# Synthesis, Structure, and Reactivity of the Heteronuclear Clusters $[Os_5H(CO)_{15}\{M(PR_3)\}]$ and $[Os_5(CO)_{15}\{M(PR_3)\}_2]$ (M = Cu, Ag, or Au; R = Ph or Me); the *X*-Ray Crystal Structure of $[Os_5H(CO)_{15}\{Au(PPh_3)\}]$ †

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Reaction of the salt $[N(PPh_3)_2][Os_5H(CO)_{15}]$ with a slight excess of $[MCl(PR_3)]$ (M = Cu, Ag, or Au; R = Ph or Me), in the presence of $TlPF_6$, proceeds instantaneously to afford a neutral brown cluster $[Os_5H(CO)_{15}\{M(PR_3)\}]$ [M = Cu, R = Ph (**1**); M = Ag, R = Ph (**2**); M = Au, R = Ph (**3**); M = Au, R = Me(**4**)]. The copper and silver complexes, (**1**) and (**2**), are less stable than the gold complexes, (**3**) and (**4**), and decompose back to the starting anion on standing in solution. Complexes (**3**) and (**4**) have been fully characterised on the basis of their i.r., $^1H$ n.m.r., and mass spectra, and the structure of (**3**) has been confirmed by a single-crystal *X*-ray analysis. The five Os atoms define a trigonal bipyramid, one face of which is asymmetrically capped by the gold triphenylphosphine group, so that the whole metal framework may be described as a bicapped tetrahedron. In co-ordinating solvents, such as MeCN, (**3**) and (**4**) dissociate with the loss of $Au(PR_3)$ to regenerate the anion $[Os_5H(CO)_{15}]^-$. With bases, such as $NEt_3$ and dbu (1,8-diazabicyclo[5.4.0]undec-7-ene) (**3**) and (**4**) deprotonate to give $[Os_5(CO)_{15}\{Au(PR_3)\}]^-$ [R = Ph (**5**) or Me (**6**)]. Careful protonation with $HBF_4$ regenerates (**3**) and (**4**). Clusters (**5**) and (**6**) can also be synthesised by the interaction of $[N(PPh_3)_2]_2[Os_5(CO)_{15}]$ with 1 equivalent of $[AuCl(PR_3)]$. Similarly, the reaction of the dianion $[Os_5(CO)_{15}]^{2-}$ with 1 equivalent of $[MCl(PPh_3)]$ (M = Cu or Ag) affords the anionic cluster $[Os_5(CO)_{15}\{M(PPh_3)\}]^-$ [M = Cu (**7**) or Ag (**8**)]. The clusters $[Os_5(CO)_{15}\{M(PR_3)\}_2]$ [M = Cu, R = Ph (**9**); M = Ag, R = Ph (**10**), M = Au, R = Ph (**11**); M = Au, R = Me (**12**)] may be synthesised in one step by the treatment of the salt $[N(PPh_3)_2]_2[Os_5(CO)_{15}]$, in the presence of $TlPF_6$, with a slight excess of $[MCl(PR_3)]$ (M = Cu, Ag, or Au; R = Ph or Me). The complexes (**9**)—(**12**) have been characterised on the basis of i.r., $^1H$ and $^{31}P$ n.m.r., and mass spectrometry. These products exhibit identical i.r. spectra and are believed to possess similar metal frameworks. The $^{31}P$ n.m.r. data show only one signal, and variable-temperature studies indicate that the $Au(PPh_3)$ groups occupy equivalent positions and are not fluxional. The clusters (**9**)—(**12**) are stable in non-co-ordinating solvents, but in co-ordinating solvents such as MeCN undergo fragmentation with the loss of a $M(PR_3)$ unit (M = Cu, Ag, or Au) to give the corresponding anionic clusters (**5**)—(**8**) in quantitative yield. With bases such as $NEt_3$ and dbu, complexes (**9**)—(**12**) react with the elimination of a $M(PR_3)$ unit to produce the anions (**5**)—(**8**).

The recent interest in the chemistry of heterometallic transition-metal clusters containing '$M(PR_3)$' units (M = Cu, Ag, or Au) has developed largely because of the proposed isolobal relationship between a hydride and '$Au(PR_3)$' unit, in which a degenerate set of *e* orbitals are too high lying to contribute significantly to the bonding.[1] It has since been shown that this analogy is not always strictly applicable with respect to the structures of hydride and gold phosphine substituted transition-metal clusters,[2] particularly in systems containing more than one $Au(PR_3)$ unit.[3] However, the introduction of $Au(PR_3)$ units into transition-metal clusters appears to enhance their stability or at least their ability to crystallise compared to their hydrido analogues, and a large number of these clusters have been successfully analysed by crystallographic techniques.

Salter and co-workers[4–8] have investigated the synthesis and reactivity of tetranuclear clusters of ruthenium and osmium with one and two $M(PR_3)$ units (M = Cu, Ag, or Au), and shown that these heterometallic systems have a rich chemistry, and that the $M(PR_3)$ units themselves may be involved in fluxional processes. In this paper we report the results of the reaction between pentaosmium clusters and $M(PR_3)$ units. These pentanuclear species should display a different reactivity to the tetranuclear systems, since in the latter all four metals in the starting material are in essentially the same chemical environment, whereas in the pentanuclear clusters the basic metal framework geometry is a trigonal bipyramid, and the equatorial and apical metals are in different environments.

## Results and Discussion

The reaction of the salt $[N(PPh_3)_2][Os_5H(CO)_{15}]$ with a slight excess of $[MCl(PR_3)]$ (M = Cu, Ag, or Au) proceeds instantaneously to afford a neutral brown cluster, formulated as $[Os_5H(CO)_{15}\{M(PR_3)\}]$ [M = Cu, R = Ph (**1**); M = Ag, R = Ph (**2**); M = Au, R = Ph (**3**); M = Au, R = Me (**4**)]. The inclusion of $TlPF_6$ increases the yield of the complex formed by abstracting the $Cl^-$ anion from the reaction mixture. The copper and silver complexes, (**1**) and (**2**), are less stable than the related gold complexes, (**3**) and (**4**), and decompose back to the starting anion in solution. The cluster (**3**) has been prepared previously from the pyrolysis of $[Os_3H(CO)_{10}\{Au(PPh_3)\}]$ in octane under reflux,[9] in low yield. The complexes have been

