Synthesis of the Cluster Dianion $[Os_{11}C(CO)_{27}]^{2-}$ by Pyrolysis and its Reactions with Electrophiles; *X*-Ray Structure Analysis of the Mixed-metal Derivative $[PMePh_3][Os_{11}C(CO)_{27}\{Cu(NCMe)\}]\cdot CH_2Cl_2$ and the Hydrido Derivative $[PMePh_3][Os_{11}C(CO)_{27}H]$ †

Simon R. Drake, Brian F. G. Johnson, Jack Lewis,* William W. J. H. Nelson, and Maria D. Vargas
University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW
Trushar Adatia, Dario Braga, Kim Henrick, Mary McPartlin,* and Angelo Sironi
School of Chemistry, Polytechnic of North London, Holloway Road, London N7 8DB

The new cluster species $[Os_{11}C(CO)_{27}]^{2-}$ (**2**) has been identified as one of the products resulting from the pyrolysis of $[Os_3(CO)_{12}]$. It reacts with $[Cu(NCMe)_4]BF_4$ to yield the monoanion $[Os_{11}C(CO)_{27}\{Cu(NCMe)\}]^-$ (**4**) and $[Os_{11}C(CO)_{27}\{Cu(NCMe)\}_2]$ (**5**). The reaction of (**2**) with iodine-iodide produces a series of iodo-clusters $[Os_{11}C(CO)_{27}I]^-$ (**8**) and $[Os_{11}C(CO)_{27}I_2]$ (**9**) which are converted back into (**2**) by addition of halide ions. The unstable monoanionic species $[Os_{11}C(CO)_{27}\{M(PMe_2Ph)\}]^-$ [M = Au (**3**) or Cu (**7**)] are obtained on reaction of (**2**) with $[M(PMe_2Ph)]^+$, and further reaction of (**3**) yields $[Os_{11}C(CO)_{27}\{Au(PMe_2Ph)\}_2]$ (**6**). The dianionic cluster (**2**) reacts with acid to give the monoanion $[Os_{11}C(CO)_{27}H]^-$ (**10**) and $[Os_{11}C(CO)_{27}H_2]$ (**11**). The reaction with $Hg(C_6Cl_5)(O_2CCF_3)$ yields initially the unstable monoanion $[Os_{11}C(CO)_{27}\{Hg(C_6Cl_5)\}]^-$ (**12**) which is rapidly converted into the known cluster dianion $[Os_{20}Hg(C)_2(CO)_{48}]^{2-}$. *X*-Ray analysis of the $[PMePh_3]^+$ salts of (**4**) and (**10**) reveal identical Os_{11} core geometries, but in (**4**) the copper ligand occupies a μ_3-bridging position, while the hydride in (**10**) appears to be located in an interstitial site.

The vacuum pyrolysis of $[Os_3(CO)_{12}]$, first reported in 1972, was shown initially to produce a range of osmium clusters containing up to eight metal atoms (see Scheme 1).[1] Subsequently the reaction of $[Os_3(CO)_{12}]$ was proved to be sensitive to temperature, time, and moisture,[2] and the range of nuclearities was extended with the isolation of $[Os_{10}C(CO)_{24}]^{2-}$ (**1**).[3] By adjusting the conditions, yields of up to 75% of $[Os_{10}C(CO)_{24}]^{2-}$ (**1**) have been obtained from $[Os_3(CO)_{10}(NCMe)_2]$.[4] The formation of carbido clusters from pyrolysis is often observed, and the carbide carbon atom has been shown to be derived from a carbonyl ligand, possibly by disproportionation of CO to CO_2 and carbon.[1] The pyrolysis of the ^{13}CO-enriched species $[Os_3(CO)_{11}(NC_5H_5)]$ and $[Re(CO)_4H_2]^-$ yields the dianions $[Os_{10}C(CO)_{24}]^{2-}$ (**1**) and $[Re_8C(CO)_{22}]^{2-}$ respectively with labelled carbide atoms.[5,6]

Details of the discovery of the largest osmium cluster obtained from the $[Os_3(CO)_{12}]$ pyrolysis reaction, the dianion $[Os_{11}C(CO)_{27}]^{2-}$ (**2**), and an extensive study of its reactions are reported here. A preliminary communication of this work has already appeared.[7]

Results and Discussion

Preparation and Structure of $[Os_{11}C(CO)_{27}]^{2-}$ (**2**).—The dianion $[Os_{11}C(CO)_{27}]^{2-}$ (**2**) was initially isolated from the residues remaining after extraction with boiling ethyl acetate of the cluster series of nuclearities Os_5–Os_8 from the products of he $[Os_3(CO)_{12}]$ pyrolysis. Addition of acetone–methanol (1 : 1), and an excess of $[PMePh_3]Br$ or $[N(PPh_3)_2]Cl$ (Scheme 1), ollowed by fractional crystallisation gave dark red crystals of he corresponding salts $[Os_{10}C(CO)_{24}]^{2-}$ (**1**) (yield *ca.* 10%), followed by dark brown crystals of the salts of $[Os_{11}C(CO)_{27}]^{2-}$ (**2**) (yield < 1%). It has now been found that by sealing the Carius tube under low vacuum (> 5 Torr), the yields of (**1**) and (**2**) may be increased to 36 and 7% respectively. The dianion (**2**) has now also been isolated in *ca.* 3% yield from the vacuum pyrolysis of $[Os_3(CO)_{11}(py)]$ (py = pyridine), originally reported as a good synthetic route to (**1**) (yield 80%).[3]

Partial *X*-ray structure analyses of the two crystalline modifications of the $[PMePh_3]^+$ salt of $[Os_{11}C(CO)_{27}]^{2-}$ (**2**) established the unusual metal core geometry, Figure 1(*a*), but gross disorder of the dianion in both crystalline modifications made satisfactory location of the light atoms impossible.[7]

The dianion (**2**) was formulated on the basis of fast atom bombardment (f.a.b.) mass spectroscopy [*m*/*z* 2 880 for (**2**) based on ^{192}Os], ^1H n.m.r. (δ +40 to −100, no hydride signals observed), and i.r. spectroscopy which reveals the presence of both terminal and bridging carbonyl ligands.

The structure of the Os_{11} core in (**2**) may be described as a bicapped square pyramid sharing its square face with a trigonal prism which is also bicapped on its triangular faces. Application of the Mingos fused-polyhedral electron-counting procedures[8] gives the correct total polyhedral electron count of 148 e.[7] This type of metal skeleton has not been previously observed but it shows some resemblance to that of $[Rh_8C(CO)_{19}]$ which also contains a square pyramid fused to a trigonal prism.[9]

Reaction of $[Os_{11}C(CO)_{27}]^{2-}$ (**2**) *with the Electrophiles* $[Au(PR_3)]^+$, $[Cu(NCMe)]^+$, *and* $[Hg(C_6Cl_5)]^+$.—The dianion $[Os_{11}C(CO)_{27}]^{2-}$ (**2**) has a rich chemistry (Scheme 2), its reactions with electrophiles bearing a striking similarity to those of the dianion $[Os_{10}C(CO)_{24}]^{2-}$ (**1**).[10] It reacts with either 1 equivalent of $[Au(PMe_2Ph)]PF_6$, $[Cu(NCMe)_4]BF_4$, or $Hg(C_6Cl_5)(O_2CCF_3)$ in dichloromethane to give the mixed-metal anions $[Os_{11}C(CO)_{27}\{Au(PMe_2Ph)\}]^-$ (**3**), $[Os_{11}C(CO)_{27}\{Cu(NCMe)\}]^-$ (**4**), and $[Os_{11}C(CO)_{27}\{Hg(C_6Cl_5)\}]^-$ (**12**) respectively. These have been characterised on the basis of the full *X*-ray structure analysis of (**4**) (see below) and of

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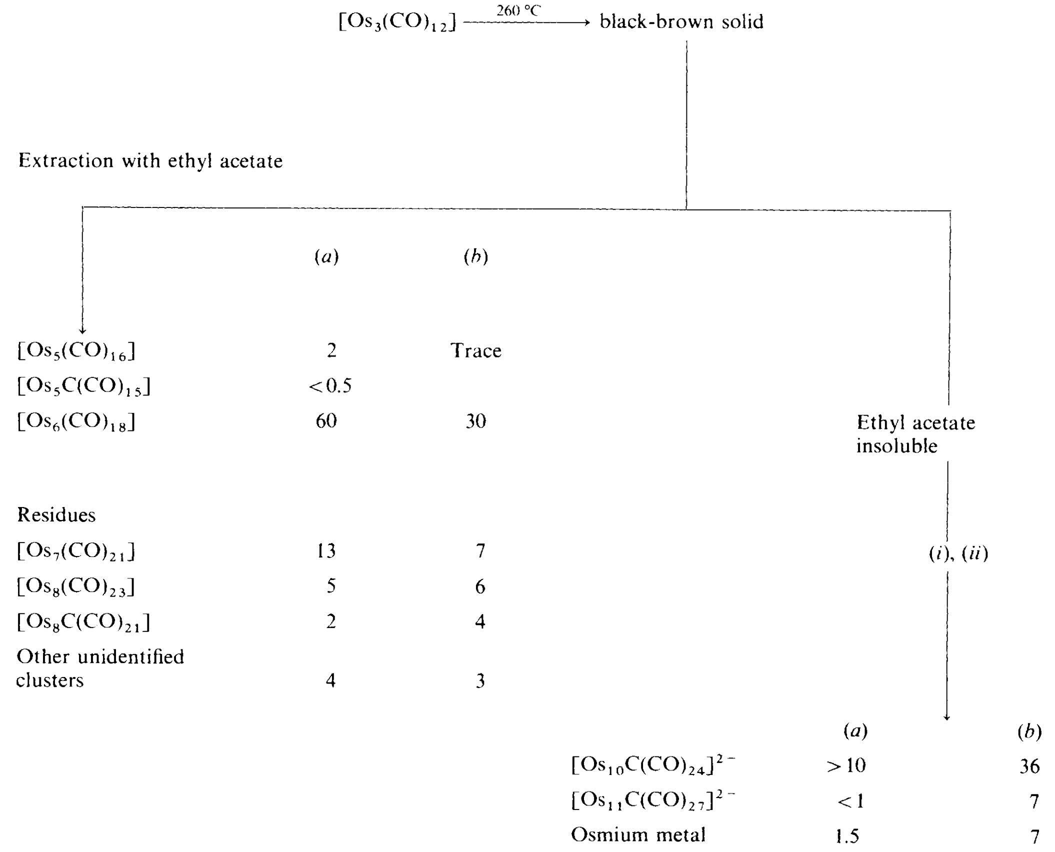
Supplementary data available: see Instructions for Authors, *J. Chem. oc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

on-S.I. unit employed: Torr ≈ 133 Pa.



