The Synthesis of the First Tetra- and Penta-gold Decaosmium Clusters, *X*-Ray Structure Analysis of $[Os_{10}Au_4C(CO)_{24}\{P(C_6H_{11})_3\}_3]$

Victoria Dearing,[a] Simon R. Drake,[b] Brian F. G. Johnson,[b] Jack Lewis,*[b] Mary McPartlin,*[a] and Harold R. Powell[a]

[a] *School of Chemistry, Polytechnic of North London, Holloway Road, London N7 8DB, U.K.*
[b] *University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K.*

The clusters $[Os_{10}Au_4C(CO)_{24}\{PR_3\}_3]$ $\{PR_3 = P(C_6H_{11})_3$ (**3a**), PPh_3 (**3b**), or PMe_2Ph (**3c**)$\}$ and $[Os_{10}Au_5C(CO)_{24}\{PPh_3\}_4]^+$ (**4**) have been prepared from the reaction of the dianion $[Os_{10}C(CO)_{24}]^{2-}$ (**1**) with $[(AuPR_3)_3O]BF_4$ which involves the corresponding intermediate monoanions $[Os_{10}C(CO)_{24}AuPR_3]^-$; the structure of the cluster (**3a**) has been fully established by *X*-ray single crystal analysis and contains a novel heterometallic polyhedron consisting of fused Au_4 and Os_{10} tetrahedra linked *via* a vertex and a capping edge, respectively.

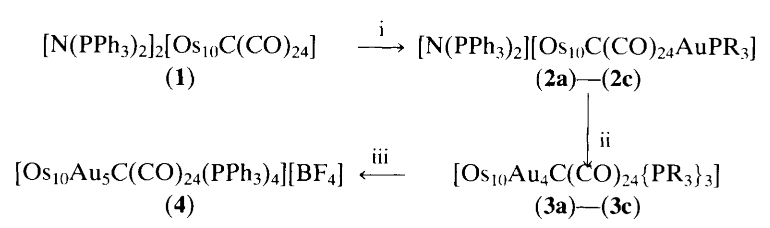
Triorganophosphine metal complexes are very widely used in the synthesis of mixed metal clusters. The treatment of Group 8 polynuclear metal carbonyl species with R_3PAu^+,[1] R_3PAuMe,[2] or $[(R_3PAu)_3O]BF_4$[3] has been shown to add up to three gold atoms to the cluster. *X*-Ray structure analysis† shows that reaction of the oxonium reagent $[(R_3PAu)_3O]^+$ with the giant tetrahedral dianion $[Os_{10}C(CO)_{24}]^{2-}$ (**1**) leads to the formation of the unusual tetra-gold decaosmium cluster $[Os_{10}Au_4C(CO)_{24}\{P(C_6H_{11})_3\}_3]$ (**3a**), illustrated in Figure 1.

The reaction of the dianion (**1**) with four equivalents of the gold oxonium salt $[\{AuPR_3\}_3O][BF_4]$ (Scheme 1) produces initially the known[4] gold–osmium cluster monoanion $[Os_{10}C(CO)_{24}AuPR_3]^-$ (**2a**)—(**2c**). If the reactants are stirred for 24 h, and then allowed to stand for 6—7 days at 0 °C, a further reaction occurs to yield the novel tetra-gold decaosmium cluster $[Os_{10}Au_4C(CO)_{24}(PR_3)_3]$ [where $PR_3 = P(C_6H_{11})_3$ (**3a**), PPh_3 (**3b**), and PMe_2Ph (**3c**)]. The clusters (**3b**) and (**3c**) were formulated on the basis of the similarity of their i.r. spectra‡ to that of the fully structurally characterised

