Polyhedral Rearrangements in Undeca- and Dodeca-nuclear Group 1B Metal Osmium Clusters

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The series of heteronuclear clusters $[Os_{10}C(CO)_{24}\{M(PR_3)\}_2]$ [M = Au, PR_3 = PMe_2Ph (**2a**); M = Ag, PR_3 = PPh_3 (**2d**)], $[Os_{10}C(CO)_{24}\{Au(PEt_3)\}\{Ag(PPh_3)\}]$ (**2e**), $[Os_{10}C(CO)_{24}\{Au(PMe_2Ph)\}_3][ClO_4]$ (**3**), and $[Os_{10}C(CO)_{24}\{M(PR_3)\}]^-$ [M = Au, PR_3 = PMe_2Ph (**4a**); M = Ag, PR_3 = PPh_3 (**4d**); M = Cu, PR_3 = PPh_3 (**4e**)] have been prepared and shown to undergo molecular rearrangement in solution; two isomeric forms of (**2a**), (**2e**), and (**4a**) have been identified and their interconversion is considered to involve a cap $\rightleftarrows$ edge bridge $\rightleftarrows$ cap (c.e.c.) pathway. The reactivity of $[Os_{10}C(CO)_{24}\{M(PR_3)\}]^-$ (M = Cu, Ag, or Au) with isolobal moieties such as H^+ and $[Cu(NCMe)]^+$ has been explored, and found to yield the mixed metal clusters $[Os_{10}C(CO)_{24}\{M(PR_3)\}\{Cu(NCMe)\}]$ [M = Au, PR_3 = PPh_3 (**5a**), or PEt_3 (**5b**); M = Ag, PR_3 = PPh_3 (**5c**)] and $[Os_{10}(H)C(CO)_{24}\{M(PPh_3)\}]$ [M = Au (**6a**), Ag (**6b**), or Cu (**6c**)]. The reaction of (**6a**) or (**6b**) with $AgClO_4$ yields the known eicosaosmium cluster $[Os_{20}M(C)_2(CO)_{48}]^{2-}$ [M = Au (**7a**) or Ag (**7b**)]. These dianionic clusters have been found to be readily reduced by sodium diphenylketyl, to yield the trianionic species $[Os_{20}M(C)_2(CO)_{48}]^{3-}$ [M = Au (**8a**) or Ag (**8b**)].

The mechanisms(s) by which framework reorganisation in clusters occurs is currently under active reconsideration.[1,2] Until recently, the generally accepted view was that cage rearrangements in both the polyhedral boranes (and carboranes) and transition-metal clusters occurred with the concerted breaking of polyhedral edges *via* a diamond–square–diamond (d.s.d.) mechanism.[3] However, this proposal now appears unacceptable for several reasons. First, theoretical studies[2] of trigonal-bipyramidal $C_2B_3H_5$ shows that d.s.d. rearrangements are blocked by crossings of filled and vacant molecular orbitals indicating that these processes face very high activation barriers. Secondly, consideration[1] of the change in the total cohesive energy of the cluster unit tends to suggest that processes involving cleavage of more than one edge *at a time* are unfavourable. This latter proposal led to the general conclusion that rearrangement might occur by a cap $\rightleftarrows$ edge bridge $\rightleftarrows$ cap (c.e.c.) pathway. Such a process has been considered to account for the isomerization of $[Os_{10}C(CO)_{24}\{Au(PR_3)\}_2]$.[4] and $[Ru_5WC(CO)_{17}\{Au(PR_3)\}_2]$.[5]

In a previous communication[4] we reported studies on a series of heteronuclear decaosmium Group 1B mixed-metal clusters of generic formula $[Os_{10}C(CO)_{24}\{M(PR_3)\}_n]^m$ [(**4**) M = Cu, Ag, or Au, $n = 1$, $m = -1$; (**2**) M = Ag or Au, $n = 2$, $m = 0$]; these mixed-metal clusters have been shown to exist in at least two isomeric forms in solution.

Results and Discussion

The mixed osmium–gold cluster anion $[Os_{10}C(CO)_{24}\{Au(PPh_3)\}]^-$ (**4b**) was first prepared several years ago from the reaction of the dianion $[Os_{10}C(CO)_{24}]^{2-}$ (**1**) with $[AuCl(PPh_3)]$ and $TlPF_6$.[6] We have now found that when the dianion (**1**) is treated with two equivalents of $[M(PR_3)]ClO_4$ {M = Au or Ag, from $[MCl(PR_3)]$ and $AgClO_4$}, the neutral mixed-metal dodecanuclear clusters $[Os_{10}C(CO)_{24}\{M(PR_3)\}_2]$ [M = Au, PR_3 = PMe_2Ph (**2a**), PPh_3 (**2b**), PEt_3 (**2c**); M = Ag, PR_3 = PPh_3 (**2d**)] are obtained in high yield.

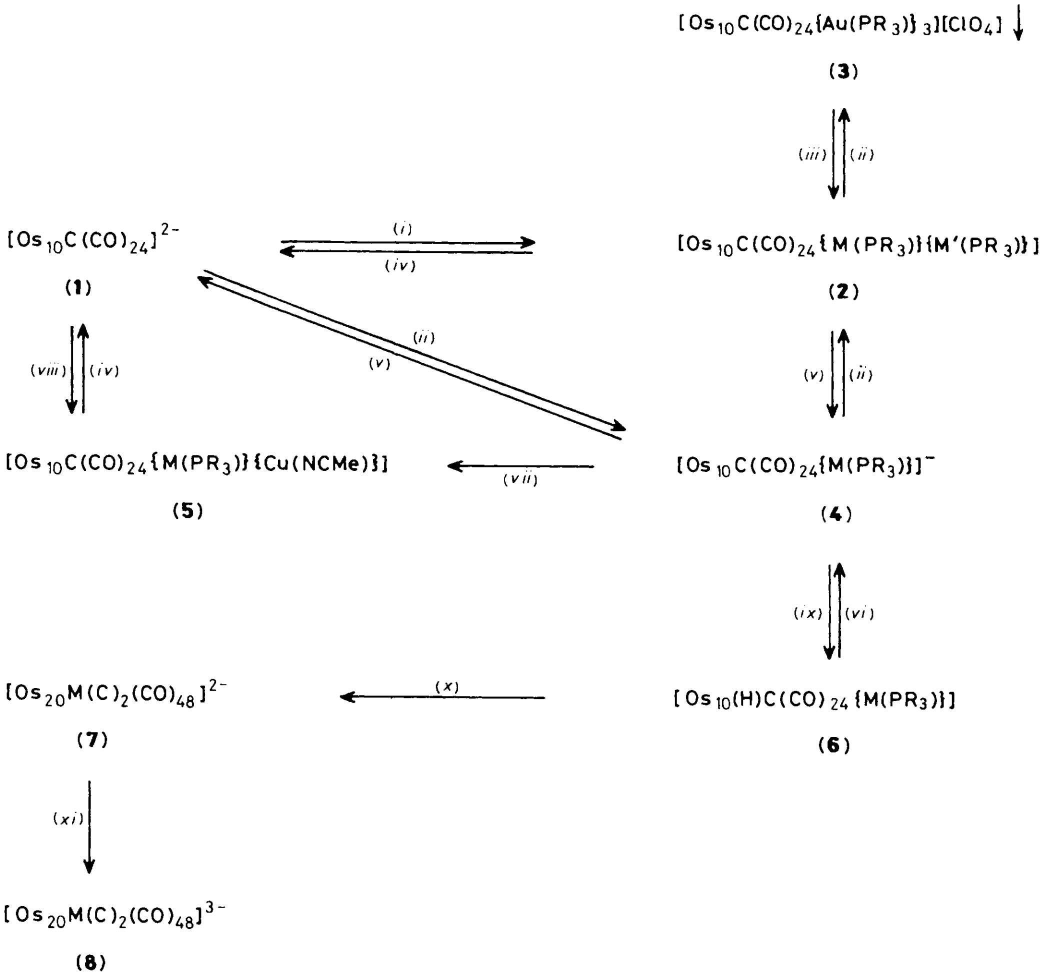
If a solution of (**2c**) and (**2d**) is stirred for 24 h, the trimetallic species $[Os_{10}C(CO)_{24}\{Au(PEt_3)\}\{Ag(PPh_3)\}]$ (**2e**) is formed, equation (1). Addition of one further equivalent of $[Au(PMe_2Ph)][ClO_4]$ to (**2a**) yields the cationic trigold species $[Os_{10}C(CO)_{24}\{Au(PMe_2Ph\}_3][ClO_4]$ (**3**) (see Scheme).

