106 74(11)	0.376 07(5)	O(61)	−0.050 9(19)	0.421 2(26)	0.356 1(12)
I	0.370 1(1)	0.450 4(2)	0.338 7(1)	C(62)	0.150 0(24)	0.473 6(34)	0.289 9(15)
C(11)	0.371 7(23)	0.380 4(32)	0.459 4(14)	O(62)	0.155 4(17)	0.582 9(24)	0.284 3(11)
O(11)	0.423 1(17)	0.419 4(23)	0.486 0(10)	C(63)	0.064 6(24)	0.259 1(35)	0.251 7(16)
C(12)	0.178 8(24)	0.466 9(34)	0.418 8(15)	O(63)	0.022 2(17)	0.230 6(24)	0.214 8(11)
O(12)	0.139 1(19)	0.553 4(27)	0.428 5(12)	C(71)	0.236 2(21)	0.216 6(28)	0.201 7(13)
C(21)	0.100 3(21)	0.033 7(29)	0.453 7(13)	O(71)	0.198 7(20)	0.167 0(27)	0.167 3(12)
O(21)	0.082 1(13)	−0.052 7(19)	0.477 4(8)	C(72)	0.395 1(30)	0.285 1(40)	0.228 1(19)
C(22)	0.024 6(22)	0.251 9(31)	0.444 4(14)	O(72)	0.476 4(19)	0.271 1(26)	0.212 4(12)
O(22)	−0.035 0(19)	0.287 2(26)	0.465 2(12)	C(73)	0.273 8(23)	0.451 2(34)	0.207 8(15)
C(23)	0.029 2(21)	0.092 3(28)	0.357 4(13)	O(73)	0.265 3(19)	0.539 0(27)	0.183 8(12)
O(23)	−0.028 1(16)	0.049 6(23)	0.326 5(10)	C(81)	0.348 5(23)	−0.244 1(34)	0.419 7(15)
C(31)	0.295 6(23)	−0.026 4(32)	0.492 9(14)	O(81)	0.362 8(18)	−0.323 5(25)	0.446 9(11)
O(31)	0.279 6(17)	−0.090 9(24)	0.529 7(11)	C(82)	0.316 5(25)	−0.183 7(35)	0.308 2(16)
C(32)	0.431 2(22)	0.115 6(29)	0.469 9(13)	O(82)	0.319 0(16)	−0.246 1(23)	0.270 5(11)
O(32)	0.501 3(14)	0.136 5(19)	0.487 0(8)	C(83)	0.437 7(21)	−0.059 0(29)	0.382 6(13)
C(41)	0.183 4(20)	0.035 5(28)	0.284 8(13)	O(83)	0.517 6(15)	−0.034 9(20)	0.386 9(9)
O(41)	0.134 2(17)	−0.019 3(23)	0.255 3(10)	C(84)	0.177 1(19)	−0.146 8(25)	0.375 5(12)
C(42)	0.359 5(21)	0.096 1(28)	0.299 2(13)	O(84)	0.102 3(17)	−0.175 3(23)	0.374 7(10)
O(42)	0.425 4(18)	0.068 8(24)	0.279 5(11)	O(1)	0.583 6(17)	0.240 1(24)	0.360 1(11)

Reaction of $[Os_6(CO)_{18}]$ *under Reflux in n-Octane or in* Bu^tOH *under a CO Atmosphere*.—No reaction was observed when $[Os_6(CO)_{18}]$ (20 mg) was heated under reflux in n-octane (15 cm^3; b.p. 125.6 °C) for 48 h nor in Bu^tOH (15 cm^3; b.p.. 108 °C) under reflux for the same time with CO passing through the solution.

Reaction of $[PMePh_3][Os_8H(CO)_{22}]$ *with* I_2.—Slow addition of a CH_2Cl_2 solution containing two equivalents of I_2 to $[PMePh_3][Os_8H(CO)_{22}]$ (15 mg) in CH_2Cl_2 (5 cm^3) gave immediately the brown species $[Os_8H(CO)_{22}I]$ (2). This was purified by t.l.c. using hexane–CH_2Cl_2(1 : 1) as eluant, and crystallized from CH_2Cl_2 by slow evaporation at 0 °C (yield 12.3 mg, 86%).

Reaction of $[Os_8H(CO)_{22}I]$ (2) *with* $[NBu_4]I$.—Addition of $[NBu_4]I$ (3 mg, 2 mol equiv.) to a solution of $[Os_8H(CO)_{22}I]$ in CH_2Cl_2 (10 mg in 5 cm^3) led to total reformation of $[Os_8H(CO)_{22}]^-$ (characterized by i.r.) after 2 h at room temperature.

