The Syntheses and *X*-Ray Structure Analyses of the Heteronuclear Monoanions $[Os_{10}C(CO)_{24}Cu(NCMe)]^-$ and $[Os_{10}C(CO)_{24}Au(PPh_3)]^-$ as Their $[PPh_3Me]^+$ Salts†

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The high nuclearity mixed-metal cluster monoanions $[Os_{10}C(CO)_{24}Cu(NCMe)]^-$ (**1**) and $[Os_{10}C(CO)_{24}Au(PPh_3)]^-$ (**2**) have been obtained by reaction of the carbido-dianion $[Os_{10}C(CO)_{24}]^{2-}$ (**3**) with one equivalent of $[Cu(NCMe)_4][BF_4]$ or $Au(PPh_3)Cl$, respectively, in CH_2Cl_2. Addition of excess $[Cu(NCMe)_4][BF_4]$ to either (**1**) or (**3**) gives the di-copper species $[Os_{10}C(CO)_{24}\{Cu(NCMe)\}_2]$ (**4**). *X*-Ray analysis of the $[PPh_3Me]^+$ salts of (**1**) and (**2**) show that the Cu and Au ligands have added to capping tetrahedra of the dianion (**3**) in μ_3- and μ-bridging positions, respectively. Crystals of $[PPh_3Me][Os_{10}C(CO)_{24}Cu(NCMe)]$ are triclinic, space group $P\bar{1}$, with $a = 16.452(3)$, $b = 13.881(3)$, $c = 13.290(3)$ Å, $\alpha = 82.12(3)$, $\beta = 93.23(3)$, $\gamma = 96.40(3)°$, $Z = 2$; refinement of atomic parameters using 4 325 absorption corrected data converged at R 0.0492. The salt $[PPh_3Me][Os_{10}C(CO)_{24}Au(PPh_3)]$ also crystallises in the triclinic space group $P\bar{1}$, with $a = 17.296(4)$, $b = 15.403(3)$, $c = 15.191(3)$ Å, $\alpha = 107.31(3)$, $\beta = 98.28(3)$, $\gamma = 88.99(3)°$, $Z = 2$; refinement of atomic co-ordinates using 5 314 absorption corrected data gave R 0.0551.

The metal core in $[Os_{10}C(CO)_{24}]^{2-}$ (3) has four large planar surfaces, each of which consists of six osmium atoms with six carbonyl ligands approximately perpendicular to each face.[1] These large cluster faces may provide the best analogy so far of carbon monoxide chemisorbed onto a metal surface, and a study of the reactions of (3) with small substrates may shed light on the interactions which occur on metal surfaces.[2] However, preliminary studies of the reactions of (3) have revealed a surprisingly high stability towards CO or H_2, the cluster resisting these gases at pressures of 1 500 atm at 250 °C.[3] This may be due in part to the fact that for (3) in each planar array the individual metal atoms each have a terminal carbonyl group attached thus 'saturating' the metal surface with a CO/M ratio of 1.0, in contrast to the situation in the bulk metal surface where the carbonyl ligands are mainly bonded in a μ_3 mode with a CO/M coverage of 0.66.[4]

The treatment of preformed cluster anions with appropriate mononuclear cations or metal halide complexes has been shown to be an efficient route to mixed-metal clusters in high yield.[5—7] These clusters may show enhanced reactivity due to the introduction of increased polarity in the molecule, *via* the heterometal bonds, together with a reduction in the ratio of carbonyl groups to metal atoms giving a less CO saturated metal core. With this in mind we have obtained the mixed-metal cluster anions $[Os_{10}C(CO)_{24}Cu(NCMe)]^-$ (1) and $[Os_{10}C(CO)_{24}Au(PPh_3)]^-$ (2) by treating the dianion (3) with one equivalent of $[Cu(NCMe)_4][BF_4]$ or $Au(PPh_3)Cl$ (in the presence of $TlPF_6$ as halide acceptor) respectively in CH_2Cl_2. The dicopper species $[Os_{10}C(CO)_{24}\{Cu(NCMe)\}_2]$ (4) is also produced on addition of excess $[Cu(NCMe)_4][BF_4]$ to either (1) or (3); these complexes were the first high nuclearity mixed-metal clusters of osmium to be reported.[8]

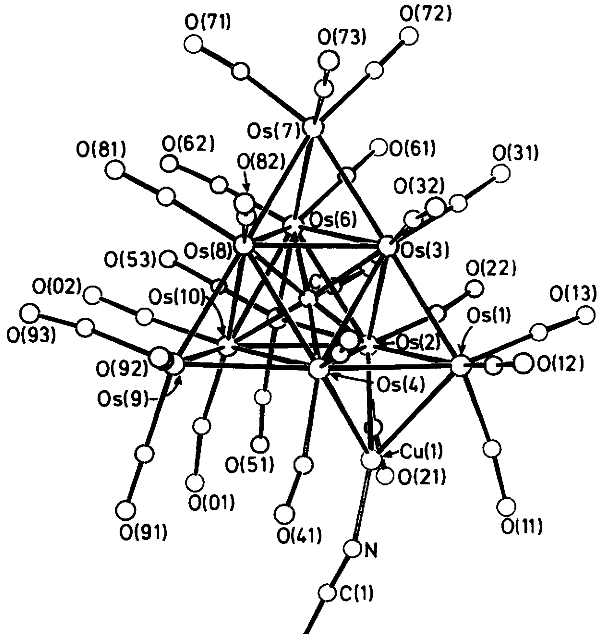

Figure 1. Molecular structure of the monoanion $[Os_{10}C(CO)_{24}Cu(NCMe)]^-$ (1). The number of each carbonyl-C atom is the same as that of the relevant O atom; the first digit of each O atom number is that of the osmium atom to which it is attached