$$\underset{\textbf{(2c)}}{[Os_{10}C(CO)_{24}\{Au(PEt_3)\}_2]} + \underset{\textbf{(2d)}}{[Os_{10}C(CO)_{24}\{Ag(PPh_3)\}_2]} \longrightarrow \underset{\textbf{(2e)}}{2[Os_{10}C(CO)_{24}\{Au(PEt_3)\}\{Ag(PPh_3)\}]} \quad (1)$$

On treatment of (**2a**)—(**2d**) with one equivalent of the base NEt_3, the monoanions $[Os_{10}C(CO)_{24}\{M(PR_3)\}]^-$ [M = Au, PR_3 = PMe_2Ph (**4a**), PPh_3 (**4b**), PEt_3 (**4c**); M = Ag, PR_3 = PPh_3 (**4d**)] are formed. The corresponding dicopper species $[Os_{10}C(CO)_{24}\{Cu(PR_3)\}_2]$ has not been prepared to date. However, the copper monoanion $[Os_{10}C(CO)_{24}\{Cu(PPh_3)\}]^-$ (**4e**) can be prepared from the reaction of (**1**) with one equivalent of $[CuCl(PPh_3)]$ in the presence of $TlPF_6$. The monoanions (**4b**) or (**4d**) react with one equivalent of $[Cu(NCMe)_4][PF_6]$ to produce the mixed-metal clusters $[Os_{10}C(CO)_{24}\{M(PPh_3)\}\{Cu(NCMe)\}]$ [M = Au (**5a**) or Ag (**5c**)]; or with H^+ to yield $[Os_{10}(H)C(CO)_{24}\{M(PPh_3)\}]$ [M = Au (**6a**) or Ag (**6b**)]. The monoanion $[Os_{10}C(CO)_{24}\{Cu(PPh_3)\}]^-$ (**4e**) does not undergo reaction with $[Cu(NCMe)_4][PF_6]$, and with H^+, a black solid tentatively formulated as $[Os_{10}(H)C(CO)_{24}\{Cu(PPh_3)\}]$ (**6c**) is obtained. Reaction of (**6a**) or (**6b**) with $AgClO_4$ in CH_2Cl_2 yields the giant eicosaosmium clusters $[Os_{20}M(C)_2(CO)_{48}]^{2-}$ [M = Au (**7a**) or Ag (**7b**)]. These dianionic species can be readily reduced with sodium diphenylketyl in tetrahydrofuran to yield the trianions $[Os_{20}M(C)_2(CO)_{48}]^{3-}$ [M = Au (**8a**) or Ag (**8b**)].

The i.r. spectra of compounds (**2**)—(**6**) are considerably more complex than the parent dianion (**1**) [in CH_2Cl_2 $\nu(CO)$ at 2 033s, 1 986s cm^{-1}] reflecting their lower symmetry. They are, however, largely insensitive to the nature of the $Au(PR_3)$, $Ag(PR_3)$, or $Cu(PR_3)$ moiety (PR_3 = PMe_2Ph, PPh_3, or PEt_3) (see Experimental section).

Studies of the ^1H and ^{31}P-$\{^1H\}$ n.m.r. spectra of $[Os_{10}C(CO)_{24}\{Au(PMe_2Ph)\}_2]$ (**2a**) in CD_2Cl_2 at room temperature (r.t.) have revealed the presence of two isomers in



Scheme. PR_3 = PMe_2Ph, PPh_3, or PEt_3; (*i*) 2[$MCl(PR_3)$] + 2$AgClO_4$ in CH_2Cl_2, 30 min at r.t.; (*ii*) [$MCl(PR_3)$] + $AgClO_4$ in CH_2Cl_2, 10 min at r.t.; (*iii*) left to stand in donor solvents, MeOH or CH_3COCH_3; (*iv*) NEt_3 (excess), or 45 °C in CH_2Cl_2; (*v*) one equivalent of NEt_3, or PR_3; (*vi*) one equivalent of NEt_3; (*vii*) [$Cu(MeCN)_4$][PF_6] in CH_2Cl_2, 20 min at r.t.; (*viii*) one equivalent each of [$MCl(PR_3)$]-$AgClO_4$ + [$Cu(MeCN)_4$][PF_6]; (*ix*) CF_3COOH, one drop; (*x*) under N_2 (two weeks), in presence of $AgClO_4$; (*xi*) sodium diphenylketyl, thf

solution, (**2a**), and (**2a′**).[4] Simple exchange with PPh_3 has been shown not to occur; instead irreversible extrusion of [$Au(PMe_2Ph)(PPh_3)$]$^+$ results and generates the monoanion [$Os_{10}C(CO)_{24}\{Au(PMe_2Ph)\}$]$^-$ (**4a**). The interconversion of isomers (**2a**) and (**2a′**) is probably the result of an intramolecular rearrangement of gold metal atoms, with the $Au(PMe_2Ph)$ moieties 'walking' across the surface of the cluster.[4,7] The cluster (**2a**) was also characterized by fast-atom bombardment (f.a.b.) mass spectroscopy [*m/z* 3 274 based on ^{192}Os and ^{197}Au]. The e.s.r. spectra of cluster (**2a**) both in frozen CH_2Cl_2 and in the solid state at liquid helium temperatures show $g_\perp = 2.018$ and $g_\parallel = 2.205$; this is consistent with a structure having axial symmetry. That this formally diamagnetic cluster shows an e.s.r. signal is not unexpected, since [$Os_{10}(H)_2C(CO)_{24}$] also exhibits temperature-dependent *intrinsic* paramagnetism.[8]