Scheme 1. (*i*) Extraction with boiling acetone–methanol (1:1); (*ii*) addition of $[PMePh_3][Br]$ or $[N(PPh_3)_2][Cl]$ in MeOH, followed by slow evaporation; (*a*) 250 °C, 48 h, high vacuum (1×10^{-4} Torr); (*b*) 270 °C, 72 h, low vacuum (>5 Torr). Numbers are yields

spectroscopic (Table 1) and analytical properties. The copper derivative (**4**) reacts with 1 equivalent of PMe_2Ph to yield $[Os_{11}C(CO)_{27}\{Cu(PMe_2Ph)\}]^-$ (**7**) (Scheme 2) which exhibits an i.r. spectrum identical in the ν(CO) region to that of the gold derivative (**3**) (Table 1). It seems possible that in solution the two monoanions have similar structures.

Full *X*-ray structure analysis of the $[PMePh_3]^+$ salt of $[Os_{11}C(CO)_{27}\{Cu(NCMe)\}]^-$ (**4**) shows the overall anionic structure illustrated in Figure 2; selected bond lengths and interbond angles are listed in Table 2. The $Os_{11}Cu(C)$ core geometry is shown in Figure 1(*b*) and it can be seen that the Os_{11} framework is very similar to that observed[7] for the dianion (**2**) [Figure 1(*a*)]. In the study of the copper derivative (**4**) the carbido atom has been located in the centre of the trigonal prismatic cavity with a mean Os–C bond length of 2.17(2) Å. Although clusters of the cobalt triad frequently favour prismatic sites for interstitial carbido atoms,[9] this class of undecaosmium cluster provides the first examples in the iron triad.

In compound (**4**) the copper atom caps a face of the square pyramid defined by Os(3), Os(4), and Os(8) with a relatively long contact to a fourth osmium atom [Os(9) ··· Cu 3.156(4) Å]. The mean Os–Cu bond length of 2.645(4) Å is similar to that in the decaosmium cluster $[Os_{10}C(CO)_{24}\{Cu(NCMe)\}]^-$ of 2.638(8) Å.[10] The three Os–Os bond lengths bridged by the copper atom [mean 2.825(2) Å] are elongated compared to those of the equivalent unbridged face, defined by Os(2), Os(3), and Os(6) [mean 2.767(2) Å].

One edge of the trigonal prismatic part of the Os_{11} core (opposite the square pyramid) is bridged by a carbonyl ligand [Os(10)–C(b) 2.15(3), Os(11)–C(b) 2.04(3) Å; Os(10)–C(b)–Os(11) 84.1°]. The μ-CO ligand is not symmetrically placed above the Os(10)–Os(11) bond but lies well over towards the square face of the trigonal prism defined by Os(6), Os(8), Os(10), and Os(11).

The remaining carbonyl ligands are essentially linear [Os–C–O range 163—179(3)°]; three are bonded to each of the four capping osmium atoms, and two to each of the remaining seven. The copper atom makes short contacts with the carbon atoms of two adjacent osmium atoms [Cu ··· C(32) 2.34(3) and Cu ··· C(81) 2.45(3), mean 2.40 Å], similar to those observed ir the structure of the decaosmium–copper monoanion $[Os_{10}C$ $(CO)_{24}\{Cu(NCMe)\}]^-$ (mean Cu ··· CO 2.44 Å).[10]

The very close similarity of the i.r. spectra, ν(CO), o $[Os_{11}C(CO)_{27}\{M(PMe_2Ph)\}]^-$ [M = Au (**3**) or Cu (**7**)] t that of (**4**) (Table 1) makes it probable that the $MPMe_2P$ groups are also adopting μ_3-bonding modes. This is in contra to the structure of the decaosmium monoanion $[Os_{10}C(CO)_2$ $\{Au(PPh_3)\}]^-$ where the heterometal is in a μ-site.[10]

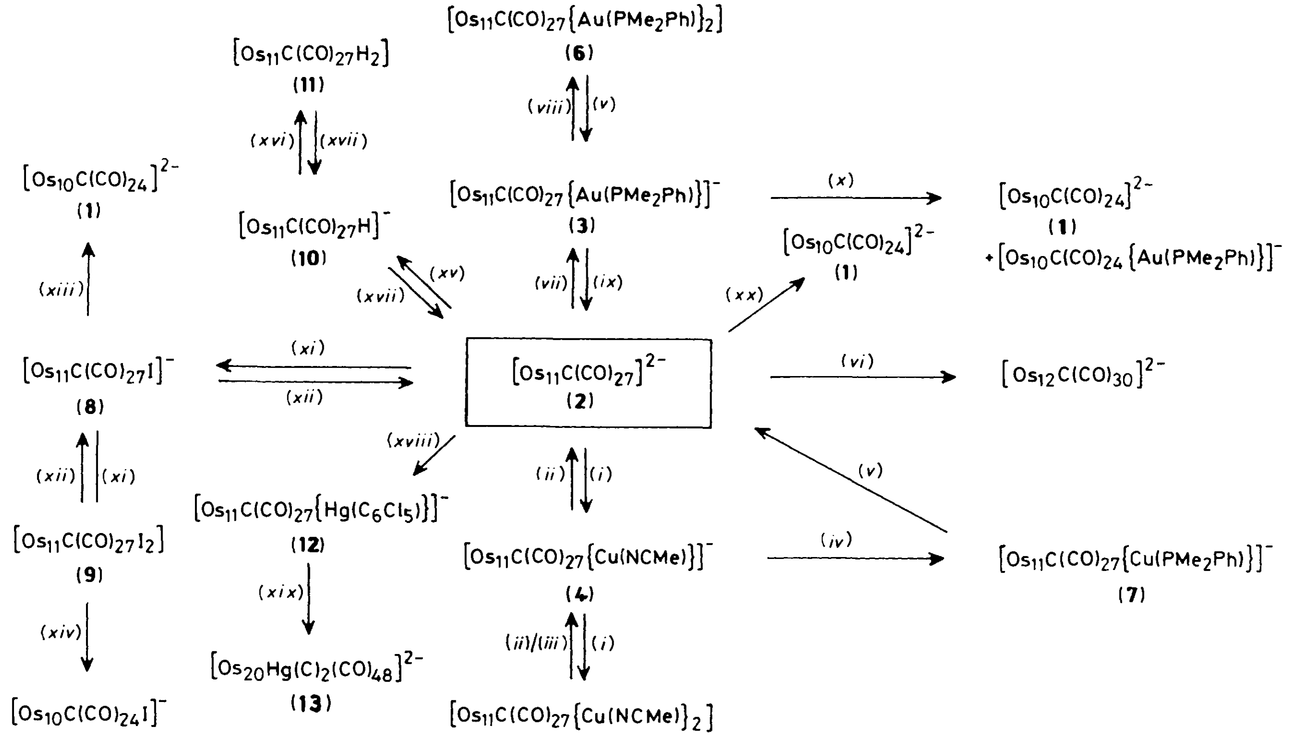
The ^1H n.m.r. spectrum of the monoanion $[Os_{11}C(CO)_2$ $\{Au(PMe_2Ph)\}]^-$ (**3**) in CD_2Cl_2 at room temperature has doublet at δ +1.92 [$^2J(PH)$ = 9.3 Hz] and a multiplet at 7.74—7.33. The spectrum does not change on cooling to 200 which is in marked contrast to the behaviour of $[Os_{10}C(CO)_2$ $\{Au(PMe_2Ph)\}]^-$ which exists in solution as two interconve ing isomers.[4] The ^{31}P-$\{^1H\}$ n.m.r. spectrum of (**3**) in CD_2Cl_2 room temperature has only one resonance for the $AuPMe_2$ group at δ −30.42, which remains unchanged on cooling 240 K.

Similar behaviour is observed in the ^1H n.m.r. spectrum of monoanion $[Os_{11}C(CO)_{27}\{Cu(PMe_2Ph)\}]^-$ (**7**) in CD_2C

Table 1. Spectroscopic data[a] (as $[PMePh_3]^+$ salts unless stated otherwise)