† 1,1,1,2,2,2,3,3,3,4,4,4-Dodecacarbonyl-2,3-μ-hydrido-2,3,4-$\mu_3$-tricarbonylosmio-1,4-μ-triphenylphosphineaurio-*tetrahedro*-tetraosmium.
*Supplementary data available*: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

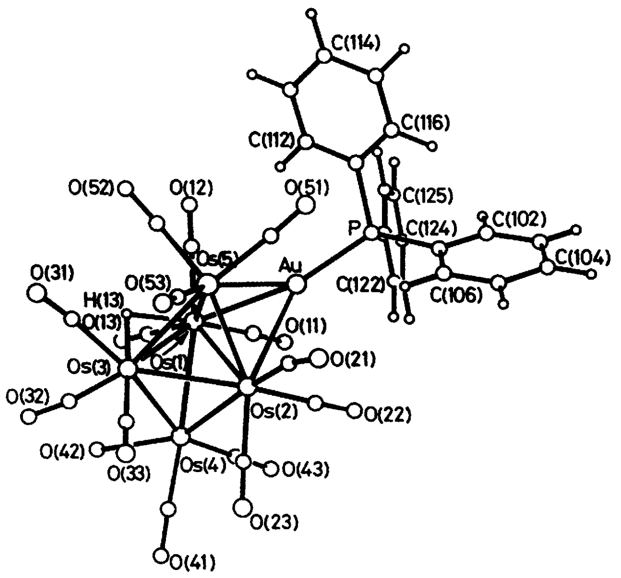


**Figure 1.** The molecular structure of $[Os_5H(CO)_{15}\{Au(PPh_3)\}]$ showing the atom numbering scheme

characterised from spectroscopic data (Table 1). The $^1H$ n.m.r. spectra of (3) and (4) show singlets at *ca.* $\delta$ $-21.0$, which suggests that the hydride occupies a bridging site. No coupling between the hydride and the phosphorus nucleus in the $Au(PR_3)$ group was observed consistent with the hydride bridging an Os–Os edge rather than an Os–Au edge. The i.r. spectra of (1) and (2) are very similar to those of (3) and (4), which indicates that the overall symmetry, and presumably the metal framework geometry, is the same in all four cases. In order to establish the full molecular geometry, a single-crystal *X*-ray analysis was performed on (3) using crystals grown by slow evaporation of a $CHCl_3$–octane solution.

The molecular structure of $[Os_5H(CO)_{15}\{Au(PPh_3)\}]$ is shown in Figure 1, while selected bond parameters are listed in Table 2. In the crystal structure the molecules exist as discrete molecular units with no abnormally short intermolecular contacts between them. Partially disordered $CHCl_3$ molecules were also observed in the crystal lattice. Within the individual cluster molecules, the five Os atoms define a trigonal bipyramid one face of which is capped asymmetrically by the Au atom of the $Au(PPh_3)$ group, so that the whole metal framework may be considered as a bicapped tetrahedron, as is found in the binary carbonyl $[Os_6(CO)_{18}]$,[10] and in a number of hexanuclear mixed-metal species.[11–14] The hydride was not located directly in the *X*-ray analysis, but was located from potential-energy-minimisation calculations,[15] and shown to bridge the Os(1)–Os(3) equatorial edge. The carbonyl ligands show some deviation from linearity consistent with the presence of incipient bridge bonding in keeping with the formal electron imbalance within the cluster. In terms of the 18-electron rule, the two apical Os atoms, Os(4) and Os(5), are electron deficient, with formally 17 $e^-$ for Os(4) and $17\frac{1}{3}$ $e^-$ for Os(5). There are short intramolecular contacts between these two metal atoms and carbonyl ligands co-ordinated to the equatorial Os atoms, Os(2) and Os(3) [Os(5) $\cdots$ C(21) 2.67(3), Os(4) $\cdots$ C(32) 2.99(3) Å], with the carbonyls bending towards and interacting with the apical metal atoms. There are also short contacts between the carbonyls C(11)O(11) and C(51)O(51) and the Au atom [Au $\cdots$ C(11) 2.72(2), Au $\cdots$ C(51) 2.72(4) Å], although studies on other gold-containing systems indicate that there is no significant bonding interaction in these cases.[16]

The Os–Os distances within the framework of (3) are in the same range as those observed in the parent binary carbonyl $[Os_5(CO)_{16}]$[17] [2.738(3)—2.889(3) Å], and in the anion $[Os_5H(CO)_{15}]^-$ [2.710(4)—2.872(4) Å],[18] with the exception of the long Os(1)–Os(5) distance of 3.072(2) Å. It is noteworthy that this long edge is not associated with the presence of a bridging hydride, which spans the shorter Os(1)–Os(3) edge [2.888(1) Å], but that it makes up one edge of the $Os_3$ triangle which is capped by the Au atom. The Au atom caps asymmetrically, with shorter distances to Os(1) and Os(5), and a longer distance to Os(2). These lengths are similar to those observed in $[Os_4H(CO)_{12}\{\mu_3\text{-}N(CO)Me\}(\mu_3\text{-}AuPPh_3)]$[19] [2.762(1)—2.940(1) Å] where the Au atom also caps an $Os_3$ triangle. In these systems, the simplest bonding picture is to consider the Au atom as being formally *sp* hybridized, with one lobe of this hybrid pointing towards the $Os_3$ triangle and donating on electron to the cluster framework. The Au–P distance of 2.291(5) Å is similar in length to the values of 2.288(12) and 2.297(12) Å found in $[Os_4H(CO)_{13}\{Au(PEt_3)\}]$ and $[Os_4H_3(CO)_{12}\{Au(PEt_3)\}]$,[9] respectively, where a similar bonding interpretation was put forward. In the context of the bonding of the $Au(PPh_3)$ fragment to the cluster, it is of interest to compare the positions of the Au atom and the hydride in (3) with the positions of the two hydrides in the pentaosmium clusters $[Os_5H_2(CO)_{14}(PEt_3)]$ and $[Os_5H_2(CO)_{13}(PEt_3)\{P(OMe)_3\}]$,[20] where there is good evidence for the hydride locations. In both these dihydrido species the hydrides bridge one equatorial–equatorial Os–Os edge and an adjacent equatorial–axial Os–Os edge. In compound (3) the hydride bridges the equatorial–equatorial Os(1)–Os(3) edge, while the Au atom could be viewed as bridging the adjacent equatorial–axial Os(1)–Os(5) edge [Os(1)–Au 2.848(1), Os(5)–Au 2.831(1) Å] but having slipped over to interact with Os(2) [Os(2)–Au 2.926(1) Å]. The distribution of the bridging ligands in the three clusters is therefore basically similar except that the greater size of the gold donor orbital favours the interaction with three Os atoms rather than with two. The carbonyl distribution in the three clusters is generally similar.