The neutral disilver cluster [$Os_{10}C(CO)_{24}\{Ag(PPh_3)\}_2$] (**2d**) is prepared in an analogous manner to (**2a**) above.[4] Attempts to prepare the neutral species [$Os_{10}C(CO)_{24}\{Cu(PPh_3)\}_2$] using [$Os_{10}C(CO)_{24}\{Cu(NCMe)\}_2$][6] as the precursor have so far proved unsuccessful, as has the reaction of the dianion [$Os_{10}C(CO)_{24}$]$^{2-}$ (**1**) with two equivalents each of [$CuCl(PPh_3)$] and $AgClO_4$, which instead produces [$Os_{10}C(CO)_{24}\{Ag(PPh_3)\}_2$] (**2d**) [equation (2)]. If a solution of (**2c**)

$$(\mathbf{1}) + 2[Cu(PPh_3)][ClO_4] \not\longrightarrow [Os_{10}C(CO)_{24}\{Cu(PPh_3)\}_2] \quad (2)$$

(PR_3 = PEt_3) and (**2d**) (PR_3 = PPh_3) is stirred for 24 h in CH_2Cl_2 exchange of $M(PR_3)$ units occurs, with the formation of [$Os_{10}C(CO)_{24}\{Au(PEt_3)\}\{Ag(PPh_3)\}$] (**2e**); $M(PR_3)$ group exchange has been previously observed.[9] The i.r. spectrum of this cluster is identical to (**2a**), indicating their probable isostructural nature.

Variable-temperature ^1H n.m.r. studies on (**2e**) revealed the presence of at least two isomers in solution in similar manner to (**2a**). The ^{31}P-$\{^1H\}$ n.m.r. spectrum of (**2e**) in CD_2Cl_2 at room temperature consists of one isomer with broad singlets at δ −46.14 and −47.92 p.p.m. (no ^{107}Ag- or ^{109}Ag–^{31}P coupling were seen at room temperature) and a second isomer with two broad singlets at δ −36.02 and −37.58 p.p.m.; the isomer ratio was 9:1. This is possibly indicative of PPh_3 dissociation at room temperature.[9] On cooling (**2e**) to 240 K, the ^{31}P-$\{^1H\}$ n.m.r. spectrum in CD_2Cl_2–freon consists of a doublet at δ − 45.7 [$Au(PEt_3)$, ^2J (AgP) 18 Hz] and two doublets at −48.12 p.p.m. [$Ag(PPh_3)$, $^1J(^{109}AgP)$ 583, $^1J(^{107}AgP)$, 506 Hz]; a second isomer with no Au–Ag bond present, shows a singlet at δ −35.61 [$Au(PEt_3)$] and two doublets at −37.40 p.p.m. [$Ag(PPh_3)$, $^1J(^{109}AgP)$ 687, $^1J(^{107}AgP)$ 611 Hz].

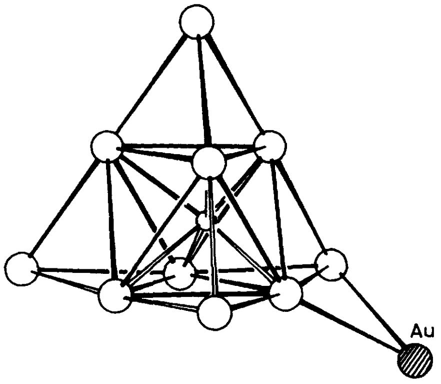


Figure 1. The 'Os$_{10}$AuP' core geometry in $[Os_{10}C(CO)_{24}\{Au(PPh_3)\}]^-$ (**4b**)

The digold cluster (**2a**) reacts with one additional equivalent of $[Au(PMe_2Ph)][ClO_4]$ to yield the trigold cluster $[Os_{10}C(CO)_{24}\{Au(PMe_2Ph)\}_3][ClO_4]$ (**3**). This cluster has been characterized on the basis of its i.r. spectroscopic and microanalytical data (see Experimental section). Interestingly, the appearance of the i.r. spectrum is not markedly different from that of (**2a**); it would therefore be interesting to determine if the three gold atoms were bonded to each other, as in the cluster $[Ru_4Au_3H(CO)_{12}(PPh_3)_3]$.[10]

The monoanions $[Os_{10}C(CO)_{24}\{Au(PR_3)\}]^-$ [$PR_3 = PMe_2Ph$ (**4a**), PPh_3 (**4b**), or PEt_3 (**4c**)] may be obtained from (**2a**)—(**2c**), by the reaction with NEt_3 (1 equivalent) or PPh_3 or by reaction of $[Os_{10}C(CO)_{24}]^{2-}$ with $[Au(PR_3)][ClO_4]$ (see Scheme). A single-crystal *X*-ray analysis of the $[PPh_3Me]^+$ salt of (**4b**) showed that the gold atom bridged the edge of a capping tetrahedron (Figure 1).[6] In previous work we have shown, on the basis of spectroscopic studies (n.m.r.), that this complex also undergoes isomerization in solution.[4] It is considered that the $[Au(PPh_3)]^+$ moiety 'moves' across the surface of the cluster *via* a μ_3 intermediate, to form (**4b**) with a μ-edge-bridging gold.[4]

The monoanions $[Os_{10}C(CO)_{24}\{M(PR_3)\}]^-$ [$M = Ag$, $PR_3 = PPh_3$ (**4d**); $M = Cu$, $PR_3 = PPh_3$ (**4e**)] may be obtained from (**2d**) by reaction with NEt_3 (one equivalent) or PPh_3 or by reaction of $[Os_{10}C(CO)_{24}]^{2-}$ with $[M(PR_3)][ClO_4]$, ($M = Ag$, $PR_3 = PPh_3$; $M = Cu$, $PR_3 = PPh_3$) [equation (3)].

$$\underset{(\mathbf{1})}{[Os_{10}C(CO)_{24}]^{2-}} + [Cu(PPh_3)][ClO_4] \longrightarrow \underset{(\mathbf{4e})}{[Os_{10}C(CO)_{24}\{Cu(PPh_3)\}]^-} \quad (3)$$