Compound	
(2) $[Os_{11}C(CO)_{27}]^{2-}$	2 079w, 2 052vs, 2 042vs, 2 011m, 1 989s, 1 982m (sh), 1 960w (sh), 1 903w, 1 781w (br); *m/z* 2 880
(3) $[Os_{11}C(CO)_{27}\{Au(PMe_2Ph)\}]^-$	2 085w, 2 061s, 2 054vs, 2 023m, 2 007s, 1 998m (sh), 1 982mw, 1 902w, 1 785w (br); $\delta(^1H)$ 1.92 [d, $^2J(PH)$ 9.3], 7.33—7.74 (m, 30 H); $\delta(^{31}P\text{-}\{^1H\})$ −30.42 (s, br)
(4) $[Os_{11}C(CO)_{27}\{Cu(NCMe)\}]^-$	2.087w, 2 061s, 2 054vs, 2 023m, 2 007s, 1 998m (sh), 1 982mw, 1 902w, 1 785w (br); $\delta(^1H)$ 2.36 (s, 3 H), 7.41—7.72 (m, 30 H); *m/z* 2 984
(5) $[Os_{11}C(CO)_{27}\{Cu(NCMe)\}_2]$	2 114vw, 2 078vs, 2 036m, 2 010s, 1 975m (sh), 1 929w, 1 792w (br); *m/z* 3 089
(6) $[Os_{11}C(CO)_{27}\{Au(PMe_2Ph)\}_2]^b$	2 109w, 2 085vs, 2 076vs, 2 038s (sh), 2 031vs, 2 013m, 1 983w (sh), 1 791w (br); $\delta(^1H)$ 1.90, 1.94 [2 d, $^2J(PH)$ = 10, 11.4]
(7) $[Os_{11}C(CO)_{27}\{Cu(PMe_2Ph)\}]^-$	2 085w, 2 065s, 2 052vs, 2 025m, 2 006s, 1 994m (sh), 1 972w (sh), 1 905w, 1 780w (br); $\delta(^1H)$ 1.93 [d, 3 H, $^2J(PH)$ 9.85], 7.36—7.78 (m, 30 H); $\delta(^{31}P\text{-}\{^1H\})$ −20.73 (s, br)
(8) $[Os_{11}C(CO)_{27}I]^{-\,b}$	2 093w, 2 070s, 2 032m, 2 014m, 2 008m (sh), 1 960w (sh), 1 933w, 1 789w (br)
(9) $[Os_{11}C(CO)_{27}I_2]^b$	2 113w, 2 083w (sh), 2 078vs, 2 071vs, 2 036s (sh), 2 029vs, 2 008m, 1 980w (sh), 1 786w (br)
(10) $[Os_{11}C(CO)_{27}H]^-$	2 096w, 2 069vs, 2 030m, 2 011m, 1 998w (sh), 1 930w, 1 786w (br); $\delta(^1H)^c$ −19.1 [s, 1 H, $^1J(^{187}Os\text{–}^1H)$ 14.16, 39.26, 49.88],[d] 1.98 [d, 3 H, $^2J(PH)$ 9]; *m/z* 2 881
(10a) $[Os_{11}C(CO)_{27}D]^-$	2 096w, 2 069vs, 2 030m, 2 011m, 1 998w (sh), 1 930w, 1 786w (br); *m/z* 2 882
(11) $[Os_{11}C(CO)_{27}H_2]$	(2 111m, 2 100w (sh), 2 086ms, 1 994m, 1 976w (sh), 1 963w, 1 952w, 1 931m, 1 790w (br); *m/z* 2 882
(11a) $[Os_{11}C(CO)_{27}D_2]$	2 111m, 2 100w (sh), 2 086ms, 1 994m, 1 976w (sh), 1 963w, 1 952w, 1 931m, 1 790w (br); *m/z* 2 883
(12) $[Os_{11}C(CO)_{27}\{Hg(C_6Cl_5)\}]^-$	2 093w, 2 070vs, 2 032m, 2 014m, 2 007m (sh), 1 993w (sh), 1 960w, 1 933w, 1 787w (br)

[a] Listed as carbonyl stretching bands (cm^{-1}) in CH_2Cl_2, 400.13-MHz ^1H n.m.r. in CD_2Cl_2 (*J* in Hz), 161.15-MHz $^{31}P\text{-}\{^1H\}$ in CD_2Cl_2 with $P(OMe)_3$ as reference (δ 0 p.p.m.), n.m.r. of $[N(PPh_3)_2]^+$ salt unless otherwise stated, M^+ in f.a.b. mass spectrum in negative-ion mode (^{192}Os, ^{197}Au). [b] Highest peak in mass spectrum, *m/z* 2 604, corresponds to $Os_{10}C(CO)_{24}$ fragment. [c] As $[PMePh_3]^+$ salt. [d] Ratio 2:1:1. *J*(CH) 2.00 Hz.



Scheme 2. Reactions of $[Os_{11}C(CO)_{27}]^{2-}$ with electrophiles (*i*) 1 equivalent of $[Cu(NCMe)_4]BF_4$ in CH_2Cl_2; (*ii*) MeCN; (*iii*) removal of CH_2Cl_2 and suspension in acetone; (*iv*) 1 equivalent of PMe_2Ph; (*v*) excess of PMe_2Ph; (*vi*) f.a.b. mass spectrometery +'$Os(CO)_3$' fragment; (*vii*) 1 equivalent each of $[Au(PMe_2Ph)]Cl + TlPF_6$ in CH_2Cl_2; (*viii*) 1 equivalent each of $[Au(PMe_2Ph)]Cl + AgClO_4$ in CH_2Cl_2; (*ix*) excess of NEt_3; (*x*) standing for up to 2 d in CH_2Cl_2; (*xi*) 2 equivalents of I_2 in CH_2Cl_2; (*xii*) 2.2 equivalents of $[NBu_4]I$ in CH_2Cl_2; (*xiii*) standing for 3 d in CH_2Cl_2; (*xiv*) standing for 2 d in CH_2Cl_2; (*xv*) 1 equivalent of CF_3CO_2H or CF_3CO_2D in CH_2Cl_2, $CHCl_3$, thf, or MeCN; (*xvi*) excess of CF_3CO_2H or CF_3CO_2D in CH_2Cl_2, $CHCl_3$, thf, or MeCN; (*xvii*) MeOH or acetone at r.t. for 40 min; (*xviii*) 1 equivalent of $Hg(C_6Cl_5)(O_2CCF_3)$ in CH_2Cl_2 for 20 min; (*xix*) standing under N_2 for up to 2 d; (*xx*) oxidation, $AgBF_4$–CH_2Cl_2

with a doublet resonance observed at δ +1.93 [$^2J(PH)$ = 9.85 Hz] which remains unchanged on cooling and exhibits no fluxional behaviour. The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum of (**7**) in CD_2Cl_2 at room temperature shows only one broad resonance at δ −20.73 relative to $P(OMe)_3$. On cooling to 240 K this resonance sharpens. Temperature-dependent line broadening has been observed previously for phosphorus atoms bonded directly to copper, and has been attributed to quadrupolar effects arising from the copper.[11]

Crystals of compound (**3**) or (**7**) suitable for *X*-ray analysis

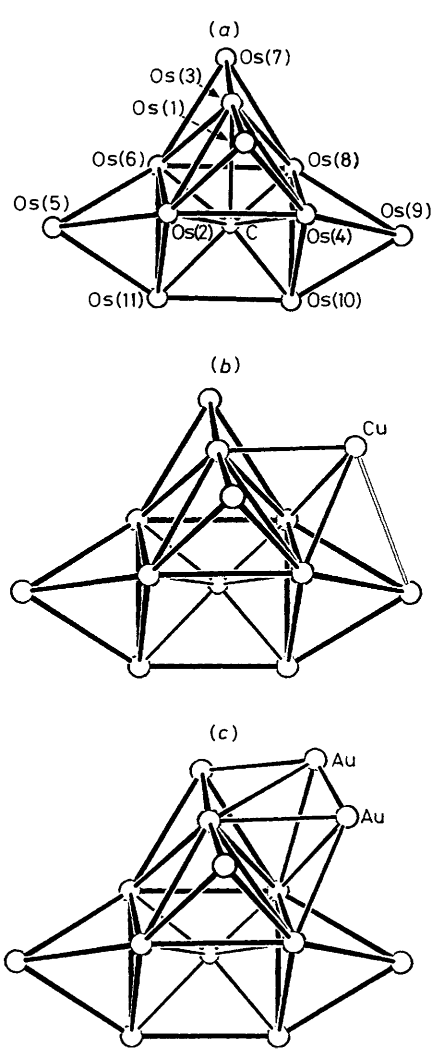


Figure 1. (*a*) The Os_{11} metal core geometry observed in $[PMePh_3]^+$ salts of the dianion $[Os_{11}C(CO)_{27}]^{2-}$ (**2**) and the monoanion $[Os_{11}C(CO)_{27}H]^-$ (**10**); (*b*) the $Os_{11}M$ metal core geometry observed in $[Os_{11}C(CO)_{27}\{Cu(NCMe)\}]^-$ (**4**), and deduced from spectroscopic evidence to be present in $[Os_{11}C(CO)_{27}\{M(PMe_2Ph)\}]^-$ [M = Au (**3**) or Cu (**7**)]; (*c*) Proposed $Os_{11}Au_2$ framework in $[Os_{11}C(CO)_{27}\{Au(PMe_2Ph)\}_2]$ (**6**)

have not been obtained, since both monoanions slowly decompose on standing in CH_2Cl_2 over a period of 4 d to give the decaosmium dianion (**1**) and $[Os_{10}C(CO)_{24}\{M(PMe_2Ph)\}]^-$ (M = Au or Cu).

On standing under nitrogen in CH_2Cl_2 for up to 2 d, the mercury monoanion $[Os_{11}C(CO)_{27}\{Hg(C_6Cl_5)\}]^-$ (**12**) condenses to form the dianion $[Os_{20}Hg(C)_2(CO)_{48}]^{2-}$. The metal framework of this eicosaosmium cluster has been well established previously, and consists of a 6:3:3:3:6 array of metal atoms with an Os_2Hg triangle fusing two Os_9 units together. [12]

Reactivity of $[Os_{11}C(CO)_{27}(MY)]^-$ [MY = Cu(NCMe) *or* $AuPMe_2Ph$].—The monoanions (**4**) and (**3**) react further with 1 equivalent of $[Cu(NCMe)_4]BF_4$ and $[Au(PMe_2Ph)]ClO_4$ respectively to yield the neutral species $[Os_{11}C(CO)_{27}\{Cu(NCMe)\}_2]$ (**5**) and $[Os_{11}C(CO)_{27}\{Au(PMe_2Ph)\}_2]$ (**6**).