Results and Discussion

X-Ray analysis of the $[PPh_3Me]^+$ salts of (1) and (2) shows that the tetracapped octahedral metal geometry of the dianion (3) is retained in both clusters, with the heterometal atom in each case bonded to Os atoms of a capping tetrahedron as shown in

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† Methyltriphenylphosphonium μ_6-carbido-tetracosacarbonyl-μ_3-methyl cyanidecuprio-decaosmate(1−) (24 *Os–Os*) and -μ-triphenylphosphineaurio-decaosmate(1−) (24 *Os–Os*) respectively.

Supplementary data available (No. SUP 56455, 30 pp.): thermal parameters, full bond lengths and angles. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

Non-S.I. unit employed: atm = 101 325 Pa.

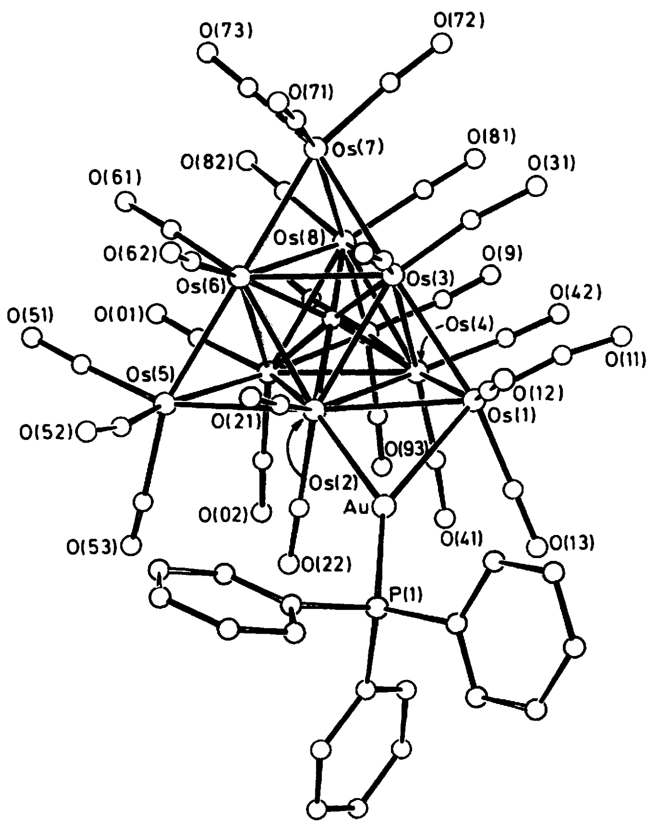

Figure 2. Molecular structure of the monoanion $[Os_{10}C(CO)_{24}Au(PPh_3)]^-$ (**2**). See caption to Figure 1 for details of numbering scheme

Figures 1 and 2 respectively. Although there is some 'pushing back' of the carbonyl ligands in the vicinity of the heteroatoms in (**1**) and (**2**), the distribution of these ligands is essentially very similar to that observed in the binary carbonyl dianion (**3**). In both structures three terminal carbonyl ligands are attached to each of the four capping osmium atoms [Os(1),Os(5),Os(7),Os(9)] and the Os atoms of the octahedral core [Os(2),Os(3),Os(4),Os(6),Os(8),Os(10)] are each co-ordinated to two terminal CO groups. Selected bond distances and angles for (**1**) and (**2**) are given in Table 1.

In the monoanion (**1**) the 'cylindrical' $[Cu(NCMe)]^+$ ligand lies between three carbonyl ligands and is attached to the metal skeleton in a slightly asymmetric μ_3-bonding mode [Cu–Os(4) 2.549 Å, mean of the Cu–Os(1) and Cu–Os(2) distances 2.683 Å]. This bonding mode is consistent with all the *s* and *p* orbitals of the Cu atom being involved in bonding. The very congested co-ordination site tolerated by the Cu atom, which gives rise to very short Cu–C(carbonyl) contacts [mean Cu–C 2.43(5) Å] may be taken as evidence of some bonding interaction between the Cu atom and the surrounding carbonyl ligands. These observations may be related to observations by Evans and Mingos,[9] from extended Hückel molecular orbital calculations on $M(PH_3)$ fragments, that a co-ordinated Cu atom can accept donation of electron density into its empty and relatively low lying p_x and p_y orbitals. In the co-ordination round the Cu atom, shown in Figure 3, the three carbonyl ligands have retained their linearity (mean Os–C–O 176.3°) and the geometry is reminiscent of the η^2-μ-CO type bridging first observed in $[Mn_2(CO)_5(Ph_2PCH_2PPh_2)]$.[10] However we have found no evidence in the i.r. spectrum of (**1**) (Table 2) for carbonyl–copper bonding.