These monoanions, like the Au species (**2a**), undergo isomerization in solution.[4] Reaction of $[Os_{10}C(CO)_{24}\{Au(PPh_3)\}]^-$ (**4b**) with one equivalent of $[Cu(MeCN)_4][PF_6]$ produces the trimetallic cluster $[Os_{10}C(CO)_{24}\{Au(PPh_3)\}\{Cu(NCMe)\}]$ (**5a**), which has been characterized by i.r. The spectrum is similar to (**2b**), suggesting that they are isostructural. ^1H N.m.r. studies on (**5a**) in CD_2Cl_2 have revealed the existence of two isomers in solution, (**5a**) and (**5a′**), in a 10:1 ratio at room temperature. On cooling this solution to 273 K the cluster (**5a**) precipitates from solution. A similar reaction of $[Os_{10}C(CO)_{24}\{Ag(PPh_3)\}]^-$ (**4d**) occurs with one equivalent of $[Cu(NCMe)_4][PF_6]$, producing the trimetallic species $[Os_{10}C(CO)_{24}\{Ag(PPh_3)\}\{Cu(NCMe)\}]$ (**5c**), which has been characterized by i.r. spectroscopy. ^1H N.m.r. studies in CD_2Cl_2 at r.t. have revealed, as for (**5a**), the presence of interconverting isomers in solution for (**5c**), (**5c**) and (**5c′**). In CD_2Cl_2–freon at 245 K the ^1H n.m.r. of the Cu(NC*Me*) signal was split into a doublet in one isomer [^2J(AgH) 6 Hz] while the other isomer (**5c′**) exhibits *no* coupling to AgP, and a broad singlet is observed. The ^{31}P-$\{^1H\}$ n.m.r. spectrum of (**5c**) in CD_2Cl_2 at r.t. exhibits two broad resonances at δ −39.44 and −41.21 p.p.m., which change on further cooling. For the ^{31}P-$\{^1H\}$ n.m.r. of (**5c**) in CD_2Cl_2–freon at 245 K, two pairs of doublets were observed with $^{107,109}Ag$–^{31}P couplings. It is possible that like (**2a**)—(**2d**), a polyhedral metal rearrangement is occurring in solution, with two isomers present [as observed for (**2a**) and (**2a′**)],[4] one possibly containing a M–Cu bond (Au, Ag), as has been seen in $[MM'Ru_4(\mu\text{-}H)_2(CO)_{12}(PPh_3)_2]$,[9] while the other isomer contains two non-bonded moieties. On addition of PPh_3 to a solution of (**5a**) or (**5c**), extrusion of $[Au(PPh_3)_2]^+$ and $[Ag(PPh_3)_2]^+$ results, generating the anion $[Os_{10}C(CO)_{24}\{Cu(PPh_3)\}]^-$. Where $M \neq M'$ [M and M′ are Group 1B metals, as in (**5a**) or (**5c**)], thermodynamic preference for the lighter atom to occupy the site of higher co-ordination number has been shown to be the norm.[9] The Cu(NCMe) ligand in (**5a**) probably μ_3 bridges a cap whilst the $Au(PPh_3)$ ligand μ bridges an edge. This is a result of the participation of lower lying *p* orbitals in the Cu than those that are found in $Au(PR_3)$.[11,12]

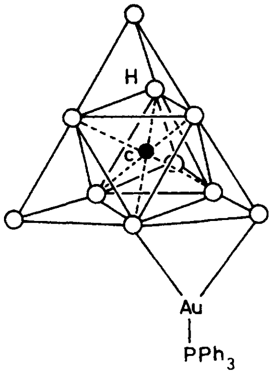


Figure 2. Proposed structure of $[Os_{10}(H)C(CO)_{24}\{Au(PPh_3)\}]$ (**6a**)

Reaction of the monoanion $[Os_{10}C(CO)_{24}\{Au(PPh_3)\}]^-$ (**4b**) with CF_3COOH produces the neutral cluster, $[Os_{10}(H)C(CO)_{24}\{Au(PPh_3)\}]$ (**6a**), which has been characterized by i.r., ^1H and ^{31}P-$\{^1H\}$ n.m.r. From the ^1H n.m.r., in CD_2Cl_2 at r.t., the hydride was located at δ −20.4 with $^1J(^{187}Os$–$^1H)$ satellites at 15.35 and 26.2 Hz, the satellite intensities being in a 3:1 ratio. This is entirely as expected for a hydride in a tetrahedral environment, as observed in $[Os_{10}(H)C(CO)_{24}]^-$.[13,14] ^{31}P-$\{^1H\}$ N.m.r. studies on (**6a**) show the presence of one broad resonance at δ −47.01 p.p.m. which did not narrow significantly on cooling to 270 K; below this (**6a**) precipitates out of CD_2Cl_2 solution. From our data (both ^1H and ^{31}P-$\{^1H\}$), we believe that the hydride is located in a tetrahedral site of the cluster, with the $Au(PPh_3)$ unit being either μ- *or* μ_3-bonded (as in Figure 2). Similar results have been obtained with the reaction of $[Os_{10}C(CO)_{24}\{Ag(PPh_3)\}]^-$ (**4d**) with CF_3COOH, to produce the neutral cluster $[Os_{10}(H)C(CO)_{24}\{Ag(PPh_3)\}]$ (**6b**), which has been characterized by i.r. [very similar to (**6a**), suggesting they are isostructural] and ^1H n.m.r. The ^1H n.m.r. spectrum of (**6b**) in CD_2Cl_2 at r.t. revealed the presence of a hydride at δ −20.1 (s, br), a very similar chemical shift to (**6a**). This neutral species was not soluble enough to obtain ^{187}Os–^1H satellites or to record a ^{31}P-$\{^1H\}$ n.m.r. spectrum. No ^1J (AgH) couplings were observed over the temperature range 270—293 K suggesting a structure for (**6b**) possibly similar to (**6a**). The reaction of $[Os_{10}C(CO)_{24}\{Cu(PPh_3)\}]^-$ (**4e**) with CF_3COOH, produces a sparingly soluble solid, $[Os_{10}(H)C(CO)_{24}\{Cu(PPh_3)\}]$ (**6c**), which has been characterized by i.r. and microanalysis.

It was observed that if a solution of (**6a**) was stirred with three equivalents of $AgClO_4$ and then left under N_2 for up to three weeks, cluster build-up occurs to give the recently characterized dianion $[Os_{20}Au(C)_2(CO)_{48}]^{2-}$ (**7a**),[15] which has two 'Os_{10}' units fused together, to create an eicosaosmium cluster. The dianion (**7a**) is we believe, the first recorded instance of an organometallic cluster compound containing Au^{II}. The e.s.r. spectrum at 10 K shows ^{197}Au hyperfine coupling (82 G) and $g_{iso} = 2.061$, which are consistent with this formulation.[15] Magnetic susceptibility measurements on (**7a**) in the range 4—300 K gave $\mu_{eff.} = 2.30 \pm 0.05$. It has now been found that this cluster can be readily reduced in an analogous manner as $[Os_{20}Hg(C)_2(CO)_{48}]^{2-}$ is reduced to $[Os_{20}Hg(C)_2(CO)_{48}]^{3-}$,[15] to give $[Os_{20}Au(C)_2(CO)_{48}]^{3-}$ (**8a**), which has at present been only characterized by i.r. and e.s.r. spectroscopy. The e.s.r. spectrum of a frozen CH_2Cl_2 solution of $[Os_{20}Au(C)_2(CO)_{48}]^{3-}$ (**8a**) at 9 K shows no ^{197}Au hyperfine coupling. This is in accord with our belief that the extra electron is added to the gold 5*d* level rather than to the osmium metal cluster core.

Similarly, if a solution of (**6b**) was stirred with $AgClO_4$, and left under N_2 for two weeks, the new dianion $[Os_{20}Ag(C)_2(CO)_{48}]^{2-}$ (**7b**) forms. This cluster is also readily reduced to give $[Os_{20}Ag(C)_2(CO)_{48}]^{3-}$ (**8b**), which has only been characterized by i.r. spectroscopy.

Experimental

The complex $[N(PPh_3)_2]_2[Os_{10}C(CO)_{24}]$ was prepared by the literature method.[16] Schlenk-tube techniques were used throughout the experiments and all reactions were performed under a N_2 atmosphere.[17] Reaction solvents were purified, dried, and deoxygenated by distillation under N_2 over appropriate drying agents. The solvents were stored under N_2. The compounds $[AgCl(PPh_3)]$,[18] $[CuCl(PPh_3)]$,[19] and $[AuCl(PMe_2Ph)]$[20] were synthesised by established procedures.