---

† *Crystal data* for (**3a**): $[Os_{10}Au_4C(CO)_{24}\{P(C_6H_{11})_3\}_3]$, $C_{79}H_{99}Au_4O_{24}Os_{10}P_3$, $M = 4215.45$, triclinic, space group $P\bar{1}$ (No. 2), $a = 23.402(4)$, $b = 15.795(3)$, $c = 15.278(3)$ Å, $\alpha = 107.21(2)$, $\beta = 99.16(2)$, $\gamma = 84.39(2)°$, $U = 5317.95$ Å^3, $Z = 2$, $D_c = 2.632$ g cm^{-3}, $R = 0.0525$ ($R_w = 0.0516$) for 9095 reflections with $I/\sigma(I) \geqslant 3.0$ corrected for absorption [μ(Mo-K_α) = 168.14 cm^{-1}]. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

‡ *I.r. spectroscopic data* [ν_{CO}/cm^{-1} in tetrahydrofuran (THF)]: (**3a**) 2059 s, 2018 vs; (**3b**) 2060s, 2018 vs; (**3c**) 2060s, 2018 vs, (**4**) 2099 w, 2078 s, 2039 vs.



$$\begin{tikzcd}
\begin{array}{c}[N(PPh_3)_2]_2[Os_{10}C(CO)_{24}]\\ (\mathbf{1})\end{array} \arrow[r, "i"] & \begin{array}{c}[N(PPh_3)_2][Os_{10}C(CO)_{24}AuPR_3]\\ (\mathbf{2a})\text{—}(\mathbf{2c})\end{array} \arrow[d, "ii"] \\
\begin{array}{c}[Os_{10}Au_5C(CO)_{24}(PPh_3)_4][BF_4]\\ (\mathbf{4})\end{array} & \begin{array}{c}[Os_{10}Au_4C(CO)_{24}\{PR_3\}_3]\\ (\mathbf{3a})\text{—}(\mathbf{3c})\end{array} \arrow[l, "iii"']
\end{tikzcd}$$

a; $PR_3 = P(C_6H_{11})_3$
b; $PR_3 = PPh_3$
c; $PR_3 = PMe_2Ph$

Scheme 1. *Reagents and conditions:* i, 4 equiv. $[\{AuPR_3\}_3O][BF_4]$, THF, 5 min; ii, 24 h stirring in THF, then 0 °C for 6—7 days; iii, 1 equiv. $[\{AuPPh_3\}_3O][BF_4]$, THF, 45 min.