If it is assumed that the $Au(PPh_3)$ unit acts as a one-electron donor in (3), then the complex has an electron count of 72, which is consistent with the trigonal-bipyramidal osmium framework geometry as predicted by Wade's rules.[21] This electron count is also consistent with a localised two-centre two-electron bonding approach for the osmium framework, since there are formally 18 electrons available for Os–Os bonding and there are nine Os–Os framework edges.

Attempts to grow single crystals of (1) and (2) have failed, but on the basis of the spectral data it is assumed that these complexes have the same structure as (3), with a bicapped tetrahedral metal framework and a $Cu(PPh_3)$ or $Ag(PPh_3)$ group capping one of the triangular faces of the osmium trigonal bipyramid.

It is of interest to compare the chemistry of the heterometallic clusters (1)—(4) with that of the isoelectronic dihydrido cluster $[Os_5H_2(CO)_{15}]$. In non-co-ordinating solvents the clusters $[Os_5H(CO)_{15}\{M(PPh_3)\}]$ [M = Cu (1) or Ag (2)] readily decompose back to the anion $[Os_5H(CO)_{15}]^-$. The corresponding gold clusters (3) and (4) are stable. The instability of (1) and (2) compared to (3) and (4) may be partly due to the different electronic demands of the metals involved.

In co-ordinating solvents such as MeCN, (3) and (4) dissociate with the loss of the $Au(PR_3)$ fragment to give the starting anion $[Os_5H(CO)_{15}]^-$ and presumably the uncharacterised cation $[Au(PR_3)(NCMe)]^+$. A similar solvent dependence has been observed for the cluster $[Os_{10}C(CO)_{24}(MX)]^-$ [MX = $Au(PR_3)$ or Cu(NCMe)].[22] Similarly, the cluster $[Os_5H_2(CO)_{15}]$ is only stable in non-co-ordinating solvents, while in co-ordinating solvents such as MeCN deprotonation occurs to give the anion $[Os_5H(CO)_{15}]^-$. However, if a stoicheiometric

**Table 1.** Analytical (%) and spectroscopic data for complexes (1)—(12)

| Cluster | I.r. spectrum[a] ν(CO) ($cm^{-1}$) | Mass spectrum[b] (*m/e*) | $^1H$ N.m.r. spectrum[c] (δ) |
|---|---|---|---|
| (1) $[Os_5H(CO)_{15}\{Cu(PPh_3)\}]$ | 2 088w, 2 053vs, 2 039s, 2 029m, 2 018m, 1 961w | *d* | |
| (2) $[Os_5H(CO)_{15}\{Ag(PPh_3)\}]$ | 2 088w, 2 053vs, 2 035s, 2 023m(sh), 2 004m, 1 961w,br | *d* | |
| (3) $[Os_5H(CO)_{15}\{Au(PPh_3)\}]$ C, 21.25 (21.60); H, 1.10 (0.85) | 2 089w, 2 055vs, 2 042s, 2 032s, 2 021m, 2 001m,br, 1 969w | 1 840 | 7.46 (m, 15 H), −20.96 (s, 1 H) |
| (4) $[Os_5H(CO)_{15}\{Au(PMe_3)\}]$ | 2 088w, 2 053vs, 2 040s, 2 031s, 2 020m, 2 000m, 1 966w | 1 654 | 1.72 (d, 9 H)[e] [*J*(P–H) = 10 Hz], −21.14 (s, 1 H) |
| (5) $[Os_5(CO)_{15}\{Au(PPh_3)\}]^-$ | 2 060w, 2 027s, 1 995s, 1 945m | *d* | |
| (6) $[Os_5(CO)_{15}\{Au(PMe_3)\}]^-$ | 2 060w, 2 025s, 1 993s, 1 958m, 1 935m | *d* | |
| (7) $[Os_5(CO)_{15}\{Cu(PPh_3)\}]^-$ | 2 060w, 2 026s, 1 992vs, 1 934w, 1 912w | *d* | |
| (8) $[Os_5(CO)_{15}\{Ag(PPh_3)\}]^-$ | 2 060w, 2 026s, 1 991s, 1 934w, 1 902vw,br | *d* | |
| (9) $[Os_5(CO)_{15}\{Cu(PPh_3)\}_2]$ C, 29.90 (30.25); H, 1.60 (1.50) | 2 073w, 2 036s, 2 010s,br, 1 965w,br, 1 947w,br | *d* | 7.50 (m) |
| (10) $[Os_5(CO)_{15}\{Ag(PPh_3)\}_2]$ C, 28.80 (28.95); H, 1.55 (1.40) | 2 071w, 2 039s, 2 007s, 1 973w, 1 951m | *d* | 7.47 (m) |
| (11) $[Os_5(CO)_{15}\{Au(PPh_3)\}_2]$ C, 26.10 (26.70); H, 1.35 (1.30) | 2 072w, 2 039s, 2 015s, 1 973w(sh), 1 961w | *d* | 7.46 (m) |
| (12) $[Os_5(CO)_{15}\{Au(PMe_3)\}_2]$ C, 13.95 (13.15); H, 1.20 (0.95) | 2 071w, 2 036s, 2 012s, 1 970w, 1 965w,br | 1 926 | 1.65 (d)[e] [*J*(P–H) = 10 Hz] |

[a] In $CH_2Cl_2$. [b] Based on $^{192}Os$. [c] In $CD_2Cl_2$. [d] Parent peak not observed. [e] In $CDCl_3$.