Infrared spectra were recorded on a Perkin-Elmer PE983 instrument. Variable-temperature i.r. spectra were recorded using a Specac P/N21.000 variable-temperature cell. Nuclear magnetic resonance spectra were recorded on Bruker 250-MHz (^1H) and 400-MHz (^{31}P-$\{^1H\}$) (observed at 162 MHz) spectrometers in CD_2Cl_2. E.s.r. spectra were recorded on a Varian E109 spectrometer, in the range 4.5—300 K, at a constant magnetic field; low-temperature work was carried out on an Oxford Instruments e.s.r. 900 helium cryostat. Mass spectra were recorded on a A.E.I. MS12 spectrometer in fast atom bombardment mode, using tris(perfluoroheptyl)-1,3,5-triazine as internal calibrant. The instrument was used in either positive or negative-ion mode, with a 3-nitrobenzyl alcohol matrix.

Preparation of $[Os_{10}C(CO)_{24}\{Au(PMe_2Ph)\}_2]$ (**2a**).—The salt $[N(PPh_3)_2]_2[Os_{10}C(CO)_{24}]$ (100 mg, 0.0272 mmol) was dissolved in CH_2Cl_2 (80 cm^3). In a separate flask, $[AuCl(PMe_2Ph)]$ (0.022 g, 0.0598 mmol) and $AgClO_4$ (12.5 mg, 0.0598 mmol) were stirred together in CH_2Cl_2 (10 cm^3) for 20 min. This solution was then filtered through Celite into the reaction vessel. I.r. monitoring showed that the reaction was complete after *ca.* 30 min at r.t. Crystals of $[Os_{10}C(CO)_{24}\{Au(PMe_2Ph)\}_2]$ (**2a**) (yield 62 mg, 70%) were obtained by slow evaporation of the CH_2Cl_2 solution at room temperature, and characterized by spectroscopy. I.r.: ν(CO) (in CH_2Cl_2) at 2 092w, 2 068vs, 2 054m, 2 016s, 2 008m(sh), 1 995w, and 1 950vw cm^{-1}. Fast atom bombardment mass spectrum: *m/e* = 3 274 (using ^{192}Os). E.s.r. (solid at 77 K): $g_\perp = 2.018$, linewidth = 315 G, and $g_\parallel = 2.205$ (Found: C, 15.75; H, 0.65. Calc. for $C_{41}H_{22}Au_2O_{24}Os_{10}P_2$: C, 16.05; H, 0.70%). The complex cannot be purified by t.l.c. techniques; the dianion (**1**) is regenerated as soon as it is put onto silica. The analogues $[Os_{10}C(CO)_{24}\{Au(PR_3)\}_2]$ [$PR_3 = PPh_3$ (**2b**) or PEt_3 (**2c**)] were obtained in comparable yield using identical techniques to the above, and also from the $[PPh_3Me]^+$ salt of (**1**).

Preparation of $[Os_{10}C(CO)_{24}\{Ag(PPh_3)\}_2]$ (**2d**).—The salt $[N(PPh_3)_2]_2[Os_{10}C(CO)_{24}]$ (40 mg, 0.0110 mmol) was dissolved in CH_2Cl_2 (20 cm^3). In a separate flask, $[AgCl(PPh_3)]$ (9 mg, 0.0221 mmol) and $AgClO_4$ (5 mg, 0.0239 mmol) were stirred together in CH_2Cl_2 (5 cm^3) for 10 min. This solution was filtered through Celite into the reaction vessel. I.r. monitoring of the reaction showed that it was complete after *ca.* 25 min at r.t. Crystals of $[Os_{10}C(CO)_{24}\{Ag(PPh_3)\}_2]$ (**2d**) (yield 25 mg, 67%) were obtained by slow evaporation of the CH_2Cl_2 solution at room temperature under N_2, and characterized by spectroscopy. I.r.: ν(CO) (in CH_2Cl_2) at 2 092w, 2 067vs, 2 053m, 2 016s, 2 006m(sh), 1 995w, and 1 950vw cm^{-1} (Found: C, 21.70; H, 0.95. Calc. for $C_{61}H_{30}Ag_2O_{24}Os_{10}P_2$: C, 21.90; H, 0.90%).

Preparation of $[Os_{10}C(CO)_{24}\{Au(PEt_3)\}\{Ag(PPh_3)\}]$ (**2e**).—The neutral compounds $[Os_{10}C(CO)_{24}\{Au(PEt_3)\}_2]$ (**2c**) (20 mg, 0.0064 mmol) and $[Os_{10}C(CO)_{24}\{Ag(PPh_3)\}_2]$ (**2d**) (20 mg, 0.0061 mmol) were dissolved in CD_2Cl_2 (10 cm^3) and left to stir for 24 h. ^1H N.m.r. monitoring of the solution showed the reaction was complete after this time. Crystals of $[Os_{10}C(CO)_{24}\{Au(PEt_3)\}\{Ag(PPh_3)\}]$ (**2e**) (yield 29 mg, 80%) were obtained by slow evaporation of the CH_2Cl_2 solution at room temperature under N_2, and characterized by spectroscopy. I.r.: ν(CO) (in CH_2Cl_2 at r.t.) at 2 091w, 2 068vs, 2 054m, 2 016s, 2 007m(sh), 1 995w, and 1 950vw cm^{-1}. ^1H N.m.r. (in CD_2Cl_2 at r.t): δ +1.3 (m, 9 H), +2.0 (m, 6 H), and +7.36—7.71 (m, 15 H). ^{31}P-$\{^1H\}$ N.m.r. (in CD_2Cl_2): δ −36.02 (s, br, $AuPEt_3$), −37.58 (s, br, $AgPPh_3$), −46.14 (s, br, $AuPEt_3$), and −47.92 p.p.m. (s, br, $AgPPh_3$) (no ^{107}Ag or ^{109}Ag couplings seen at r.t.); ratio of isomers at 293 K is 1:9 (on cooling to 275 K, ratio is 1:8). ^{31}P-$\{^1H\}$ N.m.r. in CD_2Cl_2–freon at 240 K: δ, −45.7 [d, $AuPEt_3$, $^2J(AgP)$ 18 Hz], −48.12 [2 × d, $AgPPh_3$, $^1J(^{109}AgP)$ 583, $^1J(^{107}AgP)$ 506 Hz]; −35.61 (s, br, $AuPEt_3$), −37.40 [2 × d, $AgPPh_3$, $^1J(^{109}AgP)$ 687, $^1J(^{107}AgP)$ 611 Hz]; ratio of isomers at 240 K is 1:5 (Found: C, 19.85; H, 1.25. Calc. for $C_{49}H_{33}AgAuO_{24}Os_{10}P_2$: C, 19.65; H, 1.00%).