Like its decaosmium analogue $[Os_{10}C(CO)_{24}\{Cu(NCMe)\}_2]$, the dicopper bimetallic species (**5**) is insoluble in most common organic solvents; but the digold derivative $[Os_{11}C(CO)_{27}\{Au(PMe_2Ph)\}_2]$ (**6**) has been characterised on the basis of i.r. (which was temperature independent) and ^1H n.m.r. spectroscopy (Table 1). The ^1H n.m.r. spectrum in CD_2Cl_2 at room temperature reveals the presence of one pair of doublets, at δ +1.90 and +1.94 [$^2J(PH)$ = 10 and 11.4 Hz]. This is consistent with the presence of two inequivalent $AuPMe_2Ph$ groups and at room temperature no fluxional behaviour involving Group 1b coinage-metal site exchange is observed. It seems probable that in (**6**) the gold atoms are directly bonded, adopting adjacent μ_3 sites [Figure 1(*c*)]. Direct Au–Au bonding between $AuPR_3$ groups has been observed before, in for example $[Ru_6C(CO)_{16}\{Au(PR_3)\}_2]$. [13]

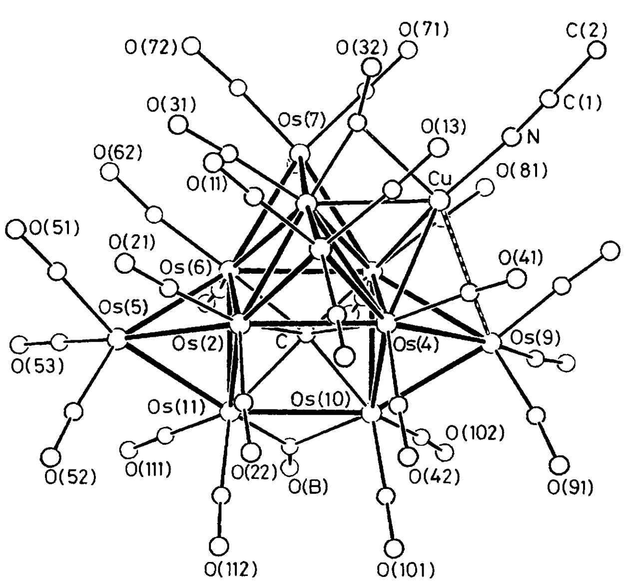


Figure 2. The structure of the monoanion $[Os_{11}C(CO)_{27}\{Cu(NCMe)\}]^-$ (**4**) in the $[PMePh_3]^+$ salt; the carbonyl C atoms have the same numbers as their O atoms, the first digits being the numbers of the corresponding osmium atoms

Crystallographic characterisation of the species (**5**) and (**6**) has not been possible due to the difficulties in obtaining crystals which result from poor solubility of these species in hydrocarbon and chlorinated solvents, and also from the ease with which dissociation of the MY units [MY = $AuPR_3$ or Cu(NCMe)] occurs in the presence of MeCN or acetone to give (**3**) or (**4**) and finally (**1**). It would be interesting to know if there is a Cu–Cu bond present in (**5**) as has previously been observed in the cluster $[Ru_6C(CO)_{16}\{Cu(NCMe)\}_2]$, [14] similar to the Au–Au bond proposed in (**6**). The reactivity of (**2**), like that of the decaosmium dianion (**1**), has been found to be solvent dependent, so that (**4**) or (**5**) are formed readily in CH_2Cl_2, but no reaction occurs in MeCN (Scheme 2).

Protonation Reactions of $[Os_{11}C(CO)_{27}]^{2-}$ (**2**).—Reaction of $[Os_{11}C(CO)_{27}]^{2-}$ (**2**) with H^+ or D^+ might be expected from the isolobal principle [15] to yield a species with the hydride capping a face of the 'Os_{11}' core, in a site similar to that observed for the μ_3-Cu(NCMe) group in (**4**). Addition of CF_3CO_2H or H_2SO_4 to (**2**) in CH_2Cl_2 or $CHCl_3$ gives the monoanion $[Os_{11}C(CO)_{27}H]^-$ (**10**) as the only product, whilst in the polar solvents tetrahydrofuran (thf) and MeCN acidification goes further giving (**2**), (**10**), and the dihydro cluster $[Os_{11}C(CO)_{27}H_2]$ (**11**) (Scheme 2). In MeCN on prolonged stirring the formation of the neutral cluster $[Os_{11}C(CO)_{27}H_2]$ (**11**) as a precipitate is quantitative (Scheme 2). This is consistent

Table 2. Selected bond lengths (Å) and angles (°) in compounds (**4**) and (**10**)

(*a*) Compound (**4**)

Os(1)–Os(2)	2.798(2)	Os(1)–Os(3)	2.733(2)	Os(7)–Os(8)	2.790(1)	Os(8)–Os(9)	2.820(2)
Os(1)–Os(4)	2.824(2)	Os(2)–Os(3)	2.755(1)	Os(8)–Os(10)	2.824(1)	Os(8)–Cu	2.627(4)
Os(2)–Os(4)	2.848(2)	Os(2)–Os(5)	2.813(2)	Os(9)–Os(10)	2.754(2)	Os(9) · · · Cu	3.156(4)
Os(2)–Os(6)	2.810(2)	Os(2)–Os(11)	2.868(2)	Os(10)–Os(11)	2.809(2)	Cu–N	1.90(3)
Os(3)–Os(4)	2.822(1)	Os(3)–Os(6)	2.735(2)	Cu–C(32)	2.34(3)	N–C(1)	1.12(4)
Os(3)–Os(7)	2.738(2)	Os(3)–Os(8)	2.827(2)	C(1)–C(2)	1.45(5)	P–CP(11)	1.774(18)
Os(3)–Cu	2.598(4)	Os(4)–Os(8)	2.826(2)	P–CP(21)	1.817(20)	P–CP(31)	1.786(20)
Os(4)–Os(9)	2.815(2)	Os(4)–Os(10)	2.904(2)	P–CP(41)	1.84(3)	Cl(1)–C(3)	1.64(8)
Os(4)–Cu	2.709(4)	Os(5)–Os(6)	2.801(2)	Cl(2)–C(3)	1.59(9)	Os–C Range	2.17—1.81(3)
Os(5)–Os(11)	2.739(2)	Os(6)–Os(7)	2.794(2)	C–O Range	1.10—1.22(3)		
Os(6)–Os(8)	2.847(2)	Os(6)–Os(11)	2.809(2)				

Os(3)–Os(1)–Os(2)	59.7(1)	Os(4)–Os(1)–Os(2)	60.9(1)	Os(7)–Os(6)–Os(2)	118.9(1)	Os(7)–Os(6)–Os(3)	59.3(1)
Os(4)–Os(1)–Os(3)	61.0(1)	Os(4)–Os(2)–Os(1)	60.0(1)	Os(7)–Os(6)–Os(5)	151.9(1)	Os(8)–Os(6)–Os(2)	90.1(1)
Os(4)–Os(2)–Os(3)	60.4(1)	Os(5)–Os(2)–Os(1)	149.9(1)	Os(8)–Os(6)–Os(3)	60.8(1)	Os(8)–Os(6)–Os(5)	143.6(1)
Os(5)–Os(2)–Os(3)	110.9(1)	Os(5)–Os(2)–Os(4)	143.8(1)	Os(8)–Os(6)–Os(7)	59.3(1)	Os(11)–Os(6)–Os(2)	61.4(1)
Os(6)–Os(2)–Os(1)	117.8(1)	Os(6)–Os(2)–Os(3)	58.9(1)	Os(11)–Os(6)–Os(3)	112.4(1)	Os(11)–Os(6)–Os(5)	58.5(1)
Os(6)–Os(2)–Os(4)	90.2(1)	Os(6)–Os(2)–Os(5)	59.7(1)	Os(11)–Os(6)–Os(7)	148.8(1)	Os(11)–Os(6)–Os(8)	90.0(1)
Os(11)–Os(2)–Os(1)	150.7(1)	Os(11)–Os(2)–Os(3)	110.0(1)	Os(6)–Os(7)–Os(3)	59.3(1)	Os(8)–Os(7)–Os(3)	61.5(1)
Os(11)–Os(2)–Os(4)	90.7(1)	Os(11)–Os(2)–Os(5)	57.6(1)	Os(8)–Os(7)–Os(6)	61.3(1)	Os(4)–Os(8)–Os(3)	59.9(1)
Os(11)–Os(2)–Os(6)	59.3(1)	Os(4)–Os(3)–Os(1)	61.1(1)	Os(6)–Os(8)–Os(3)	57.6(1)	Os(6)–Os(8)–Os(4)	89.9(1)
Os(4)–Os(3)–Os(2)	61.4(1)	Os(6)–Os(3)–Os(1)	122.9(1)	Os(7)–Os(8)–Os(3)	58.3(1)	Os(7)–Os(8)–Os(4)	118.2(1)
Os(6)–Os(3)–Os(2)	61.6(1)	Os(6)–Os(3)–Os(4)	92.3(1)	Os(7)–Os(8)–Os(6)	59.4(1)	Os(9)–Os(8)–Os(3)	113.7(1)
Os(7)–Os(3)–Os(1)	175.7(1)	Os(7)–Os(3)–Os(2)	123.0(1)	Os(9)–Os(8)–Os(4)	59.8(1)	Os(9)–Os(8)–Os(6)	142.7(1)
Os(7)–Os(3)–Os(4)	120.1(1)	Os(7)–Os(3)–Os(6)	61.4(1)	Os(9)–Os(8)–Os(7)	152.2(1)	Os(10)–Os(8)–Os(3)	110.9(1)
Os(8)–Os(3)–Os(1)	121.1(1)	Os(8)–Os(3)–Os(2)	91.6(1)	Os(10)–Os(8)–Os(4)	61.9(1)	Os(10)–Os(8)–Os(6)	89.3(1)
Os(8)–Os(3)–Os(4)	60.0(1)	Os(8)–Os(3)–Os(6)	61.5(1)	Os(10)–Os(8)–Os(7)	148.3(1)	Os(10)–Os(8)–Os(9)	58.4(1)
Os(8)–Os(3)–Os(7)	60.1(1)	Cu–Os(3)–Os(1)	91.2(1)	Cu–Os(8)–Os(3)	56.7(1)	Cu–Os(8)–Os(4)	59.4(1)
Cu–Os(3)–Os(2)	121.2(1)	Cu–Os(3)–Os(4)	59.8(1)	Cu–Os(8)–Os(6)	114.3(1)	Cu–Os(8)–Os(7)	84.6(1)
Cu–Os(3)–Os(6)	119.2(1)	Cu–Os(3)–Os(7)	86.3(1)	Cu–Os(8)–Os(9)	70.7(1)	Cu–Os(8)–Os(10)	115.6(1)
Cu–Os(3)–Os(8)	57.7(1)	Os(2)–Os(4)–Os(1)	59.1(1)	Os(8)–Os(9)–Os(4)	60.2(1)	Os(10)–Os(9)–Os(4)	62.8(1)
Os(3)–Os(4)–Os(1)	57.9(1)	Os(3)–Os(4)–Os(2)	58.1(1)	Os(10)–Os(9)–Os(8)	60.9(1)	Cu–Os(9)–Os(4)	53.6(1)
Os(8)–Os(4)–Os(1)	118.0(1)	Os(8)–Os(4)–Os(2)	89.8(1)	Cu–Os(9)–Os(8)	51.8(1)	Cu–Os(9)–Os(10)	102.4(1)
Os(8)–Os(4)–Os(3)	60.1(1)	Os(9)–Os(4)–Os(1)	153.2(1)	Os(8)–Os(10)–Os(4)	59.1(1)	Os(9)–Os(10)–Os(4)	59.6(1)
Os(9)–Os(4)–Os(2)	142.3(1)	Os(9)–Os(4)–Os(3)	114.0(1)	Os(9)–Os(10)–Os(8)	60.7(1)	Os(11)–Os(10)–Os(4)	90.8(1)
Os(9)–Os(4)–Os(8)	60.0(1)	Os(10)–Os(4)–Os(1)	147.5(1)	Os(11)–Os(10)–Os(8)	90.4(1)	Os(11)–Os(10)–Os(9)	145.8(1)
Os(10)–Os(4)–Os(2)	88.5(1)	Os(10)–Os(4)–Os(3)	108.8(1)	Os(5)–Os(11)–Os(2)	60.2(1)	Os(6)–Os(11)–Os(2)	59.3(1)
Os(10)–Os(4)–Os(8)	59.0(1)	Os(10)–Os(4)–Os(9)	57.6(1)	Os(6)–Os(11)–Os(5)	60.6(1)	Os(10)–Os(11)–Os(2)	90.0(1)
Cu–Os(4)–Os(1)	87.0(1)	Cu–Os(4)–Os(2)	114.1(1)	Os(10)–Os(11)–Os(5)	145.5(1)	Os(10)–Os(11)–Os(6)	90.3(1)
Cu–Os(4)–Os(3)	56.0(1)	Cu–Os(4)–Os(8)	56.6(1)	Os(4)–Cu–Os(3)	64.2(1)	Os(8)–Cu–Os(3)	65.5(1)
Cu–Os(4)–Os(9)	69.7(1)	Cu–Os(4)–Os(10)	110.5(1)	Os(8)–Cu–Os(4)	69.1(1)	Os(9)–Cu–Os(3)	110.1(1)
Os(6)–Os(5)–Os(2)	60.1(1)	Os(11)–Os(5)–Os(2)	62.2(1)	Os(9)–Cu–Os(4)	56.8(1)	Os(9)–Cu–Os(8)	57.5(1)
Os(11)–Os(5)–Os(6)	60.9(1)	Os(3)–Os(6)–Os(2)	59.6(1)	Os–C–O Range	163—179(3)		
Os(5)–Os(6)–Os(2)	60.2(1)	Os(5)–Os(6)–Os(3)	111.9(1)				