**Table 2.** Selected bond lengths (Å) and angles (°) for complex (3)

| | | | |
|---|---|---|---|
| Os(1)–Os(2) | 2.890(1) | Os(1)–Os(3) | 2.888(1) |
| Os(1)–Os(4) | 2.868(1) | Os(1)–Os(5) | 3.072(2) |
| Os(1)–Au | 2.848(1) | Os(2)–Os(3) | 2.855(1) |
| Os(2)–Os(4) | 2.750(1) | Os(2)–Os(5) | 2.728(1) |
| Os(2)–Au | 2.926(1) | Os(3)–Os(4) | 2.852(1) |
| Os(3)–Os(5) | 2.828(1) | Os(5)–Au | 2.831(1) |
| Au–P | 2.291(5) | | |
| Os(3)–Os(1)–Os(2) | 59.2(1) | Os(4)–Os(1)–Os(2) | 57.1(1) |
| Os(4)–Os(1)–Os(3) | 59.4(1) | Os(5)–Os(1)–Os(2) | 54.4(1) |
| Os(5)–Os(1)–Os(3) | 56.5(1) | Os(5)–Os(1)–Os(4) | 101.9(1) |
| Au–Os(1)–Os(2) | 61.3(1) | Au–Os(1)–Os(3) | 107.7(1) |
| Au–Os(1)–Os(4) | 112.8(1) | Au–Os(1)–Os(5) | 57.0(1) |
| Os(3)–Os(2)–Os(1) | 60.4(1) | Os(4)–Os(2)–Os(1) | 61.1(1) |
| Os(4)–Os(2)–Os(3) | 61.1(1) | Os(5)–Os(2)–Os(1) | 66.2(1) |
| Os(5)–Os(2)–Os(3) | 60.8(1) | Os(5)–Os(2)–Os(4) | 114.8(1) |
| Au–Os(2)–Os(1) | 58.6(1) | Au–Os(2)–Os(3) | 106.5(1) |
| Au–Os(2)–Os(4) | 114.0(1) | Au–Os(2)–Os(5) | 60.0(1) |
| Os(2)–Os(3)–Os(1) | 60.4(1) | Os(4)–Os(3)–Os(1) | 59.9(1) |
| Os(4)–Os(3)–Os(2) | 57.6(1) | Os(5)–Os(3)–Os(1) | 65.0(1) |
| Os(5)–Os(3)–Os(2) | 57.4(1) | Os(5)–Os(3)–Os(4) | 108.7(1) |
| Os(2)–Os(4)–Os(1) | 61.9(1) | Os(3)–Os(4)–Os(1) | 60.7(1) |
| Os(3)–Os(4)–Os(2) | 61.2(1) | Os(2)–Os(5)–Os(1) | 59.4(1) |
| Os(3)–Os(5)–Os(1) | 58.4(1) | Os(3)–Os(5)–Os(2) | 61.8(1) |
| Au–Os(5)–Os(1) | 57.5(1) | Au–Os(5)–Os(2) | 63.5(1) |
| Au–Os(5)–Os(3) | 109.9(1) | Os(2)–Au–Os(1) | 60.1(1) |
| Os(5)–Au–Os(1) | 65.5(1) | Os(5)–Au–Os(2) | 56.6(1) |
| P–Au–Os(1) | 144.0(2) | P–Au–Os(2) | 150.2(2) |
| P–Au–Os(5) | 138.4(2) | C(101)–P–Au | 117.9(6) |
| C(111)–P–Au | 106.6(5) | C(111)–P–C(101) | 107.2(7) |
| C(121)–P–Au | 114.8(5) | C(121)–P–C(101) | 103.6(8) |
| C(121)–P–C(111) | 106.0(8) | | |

amount of MeCN is added to a n-octane solution of $[Os_5H_2(CO)_{15}]$, the addition product $[Os_5H_2(CO)_{15}(NCMe)]$ is obtained in 10% yield.[23] The reactions of (3) and (4) with $[N(PPh_3)_2]Cl$ produce the anionic cluster $[Os_5H(CO)_{15}]^-$, which contrasts with the behaviour of the unsaturated cluster $[Os_3H(CO)_{10}\{Au(PPh_3)\}]$ under the same reaction conditions where the heptanuclear product $[Os_6AuH_2(CO)_{20}]^-$ is obtained.[24]

Complex (3) may also be obtained, in 35% yield, from the direct reaction of $[Os_5H_2(CO)_{15}]$ with $[AuCl(PPh_3)]$, in $CH_2Cl_2$, under reflux. In order to test the reversibility of this reaction, complex (3) was treated with HCl, and $[Os_5H_2(CO)_{15}]$ obtained in 15% yield. Other products from this reaction include $[Os_5H(CO)_{15}]^-$ (35—40% yield) and the known tetranuclear hydrido carbonyl $[Os_4H_4(CO)_{12}]$[25] (30% yield). In contrast, the dihydride $[Os_5H_2(CO)_{15}]$ reacts with HCl or HI in $CH_2Cl_2$, under reflux, to afford the addition product $[Os_5H_2(CO)_{15}X]$ (X = Cl or I),[26] and no tetranuclear products are observed. On the basis of these observations, it appears that the cluster $[Os_4H_4(CO)_{12}]$ must have been formed from $[Os_5H(CO)_{15}\{Au(PR_3)\}]$. This suggests a competitive attack by $Cl^-$ at either the gold atom or at an osmium atom as the initial step in the reaction. The attack at the Au atom is slightly preferred, from the yields obtained, and may reflect the greater orbital availability at gold. However, it may be that the presence of a gold-containing ligand facilitates the cleavage of an '$Os(CO)_3$' unit prior to $Au(PR_3)$ loss. While the exact mechanism is not known, initial attack at the Au atom by $Cl^-$ (from excess of HCl) could give the anion '$Os_4H_3(CO)_{12}^-$' and $[AuCl(PR_3)]$, then the cluster anion might react *in situ* with $H^+$ (from excess of HCl) to give the required neutral cluster $[Os_4H_4(CO)_{12}]$. Alternatively, if it is assumed that the initial step involves attack of $Cl^-$ (from HCl) at a capping Os atom, which is formally electron deficient, and this results in the elimination of an $Os(CO)_3$ unit to produce a species which then reacts *in situ* with $H^+$ (from HCl) to produce '$Os_4H_3(CO)_{12}\{Au(PR_3)\}$'.