Attempted Preparation of $[Os_{10}C(CO)_{24}\{Cu(PPh_3)\}_2]$.—The salt $[N(PPh_3)_2]_2[Os_{10}C(CO)_{24}]$ (40 mg, 0.110 mmol) was dissolved in CH_2Cl_2 (20 cm^3). In a separate flask $[CuCl(PPh_3)]$ (7.2 mg, 0.0220 mmol) and $AgClO_4$ (5 mg, 0.0239 mmol) were stirred in CH_2Cl_2 (5 cm^3) for 5 min; this solution was then filtered through Celite into the reaction vessel. I.r. monitoring of the reaction showed it was complete after *ca.* 25 min at r.t. Crystals of '$[Os_{10}C(CO)_{24}\{Cu(PPh_3)\}_2]$' were obtained by slow evaporation of the CH_2Cl_2 solution at r.t. under N_2 and found to have an i.r. spectrum identical to (**2d**). The ^{31}P-$\{^1H\}$ n.m.r. spectrum in CH_2Cl_2 at r.t. showed that the disilver cluster (**2d**) had formed instead of the desired dicopper species.

The reaction of $[Os_{10}C(CO)_{24}\{Cu(NCMe)\}_2]$ (20 mg, 0.0071 mmol) suspended in CH_2Cl_2 (10 cm^3) with two equivalents of PPh_3 (3.6 mg, 0.0142 mmol) was instantaneous and produced quantitatively the monoanion $[Os_{10}C(CO)_{24}\{Cu(PPh_3)\}]^-$ (**4e**); there was no evidence of formation of $[Os_{10}C(CO)_{24}\{Cu(PPh_3)\}_2]$.

Preparation of $[Os_{10}C(CO)_{24}\{Au(PMe_2Ph)\}_3][ClO_4]$ (**3**).—The cluster $[Os_{10}C(CO)_{24}\{Au(PMe_2Ph)\}_2]$ (**2a**) (20 mg, 0.0061 mmol) was dissolved in CH_2Cl_2 (10 cm^3). In a separate flask, $[AuCl(PMe_2Ph)]$ (2.5 mg, 0.0073 mmol) and $AgClO_4$ (1.3 mg, 0.0073 mmol) were stirred together in CH_2Cl_2 (5 cm^3) for 20 min. This solution was then filtered through Celite into the reaction vessel. The complex $[Os_{10}C(CO)_{24}\{Au(PMe_2Ph)\}_3]$-

$[ClO_4]$ (**3**) was isolated by filtration as an insoluble red-brown powder (yield 22 mg, 95%), and characterized by spectroscopy. I.r.: ν(CO) (KBr disc) at 2 101w, 2 078w, 2 058m, 2 026s, and 2 020m(sh) cm^{-1} (Found: C, 15.75; H, 0.65. Calc. for $C_{57}H_{44}Au_3ClO_{28}Os_{10}P_3$: C, 15.90; H, 0.90%).

Preparation of $[PPh_3Me][Os_{10}C(CO)_{24}\{Au(PMe_2Ph)\}]$ (**4a**).—The salt $[PPh_3Me]_2[Os_{10}C(CO)_{24}]$ (40 mg, 0.0126 mmol) was dissolved in CH_2Cl_2 (20 cm^3). In a separate flask, $[AuCl(PMe_2Ph)]$ (7 mg, 0.0138 mmol) and $AgClO_4$ (2.6 mg, 0.013 mmol) were stirred in CH_2Cl_2 (5 cm^3) for 20 min and then filtered through Celite into the reaction vessel. I.r. spectroscopy showed that the reaction was complete after stirring for *ca.* 10 min at r.t. Crystals of $[PPh_3Me][Os_{10}C(CO)_{24}\{Au(PMe_2Ph)\}]$ (**4a**) (yield 37 mg, 90%) were obtained by slow evaporation of the CH_2Cl_2 solution at room temperature and characterized by spectroscopy. I.r.: ν(CO) (in CH_2Cl_2) at 2 082w, 2 052s, 2 038m, 2 002s; 2 090w, 2 054s, 2 038m, and 2 000s cm^{-1} (Found: C, 22.5; H, 1.15. Calc. for $C_{62}H_{33}AuO_{24}Os_{10}P_2$: C, 22.4; H, 1.0%). The analogues $[PPh_3Me][Os_{10}C(CO)_{24}\{Au(PR_3)\}]$ $[PR_3 = PPh_3$ (**4b**) or PEt_3 (**4c**)] were also obtained in comparable yield using identical techniques to the above, and also from the $[N(PPh_3)_2]^+$ salt of (**1**).

Preparation of $[N(PPh_3)_2][Os_{10}C(CO)_{24}\{Ag(PPh_3)\}]$ (**4d**).—The salt $[N(PPh_3)_2][Os_{10}C(CO)_{24}]$ (40 mg, 0.0110 mmol) was dissolved in CH_2Cl_2 (20 cm^3). In a separate flask, $[AgCl(PPh_3)]$ (4.1 mg, 0.0110 mmol) and $AgClO_4$ (2.6 mg, 0.13 mmol) were stirred for 20 min in CH_2Cl_2 (5 cm^3) and then filtered through Celite into the reaction vessel. I.r. monitoring of the solution showed that the reaction was complete after stirring for *ca.* 10 min at r.t. Crystals of $[N(PPh_3)_2][Os_{10}C(CO)_{24}\{Ag(PPh_3)\}]$ (**4d**) (yield 30 mg, 77%) were obtained by slow evaporation of the CH_2Cl_2 solution at room temperature under N_2, and characterized by spectroscopy. I.r.: ν(CO) (in CH_2Cl_2) at 2 082w, 2 052vs, 2 038m, and 2 000s cm^{-1} (Found: C, 27.30; H, 1.35; N, 0.45. Calc. for $C_{79}H_{45}AgNO_{24}Os_{10}P_3$: C, 27.00; H, 1.30; N, 0.40%).

Preparation of $[N(PPh_3)_2][Os_{10}C(CO)_{24}\{Cu(PPh_3)\}]$ (**4e**).—The cluster $[N(PPh_3)_2][Os_{10}C(CO)_{24}\{Cu(NCMe)\}]$[7,13] (20 mg, 0.0062 mmol) was suspended in CH_2Cl_2 (10 cm^3) and one equivalent of PPh_3 (1.8 mg, 0.0071 mmol) added. I.r. monitoring of the solution at room temperature showed the reaction was instantaneous, with formation of the monoanion $[Os_{10}C(CO)_{24}\{Cu(PPh_3)\}]^-$. Crystals of $[N(PPh_3)_2][Os_{10}C(CO)_{24}\{Cu(PPh_3)\}]$ (**4e**) (yield 19 mg, 90%) were obtained by slow evaporation of the CH_2Cl_2 solution at room temperature under N_2, and characterized by spectroscopy. I.r.: ν(CO) (in CH_2Cl_2) at 2 082w, 2 052vs, 2 038m, and 2 000s cm^{-1} (Found: C, 26.85; H, 1.00; N, 0.50. Calc. for $C_{79}H_{45}CuNO_{24}Os_{10}P_3$: C, 27.0; H, 1.30; N, 0.45%). $[Os_{10}C(CO)_{24}\{Cu(PEt_3)\}]^-$ was also obtained in a similar manner and in a similar yield.