(*b*) Compound (**10**)

Os(1)–Os(2)	2.773(7)	Os(1)–Os(3)	2.883(8)	Os(4)–Os(10)	2.827(7)	Os(5)–Os(6)	2.777(6)
Os(1)–Os(4)	2.764(7)	Os(2)–Os(3)	2.759(6)	Os(5)–Os(11)	2.728(7)	Os(6)–Os(7)	2.706(6)
Os(2)–Os(4)	2.796(6)	Os(2)–Os(5)	2.773(7)	Os(6)–Os(8)	2.800(6)	Os(6)–Os(11)	2.790(6)
Os(2)–Os(6)	2.703(8)	Os(2)–Os(11)	2.848(6)	Os(7)–Os(8)	2.745(7)	Os(8)–Os(9)	2.788(7)
Os(3)–Os(4)	2.767(7)	Os(3)–Os(6)	2.754(7)	Os(8)–Os(10)	2.796(6)	Os(9)–Os(10)	2.703(6)
Os(3)–Os(7)	2.814(8)	Os(3)–Os(8)	2.764(7)	Os(10)–Os(11)	2.784(6)		
Os(4)–Os(8)	2.703(8)	Os(4)–Os(9)	2.771(7)				

with previous observations that the protonation of large clusters gives different product ratios in solvents of different basicity.[16,17] The deuteriated species $[Os_{11}C(CO)_{27}D]^-$ (**10a**) and $[Os_{11}C(CO)_{27}D_2]$ (**11a**) can be made by identical procedures to the above, by the use of CF_3CO_2D.

A partial *X*-ray structure analysis of the $[PMePh_3]^+$ salt of $[Os_{11}C(CO)_{27}H]^-$ (**10**) clearly establishes an 'Os_{11}' metal core geometry, which is very similar to that found for (**2**) and (**4**) [Figure 1(*a*)], but poor crystallographic data meant that the positions of all the light atoms had not been located with certainty.

The ^1H n.m.r. spectrum of compound (**10**) has a hydride resonance at δ −19.1, downfield by 4 p.p.m. from the hydride in the decaosmium monoanion $[Os_{10}C(CO)_{24}H]^-$, and the spectra of both monoanions are unchanged over the temperature range 193—295 K.[17] The ^1H n.m.r. spectrum of (**10**) also shows ^{187}Os–^1H satellites in the ratio of 2:1:1 (Table 1). From this data and by analogy with $[Os_{10}C(CO)_{24}H]^-$ (where from *X*-ray analysis and ^1H n.m.r. studies the hydride was deduced to be in an interstitial tetrahedral site[17,18]) it is thought that the hydride ligand in (**10**) is in one of the capping tetrahedra.

The tetrahedral cavity size in compounds (**4**) and (**10**) may be assessed from the mean of the three Os–Os bond lengths from each of the capping osmium atoms [thus excluding three Os–Os bonds in (**4**) known to be elongated by the presence of the μ_3-Cu(NCMe) ligand].

	Mean capping Os–Os bond length/Å	
	(4)	(10)
Os(1)	2.785	2.807
Os(5)	2.784	2.759
Os(7)	2.774	2.755
Os(9)	2.796	2.754

It can be seen that three of the tetrahedral caps are markedly larger in the copper derivative (**4**) than in the hydrido monoanion (**10**). For the fourth capping atom the opposite is observed, and the cap formed by Os(1) in the hydride (**10**) is larger (mean Os–Os 2.807 Å) than any other tetrahedral cap in either structure (range of other mean Os–Os is 2.754—2.796 Å). Assuming that the tetrahedral location deduced for the hydride ligand in solution from ^{187}Os–^{1}H n.m.r. data (see above) is maintained in the solid state, it appears that the hydrido ligand is located in the tetrahedron formed by the capping of a triangular face of the square pyramid by Os(1).

Reaction of $[Os_{11}C(CO)_{27}]^{2-}$ (**2**) *with Iodine–Iodide.*—The dianion (**2**) reacts with I_2 to give $[Os_{11}C(CO)_{27}I]^-$ (**8**) and $[Os_{11}C(CO)_{27}I_2]$ (**9**) *via* sequential oxidative addition of I^+ (Scheme 2).

Sequential loss of the iodine ligands as I_3^- has been achieved on reaction of (**8**) and (**9**) with slightly more than 2 equivalents of $[NBu_4]I$. A similar reversible pattern of reactivity was reported for the decaosmium dianion (**1**), which upon reaction with X_2 (X = Cl, Br, or I) yields first $[Os_{10}C(CO)_{24}X]^-$ and then $[Os_{10}C(CO)_{24}X_2]$[19] [equation (1)].

$$\underset{(\mathbf{1})}{[Os_{10}C(CO)_{24}]^{2-}} \underset{2.2X}{\overset{2X_2}{\rightleftharpoons}} [Os_{10}C(CO)_{24}X]^- \underset{2.2X}{\overset{2X_2}{\rightleftharpoons}} [Os_{10}C(CO)_{24}X_2] \quad (1)$$

Crystallographic studies of both iodo decaosmium species show opening up of caps of the basic tetracapped octahedron in (**1**) by I^+ donors, to produce iodine-bridged Os_4 butterflies on the cluster surface.[19] It is envisaged that in formation of $[Os_{11}C(CO)_{27}I]^-$ (**8**) and $[Os_{11}C(CO)_{27}I_2]$ (**9**) opening up of capping tetrahedra also occurs. Support for this proposal comes from the fact that reversible Os–Os bond reforming must occur upon addition of halide ion to (**8**) or (**9**) to regenerate the dianion $[Os_{11}C(CO)_{27}]^{2-}$ (**2**).

Both Os_{11} iodo derivatives (**8**) and (**9**) were characterised by i.r. spectroscopy only; f.a.b. mass spectroscopy gave only peaks for (**1**) and no peaks for the parent cluster. Furthermore attempts to obtain crystals for *X*-ray structure analysis failed because of the readiness with which both species break down on standing in CH_2Cl_2 solution to yield the dianion (**1**). The fate of the osmium mononuclear fragment released by this process has not been established although monitoring of the reaction indicates that the monoanion (**8**) is an intermediate in the formation of (**1**) from the neutral di-iodide (**9**). Specific fragmentation of a high-nuclearity metal carbonyl cluster carbide has also been observed previously in the reaction of $[Re_7C(CO)_{21}]^{3-}$ with stoicheiometric amounts of iodine,[20] which results in the cleavage of the $Re(CO)_3$ capping unit to form $[Re_6C(CO)_{19}]^{2-}$. In contrast to the reversible reactions of the dianion $[Os_{10}C(CO)_{24}]^{2-}$, formed in the fragmentation of the undecaosmium species, further reaction of the hexanuclear rhenium cluster with iodine leads to further breakdown to give a mixture of mononuclear compounds, $[Re(CO)_3I_n(MeCN)_{3-n}]^{n-}$ and $[Re_4C(CO)_{15}I]^-$.[20]

Reaction of $[Os_{11}C(CO)_{27}]^{2-}$ (**2**) *with* Ag^+.—The dianion (**2**) reacts with 1 equivalent of $AgBF_4$ to yield the decaosmium cluster (**1**) quantitatively (Scheme 2); the two prismatic capping groups on the trigonal prism of (**2**) may be envisaged as swinging down to generate the tetracapped octahedral structure of (**1**) [with ejection of '$Os(CO)_3$' group], the carbido atom moving up to the centre of the octahedron (Figure 3). The reactions of (**2**) are in contrast to those of the dianion $[Os_{10}C(CO)_{24}]^{2-}$ (**1**) which reacts with 1 equivalent of Ag^+ to yield a radical monoanion $[Os_{10}C(CO)_{24}]^{-}$.[21] A third type of reactivity pattern has been observed in the reaction of $[Rh_6C(CO)_{15}]^{2-}$ with Ag^+, which gives oligomeric chains of general formula $[\{Rh_6C(CO)_{15}\}_mAg_n]^{n-}$.[22]