With the bases $NEt_3$ and dbu (1,8 diazabicyclo[5.4.0]undec-7-ene) the clusters (3) and (4) are deprotonated to produce anionic complexes formulated as $[Os_5(CO)_{15}\{Au(PR_3)\}]^-$ [R = Ph (5) or Me (6)]. These have been characterised from spectroscopic data (Table 1). It is interesting that the addition of bases such as $NEt_3$ and dbu to (3) and (4) initially removes the $Au(PR_3)$ fragment, presumably as '$[\{Au(PR_3)\}NEt_3]^+$' or '$[\{Au(PR_3)\}dbu]^+$', to give the hydrido anion $[Os_5H(CO)_{15}]^-$, but if left stirring for longer periods deprotonation followed by attack of $Au(PR_3)$ occurs *in situ* to produce the anionic clusters (5) or (6). Careful protonation of (5) and (6) with $HBF_4$

**Table 3.** Variable-temperature $^{31}$P-{$^{1}$H} n.m.r. data for complexes (**9**), (**10**), and (**12**)

| Cluster | Temperature (°C) | $^{31}$P-{$^{1}$H} N.m.r.* |
|---|---|---|
| (**9**) [$Os_5(CO)_{15}\{Cu(PPh_3)\}_2$] | 25 | −118(s) |
| | −30 | −118(s) |
| (**10**) [$Os_5(CO)_{15}\{Ag(PPh_3)\}_2$] | 25 | −111.36 (d of d) $J(^{107}Ag–P)$ = 472.3, $J(^{109}Ag–P)$ = 544.5 Hz |
| (**12**) [$Os_5(CO)_{15}\{Au(PMe_3)\}_2$] | 25 | −94.9 (s) |
| | −80 | −94.45(s) |

* Measured in $CD_2Cl_2$, chemical shifts referenced to trimethyl phosphite (external).

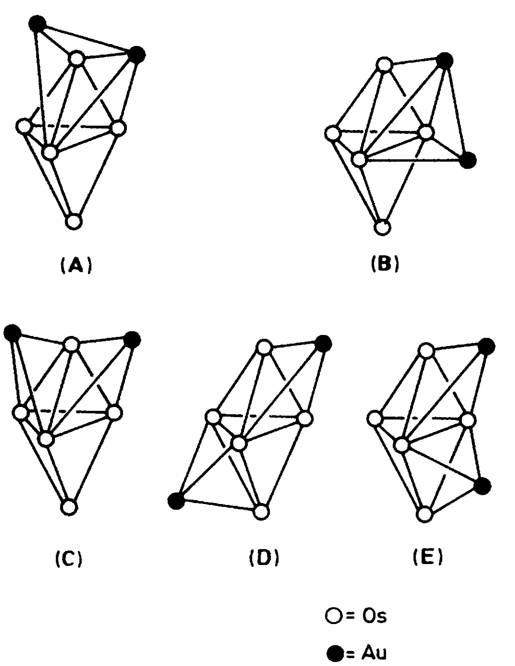


**Figure 2.** Possible isomeric structures for [$Os_5(CO)_{15}\{M(PR_3)\}_2$]

produces quantitative yields of (**3**) and (**4**) again. The clusters (**5**) and (**6**) may also be synthesised by the reaction of [$N(PPh_3)_2]_2[Os_5(CO)_{15}$] with 1 equivalent of [$AuCl(PR_3)$]. In a similar manner, the reaction of the dianion [$Os_5(CO)_{15}]^{2-}$ with 1 equivalent of [$MCl(PPh_3)$] (M = Cu or Ag) gives good yields of [$Os_5(CO)_{15}\{M(PPh_3)\}]^-$ [M = Cu (**7**) or Ag (**8**)], but protonation of these anions does not afford any stable products.

Although it has not been possible to obtain crystals of complexes (**5**)—(**8**) suitable for *X*-ray analysis the spectroscopic data are consistent with their adopting the same framework geometry as observed for (**3**), but with no hydride.

The clusters [$Os_5(CO)_{15}\{M(PR_3)\}]^-$ (M = Au, R = Ph (**5**); M = Au, R = Me (**6**); M = Cu, R = Ph (**7**); M = Ag, R = Ph (**8**)] react further with 1 equivalent of [$MCl(PR_3)$], in the presence of $TlPF_6$, to afford the neutral heptanuclear clusters [$Os_5(CO)_{15}\{M(PR_3)\}_2$] [M = Cu, R = Ph (**9**); M = Ag, R = Ph (**10**); M = Au, R = Ph (**11**); M = Au, R = Me (**12**)], which have been characterised on the basis of i.r., $^{1}$H and $^{31}$P n.m.r., and, in the case of (**12**), mass spectroscopic data (Tables 1 and 3). These products (**9**)—(**12**) may also be obtained by the reaction of [$N(PPh_3)_2]_2[Os_5(CO)_{15}$] with a slight excess of the appropriate [$MCl(PR_3)$] complex. The similarity of the i.r. pattern for the four complexes (**9**)—(**12**) suggests that all of them have the same overall structure. The $^{1}$H n.m.r. specta of (**9**)—(**11**) show a multiplet in the phenyl region, whereas the $^{1}$H n.m.r. spectrum of (**12**) displays a doublet at δ 1.65 [$J$(P–H) = 10 Hz] due to the co-ordinated $PMe_3$ groups. The presence of only one signal in the spectrum of (**12**) suggests that either both the $Au(PMe_3)$ units are in equivalent chemical environments or that the metal framework in (**12**) is undergoing an intramolecular rearrangement which exchanges two $Au(PMe_3)$ units rapidly (on the n.m.r. time-scale) at room temperature and makes them equivalent. If it is assumed that the metal framework in (**9**)—(**12**) is related to that of (**3**), then it is likely that two faces of the $Os_5$ trigonal bipyramid are capped by $M(PR_3)$ units, or that the second $M(PR_3)$ unit caps an $Os_2M$ triangle, as has been observed in the structure of [$Os_4H_2(CO)_{12}\{Au(PPh_3)\}_2$].[14] If this is so, then there are five possible isomeric metal framework arrangements for the structures of (**9**)—(**12**), and these are shown as structures (**A**)—(**E**) in Figure 2. In the isomers (**C**)—(**E**) the two $M(PR_3)$ units are in equivalent environments, and in the case of (**12**) only one signal in the $^{1}$H n.m.r. spectrum would be expected. In the structures (**A**) and (**B**) there are two different $M(PR_3)$ environments and two distinct signals in the ratio 1:1 would be expected in the $^{1}$H n.m.r. spectrum of (**12**) unless the two $Au(PMe_3)$ units are undergoing metal site exchange. Metal site exchange has been observed previously in other heterometallic clusters containing $M(PR_3)$ groups.[4,5]