Preparation of $[Os_{10}C(CO)_{24}\{Au(PPh_3)\}\{Cu(NCMe)\}]$ (**5a**).—The salt $[PPh_3Me][Os_{10}C(CO)_{24}\{Au(PPh_3)\}]$ (**4b**) (20 mg, 0.0064 mmol) was dissolved in CH_2Cl_2 (15 cm^3), and one equivalent of $[Cu(NCMe)_4][PF_6]$ (2.7 mg, 0.0064 mmol) added as a solid. I.r. monitoring of the solution showed that the reaction was complete after *ca.* 5 min at r.t. Crystals of $[Os_{10}C(CO)_{24}\{Au(PPh_3)\}\{Cu(NCMe)\}]$ (**5a**) (yield 12.5 mg, 65%) were obtained by slow evaporation of the CH_2Cl_2 solution at r.t. and characterized by spectroscopy. I.r.: ν(CO) (in CH_2Cl_2) at 2 093w, 2 067s, 2 054m, 2 016s, 2 009m(sh), 1 995w, 1 970w, and 1 927w cm^{-1}. ^1H N.m.r. (in CD_2Cl_2): δ +2.12 [s, (**5a**)], +2.14 [s, (**5a′**)], +7.46—7.67 (m); ratio of isomers at 293 K is 10:1 (Found: C, 17.4; H, 0.6; N, 0.30. Calc. for $C_{45}H_{18}AuCuNO_{24}Os_{10}P$: C, 17.10; H, 0.60; N, 0.45%). $[Os_{10}C(CO)_{24}\{Au(PEt_3)\}\{Cu(NCMe)\}]$ (**5b**) was also obtained in a similar manner and comparable yield.

Preparation of $[Os_{10}C(CO)_{24}\{Ag(PPh_3)\}\{Cu(NCMe)\}]$ (**5c**).—The salt $[N(PPh_3)_2][Os_{10}C(CO)_{24}\{Ag(PPh_3)\}]$ (**4d**) (20 mg, 0.0058 mmol) was dissolved in CH_2Cl_2 (15 cm^3) and one equivalent of $[Cu(NCMe)_4][PF_6]$ (2.4 mg, 0.058 mmol) added as a solid. I.r. monitoring of the solution showed that the reaction was complete after *ca.* 2 min at r.t. Crystals of $[Os_{10}C(CO)_{24}\{Ag(PPh_3)\}\{Cu(NCMe)\}]$ (**5c**) (yield 14 mg, 75%) were obtained by slow evaporation of the CH_2Cl_2 solution at room temperature under N_2, and characterized by spectroscopy. I.r.: ν(CO) (in CH_2Cl_2) at 2 093w, 2 066s, 2 054m, 2 015s, 2 008m, 1 995w, 1 971w, and 1 927w cm^{-1}. ^1H N.m.r. (in CD_2Cl_2-freon at 245 K): γ, +2.13[s, (**5c**)], +2.16 [d, (**5c′**), J(AgH) 6 Hz], and +7.42—7.65 (m, 15 H). ^{31}P-$\{^1H\}$ N.m.r. (in CD_2Cl_2): δ, −39.44 and −41.21 p.p.m. (2 × s, br). ^{31}P-$\{^1H\}$ N.m.r. (245 K in CD_2Cl_2–freon): δ, −38.63 [2 × d, $J(^{109}AgP)$ 568, $J(^{107}AgP)$ 490 Hz], and −41.97 [2 × d, $J(^{109}AgP)$ 483, $J(^{107}AgP)$ 411 Hz] (Found: C, 15.70; H, 0.70; N, 0.45. Calc. for $C_{45}H_{18}AgCuNO_{24}Os_{10}P$: C, 15.55; H, 0.50; N, 0.40%).

Preparation of $[Os_{10}(H)C(CO)_{24}\{Au(PPh_3)\}]$ (**6a**).—The salt $[N(PPh_3)_2][Os_{10}C(CO)_{24}\{Au(PPh_3)\}]$ (**4b**) (40 mg, 0.011 mmol) was dissolved in CH_2Cl_2 (30 cm^3) and CF_3COOH (one equivalent) in CH_2Cl_2 (5 cm^3) slowly added. The reaction was found to be complete after 10 min by i.r. monitoring of the solution at r.t. A sparingly soluble red-brown compound, $[Os_{10}(H)C(CO)_{24}\{Au(PPh_3)\}]$ (**6a**), formed which was characterized by spectroscopy. I.r.: ν(CO) (in CH_2Cl_2) at 2 091w, 2 065s, 2 056m, 2 015s, 2 007m (sh), 1 995w, and 1 950vw cm^{-1}. ^1H N.m.r. (in CD_2Cl_2): δ, +7.31—7.67 (m) and −20.4(s); $^1J(^{187}Os$–$^1H)$ satellites at 15.35 and 26.2 Hz in a 3:1 ratio at 296 K, remaining unchanged on cooling to 270 K. ^{31}P-$\{^1H\}$ N.m.r. (in CD_2Cl_2): δ, −47.01 p.p.m. (s, br).

Preparation of $[Os_{10}(H)C(CO)_{24}\{Ag(PPh_3)\}]$ (**6b**).—The salt $[N(PPh_3)_2][Os_{10}C(CO)_{24}\{Ag(PPh_3)\}]$ (**4d**) (20 mg, 0.0056 mmol) was dissolved in CH_2Cl_2 (5 cm^3) and CF_3COOH (one equivalent) slowly added. The reaction was found to be complete after 10 min by i.r. monitoring of the solution at r.t. A *very* sparingly soluble red-brown compound, $[Os_{10}(H)C(CO)_{24}\{Ag(PPh_3)\}]$ (**6b**), formed which was characterized by spectroscopy. I.r.: ν(CO) (in CH_2Cl_2) at 2 090w, 2 064s, 2 056m, 2 015s, 2 006m (sh), 1 995w, and 1 950vw cm^{-1}. ^1H N.m.r. (in CD_2Cl_2 at 250 K): δ, +7.38—7.78 (m, 15 H) and δ, −20.1 (s, br *no* AgH coupling seen in the temperature range 250—293 K).

Preparation of $[Os_{10}(H)C(CO)_{24}\{Cu(PPh_3)\}]$ (**6c**).—The salt $[N(PPh_3)_2][Os_{10}C(CO)_{24}\{Cu(PPh_3)\}]$ (**4e**) (20 mg, 0.0058 mmol) was dissolved in CH_2Cl_2 (10 cm^3) and CF_3COOH (one equivalent) in CH_2Cl_2 (5 cm^3) slowly added. As the acid was added a precipitate of $[Os_{10}(H)C(CO)_{24}\{Cu(PPh_3)\}]$ (**6c**) slowly formed over 15 min. The complex (**6c**) was isolated by filtration as a near insoluble red-brown powder (yield 16 mg, 90%), and characterized by spectroscopy. I.r.: ν(CO) (in CH_2Cl_2) at 2 090w, 2 065s, 2 056m, 2 015s, 2 007m (sh), 1 995w, and 1 950vs cm^{-1} (Found: C, 17.85; H, 0.60. Calc. for $C_{43}H_{15}CuO_{24}Os_{10}P$: C, 17.60; H, 0.50%).