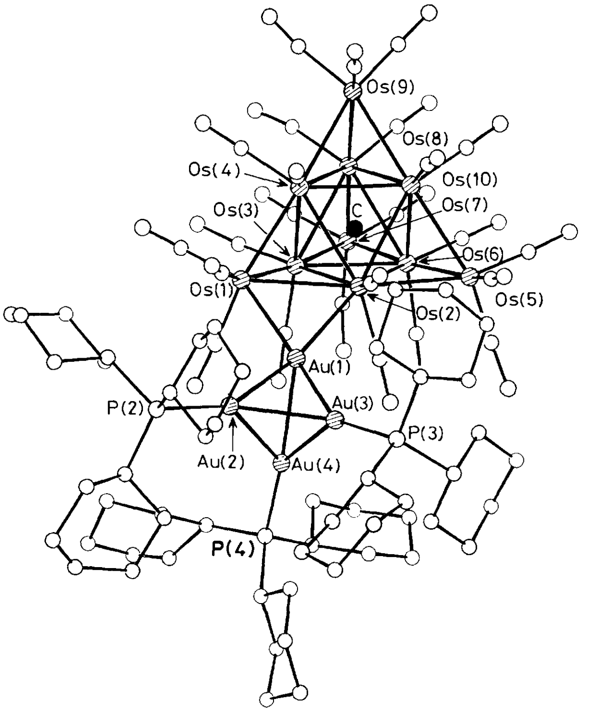


Figure 1. Molecular structure of $[Au_4Os_{10}C(CO)_{24}\{P(C_6H_{11})_3\}]$ (**3a**). Principal bond distances are (Å) (max. e.s.d. 0.002 Å): Os(1)–Os(2) 3.025, Os(1)–Os(3) 2.762, Os(1)–Os(4) 2.754, Os(2)–Os(3) 2.927, Os(2)–Os(4) 2.909, Os(2)–Os(5) 2.873, Os(2)–Os(6) 2.886, Os(2)–Os(10) 2.893, Os(3)–Os(4) 2.890, Os(3)–Os(6) 2.859, Os(3)–Os(7) 2.810, Os(3)–Os(8) 2.856, Os(4)–Os(8) 2.850, Os(4)–Os(9) 2.796, Os(4)–Os(10) 2.852, Os(5)–Os(6) 2.753, Os(5)–Os(10) 2.756, Os(6)–Os(7) 2.777, Os(6)–Os(8) 2.877, Os(6)–Os(10) 2.875, Os(7)–Os(8) 2.762, Os(8)–Os(9) 2.763, Os(8)–Os(10) 2.858, Os(9)–Os(10) 2.802, Os(2)–Au(1) 2.759, Os(1)–Au(1) 2.808, Au(1)–Au(2) 2.692, Au(1)–Au(3) 2.665, Au(1)–Au(4) 2.678, Au(2)–Au(3) 2.758, Au(2)–Au(4) 2.733, Au(3)–Au(4) 2.752; mean Os–C(carbide) 2.03(3).

cyclohexyl species (**3a**). The fast atom bombardment (f.a.b.) mass spectrum of (**3a**) shows a molecular ion at 4231 daltons for $[Os_{10}Au_4C(CO)_{24}\{P(C_6H_{11})_3\}_3]$ based on ^{192}Os, which corresponds to the established molecular formula.§

In the heteronuclear cluster (**3a**) the tetracapped octahedral metal geometry of the Os_{10} dianion (**1**) is retained, and one gold atom of the Au_4 tetrahedron bridges the outer edge of an Os_4 capping group (Figure 1), so that the bridging gold atom is in an unusual five co-ordinate site, The Os–Os bond bridged by the gold atom of 3.025(2) Å is the longest in the structure and is very much longer than the other Os–Os capping bonds {mean 2.783(2) Å}. This bond is also considerably longer than the bridged Os–Os bond length of 2.962(1) Å observed for $[Os_{10}C(CO)_{24}AuPPh_3]$ (**2b**).[4] The unsymmetrical edge-bridging bonding mode adopted by the gold atom in (**3a**) [Au–Os(1) 2.808(2) and Au–Os(2) 2.759(1) Å] may be the result of short contacts between the gold atom and the effectively close packed carbonyls [Au · · · C(carbonyl) 2.66—2.76 Å].

Homonuclear tetragold species are rare and the mean Au–Au bond length in the gold tetrahedron of (**3a**) is 2.713(2) Å which is considerably shorter than that in the tetrahedral cluster $[Au_4(\mu\text{-}I)_2(PPh_3)_2]$ of 2.793(2) Å.[5]

The ^1H and $^{31}P\text{-}\{^1H\}$ n.m.r. spectra in CD_2Cl_2 for the derivatives (**3a**)—(**3c**) show evidence of fluxional behaviour. For example the ^1H n.m.r. spectrum of (**3c**) shows one doublet down to 240 K [δ +1.94, $^2J(PH)$ 10.2 Hz],¶ and the $^{31}P\text{-}\{^1H\}$ n.m.r. spectra of all three derivatives in CD_2Cl_2 show only one broad resonance down to 220 K.‖ Dynamic behaviour of the $AuPR_3$ group is frequently observed for homo- and heteronuclear clusters, and results from the ease with which the Au–Au bond may be broken or re-formed.[6—8] For each of the compounds (**3a**)—(**3c**) the equivalence of the three $AuPR_3$ groups on the n.m.r. time scale may result from a simple rotation of the triangle Au(2), Au(3), and Au(4) round the multicentre bond to the sp hybrid orbital of Au(1). On addition of PPh_3 to (**3b**) $[Os_{10}C(CO)_{24}AuPPh_3]^-$ (**2b**) is formed irreversibly, ruling out the possibility that the equivalence of the organophosphine ligands in solution results from an intermolecular process.[7]