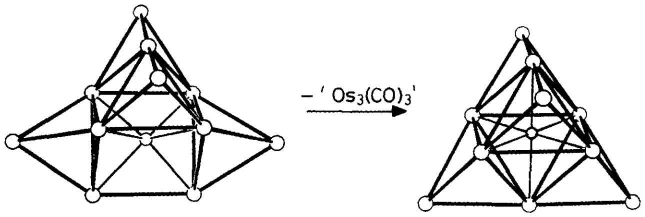


Figure 3. The metal framework rearrangement resulting from reaction of $[Os_{11}C(CO)_{27}]^{2-}$ (**2**) with Ag^+ to give $[Os_{10}C(CO)_{24}]^{2-}$ (**1**)

Cluster Fragmentation or Aggregation.—In f.a.b. mass spectroscopy the dianion (**2**) has been found to give clusters of higher and lower mass, by gain or loss of '$Os(CO)_3$' fragments. Both $[Os_{10}C(CO)_{24}]^{2-}$ (**1**) and the new, so far unisolated, dianion $[Os_{12}C(CO)_{30}]^{2-}$ are observed [equation (2)]. Similar

$$\underset{m/z\ 2\,604}{[Os_{10}C(CO)_{24}]^{2-}} \xleftarrow{-Os(CO)_3} \underset{2\,880}{[Os_{11}C(CO)_{27}]^{2-}} \xrightarrow{+Os(CO)_3} \underset{3\,156}{[Os_{12}C(CO)_{30}]^{2-}} \quad (2)$$

cluster aggregation and fragmentation behaviour was observed in f.a.b. mass spectrometery with $[Ru_5C(CO)_{14}\{Au(PPh_3)\}_2]$,[23] where the known clusters $[Ru_6C(CO)_{16}\{Au(PPh_3)\}_2]$ and $[Ru_4C(CO)_{12}\{Au(PPh_3)\}_2]$ were also detected.

The chemistry of the dianion $[Os_{11}C(CO)_{27}]^{2-}$ (**2**) is dominated by the tendency to lose an '$Os(CO)_3$' group to give decaosmium species (Scheme 2), and from this it appears probable that in the pyrolysis of $[Os_3(CO)_{12}]$ (Scheme 1) the $[Os_{11}C(CO)_{27}]^{2-}$ dianion represents a step in the sequence of cluster growth immediately *before* the formation of the extremely stable dianion $[Os_{10}C(CO)_{24}]^{2-}$ (**1**).

Experimental

All reactions were carried out under nitrogen using dry degassed solvents distilled from an appropriate drying agent, stored over 4A molecular sieves.

Infrared spectra were recorded in CH_2Cl_2 on a Perkin-Elmer PE 983 spectrometer, unless otherwise stated. N.m.r. (^{1}H and ^{31}P-{^{1}H}) spectra were recorded on a Bruker WH400 instrument using solvent references or $P(OMe)_3$ as internal standards. F.a.b. mass spectrometry was performed in a N.E.I. MS 12 spectrometer using tris(perfluoroheptyl)-s-triazine as calibrant. The instrument was run in negative-ion mode with a 3-nitrobenzyl alcohol matrix. Microanalysis were performed in the University Chemical Laboratory, Cambridge. The compounds $[Os_3(CO)_{12}]$,[24] $[AuCl(PMe_2Ph)]$,[25] $[CuCl(PMe_2Ph)]$,[26] $[Cu(NCMe)_4]PF_6$,[27] and $Hg(C_6Cl_5)(O_2CCF_3)$[28] were prepared by literature procedures.

All other reagents were obtained from the usual commercial suppliers and used without further purification.

Preparation of $[N(PPh_3)_2]_2[Os_{11}C(CO)_{27}]$ (**2**).—Finely powdered $[Os_3(CO)_{12}]$ (2 g, 2.20 mmol) was placed into a dried Carius tube (170 cm^3). The tube was *not* evacuated but sealed under atmospheric pressure, then placed in a steel liner on its side in an oven at 270 °C for 72 h. The resulting dark brown solid was extracted with ethyl acetate until the solvent was pale pink, when all of the neutral clusters had been extracted. The insoluble residue was heated under reflux in acetone–methanol (1 : 1) (200 cm^3) for 24 h. The hot red-brown solution was filtered to remove any osmium metal (90 mg, 7%) and reduced in volume to 30 cm^3. An excess of $[N(PPh_3)_2]Cl$ (200 mg, 0.350 mmol) in MeOH (30 cm^3) was then added to the filtrate which was stirred for a further 3 h. Column chromatography using acetone–hexane (1 : 1) as eluant afforded first a pink-red band of $[N(PPh_3)_2]_2[Os_{10}C(CO)_{24}]$ (**1**), which was crystallised from acetone–methanol at −20 °C (720 mg, 29.5%), followed closely by a dark brown band containing a mixture of (**1**) and $[N(PPh_3)_2]_2[Os_{11}C(CO)_{27}]$ (**2**). Slow evaporation of an acetone–methanol solution of the second band at −20 °C over 3—4 d afforded an additional amount of (**1**) (180 mg, 7.5%) as red-black crystals, followed by dark brown crystals of the dianion (**2**) (200 mg, 7%) (Found: C, 30.05; H, 1.55; N, 0.60. Calc. for $C_{100}H_{60}N_2O_{27}Os_{11}P_4$: C, 30.50; H, 1.50; N, 0.70%). An identical procedure is used for the preparation of both the $[PMePh_3]^+$ and $[AsPh_4]^+$ salts of (**2**).

Reactions of $[Os_{11}C(CO)_{27}]^{2-}$ (**2**).—*With* $[Au(PMe_2Ph)]PF_6$. The salt $[N(PPh_3)_2]_2[Os_{11}C(CO)_{27}]$ (60 mg, 0.015 mmol) was dissolved in CH_2Cl_2 (15 cm^3) to give an orange-brown solution and 1 equivalent each of $[Au(PMe_2Ph)]Cl$ (5.7 mg, 0.0153 mmol) and $TlPF_6$ (6.0 mg, 0.0172 mmol) (as the halide acceptor) were added as solids to the reaction mixture. The reaction was monitored by i.r. spectroscopy and was complete after stirring for *ca.* 45 min at room temperature (r.t.) to form a chocolate brown solution of the monoanion $[Os_{11}C(CO)_{27}\{Au(PMe_2Ph)\}]^-$ (**3**). Attempts to obtain crystals of (**3**) in CH_2Cl_2 under N_2 at r.t. resulted in the dissociation of $[Au(PMe_2Ph)]^+$ to give a mixture of (**1**) and $[Os_{10}C(CO)_{24}\{Au(PMe_2Ph)\}]^-$. Similar analogues have been prepared for $PR_3 = PPh_3$ or PEt_3 which exhibit identical i.r. spectra to that of the PMe_2Ph derivative. Reaction of compound (**3**) with NEt_3 (excess) in CH_2Cl_2 produces the dianion (**2**) in *ca.* 2 min as shown by i.r. spectroscopic monitoring of the reaction.

With $AgBF_4$. The salt $[N(PPh_3)_2]_2[Os_{11}C(CO)_{27}]$ (60 mg, 0.015 mmol) was dissolved in CH_2Cl_2 (15 cm^3) and 2 equivalents of $AgBF_4$ (6 mg, 0.0324 mmol) added as a solid in a plastic vial cap. The reaction was monitored by i.r. spectroscopy and was complete after stirring for 30 min at r.t. with quantitative formation of the dianion (**1**).

With $[Cu(NCMe)_4]PF_6$. The salt $[PMePh_3]_2[Os_{11}C(CO)_{27}]$ (60 mg, 0.0174 mmol) was dissolved in CH_2Cl_2 (15 cm^3) and 1 equivalent of $[Cu(NCMe)_4]PF_6$ (6.7 mg, 0.0180 mmol) added as a solid in a plastic vial. The reaction was instantaneous at room temperature and crystals of $[PMePh_3][Os_{11}C(CO)_{27}\{Cu(NCMe)\}]$ (**4**) were obtained by slow evaporation of the dark brown CH_2Cl_2 solution under N_2 over a period of 3 d (yield 51 mg, 90%) (Found: C, 18.30; H, 0.65; N, 0.70. Calc. for $C_{49}H_{21}CuNO_{27}Os_{11}P$: C, 18.15; H, 0.65; N, 0.45%).

The salt $[PMePh_3]_2[Os_{11}C(CO)_{27}]$ (60 mg, 0.0174 mmol) was dissolved in CH_2Cl_2 (15 cm^3) and 2 equivalents of $[Cu(NCMe)_4]PF_6$ (13.4 mg, 0.036 mmol) added as a solid in a plastic vial. The reaction was instantaneous at room temperature and the complex $[Os_{11}C(CO)_{27}\{Cu(NCMe)\}_2]$ (**5**) was isolated in quantitative yield by filtration as an insoluble red-brown solid (Found: C, 12.50; H, 0.25; N, 1.00. Calc. for $C_{32}H_6Cu_2N_2O_{27}Os_{11}$: C, 12.45; H, 0.20; N, 0.90%). In coordinating solvents such as MeCN the cluster (**5**) slowly dissociates back to (**4**) and finally after 10—15 min to (**2**).

With $[Au(PMe_2Ph)]ClO_4$. The salt $[N(PPh_3)_2]_2[Os_{11}C(CO)_{27}]$ (60 mg, 0.015 mmol) was dissolved in CH_2Cl_2 (15 cm^3) to give an orange-brown solution and 1 equivalent each of $[Au(PMe_2Ph)]Cl$ (11.4 mg, 0.0300 mmol) and $AgClO_4$ (6.9 mg, 0.0330 mmol) (as the halide acceptor) were stirred together in CH_2Cl_2 (5 cm^3) for 20 min then filtered through Celite into the reaction mixture. The reaction was monitored by i.r. spectroscopy and was complete after stirring for *ca.* 1 h at r.t. forming a pale brown solution. Slow addition of hexane (10 cm^3) led to the precipitation of $[Os_{11}C(CO)_{27}\{Au(PMe_2Ph)\}_2]$ (**6**) as a black crystalline powder (Found: C, 18.50; H, 1.10. Calc. for $C_{44}H_{22}Au_2O_{27}Os_{11}P_2$: C, 17.20; H, 0.50%). Attempts to obtain crystals of (**2**)—(**6**) in CH_2Cl_2 under N_2 at r.t. over 4 d resulted in the dissociation of $[Au(PMe_2Ph)]^+$ to give a mixture of (**3**) and the monoanion $[Os_{10}C(CO)_{24}\{Au(PMe_2Ph)\}]^-$.