Crystal Data for (1), $[PMePh_3]^+$ *Salt*.—$C_{41}H_{19}O_{22}Os_8P$, M = 2 416.2, triclinic, space group $P\bar{1}$, a = 16.775(3), b = 13.509(2), c = 11.267(2) Å, α = 89.88(1), β = 103.97(1), γ = 96.99(1)°, U = 2 458.3 $Å^3$, $F(000)$ = 2 128, Z = 2, D_c = 3.26 g cm^{-3}, Mo-K_α radiation, λ = 0.710 69 Å, μ(Mo-K_α) = 198.9 cm^{-1}. The space group was assumed and confirmed by satisfactory refinement. The crystal selected for data collection had dimensions 0.20 × 0.15 × 0.21 mm. Data were collected in the θ range 3—25°, with scan width 0.8°. 482 Azimuthal scan data were used in the absorption correction and relative transmission factors varied from 1.00 to 0.54. Equivalent reflections were averaged to give 5 615 absorption-corrected reflections with $I/\sigma(I) \geqslant 3.0$.

Crystal Data for (2) (*as a Monohydrate*).—$C_{22}H_3IO_{23}Os_8$, M = 2 283.7, monoclinic, space group $P2_1/c$, a = 14.386(2), b = 11.037(1), c = 24.629(3) Å, β = 94.30(2)°, U = 3 899.5 $Å^3$, $F(000)$ = 3 920, Z = 4, D_c = 3.89 g cm^{-3}, Mo-K_α radiation, λ = 0.710 69 Å, μ(Mo-K_α) = 257.7 cm^{-1}. The space group was assigned from systematic absences in the data $h0l$ ($l = 2n + 1$) and $0k0$ ($k = 2n + 1$). The crystal selected for data collection had dimensions 0.35 × 0.20 × 0.10 mm. Data were collected in the θ range 3—25°, with scan width 0.90°. 406 Azimuthal scan data were used in the absorption correction and relative transmission factors varied from 1.00 to 0.42. Equivalent reflections were averaged to give 4 644 reflections with $I/\sigma(I) \geqslant 3.0$.

The method of data collection, data processing, and absorption correction used for the $[PMePh_3]^+$ salt of (1) and for (2) have been described previously.[36]

Structure Solution and Refinement.[37]—The position of three osmium atoms for the $[PMePh_3]^+$ salt of (1) (defining a triangle) were found from a Patterson synthesis; the remaining five osmium atoms were found from subsequent Fourier syntheses. The non-hydrogen atoms were located from difference-Fourier syntheses, establishing the formulation of (1) as $[Os_8H(CO)_{22}]^-$. Blocked full-matrix refinement of the atomic positional and thermal parameters converged at a final R = 0.0359 and R' of 0.0366. The phenyl groups were treated as rigid hexagons [d(C–C) = 1.395, d(C–H) = 1.08 Å]. Anisotropic thermal parameters were assigned to the Os and P atoms, and a common thermal parameter [refined value 0.108(20) $Å^2$] to the H atoms in the final cycles of refinement. Final difference-Fourier syntheses showed a few residual peaks of *ca.* 1 e $Å^{-3}$ in the region of the osmium atoms.

For (2) four osmium atoms (defining a tetrahedron) were located from a Patterson map and the remaining osmium and other non-hydrogen atoms were found in subsequent difference-Fourier syntheses. With all atoms included, a difference-Fourier synthesis showed several residual peaks of *ca.* 2—3 e $Å^{-3}$ in the vicinity of the Os atoms. One higher peak of *ca.* 6 e $Å^{-3}$ was located between the I atom (3.85 Å) and a carbonyl oxygen O(83) (3.26 Å). This was attributed to the oxygen atom of a water molecule and as such refined satisfactorily. No independent evidence of the presence of water of crystallization was obtained from the i.r. spectrum. Blocked full-matrix refinement, with anisotropic thermal parameters assigned to the osmium and iodine atoms, converged to a final R of 0.0569 and R' of 0.0570. A final difference-Fourier synthesis showed residual peaks of *ca.* 2 e Å^{-3} in the region of the osmium atoms.

The final atomic co-ordinates for the $[PMePh_3]^+$ salt of (1), and for (2), are given in Tables 6 and 7 respectively.

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