The treatment of $[Os_{10}Au_4C(CO)_{24}(PPh_3)_3]$ (**3b**) with a further one equivalent of $[(AuPPh_3)_3O]\,[BF_4]$ (see Scheme 1) affords the penta-gold decaosmium cluster $[Os_{10}Au_5C(CO)_{24}(PPh_3)_4]^+$ (**4**) in 80% yield (on recrystallisation).‡ This cluster has been characterised on the basis of its f.a.b. mass spectrum, which has *m/z* 4637 daltons corresponding to this formulation.¶ Variable temperature $^{31}P\text{-}\{^1H\}$ n.m.r. studies reveal the presence of four resonances at room temperature consistent with a structure containing four inequivalent phosphorus environments.‖ This is in marked contrast to the

---

§ *F.a.b. mass spectral data* (using nitrobenzyl alcohol matrix): (**3b**) *m/z* 4232 corresponds to $[Os_{10}Au_4C(CO)_{24}\{P(C_6H_{11})_3\}_3]$ (negative ion); (**4**) *m/z* 4637 corresponds to $[Os_{10}Au_5C(CO)_{24}\{PPh_3\}_4]$ (positive ion).

¶ *^1H N.m.r. spectroscopic data* ($[^2H_4]$-THF, 400.13 MHz): (**3a**) δ +1.11—2.42 (m); (**3b**) δ +7.42—7.83 (m); (**3c**) δ +1.94 [d, ^2J (PH) 10.2 Hz], δ +7.44—7.81 (m); (**4**) δ +7.39—7.86 (m).

‖ *$^{31}P\text{-}\{^1H\}$ n.m.r. spectroscopic data* ($[^2H_4]$-THF, 400.13 MHz, referenced to trimethyl phosphite): (**3a**) δ −45.34 (s, br.); (**3b**) δ −47.10 (s, br.); (**3c**) δ −40.27 (s, br.); (**4**) δ −43.22 (s), δ −44.83 (s), δ −46.19 (s), δ −49.86 (s) p.p.m.

fluxional behaviour of the tetra-gold decaosmium clusters (**3a**)—(**3c**), indicating that the fifth gold atom in (**4**) may be attached to both the gold tetrahedron *via* a gold–gold bond and to the Os_4 capping group in such a way as to impart rigidity to the metal framework.

We thank the S.E.R.C. (H.R.P.) and St. John's College, Cambridge, for the award of a Research Fellowship to S.R.D.

Received, 5th May 1988; Com. 8/01767K

References

1 M. J. Freeman, A. G. Orpen, and I. D. Salter, *J. Chem. Soc., Dalton Trans.*, 1987, 379, and references therein.

2 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.

3 M. I. Bruce and B. K. Nicholson, *Organometallics*, 1984, **3**, 101.

4 D. Braga, B. F. G. Johnson, J. Lewis, M. McPartlin, W. J. H. Nelson, and M. D. Vargas, *J. Organomet. Chem.*, 1983, **246**, C69.

5 F. Demartin, M. Manassero, L. Naldini, R. Ruggeri, and M. Sansoni, *J. Chem. Soc., Chem. Commun.*, 1981, 22.

6 K. P. Hall, B. R. C. Theobald, D. I. Guilmour, D. M. P. Mingos, and A. J. Welsh, *J. Chem. Soc., Chem. Commun.*, 1982, 528.

7 L. J. Farrugia, M. J. Freeman, M. Green, A. G. Orpen, F. G. A. Stone, and I. D. Salter, *J. Organomet. Chem.*, 1983, **249**, 273.

8 S. R. Bunkall, 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, 26.