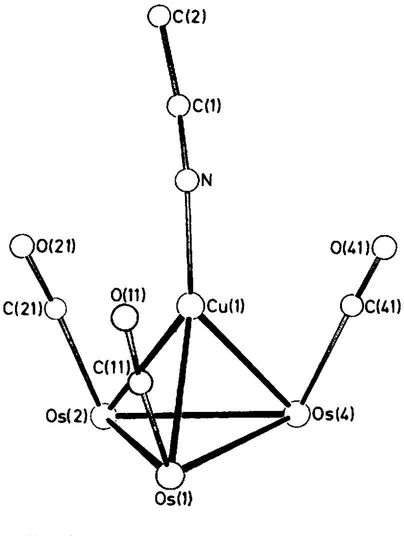

Figure 3. Co-ordination geometry around the Cu atom in the anion (**1**); the major site of occupancy for the copper atom is shown

The structure of (**1**) may be compared with those of the bis-$[Cu(NCMe)]^+$ adduct of $[Ru_6C(CO)_{16}]^{2-}$, $[Ru_6C(CO)_{16}\{Cu(NCMe)\}_2]$ (**5**),[7] and that of $[Rh_6C(CO)_{15}]^{2-}$, $[Rh_6C(CO)_{15}\{Cu(NCMe)\}_2]$ (**6**).[5b] In the neutral compound (**5**) one Cu atom adopts a μ_3 position above one of the triangular faces of the octahedral Ru_6C core forming a tetrahedral capping group similar to the capping $Os(CO)_3$ group in (**3**); the second copper ligand bridges a triangular face of the $CuRu_3$ cap (forming a direct Cu–Cu bond). Short Cu ··· C distances (minimum 2.471 Å) similar to those observed in (**1**) were also observed in the structure of (**5**). In the rhodium compound (**6**) the two triangular ends of the trigonal prismatic Rh_6C core are capped by individual $[Cu(NCMe)]^+$ leaving the carbonyl distribution of the parent dianion virtually unchanged. The shortest Cu ··· C contact is 2.93 Å which may reflect the relatively larger surface area of the trigonal-prismatic metal polyhedron compared to the triangulated surfaces of (**1**) and (**5**).

The neutral dicopper compound $[Os_{10}C(CO)_{24}\{Cu(NCMe)\}_2]$ (**4**) is insoluble in most common solvents, so attempts to grow crystals suitable for *X*-ray analysis have failed. It would be interesting to know if there is a direct Cu–Cu bond present in this complex similar to that in the hexaruthenium compound (**5**), particularly since the latter compound is useful as a homogeneous catalyst for converting 'synthesis gas' ($CO + H_2$) into methanol.[11]

In the structure of $[Os_{10}C(CO)_{24}Au(PPh_3)]^-$ (**2**) the gold atom bridges the outer edge of a capping tetrahedron. In this case the heteroatom may be regarded as using an *sp* hybrid orbital for bonding and attack at the metal cage results in the formation of a three-centre, two-electron Os–Au–Os bond. Consistent with this view is the fact that the Os(1)–Os(2) distance bridged by the Au species (2.962 Å), is the longest in the structure and is very much longer than the other Os–Os capping bonds (mean 2.808 Å).

The symmetrical edge-bridging position adopted by the $[Au(PPh_3)]^+$ ligand in (**2**) [Au ··· Os(4) 4.591(2), Au ··· Os(3) 4.554(2) Å] reduces contact between the gold atom and the effectively close-packed carbonyls, compared to the copper–carbonyl interaction in (**1**), but there are nevertheless two very short Au ··· C(carbonyl) distances [Au ··· C(21) 2.66, Au ··· C(22) 2.67 Å]. The difference in bonding mode adopted by the Cu and Au species may be related to calculations by Evans and Mingos[9] which show that for $Au(PH_3)$ fragments,

Table 1. Selected bond lengths (Å) and angles (°)

(*a*) Os–Os (all e.s.d.s 0.002 Å)

(*i*) Within octahedron

	(1)	(2)		(1)	(2)
Os(2)–Os(3)	2.884	2.895	Os(3)–Os(8)	2.868	2.861
Os(2)–Os(4)	3.012	2.909	Os(4)–Os(8)	2.849	2.877
Os(2)–Os(6)	2.872	2.875	Os(4)–Os(10)	2.964	2.867
Os(2)–Os(10)	2.885	2.906	Os(6)–Os(8)	2.844	2.871
Os(3)–Os(4)	2.883	2.900	Os(6)–Os(10)	2.859	2.878
Os(3)–Os(6)	2.857	2.877	Os(8)–Os(10)	2.904	2.886
			Mean	2.890	2.884

(*ii*) Os–Os from 'caps'

	(1)	(2)		(1)	(2)
Os(1)–Os(2)	2.808	2.962	Os(7)–Os(3)	2.793	2.805
Os(1)–Os(3)	2.778	2.780	Os(7)–Os(6)	2.782	2.786
Os(1)–Os(4)	2.880	2.776	Os(7)–Os(8)	2.799	2.788
Os(5)–Os(2)	2.801	2.876	Os(9)–Os(4)	2.854	2.807
Os(5)–Os(6)	2.761	2.762	Os(9)–Os(8)	2.770	2.777
Os(5)–Os(10)	2.799	2.772	Os(9)–Os(10)	2.788	2.799
			Mean	2.801	2.808