Preparation of $[N(PPh_3)_2]_2[Os_{20}Au(C)_2(CO)_{48}]$ (**7a**).—The cluster $[Os_{10}(H)C(CO)_{24}\{Au(PPh_3)\}]$ (**6a**) made above was assumed to be present in 100% yield. To the reaction mixture was added three equivalents of $AgClO_4$ (6.6 mg, 0.0318 mmol), and the solution stirred for 5 min. The resulting solution was then allowed to stand for 2—3 weeks under nitrogen in CH_2Cl_2 at r.t. during which time black crystals of $[N(PPh_3)_2]_2[Os_{20}Au(C)_2(CO)_{48}]$ (**7a**) slowly formed, (yield 23 mg, 65%), which were characterized by spectroscopy. I.r.: ν(CO) (in CH_2Cl_2) at 2 072m, 2 057s, and 2 005s cm^{-1}. Low-temperature e.s.r. (at 10 K, solid state): $g_{iso} = 2.061$, A_{av} (^{197}Au) = 82 G, $g_{\parallel} = 2.271$ (Found: C, 22.5; H, 1.05; N, 0.50. Calc. for $C_{122}H_{60}AuN_2O_{48}Os_{20}P_4$: C, 22.5; H, 1.05; N, 0.50%). The dianion of (**7a**) was also crystallized as its $[PPh_3Me]^+$ salt.

Preparation of $[N(PPh_3)_2]_2[Os_{20}Ag(C)_2(CO)_{48}]$ (**7b**).—The cluster $[Os_{10}(H)C(CO)_{24}\{Ag(PPh_3)\}]$ (**6b**) made above was assumed to be present in 100% yield (as was $[N(PPh_3)_2][ClO_4]$). To the reaction mixture was added $AgClO_4$ (6.6 mg, 0.0318 mmol) and the solution was then allowed to stand for two weeks under N_2 in CH_2Cl_2 at r.t., during which time black crystals of $[N(PPh_3)_2]_2[Os_{20}Ag(C)_2(CO)_{48}]$ (**7b**) slowly formed (yield 8 mg, 45%), which were characterized by spectroscopy. I.r.: ν(CO) (in CH_2Cl_2) at 2 072m, 2 057s, and 2 005s cm^{-1} (Found: C, 26.60; H, 1.05; N, 0.50. Calc. for $C_{122}H_{60}AgN_2O_{48}Os_{20}P_4$: C, 26.45; H, 0.95; N, 0.45%).

Preparation of $[Os_{20}Au(C)_2(CO)_{48}]^{3-}$ (**8a**).—The salt $[N(PPh_3)_2]_2[Os_{20}Au(C)_2(CO)_{48}]$ (**7a**) (20 mg, 0.0031 mmol) was dissolved in tetrahydrofuran (thf) (10 cm^3) and one equivalent of sodium diphenylketyl in thf slowly added dropwise. I.r. spectroscopy showed that the reaction was complete after 15 min at r.t., with a change in colour from red to burgundy, and the formation of a new species $[Os_{20}Au(C)_2(CO)_{48}]^{3-}$ (**8a**). This species was stable under N_2, and characterized by spectroscopy. I.r.: ν(CO) (in CH_2Cl_2) at 2 049m, 2 032s, and 1 979s cm^{-1}. Low-temperature e.s.r. (at 9 K in frozen CH_2Cl_2 solution): no ^{197}Au hyperfine coupling observed, but a broad line observed at $g = 2.288$.

Preparation of $[Os_{20}Ag(C)_2(CO)_{48}]^{3-}$ (**8b**).—The salt $[N(PPh_3)_2]_2[Os_{20}Ag(C)_2(CO)_{48}]$ (**7b**) (10 mg, 0.0015 mmol) was dissolved in thf (6 cm^3) and one equivalent of sodium benzophenone in thf added. I.r. spectroscopy showed that the reaction was complete after 10 min with the formation of $[Os_{20}Ag(C)_2(CO)_{48}]^{3-}$ (**8b**). This species was stable under N_2, and characterized on the basis of its i.r. spectrum only: ν(CO) (in CH_2Cl_2) at 2 049m, 2 032s, and 1 979s cm^{-1}.

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References

1 B. F. G. Johnson, *J. Chem. Soc., Chem. Commun.*, 1986, 27.
2 B. M. Gimarc and J. J. Ott, *Inorg. Chem.*, 1986, **25**, 83, and refs. therein.
3 W. N. Lipscomb, *Science*, 1966, **153**, 373.
4 S. R. Drake, B. F. G. Johnson, and J. Lewis, *J. Organomet. Chem.*, 1988, **340**, C31.
5 S. R. Bunkhall, H. D. Holden, B. F. G. Johnson, J. Lewis, G. N. Pain, P. R. Raithby, and M. J. Taylor, *J. Chem. Soc., Chem. Commun.*, 1984, 25.
6 B. F. G. Johnson, J. Lewis, W. J. H. Nelson, M. McPartlin, and M. D. Vargas, *J. Organomet. Chem.*, 1983, **243**, C69.
7 B. F. G. Johnson, D. A. Kaner, J. Lewis, P. R. Raithby, and M. J. Taylor, *Polyhedron*, 1982, **1**, 105.
8 R. E. Benfield, P. P. Edwards, and A. M. Stacy, *J. Chem. Soc., Chem. Commun.*, 1982, 525.
9 M. J. Freeman, M. Green, A. G. Orpen, I. D. Salter, and F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 1983, 1332.
10 L. W. Bateman, M. Green, J. A. K. Howard, K. A. Mead, R. M. Mills, I. D. Salter, F. G. A. Stone, and P. Woodward, *J. Chem. Soc., Chem. Commun.*, 1982, 773; J. A. K. Howard, I. D. Salter, and F. G. A. Stone, *Polyhedron*, 1984, **3**, 567.
11 S. R. Bunkhall, Ph.D. Thesis, University of Cambridge, 1984.
12 D. G. Evans and D. M. P. Mingos, *J. Organomet. Chem.*, 1982, **232**, 171.
13 E. C. Constable, B. F. G. Johnson, J. Lewis, G. N. Pain, and M. J. Taylor, *J. Chem. Soc., Chem. Commun.*, 1982, 754.
14 P. F. Jackson, B. F. G. Johnson, J. Lewis, M. McPartlin, and W. J. H. Nelson, *J. Chem. Soc., Chem. Commun.*, 1982, 4911.
15 S. R. Drake, B. F. G. Johnson, J. Lewis, K. Henrick, M. McPartlin, and J. Morris, *J. Chem. Soc., Chem. Commun.*, 1986, 928.
16 P. F. Jackson, B. F. G. Johnson, J. Lewis, W. J. H. Nelson, and M. McPartlin, *J. Chem. Soc., Dalton Trans.*, 1982, 2099.
17 D. F. Shriver, 'The Manipulation of Air-sensitive Compounds,' McGraw-Hill, New York, 1969.
18 F. G. Mann, D. Purdie, and A. F. Wells, *J. Chem. Soc.*, 1937, 1828.
19 J. H. Osborne, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc. A*, 1966, 1711.
20 C. K. Ingold and B. J. Gregory, *J. Chem. Soc. B*, 1969, 276.

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