In order to investigate whether the $Au(PMe_3)$ groups in compound (**12**) are undergoing fluxional processes, variable-temperature $^{1}$H and $^{31}$P n.m.r. studies have been carried out. The $^{1}$H n.m.r. spectrum of (**12**) shows no change over the temperature range −75 to 25 °C, and it seems likely that the two $Au(PMe_3)$ groups are not involved in any dynamic processes. This is confirmed by the $^{31}$P n.m.r. spectral studies. At room temperature, the spectrum displays a sharp singlet at δ −94.9 (referenced to trimethyl phosphite) and shows no change on cooling to −80 °C (Table 3). These results rule out structures (**A**) and (**B**) where the $Au(PMe_3)$ environments are different. However, on the basis of these data it is not possible to distinguish between the three remaining structures (**C**)—(**E**), and it has not been possible to grow suitable single crystals of any of these complexes.

The clusters (**9**)—(**12**) are stable to decomposition in non-co-ordinating solvents, but in co-ordinating solvents such as MeCN they undergo fragmentation with the loss of a $M(PR_3)$ unit (M = Cu, Ag, or Au) to give the corresponding anionic clusters (**5**)—(**8**) in quantitative yields. The clusters (**9**)—(**12**) also react with nucleophiles such as CO, $P(OMe)_3$, or $Cl^-$ to afford (**5**)—(**8**). This suggests that the nucleophiles tend to attack at the heterometal rather than at an Os atom, presumably because of the greater orbital availability at the former site. The reaction of the clusters (**9**)—(**12**) with bases such as $NEt_3$ or dbu results in the elimination of a $M(PR_3)$ unit to produce the corresponding anionic clusters (**5**)—(**8**). It is interesting that even in the presence of excess of nucleophile or base only one $M(PR_3)$ fragment dissociates. It appears that the anionic cluster [$Os_5(CO)_{15}\{M(PR_3)\}]^-$, which results from the elimination of one $M(PR_3)$ unit, is less susceptible to further nucleophilic attack.

The cluster [$Os_5(CO)_{15}\{Au(PPh_3)\}_2$] (**11**) may also be synthesised, in 40—50% yield, by the reaction of [$Os_5H_2(CO)_{15}$] or [$Os_5H(CO)_{15}\{Au(PPh_3)\}$] with excess of [$AuCl(PPh_3)$], in $CH_2Cl_2$, under reflux. The reversibility of this reaction was tested by the reaction of (**11**) with HCl. Although, [$Os_5H_2(CO)_{15}$] was obtained in low yield (5—10%), the major product was the tetranuclear cluster [$Os_4H_4(CO)_{12}$].[25] This reaction is believed to proceed in a fashion parallel to that of (**3**) with HCl, where [$Os_4H_4(CO)_{12}$] is also a major product.

## Experimental

All reactions were performed under dry nitrogen using standard Schlenk techniques. All solvents were freshly distilled from the usual drying agents prior to use. The neutral products containing gold are sufficiently air stable to be separated by t.l.c. on silica plates. The starting materials $[Os_5H_2(CO)_{15}]$ and $[Os_5H(CO)_{15}]^-$ were prepared by standard literature methods.[27] Other reagents were prepared as supplied. I.r. spectra were obtained using a Perkin-Elmer 1700 Fourier-transform i.r. spectrometer, n.m.r. spectra on a Bruker WM250 spectrometer, and mass spectra on a Kratos MS12.

*Reactions.*—$[N(PPh_3)_2][Os_5H(CO)_{15}]$ *with* $[MCl(PR_3)]$ (M = Cu *or* Ag, R = Ph; M = Au, R = Ph *or* Me). To a solution of $[N(PPh_3)_2][Os_5H(CO)_{15}]$ (50 mg), in $CH_2Cl_2$, 1 molar equivalent of $[MCl(PR_3)]$ [M = Cu or Ag, R = Ph; M = Au, R = Ph or Me), and $TlPF_6$, was added, and stirred at room temperature for 0.5 h. The solvent was then removed and the resulting mixture was separated by t.l.c. using a $CH_2Cl_2$–hexane (1:1) solution as eluant. The only brown band collected was identified as $[Os_5H(CO)_{15}\{M(PR_3)\}]$ [M = Cu, R = Ph (**1**); M = Ag, R = Ph (**2**); M = Au, R = Ph (**3**); M = Au, R = Me (**4**)].

$[Os_5H_2(CO)_{15}]$ *with* $[AuCl(PPh_3)]$. To a solution of $[Os_5H_2(CO)_{15}]$ (50 mg) in $CH_2Cl_2$ were added 2.1 molar equivalents of $[AuCl(PPh_3)]$ and $TlPF_6$. The reaction mixture was heated to 45 °C for 10—12 h. Purification of the resulting mixture by t.l.c. yielded two bands. These were characterised as $[Os_5H(CO)_{15}\{Au(PPh_3)\}]$ (**3**) (35%) and $[Os_5(CO)_{15}\{Au(PPh_3)\}_2]$ (**11**) (50% yield).

$[Os_5H(CO)_{15}\{Au(PR_3)\}]$ [R = Ph (**3**) *or* Me (**4**)] *with* MeCN. When $[Os_5H(CO)_{15}\{Au(PR_3)\}]$ [R = Ph (**3**) or Me (**4**)] was dissolved in MeCN the anion $[Os_5H(CO)_{15}]^-$ was formed in quantitative yield.

$[Os_5H(CO)_{15}\{Au(PPh_3)\}]$ (**3**) *with* HCl. Hydrogen chloride was bubbled through a solution of $[Os_5H(CO)_{15}\{Au(PPh_3)\}]$ (**3**) in $CH_2Cl_2$ for 0.25 h. Excess of HCl was removed by a fast stream of $N_2$ and the reaction mixture purified by t.l.c. using $CH_2Cl_2$–hexane (2:3) solution as eluant. Three bands were collected and identified as $[Os_5H_2(CO)_{15}]$ (15%), $[Os_5H(CO)_{15}]^-$ (40%), and $[Os_4H_4(CO)_{12}]$ (30% yield).