(*b*) Heterometal–Os

(1)		(2)	
Cu–Os(1)	2.690(8)	Au–Os(1)	2.851(2)
Cu–Os(2)	2.676(9)	Au–Os(2)	2.781(2)
Cu–Os(4)	2.549(8)	Au ··· Os(4)	4.591(2)
Cu′–Os(4)	2.508	Au ··· Os(3)	4.554(2)
Cu′–Os(9)	2.771		
Cu′–Os(10)	2.633		

(*c*) The carbido ligand

	(1)	(2)
Os–C range	1.96(3)—2.14(3)	2.00(3)—2.08(3)
Mean Os–C	2.05(3)	2.04(3)

(*d*) The carbonyl ligands

	(1)	(2)
Os–C range	1.70(5)—1.97(7)	1.74(4)—1.94(3)
Mean Os–C	1.84(4)	1.84(4)
C–O range	1.06(9)—1.28(6)	1.10(4)—1.39(5)
C–O mean	1.18(5)	1.19(5)
Os–C–O range	169(4)—180(2)	165(5)—178(3)
Os–C–O mean	174(3)	173(3)

(*e*) Ligands on the heteroatoms

	(1)	(2)
Cu–N	1.911(7)	
N–C(1)	1.18(8)	
C(1)–C(2)	1.42(8)	
Au–P		2.267(10)
Cu(1)–N–C(1)	156(5)	
C(2)–C(1)–N	172(6)	
P(1)–Au–Os(1)		149.9(3)
P(1)–Au–Os(2)		148.6(3)

Table 2. Infrared data for the complexes

Compound[a]	ν(CO)/cm^{-1} [b]
(1) $[Os_{10}C(CO)_{24}Cu(NCMe)]^-$	2 082w, 2 051vs, 2 043s (sh), 2 001s, 1 991m, 1 976mw, 1 934w
(2) $[Os_{10}C(CO)_{24}Au(PPh_3)]^-$	2 081w, 2 050s, 2 040m, 1 999s
(3) $[Os_{10}C(CO)_{24}]^{2-}$	2 035s, 1 987s
(7) '$Os_{10}C(CO)_{24}(H)Au(PPh_3)$'	2 094w, 2 068vs, 2 054m, 2 018s, 2 009m, 1 995w, 1 975w

[a] $[PPh_3Me]^+$ salts where appropriate. [b] In CH_2Cl_2.

unlike their copper analogues, the p_x and p_y orbitals are relatively high lying and cannot accept electron density effectively. The monoanion (2) does not react with further $Au(PPh_3)Cl$ in the presence of $TlPF_6$ so that the digold neutral molecule has not been obtained.

Formally the cations $[Cu(NCMe)]^+$ and $[Au(PPh_3)]^+$ may be regarded as 12-electron groups and therefore from current skeletal electron-counting procedures would be regarded as contributing no electrons to skeletal bonding.[12] Although such groups may add to clusters without change of core geometry, it has been observed that addition of these cations to binary carbonyl anions, particularly to the larger ones, often leads to drastic changes in the geometries of the metal polyhedra.[13] The retention of the tetracapped octahedral core in (1) and (2) is a further example of the previous observation that carbido-centred clusters are more resistant to changes in structure of their core geometry than their non-carbido analogues.[14] The $[Au(PR_3)]^+$ ligand is isolobal with the H^+ ligand and has been observed both in the μ bridging mode found here and more frequently in rather distorted μ_3 bridging sites.[15] The low barrier to interchange between these bonding modes is demonstrated in the recent observation of two skeletal isomers of $[Ru_5C(CO)_{13}(NO)Au(PEt_3)]$ in which the change from μ to μ_3 bonding of the gold atom is produced by the nitrosyl and a carbonyl ligand interchanging positions.[16]

In both (1) and (2) the Os–Os bonds spanned by the heterometal are longer than comparable unbridged bonds. For example, in (1), the Os(2)–Os(4) length of 3.012 Å is the longest edge of the central octahedron (mean Os–Os 2.890 Å), and the two other bridged bonds Os(1)–Os(2) and Os(1)–Os(4), 2.808 and 2.880 Å respectively, are longer than the mean capping Os

Table 3. Fractional atomic co-ordinates for the anion of $[PPh_3Me][Os_{10}C(CO)_{24}Cu(NCMe)]$ (**1**)