With I_2. The salt $[N(PPh_3)_2][Os_{11}C(CO)_{27}]$ (60 mg, 0.015 mmol) was dissolved in CH_2Cl_2 (15 cm^3) and 2 equivalents of iodine (8 mg, 0.0315 mmol) in CH_2Cl_2 (10 cm^3) slowly added over 2.5 h at r.t. After *ca.* 3 h the monoanion $[Os_{11}C(CO)_{27}I]^-$ (**8**) was formed in quantitative yield according to i.r. spectroscopy. On standing in CH_2Cl_2 for up to 3 d under N_2, (**8**) *fragmented to give the dianion* (**1**). On addition of 2.2 equivalents of $[NBu_4]I$ (14.1 mg, 0.0380 mmol) to the above solution regeneration of the dianion (**2**) occurred.

The salt $[N(PPh_3)_2]_2[Os_{11}C(CO)_{27}]$ (60 mg, 0.015 mmol) was dissolved in CH_2Cl_2(15 cm^3) and 4 equivalents of iodine (16 mg, 0.0630 mmol) in CH_2Cl_2 (10 cm^3) slowly added over 3.5 h at r.t. After this time the only species present in solution was $[Os_{11}C(CO)_{27}I_2]$ (**9**) according to i.r. spectroscopy. This species disproportionates in CH_2Cl_2 at r.t. to give $[Os_{10}C(CO)_{24}I]^-$ quantitatively after 2 d. The same behaviour is observed when (**9**) is subject to t.l.c. on silica plates. On addition of 4.4 equivalents of $[NBu_4]I$ (28.2 mg, 0.0760 mmol) to the above solution regeneration of the dianion (**2**) occurred.

With H^+. The salt $[PMePh_3]_2[Os_{11}C(CO)_{27}]$ (20 mg, 0.0058 mmol) was dissolved in CH_2Cl_2 (15 cm^3) and CF_3CO_2H (1 drop) added. The reaction was monitored by i.r. spectroscopy and was complete after 5 min with a change in colour from olive to chocolate brown. Black crystals of $[PMePh_3][Os_{11}C(CO)_{27}H]$ (**10**) were obtained by slow evaporation of the solvent under N_2 (yield 17.2 mg, 90%) (Found: C, 18.00; H, 0.60. Calc. for $C_{47}H_{19}O_{27}Os_{11}P$: C, 17.85; H, 0.60%). The monoanion (**10**) is unstable on silica decomposing to $[Os_{10}C(CO)_{24}H]^-$ which dissociates back to (**2**) in donor solvents such as acetone or MeOH at r.t. over a period of 40 min.

When the protonation of compound (**2**) was attempted in thf a mixture of (**2**), (**10**), and (**11**) resulted.

With D^+ *in* CH_2Cl_2. The salt $[PMePh_3]_2[Os_{11}C(CO)_{27}]$ (20 mg, 0.0058 mmol) was dissolved in CH_2Cl_2 (15 cm^3) and CF_3CO_2D (1 drop) added. The reaction was monitored by i.r. spectroscopy and was complete after 5 min with a change in colour from olive to chocolate brown. Black crystals of $[PMePh_3][Os_{11}C(CO)_{27}D]$ (**10a**) were obtained by slow evaporation of the solvent under N_2 (yield 16.5 mg, 86%) (Found: C, 18.00; H, 0.60. Calc. for $C_{47}H_{18}DO_{27}Os_{11}P$: C, 17.85; H, 0.60%). The monoanion (**10a**) is unstable on silica decomposing to $[Os_{10}C(CO)_{24}D]^-$.

The salt $[PMePh_3]_2[Os_{11}C(CO)_{27}]$ (20 mg, 0.0058 mmol) was dissolved in MeCN (15 cm^3) and CF_3CO_2H (1 drop) added. The reaction was monitored by i.r. spectroscopy; initially the monoanion (**10**) formed but on prolonged stirring (3—4 h) the neutral species $[Os_{11}C(CO)_{27}H_2]$ (**11**) precipitated quantitatively as an insoluble black-brown powder. This was collected by filtration, washed with cold MeCN(3 × 5 cm^3), and dried *in vacuo* for 2 h (Found: C, 11.60; H, 0.30. Calc. for

Table 3. Fractional atomic co-ordinates for compounds (**4**) and (**10**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
(*a*) Compound (**4**)							
Os(1)	0.014 29(7)	0.095 87(9)	0.199 58(4)	C(71)	0.147 2(16)	−0.037 6(21)	0.025 4(9)
Os(2)	0.154 45(7)	0.215 89(8)	0.199 19(4)	O(71)	0.113 4(15)	−0.106 9(19)	0.008 3(8)
Os(3)	0.106 72(7)	0.090 15(8)	0.127 68(4)	C(72)	0.126 0(19)	0.145 1(23)	0.010 5(10)
Os(4)	0.175 43(7)	0.011 84(8)	0.212 88(4)	O(72)	0.082 2(17)	0.202 0(21)	−0.016 1(9)
Os(5)	0.229 33(8)	0.383 93(9)	0.167 93(4)	C(73)	0.284 1(20)	0.067 5(24)	0.020 8(10)
Os(6)	0.243 14(7)	0.206 33(9)	0.122 80(4)	O(73)	0.345 8(17)	0.064 8(21)	0.004 9(9)
Os(7)	0.191 43(7)	0.073 88(9)	0.052 85(4)	C(81)	0.260 0(15)	−0.113 5(19)	0.104 9(8)
Os(8)	0.266 78(7)	0.002 81(8)	0.136 90(3)	O(81)	0.263 3(15)	−0.186 3(18)	0.083 9(8)
Os(9)	0.289 62(8)	−0.140 75(9)	0.205 87(4)	C(82)	0.376 6(18)	0.012 8(21)	0.118 0(9)
Os(10)	0.355 16(7)	0.042 17(10)	0.224 10(4)	O(82)	0.439 9(15)	0.027 5(18)	0.108 6(8)
Os(11)	0.332 29(7)	0.242 80(9)	0.209 46(4)	C(91)	0.302 9(21)	−0.175 7(26)	0.268 8(12)
Cu	0.127 5(2)	−0.096 5(3)	0.137 1(1)	O(91)	0.311 5(17)	−0.191 0(20)	0.308 2(9)
P	0.351 9(5)	−0.290 4(6)	0.948 6(3)	C(92)	0.388 6(21)	−0.210 6(26)	0.194 1(11)
Cl(1)	0.357 5(13)	0.095 7(14)	0.502 1(7)	O(92)	0.441 2(15)	−0.263 2(18)	0.184 1(8)
Cl(2)	0.287 0(11)	0.171 8(28)	0.416 5(7)	C(93)	0.229 0(22)	−0.250 5(28)	0.189 2(12)
C	0.254 2(16)	0.119 9(19)	0.183 7(9)	O(93)	0.191 2(19)	−0.321 4(24)	0.181 0(10)
N	0.059 1(15)	−0.206 5(19)	0.120 0(8)	C(101)	0.382 2(20)	0.047 1(24)	0.286 4(11)
C(1)	0.008 3(23)	−0.261 7(27)	0.112 4(12)	O(101)	0.393 4(15)	0.052 3(19)	0.325 6(9)
C(2)	−0.058 3(24)	−0.332 2(30)	0.102 1(13)	C(102)	0.452 0(20)	−0.032 3(25)	0.220 0(11)
C(11)	−0.078 5(19)	0.178 9(23)	0.181 7(10)	O(102)	0.515 7(17)	−0.069 6(20)	0.215 9(9)
O(11)	−0.133 0(16)	0.224 1(19)	0.169 6(9)	C(111)	0.404 6(25)	0.340 0(30)	0.195 7(13)
C(12)	−0.004 8(20)	0.099 4(24)	0.261 5(11)	O(111)	0.458 4(20)	0.391 7(25)	0.186 0(11)
O(12)	−0.018 9(15)	0.101 1(19)	0.298 8(9)	C(112)	0.348 9(18)	0.279 8(22)	0.271 3(10)
C(13)	−0.053 5(18)	−0.010 6(22)	0.187 2(10)	O(112)	0.356 4(17)	0.297 8(21)	0.309 9(10)
O(13)	−0.093 4(18)	−0.080 5(23)	0.174 0(10)	CB	0.438 0(21)	0.159 6(25)	0.212 8(11)
C(21)	0.069 0(16)	0.307 8(20)	0.189 0(9)	OB	0.507 7(14)	0.161 4(16)	0.208 7(7)
O(21)	0.013 1(14)	0.363 2(18)	0.183 3(8)	CP(11)	0.413 0(11)	−0.262 9(15)	1.001 5(6)
C(22)	0.154 8(19)	0.235 5(22)	0.262 8(10)	CP(12)	0.428 2(11)	−0.335 2(15)	1.034 8(6)
O(22)	0.160 4(15)	0.241 0(18)	0.301 1(8)	CP(13)	0.478 2(11)	−0.315 2(15)	1.076 0(6)
C(31)	0.038 6(19)	0.189 6(24)	0.100 1(11)	CP(14)	0.513 0(11)	−0.222 9(15)	1.083 9(6)
O(31)	−0.003 6(17)	0.249 9(21)	0.083 2(9)	CP(15)	0.497 7(11)	−0.150 6(15)	1.050 6(6)
C(32)	0.025 0(17)	0.001 5(20)	0.096 4(9)	CP(16)	0.447 7(11)	−0.170 5(15)	1.009 4(6)
O(32)	−0.033 7(15)	−0.029 7(18)	0.075 5(8)	CP(21)	0.327 1(13)	−0.179 1(13)	0.916 4(7)
C(41)	0.111 1(20)	−0.102 3(24)	0.222 2(11)	CP(22)	0.257 8(13)	−0.126 2(13)	0.926 5(7)
O(41)	0.070 8(13)	−0.164 6(17)	0.231 7(7)	CP(23)	0.238 2(13)	−0.037 6(13)	0.904 6(7)
C(42)	0.184 5(18)	0.020 7(22)	0.278 5(10)	CP(24)	0.287 8(13)	−0.001 8(13)	0.872 7(7)
O(42)	0.194 6(15)	0.026 0(18)	0.317 0(8)	CP(25)	0.357 2(13)	−0.054 8(13)	0.862 7(7)
C(51)	0.137 4(18)	0.452 0(22)	0.135 6(10)	CP(26)	0.376 8(13)	−0.143 4(13)	0.884 5(7)
O(51)	0.083 3(14)	0.498 0(17)	0.114 6(8)	CP(31)	0.255 4(10)	−0.347 9(15)	0.956 7(7)
C(52)	0.228 6(19)	0.465 7(24)	0.221 9(11)	CP(32)	0.209 3(10)	−0.386 8(15)	0.917 6(7)
O(52)	0.231 6(18)	0.508 7(22)	0.255 3(10)	CP(33)	0.131 3(10)	−0.428 8(15)	0.920 5(7)
C(53)	0.296 7(22)	0.464 9(27)	0.138 6(12)	CP(34)	0.099 4(10)	−0.431 7(15)	0.962 4(7)
O(53)	0.341 9(19)	0.519 1(23)	0.120 2(10)	CP(35)	0.145 5(10)	−0.392 8(15)	1.001 5(7)
C(61)	0.345 9(21)	0.219 2(25)	0.101 1(11)	CP(36)	0.223 5(10)	−0.350 9(15)	0.998 7(7)
O(61)	0.409 4(16)	0.236 5(18)	0.089 1(8)	CP(41)	0.413 7(20)	−0.375 1(24)	0.917 6(11)
C(62)	0.198 1(18)	0.296 7(22)	0.080 0(10)	C(3)	0.302 1(50)	0.177 1(62)	0.471 0(29)
O(62)	0.167 6(14)	0.348 9(17)	0.048 5(8)				
(*b*) Compound (**10**)							
Os(1)	−0.201 1(3)	0.073 4(3)	0.106 1(4)	Os(7)	−0.204 5(3)	0.395 1(3)	0.041 4(5)
Os(2)	−0.288 2(3)	0.102 3(3)	−0.095 8(4)	Os(8)	−0.118 4(2)	0.293 1(3)	−0.098 3(4)
Os(3)	−0.202 3(2)	0.239 0(3)	0.085 3(4)	Os(9)	0.019 0(3)	0.227 4(3)	−0.146 4(5)
Os(4)	−0.117 0(2)	0.140 4(3)	−0.066 9(4)	Os(10)	−0.118 2(3)	0.166 5(3)	−0.311 2(4)
Os(5)	−0.426 1(3)	0.127 7(3)	−0.220 4(4)	Os(11)	−0.288 6(3)	0.131 9(3)	−0.339 9(4)
Os(6)	−0.289 8(2)	0.255 5(3)	−0.124 3(4)				