$[Os_5H(CO)_{15}\{Au(PR_3)\}]$ [R = Ph (**3**) *or* Me (**4**)] *with* $NEt_3$ *or* dbu. Three drops of $NEt_3$ or dbu were added to a $CH_2Cl_2$ solution of $[Os_5H(CO)_{15}\{Au(PR_3)\}]$ (25 mg) at room temperature. The i.r. spectrum of the reaction mixture showed the formation of $[Os_5H(CO)_{15}]^-$. When the reaction mixture was left stirring at room temperature for 12—14 h the anionic cluster $[Os_5(CO)_{15}\{Au(PR_3)\}]^-$ was obtained.

$[Os_5(CO)_{15}\{Au(PR_3)\}]^-$ *with* $HBF_4$. The addition of 2—3 drops of $HBF_4$ to a $CH_2Cl_2$ solution of $[Os_5(CO)_{15}\{Au(PR_3)\}]^-$ resulted in the formation of the neutral cluster $[Os_5H(CO)_{15}\{Au(PR_3)\}]$.

$[N(PPh_3)_2]_2[Os_5(CO)_{15}]$ *with* $[MCl(PR_3)]$. The cluster $[N(PPh_3)_2]_2[Os_5(CO)_{15}]$ (50 mg) was stirred with 1 molar equivalent of $[MCl(PR_3)]$ and $TlPF_6$ in $CH_2Cl_2$ at room temperature for 0.5 h. The i.r. spectrum of the reaction mixture showed it to be $[Os_5(CO)_{15}\{M(PR_3)\}]^-$.

$[N(PPh_3)_2][Os_5(CO)_{15}\{M(PR_3)\}]$ *with* $[MCl(PR_3)]$. The cluster $[N(PPh_3)_2][Os_5(CO)_{15}\{M(PR_3)\}]$ (50 mg) was stirred with 1 molar equivalent of $[MCl(PR_3)]$ and $TlPF_6$ in $CH_2Cl_2$ at room temperature for 0.5 h. Removal of solvent followed by t.l.c., using $CH_2Cl_2$–hexane (1:1) solution as eluant afforded a neutral cluster characterised as $[Os_5(CO)_{15}\{M(PR_3)\}_2]$ [M = Cu, R = Ph (**9**); M = Ag, R = Ph (**10**); M = Au, R = Ph (**11**); M = Au, R = Me (**12**)].

$[N(PPh_3)_2]_2[Os_5(CO)_{15}]$ *with* $[MCl(PR_3)]$. The cluster $[N(PPh_3)_2]_2[Os_5(CO)_{15}]$ (50 mg) was stirred with 2 molar equivalents of $[MCl(PR_3)]$ and $TlPF_6$, in $CH_2Cl_2$, at room temperature for 0.5 h. Purification of the reaction mixture by t.l.c., using $CH_2Cl_2$–hexane (1:1) as eluant, afforded a neutral cluster characterised as $[Os_5(CO)_{15}\{M(PR_3)\}_2]$.

$[Os_5(CO)_{15}\{M(PR_3)\}_2]$ *with* MeCN. When $[Os_5(CO)_{15}\{M(PR_3)\}_2]$ [M = Cu, R = Ph (**9**), M = Ag, R = Ph (**10**); M = Au, R = Ph (**11**); M = Au, R = Me (**12**) was dissolved in MeCN the known cluster $[Os_5(CO)_{15}\{M(PR_3)\}]^-$ was obtained.

*With* CO. Carbon monoxide was bubbled through a $CH_2Cl_2$ solution of $[Os_5(CO)_{15}\{M(PR_3)\}_2]$ at room temperature for 2 h. The i.r. spectrum of the reaction mixture showed the formation of the anion $[Os_5(CO)_{15}\{M(PR_3)\}]^-$.

*With* $P(OMe)_3$. Two drops of $P(OMe)_3$ were added to a $CH_2Cl_2$ solution of $[Os_5(CO)_{15}\{M(PR_3)\}_2]$ (10 mg) at room temperature and stirred for 0.1 h. The i.r. spectrum of the reaction mixture showed the formation of the anion $[Os_5(CO)_{15}\{M(PR_3)\}]^-$.

*With* $[N(PPh_3)_2]Cl$. To a $CH_2Cl_2$ solution of $[Os_5(CO)_{15}\{M(PR_3)\}_2]$ (20 mg) was added a large excess of $[N(PPh_3)_2]Cl$. The reaction mixture was stirred at room temperature for 0.5 h. The i.r. spectrum showed the presence of the anion $[Os_5(CO)_{15}\{M(PR_3)\}]^-$.

*With* $NEt_3$ *or* dbu. Three drops of $NEt_3$ or dbu were added to a $CH_2Cl_2$ solution of $[Os_5(CO)_{15}\{M(PR_3)\}_2]$ (10 mg), and the reaction mixture stirred at room temperature for 0.5 h. The i.r. spectrum showed the formation of the anion $[Os_5(CO)_{15}\{M(PR_3)\}]^-$.

*With* HCl. Hydrogen chloride was bubbled through a $CH_2Cl_2$ solution of $[Os_5(CO)_{15}\{M(PR_3)\}_2]$ (20 mg) at room temperature for 0.25 h. Excess of HCl was removed by a gentle stream of $N_2$, and the reaction mixture separated by t.l.c. using $CH_2Cl_2$–hexane (2:3) as eluant. Three bands were collected and characterised as $[Os_5H_2(CO)_{15}]$ (10%) $[Os_5H(CO)_{15}]^-$ (30%), and $[Os_4H_4(CO)_{12}]$ (50% yield).

*Crystal Structure Determination of* $[Os_5H(CO)_{15}\{Au(PPh_3)\}]\cdot 0.5CHCl_3$ (**3**).—Suitable crystals were grown by slow evaporation of $CHCl_3$–octane solution at −5 °C and a single crystal mounted on a glass fibre with epoxy resin.