Atom	*x*	*y*	*z*
Os(1)	0.417 02(9)	0.104 15(13)	0.224 58(11)
Os(2)	0.353 56(8)	−0.070 26(12)	0.339 48(10)
Os(3)	0.326 26(8)	−0.035 82(12)	0.121 84(10)
Os(4)	0.242 00(9)	0.076 84(12)	0.241 56(10)
Os(5)	0.285 04(9)	−0.247 89(13)	0.442 15(11)
Os(6)	0.258 61(8)	−0.214 49(12)	0.233 84(10)
Os(7)	0.234 89(9)	−0.180 14(13)	0.023 58(10)
Os(8)	0.152 87(8)	−0.074 94(12)	0.143 91(10)
Os(9)	0.071 75(8)	0.021 33(13)	0.270 63(11)
Os(10)	0.179 28(8)	−0.109 01(12)	0.363 19(10)
Cu(1)	0.337 0(5)	0.104 2(6)	0.395 6(6)
Cu(1′)*	0.190 8(11)	0.067 7(15)	0.417 2(13)
N	0.332 6(35)	0.156 2(48)	0.521 0(45)
C(1)	0.313 9(32)	0.156 0(45)	0.605 4(43)
C(2)	0.303 1(35)	0.156 1(49)	0.710 6(44)
N′*	0.221 50	0.100 00	0.541 20
C(1′)*	0.227 60	0.089 10	0.630 70
C(2′)*	0.226 00	0.121 50	0.720 90
C	0.254 4(17)	−0.074 9(25)	0.241 8(21)
C(11)	0.463 0(22)	0.176 1(32)	0.321 1(28)
O(11)	0.488 4(22)	0.224 2(32)	0.384 1(29)
C(12)	0.414 1(30)	0.200 6(44)	0.131 3(39)
O(12)	0.422 8(20)	0.277 2(29)	0.066 3(26)
C(13)	0.517 3(26)	0.082 1(35)	0.195 1(31)
O(13)	0.583 0(18)	0.058 6(24)	0.180 9(21)
C(21)	0.387 5(23)	−0.037 2(32)	0.471 2(29)
O(21)	0.411 5(21)	−0.021 2(29)	0.549 1(26)
C(22)	0.450 4(23)	−0.110 5(32)	0.324 6(28)
O(22)	0.513 5(15)	−0.154 3(22)	0.317 6(19)
C(31)	0.419 7(22)	−0.083 0(30)	0.087 0(26)
O(31)	0.480 6(16)	−0.113 9(22)	0.065 0(19)
C(32)	0.318 1(20)	0.045 9(29)	0.005 4(26)
O(32)	0.316 9(17)	0.107 7(24)	−0.067 2(22)
C(41)	0.213 9(37)	0.177 1(51)	0.321 7(45)
O(41)	0.195 8(24)	0.230 9(35)	0.362 5(31)
C(41′)*	0.273 1(64)	0.200 5(86)	0.309 7(74)
O(41′)*	0.290 3(48)	0.263 0(68)	0.362 3(60)
C(42)	0.228 9(21)	0.171 0(30)	0.132 0(26)
O(42)	0.213 9(16)	0.221 9(22)	0.0558 (20)
C(51)	0.289 4(25)	−0.220 8(36)	0.580 1(32)
O(51)	0.301 8(18)	−0.214 7(25)	0.664 2(23)
C(52)	0.376 9(23)	−0.318 5(31)	0.448 3(27)
O(52)	0.434 6(17)	−0.354 5(23)	0.449 0(20)
C(53)	0.226 8(28)	−0.357 4(39)	0.471 7(34)
O(53)	0.173 5(19)	−0.431 7(26)	0.483 5(23)
C(61)	0.336 1(21)	−0.289 3(29)	0.209 3(25)
O(61)	0.388 3(18)	−0.338 5(26)	0.196 5(22)
C(62)	0.179 4(21)	−0.323 4(29)	0.243 9(25)
O(62)	0.121 6(17)	−0.380 9(23)	0.246 5(20)
C(71)	0.155 0(21)	−0.282 8(28)	0.006 6(24)
O(71)	0.101 3(15)	−0.342 8(21)	−0.000 5(18)
C(72)	0.317 5(21)	−0.242 2(30)	−0.024 1(26)
O(72)	0.364 4(20)	−0.280 4(28)	−0.054 3(25)
C(73)	0.211 7(19)	−0.114 8(27)	−0.097 5(25)
O(73)	0.195 6(19)	−0.072 3(27)	−0.178 2(24)
C(81)	0.062 8(20)	−0.167 4(28)	0.132 3(24)
O(81)	0.007 8(17)	−0.229 3(24)	0.129 8(21)
C(82)	0.120 9(18)	0.002 5(26)	0.027 7(23)
O(82)	0.096 6(16)	0.051 9(22)	−0.043 5(20)
C(91)	0.048 2(24)	0.080 6(34)	0.385 2(30)
O(91)	0.030 1(17)	0.113 0(24)	0.453 0(22)
C(92)	0.028 0(21)	0.118 3(30)	0.175 8(27)
O(92)	0.002 2(17)	0.173 5(25)	0.114 8(22)
C(93)	−0.024 7(24)	−0.062 7(32)	0.274 8(28)
O(93)	−0.088 2(17)	−0.110 1(22)	0.283 7(19)
C(01)	0.168 5(24)	−0.081 2(34)	0.494 0(30)
O(01)	0.169 6(18)	−0.050 9(26)	0.574 8(23)
C(02)	0.086 4(19)	−0.200 2(27)	0.383 0(23)
O(02)	0.032 8(14)	−0.266 9(19)	0.395 5(17)

* Site occupancy 0.3.

to octahedral core distance of 2.801 Å. Similarly, in (**2**) the Os(1)–Os(2) distance, bridged by the μ-Au atom, is the longest in the structure and is very much longer than the other Os–Os 'capping' bonds, mean 2.808 Å.