$C_{28}H_2O_{27}Os_{11}$: C, 11.65; H, 0.05%). This neutral species (**11**) is insoluble in most organic solvents but in acetone or MeOH it slowly dissociates to (**10**) at r.t. over a period of 30 min.

The salt $[PMePh_3]_2[Os_{11}C(CO)_{27}]$ (20 mg, 0.0058 mmol) was dissolved in MeCN (15 cm^3) and CF_3CO_2D (1 drop) added. The reaction was monitored by i.r. spectroscopy; initially the monoanion (**10a**) formed but on prolonged stirring (3—4 h) the neutral species $[Os_{11}C(CO)_{27}D_2]$ (**11a**) precipitated quantitatively as an insoluble black-brown powder. This was collected by filtration, washed with cold MeCN (3 × 5 cm^3), and dried *in vacuo* for 2 h (Found: C, 11.60. Calc. for $C_{28}D_2O_{27}Os_{11}$: C, 11.70%). This neutral species (**11a**) is insoluble in most organic solvents but in acetone or MeOH it slowly dissociates to (**10a**) at r.t. over a period of 30 min.

With $Hg(C_6Cl_5)(O_2CCF_3)$. The salt $[N(PPh_3)_2]_2[Os_{11}C(CO)_{27}]$ (20 mg, 0.005 mmol) was dissolved in CH_2Cl_2 (15 cm^3) and 1 equivalent of $Hg(C_6Cl_5)(O_2CCF_3)$ (3.3 mg, 0.0058 mmol) added. The reaction was monitored by i.r. spectroscopy and was complete after 20 min with a change in colour of the solution from olive to chocolate brown. The resulting monoanion $[N(PPh_3)_2][Os_{11}C(CO)_{27}\{Hg(C_6Cl_5)\}]$ **(12)** is air sensitive and was characterised by i.r. spectroscopy only.

Reaction of $[Os_{11}C(CO)_{27}\{Cu(NCMe)\}]^-$ **(4)** + PMe_2Ph.—The salt $[PMePh_3][Os_{11}C(CO)_{27}\{Cu(NCMe)\}]$ (60 mg, 0.0185 mmol) was dissolved in CH_2Cl_2 (15 cm^3) and 1 equivalent of PMe_2Ph (3 μl, 0.0218 mmol) was added to the solution. The reaction was monitored by i.r. spectroscopy and found to be complete after *ca.* 1 h at r.t. with the formation of the monoanion $[Os_{11}C(CO)_{27}\{Cu(PMe_2Ph)\}]^-$ **(7)**. Attempts to obtain crystals of **(7)** in CH_2Cl_2 under N_2 at r.t. over 3 d resulted in the dissociation of $[Cu(PMe_2Ph)]^+$ to give a mixture of **(3)** and the monoanion $[Os_{10}C(CO)_{24}\{Cu(PMe_2Ph)\}]^-$.

Redistribution Reaction of $[N(PPh_3)_2][Os_{11}C(CO)_{27}\{Hg(C_6Cl_5)\}]$ **(12)**.—The monoanion $[N(PPh_3)_2][Os_{11}C(CO)_{27}\{Hg(C_6Cl_5)\}]$ **(12)** was allowed to stand in CH_2Cl_2 at r.t. for up to 2 d after which time black crystals of the dianion $[N(PPh_3)_2]_2[Os_{20}Hg(C)_2(CO)_{48}]$ had formed (yield 12.5 mg, 70%) (Found: C, 22.40; H, 1.05; N, 0.55. Calc. for $C_{122}H_{60}HgN_2O_{48}Os_{20}P_4$: C, 22.60; H, 0.95; N, 0.45%).

Crystallography.—Crystal data for $[MePPh_3][Os_{11}C(CO)_{27}Cu(NCMe)]\cdot 0.5CH_2Cl_2$ **(4)**. $C_{49.5}H_{22}ClCuNO_{27}Os_{11}P$, M = 3 284.9, monoclinic space group $P2_1/c$, a = 16.114(3), b = 13.748(2), c = 29.382(4) Å, β = 97.15(2)°, U = 6 458.53 Å^3, $F(000)$ = 5 756, $\mu(\text{Mo-}K_\alpha)$ = 211.60 cm^{-1}, Z = 4, D_c = 2.70 g cm^{-3}.

Crystal data for $[PMePh_3][Os_{11}C(CO)_{27}H]$ **(10)**. $C_{47}H_{19}O_{27}Os_{11}P$, M = 3 138.81, triclinic, space group $P\bar{1}$ (no. 2), a = 16.788(3), b = 17.019(3), c = 11.019(2) Å, α = 103.34(2), β = 93.77(2), γ = 101.54(2)°, U = 2 980.67 Å^3, $F(000)$ = 2 736, $\mu(\text{Mo-}K_\alpha)$ = 225.35 cm^{-1}, Z = 2, D_c = 2.68 g cm^{-3}.

Data collection. Data sets for both compounds **(4)** and **(10)** were collected by the method previously described,[29] using single crystals of dimensions 0.25 × 0.18 × 0.15 **(4)** and 0.50 × 0.48 × 0.15 mm **(10)** on a Phillips four-circle diffractometer, in the range θ 3—25°, with a constant scan width of 0.80° and a scan speed of 0.05°. Lorentz and polarisation corrections were applied to both data sets, and for **(4)** 396 azimuthal scan data were used in absorption correction.[29] Crystals of **(10)** diffracted very weakly so that a relatively large crystal was necessary; azimuthal scan data could not be collected due to the onset of decomposition in the last stages of data collection. Equivalent reflections were merged to give a total of 5 717 **(4)** and 3 266 **(10)** with $I/\sigma(I) \geqslant 3.0$.

Structure solution and refinement.[30] The structure of compound **(4)** was solved from a Patterson synthesis from which all 11 osmium atoms were located. The remaining non-hydrogen atoms were found from subsequent Fourier difference syntheses. Anisotropic thermal parameters were assigned to the Os, Cu, P, and Cl atoms in the final stages of refinement. Partial occupancy by the solvent molecule was indicated by extremely high thermal parameters for these atoms, and as a result they were assigned occupancy factors of 0.5 in the final cycles of full-matrix refinement which converged at R = 0.049 and R' = 0.054 with weights of $1/\sigma^2(F_o)$ assigned to individual reflections. The atomic co-ordinates for **(4)** are listed in Table 3.

The structure of compound **(10)** was solved from a Patterson synthesis from which four osmium atoms forming one tetrahedron were located. The remaining seven atoms were located from an observed Fourier map. The positions of most of the non-hydrogen atoms were located with some difficulty from subsequent Fourier difference syntheses. No suitable maxima could be located for the atoms of one phenyl ring of the $[PMePh_3]^+$ cation, nor for one carbonyl group thought to bridge the bond Os(10)–Os(11), by comparison with **(4)** and from i.r. data. Several strategies were employed in attempting to deduce the positions of these atoms, but they could not be located with certainty. An empirical absorption correction was applied to the data set at this stage.[31] This allowed relatively satisfactory refinement of the parameters of the atoms that had been located, but did not help with the location of the missing atoms. Anisotropic thermal parameters were assigned to the Os and P atoms, and full-matrix refinement of the parameters of located non-hydrogen atoms gave R = 0.109 and R' = 0.1096 with weights of $1/\sigma^2(F_o)$ assigned to individual reflections. All attempts to obtain better crystals and an improved data set for **(2)** have failed so far. The metal core geometry for **(10)** is well established and is important in discussing the other data for this compound and therefore the fractional co-ordinates for the osmium atoms are listed in Table 3.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

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