*Crystal data.* $C_{33}H_{16}AuO_{15}Os_5P\cdot 0.5CHCl_3$, $M$ = 1 891.6, monoclinic, $a$ = 32.967(3), $b$ = 9.699(1), $c$ = 28.936(3) Å, $\beta$ = 118.50(1)°, $U$ = 8 131.3 Å$^3$ (by constrained least-squares refinement on diffractometer angles for 70 automatically centred reflections in the range $15 < 2\theta < 25°$, $\lambda$ = 0.710 69 Å, $T$ = 297 K), space group $C2/c$ (no. 15), $Z$ = 8, $D_c$ = 3.09 g cm$^{-3}$, $F(000)$ = 6 542. Red irregular blocks. Crystal dimensions (distance to face from centre); 0.146 (110, $\bar{1}\bar{1}0$) × 0.0627 (001, $00\bar{1}$) × 0.057 (100, $\bar{1}00$) × 0.053 ($20\bar{1}$) × 0.065 ($\bar{1}01$) mm, $\mu$(Mo-$K_\alpha$) = 192.71 cm$^{-1}$.

*Data collection and processing.* Stoe–Siemens diffractometer, 24 step $\omega$ scan mode with step width 0.04°, scan time 0.75—3.0 s per step, graphite-monochromated Mo-$K_\alpha$ radiation; 13 416 reflections measured ($5.0 \leqslant 2\theta \leqslant 47.5°$, $\pm h$, $-k$, $\pm l$), 6 193 unique [merging $R$ = 0.061 after a numerical absorption correction (maximum, minimum transmission factors 0.191, 0.114] giving 4 880 with $F > 4\sigma(F)$. No significant variation of intensity of the check reflections during data collection.

*Structure analysis and refinement.* Direct methods (Os and Au) followed by Fourier difference techniques. Blocked full-matrix least-squares refinement with Os, Au, P, and O atoms assigned anisotropic thermal parameters. Phenyl rings refined as idealised rigid groups (C–C 1.395 Å, C–C–C 120.0°), phenyl H fixed at C–H 1.08 Å and refined with one overall thermal parameter $U_{iso}$ = 0.13(3) Å$^2$. Hydride not located directly, but by potential-energy minimisation calculations, and not included in refinement. The weighting scheme $w = 3.951/[\sigma^2(F) + 0.0013F^2]$, with $\sigma(F)$ from counting statistics, gave satisfactory agreement analyses. Final $R$ and $R'$ values are 0.052 and 0.052. Maximum residual

**Table 4.** Atomic co-ordinates ( $\times 10^4$) for complex (**3**)

| Atom | *x* | *y* | *z* | Atom | *x* | *y* | *z* |
|---|---|---|---|---|---|---|---|
| Os(1) | 2 926(1) | 609(1) | 2 030(1) | C(13) | 2 266(8) | 447(23) | 1 777(8) |
| Os(2) | 3 543(1) | 2 361(1) | 1 845(1) | O(13) | 1 890(5) | 354(18) | 1 638(7) |
| Os(3) | 2 949(1) | 493(1) | 1 046(1) | C(21) | 4 171(9) | 2 087(26) | 2 040(9) |
| Os(4) | 2 611(1) | 2 899(1) | 1 317(1) | O(21) | 4 551(6) | 2 179(26) | 2 142(9) |
| Os(5) | 3 769(1) | −368(1) | 1 935(1) | C(22) | 3 673(8) | 3 709(27) | 2 385(9) |
| Au | 3 850(1) | 941(1) | 2 850(1) | O(22) | 3 754(9) | 4 462(20) | 2 710(7) |
| P | 4 316(1) | 838(7) | 3 742(2) | C(23) | 3 520(9) | 3 699(27) | 1 352(10) |
| C(102) | 5 041(5) | 2 263(18) | 4 559(5) | O(23) | 3 520(7) | 4 519(17) | 1 073(7) |
| C(103) | 5 455 | 2 997 | 4 783 | C(31) | 2 983(8) | −1 307(28) | 786(9) |
| C(104) | 5 659 | 3 369 | 4 476 | O(31) | 2 999(9) | −2 292(21) | 600(8) |
| C(105) | 5 450 | 3 008 | 3 945 | C(32) | 2 319(9) | 570(26) | 548(10) |
| C(106) | 5 036 | 2 274 | 3 721 | O(32) | 1 933(6) | 447(24) | 221(8) |
| C(101) | 4 831 | 1 902 | 4 028 | C(33) | 3 185(9) | 1 329(28) | 620(10) |
| C(112) | 4 168(4) | −1 977(18) | 3 708(6) | O(33) | 3 329(7) | 1 812(21) | 377(7) |
| C(113) | 4 301 | −3 359 | 3 785 | C(41) | 2 542(9) | 4 154(27) | 778(10) |
| C(114) | 4 768 | −3 705 | 4 051 | O(41) | 2 471(7) | 4 969(19) | 458(7) |
| C(115) | 5 102 | −2 669 | 4 240 | C(42) | 1 972(10) | 2 638(28) | 1 012(10) |
| C(116) | 4 969 | −1 287 | 4 163 | O(42) | 1 575(6) | 2 444(21) | 814(7) |
| C(111) | 4 502 | −941 | 3 896 | C(43) | 2 593(10) | 4 273(31) | 1 770(11) |
| C(122) | 3 829(6) | 2 574(15) | 4 057(6) | O(43) | 2 623(8) | 5 156(21) | 2 061(7) |
| C(123) | 3 604 | 2 973 | 4 340 | C(51) | 4 348(10) | −686(29) | 2 540(11) |
| C(124) | 3 579 | 2 066 | 4 699 | O(51) | 4 717(6) | −964(22) | 2 855(7) |
| C(125) | 3 777 | 760 | 4 776 | C(52) | 3 570(9) | −2 233(30) | 1 902(10) |
| C(126) | 4 002 | 360 | 4 493 | O(52) | 3 443(9) | −3 350(21) | 1 863(9) |
| C(121) | 4 028 | 1 267 | 4 134 | C(53) | 3 996(9) | −694(28) | 1 438(10) |
| C(11) | 2 978(7) | 1 803(24) | 2 578(8) | O(53) | 4 161(7) | −843(24) | 1 169(8) |
| O(11) | 2 965(5) | 2 534(17) | 2 888(6) | Cl | 439(6) | 890(18) | 2 937(9) |
| C(12) | 3 044(7) | −1 067(24) | 2 421(8) | C(100) | 73(32) | 654(89) | 2 282(33) |
| O(12) | 3 068(6) | −2 001(17) | 2 667(7) | | | | |

electron density 2 e Å$^{-3}$ in the region of the metal atoms. Structure solved and refined using SHELX 76,[28] scattering factors from ref. 29. Final atomic co-ordinates in Table 4.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

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