In the mixed-metal monoanions (**1**) and (**2**), and in $[Os_{10}C(CO)_{24}\{Cu(NCMe)\}_2]$ (**4**), the $[Cu(NCMe)]^+$ and $[Au(PPh_3)]^+$ groups dissociate readily in co-ordinating solvents to regenerate the dianion (**3**). Although (**1**) and (**2**) appear to be indefinitely stable in dry chlorinated hydrocarbon solvents, addition of X_2 or X^- (X = Cl, Br, or I) gives $[Os_{10}C(CO)_{24}(\mu\text{-}X)]^-$ (ref. 17) and the dianion (**3**), respectively. Careful protonation of (**2**) with one equivalent of concentrated H_2SO_4 in CH_2Cl_2 gives a neutral compound,* tentatively formulated as $[Os_{10}C(CO)_{24}(H)Au(PPh_3)]$ (**7**), but attempts to characterise this complex fully have been hampered by its very low solubility in most common solvents.

Experimental

Infrared spectra were recorded on a Perkin-Elmer 257 instrument using carbon monoxide gas calibrant (central position 2 143 cm^{-1}). Thin-layer chromatography (t.l.c.) plates were purchased from Merck and consisted of glass plates (20 × 20 cm) coated with a layer (0.25 mm) of silica gel.

Preparation of $[PPh_3Me][Os_{10}C(CO)_{24}Cu(NCMe)]$.—The salt $[PPh_3Me]_2[Os_{10}C(CO)_{24}]$ (50 mg) was dissolved in CH_2Cl_2 (40 cm^3) and 1 mol equiv. of $[Cu(NCMe)_4][BF_4]$ (5 mg) added as a solid. Reduction of the solution in volume (to *ca.* half) followed by cooling to −20 °C gave crystals of $[PPh_3Me][Os_{10}C(CO)_{24}Cu(NCMe)]$ (**1**) (yield 38 mg, 81%) which were characterised by i.r. spectroscopy (Table 2) and microanalysis (Found: C, 18.5; H, 0.80; N, 0.50. Calc. for $C_{46}H_{21}CuNO_{24}Os_{10}P$: C, 18.6; H, 0.70; N, 0.45%). This complex cannot be purified by t.l.c. techniques; the dianion (**3**) is regenerated as soon as it is put onto silica gel.

Preparation of $[Os_{10}C(CO)_{24}\{Cu(NCMe)\}_2]$.—The salt $[PPh_3Me]_2[Os_{10}C(CO)_{24}]$ (20 mg) was dissolved in CH_2Cl_2 (30 cm^3) and excess $[Cu(NCMe)_4][BF_4]$ was added as a solid. The complex $[Os_{10}C(CO)_{24}\{Cu(NCMe)\}_2]$ was isolated in quantitative yield as an insoluble red-brown powder by filtration, and characterised by microanalysis (Found: C, 12.6; H, 0.20; N, 1.05. Calc. for $C_{29}H_6Cu_2N_2O_{24}Os_{10}$: C, 12.5; H, 0.20; N, 1.00%).

Preparation of $[PPh_3Me][Os_{10}C(CO)_{24}Au(PPh_3)]$.—The salt $[PPh_3Me]_2[Os_{10}C(CO)_{24}]$ (50 mg) was dissolved in CH_2Cl_2 and 1 mol equiv. each of $Au(PPh_3)Cl$ and $TlPF_6$ added as a solid. I.r. spectroscopy showed that the reaction was complete after stirring for *ca.* 1 h at room temperature. Crystals of $[PPh_3Me][Os_{10}C(CO)_{24}Au(PPh_3)]$ (yield 49 mg, 92%), which were characterised by i.r. spectroscopy (Table 2) and microanalysis (Found: C, 22.5; H, 1.15. Calc. for $C_{62}H_{33}AuO_{24}$-

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* If an excess of concentrated H_2SO_4 is added quickly to a solution of (**2**) in CH_2Cl_2, the major products are $[Os_{10}C(CO)_{24}H]^-$ (ref. 18) and the dihydride $[Os_{10}C(CO)_{24}H_2]$. Presumably better yields of (**7**) could be obtained by the use of a non-co-ordinating acid such as HBF_4.

Table 4. Fractional atomic co-ordinates for the anion of $[PPh_3Me][Os_{10}C(CO)_{24}Au(PPh_3)]$ (**2**)

Atom	*x*	*y*	*z*
Os(1)	0.120 11(8)	0.171 24(10)	0.311 76(10)
Os(2)	0.270 27(8)	0.159 04(10)	0.237 06(9)
Os(3)	0.231 06(8)	0.050 04(10)	0.351 00(9)
Os(4)	0.145 85(8)	0.020 75(10)	0.165 22(9)
Os(5)	0.413 05(8)	0.119 26(10)	0.158 19(10)
Os(6)	0.375 20(8)	0.022 99(10)	0.273 82(9)
Os(7)	0.336 51(9)	−0.081 27(11)	0.383 64(10)
Os(8)	0.251 73(8)	−0.112 90(10)	0.206 01(0)
Os(9)	0.170 91(8)	−0.140 96(10)	0.027 71(9)
Os(10)	0.290 05(8)	−0.006 83(10)	0.089 59(9)
Au	0.200 88(9)	0.326 10(10)	0.299 70(10)
P(1)	0.202 8(5)	0.478 1(6)	0.320 2(7)
C	0.258 6(20)	0.023 0(25)	0.222 0(22)
C(11)	0.039 8(24)	0.118 7(28)	0.343 2(25)
O(11)	−0.016 8(18)	0.086 8(22)	0.359 6(20)
C(12)	0.141 9(19)	0.253 2(24)	0.426 8(22)
O(12)	0.144 0(15)	0.300 8(18)	0.505 3(17)
C(13)	0.051 2(24)	0.236 3(30)	0.252 2(27)
O(13)	0.008 6(16)	0.272 5(20)	0.206 7(18)
C(21)	0.332 2(21)	0.241 2(26)	0.333 1(24)
O(21)	0.376 9(15)	0.291 7(18)	0.396 0(16)
C(22)	0.253 8(23)	0.222 4(28)	0.147 1(26)
O(22)	0.243 1(16)	0.252 1(21)	0.085 5(19)
C(31)	0.168 2(22)	0.002 2(26)	0.404 5(24)
O(31)	0.108 0(18)	−0.039 5(22)	0.430 4(20)
C(32)	0.275 8(25)	0.126 6(32)	0.461 1(29)
O(32)	0.308 8(18)	0.191 2(22)	0.531 7(20)
C(41)	0.093 0(18)	0.070 0(23)	0.078 1(21)
O(41)	0.061 6(15)	0.106 1(19)	0.024 7(17)
C(42)	0.056 2(21)	−0.036 1(25)	0.178 1(22)
O(42)	0.003 6(15)	−0.076 7(18)	0.190 5(16)
C(51)	0.498 2(22)	0.052 4(26)	0.118 9(23)
O(51)	0.554 0(15)	0.013 1(19)	0.103 3(17)
C(52)	0.467 4(27)	0.226 0(34)	0.230 5(31)
O(52)	0.511 3(19)	0.277 0(24)	0.278 8(22)
C(53)	0.399 9(28)	0.173 1(35)	0.060 6(33)
O(53)	0.392 3(19)	0.192 8(24)	−0.007 4(23)
C(61)	0.451 2(20)	−0.056 9(25)	0.239 7(22)
O(61)	0.495 1(16)	−0.113 8(20)	0.208 7(18)
C(62)	0.451 5(21)	0.096 9(26)	0.370 3(25)
O(62)	0.488 5(16)	0.148 7(21)	0.439 2(19)
C(71)	0.388 2(23)	−0.020 0(28)	0.491 3(26)
O(71)	0.423 4(16)	0.029 4(20)	0.564 3(19)
C(72)	0.280 7(22)	−0.144 7(27)	0.437 3(24)
O(72)	0.236 8(16)	−0.187 9(20)	0.467 5(18)
C(73)	0.412 0(24)	−0.166 5(30)	0.366 1(26)
O(73)	0.457 9(15)	−0.223 2(19)	0.348 2(17)
C(81)	0.181 5(24)	−0.185 0(29)	0.236 3(26)
O(81)	0.128 8(16)	−0.227 4(19)	0.251 3(17)
C(82)	0.315 8(20)	−0.210 2(25)	0.163 1(22)
O(82)	0.354 2(15)	−0.269 3(19)	0.134 9(17)
C(91)	0.090 4(24)	−0.211 3(29)	0.026 5(26)
O(91)	0.037 0(16)	−0.262 0(19)	0.025 4(17)
C(92)	0.219 9(24)	−0.240 9(30)	−0.042 6(27)
O(92)	0.259 6(19)	−0.300 2(23)	−0.073 3(21)
C(93)	0.120 0(22)	−0.112 4(27)	−0.079 4(26)
O(93)	0.094 9(15)	−0.091 0(19)	−0.141 7(18)
C(01)	0.360 8(21)	−0.094 3(25)	0.026 4(23)
O(01)	0.401 1(15)	−0.146 0(19)	−0.006 6(17)
C(02)	0.261 6(19)	0.032 6(23)	−0.015 3(22)
O(02)	0.238 7(16)	0.056 8(20)	−0.080 0(19)
C(111)	0.140 7(15)	0.546 8(17)	0.402 1(16)
C(112)	0.131 2(15)	0.521 3(17)	0.480 7(16)
C(113)	0.089 9(15)	0.576 4(17)	0.548 0(16)
C(114)	0.058 2(15)	0.656 9(17)	0.536 7(16)
C(115)	0.067 7(15)	0.682 4(17)	0.458 1(16)
C(116)	0.108 9(15)	0.627 3(17)	0.390 8(16)
C(121)	0.302 0(11)	0.529 4(17)	0.365 3(16)
C(122)	0.310 8(11)	0.615 0(17)	0.431 4(16)
C(123)	0.385 4(11)	0.652 3(17)	0.469 9(16)
C(124)	0.451 2(11)	0.604 1(17)	0.442 2(16)
C(125)	0.442 4(11)	0.518 4(17)	0.376 2(16)
C(126)	0.367 8(11)	0.481 1(17)	0.337 7(16)
C(131)	0.175 8(15)	0.499 4(18)	0.207 2(14)
C(132)	0.210 1(15)	0.569 1(18)	0.183 7(14)
C(133)	0.186 4(15)	0.582 2(18)	0.096 9(14)
C(134)	0.128 4(15)	0.525 6(18)	0.033 7(14)
C(135)	0.094 0(15)	0.455 9(18)	0.057 2(14)
C(136)	0.117 7(17)	0.442 8(18)	0.144 0(14)

$Os_{10}P_2$: C, 22.4; H, 1.00%) were obtained by slow evaporation of the CH_2Cl_2 at room temperature. The complex $[PPh_3Me][Os_{10}C(CO)_{24}Au(PPh_3)]$ can also be purified by t.l.c. (CH_2Cl_2 eluant, R_f *ca.* 0.4), unlike the Cu monoanion (**1**).

Preparation of '$[Os_{10}C(CO)_{24}(H)Au(PPh_3)]$'.—The salt $[PPh_3Me][Os_{10}C(CO)_{24}Au(PPh_3)]$ (20 mg) was dissolved in CH_2Cl_2 and concentrated H_2SO_4 (1 mol equiv.) in CH_2Cl_2 slowly added. A sparingly soluble red-brown neutral compound was formed which was characterised on the basis of its i.r. spectrum only (Table 2). If the protonation is not performed carefully, the major product of the reaction is $[PPh_3Me][Os_{10}C(CO)_{24}H]$.

Reaction of (**1**) *and* (**2**) *with* X_2 (X = Cl, Br, *or* I).—Addition of 1 mol equiv. of X_2 in CH_2Cl_2 to solutions of (**1**) or (**2**) in CH_2Cl_2 gives the monoanions $[Os_{10}C(CO)_{24}(\mu\text{-}X)]^-$ which were characterised on the basis of spot t.l.c. techniques and i.r. spectroscopy.[17]

Reaction of (**1**) *and* (**2**) *with* X^- (X = Cl, Br *or* I).—Addition of 1 mol equiv. of X^- $\{[N(PPh_3)_2]^+, [PPh_3Me]^+$, or $[NBu_4]^+$ salts$\}$ in CH_2Cl_2 to solutions of (**1**) or (**2**) in CH_2Cl_2, immediately gives the dianion (**3**) in quantitative yield which was characterised by i.r. spectroscopy (Table 2).

Crystal Data for (**1**).—$C_{46}H_{21}CuNO_{24}Os_{10}P$, M = 2 968.18, triclinic, space group $P\bar{1}$, a = 16.452(3), b = 13.881(3), c = 13.290(3) Å, α = 82.12(3), β = 93.23(3), γ = 96.40(3)°, U = 2 985.04 Å^3, Z = 2, D_c = 3.301 g cm^{-3}, $F(000)$ = 2 666, Mo-K_α radiation, λ = 0.710 69 Å, μ(Mo-K_α) = 208.02 cm^{-1}.

Crystal Data for (**2**).—$C_{62}H_{33}AuO_{24}Os_{10}P_2$, M = 3 322.85, triclinic, space group $P1$, a = 17.296(4), b = 15.403(3), c = 15.191(3) Å, α = 107.31(3), β = 98.28(3), γ = 88.99(3)°, U = 3 822.06 Å^3, Z = 2, $F(000)$ = 2 920, D_c = 2.886 g cm^{-3}, Mo-K_α radiation, λ = 0.710 69 Å, μ(Mo-K_α) = 178.44 cm^{-1}.

The methods of data collection, data processing, and absorption correction used for the salts (**1**) and (**2**) were similar to those described previously.[1] The crystals selected for data collection had dimensions 0.28 × 0.20 × 0.11 mm for (**1**) and 0.23 × 0.12 × 0.15 mm for (**2**). A scan width of 0.80° was used to collect data in the θ range 3—25° for both crystals. 422 Azimuthal scan data for (**1**) and 316 for (**2**) were used in absorption correction and relative transmission factors varied from 1.000 to 0.435 for (**1**) and 1.000 to 0.356 for (**2**). Equivalent reflections were averaged to give 4 325 and 5 314 data with $I/\sigma(I) > 3.0$ for (**1**) and (**2**) respectively.

Structure Solution and Refinement.[19]—For both (**1**) and (**2**) the position of six osmium atoms (defining an octahedron) were found from Patterson syntheses. The remaining osmium atoms together with the other non-hydrogen atoms were found from subsequent difference-Fourier syntheses. For the copper derivative there is a disorder of the monoanion corresponding to two orientations of the cluster, of occupancies 0.7 and 0.3, related by a virtual mirror plane through Os(4), Os(5), Os(6), Os(7), and the carbido-C atom. The disorder was mainly apparent in the location of two well defined sites for the Cu(NCMe) ligand in the difference-Fourier syntheses, together with two equivalent sites for the adjacent CO(41) ligand. The remaining metal atoms and ligand atoms were indistinguishable in the two orientations. The atoms of the minor component of the disorder were included in the structure factor calculation but only the parameters of the copper atom and CO(41′) were refined. Blocked full-matrix refinement of the atomic positional and thermal parameters converged at final *R* and *R′* values of 0.0492 and 0.0489 for (**1**) and 0.0551 and 0.0583 for (**2**). The phenyl groups were treated as rigid hexagons [d(C–C) = 1.395 Å] and the hydrogen atoms were included in the structure factor calculations at calculated positions with d(C–H) = 1.08 Å. Anisotropic thermal parameters were assigned to the Os, Cu, or Au, and P atoms in the final cycles of refinement for both (**1**) and (**2**).

Selected bond lengths and bond angles for (**1**) and (**2**) are given in Table 1. The final atomic co-ordinates for the anions in (**1**) and (**2**) are listed in Tables 3 and 4 respectively.

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