

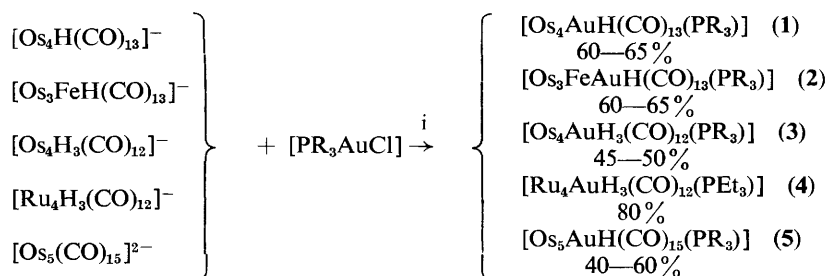
Synthesis and Characterisation of Mixed-metal Clusters containing Elements of the Iron Triad and Gold: X-Ray Crystal Structures of $[\text{Os}_4\text{Au}(\mu\text{-H})(\text{CO})_{13}(\text{PEt}_3)]$ and $[\text{Os}_4\text{Au}(\mu\text{-H})_3(\text{CO})_{12}(\text{PEt}_3)]$

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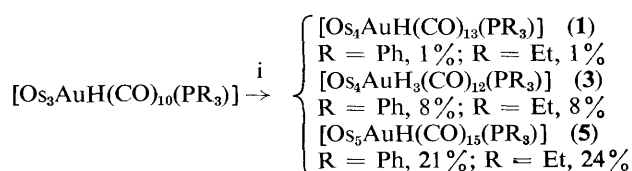
The clusters $[\text{Os}_4\text{AuH}(\text{CO})_{13}(\text{PR}_3)]$ (1), $[\text{Os}_3\text{FeAuH}(\text{CO})_{13}(\text{PR}_3)]$ (2), $[\text{Os}_4\text{AuH}_3(\text{CO})_{12}(\text{PR}_3)]$ (3), $[\text{Ru}_4\text{AuH}_3(\text{CO})_{12}(\text{PEt}_3)]$ (4), and $[\text{Os}_5\text{AuH}(\text{CO})_{15}(\text{PR}_3)]$ (5) (R = Ph, Et) have been synthesised by the reaction of the appropriate cluster anion with $[\text{PR}_3\text{AuCl}]$; the structures of (1) and (3) have been established by single-crystal X-ray analyses.

Although a great variety of mixed-metal clusters are known, most are obtained in low yield.¹ One possible method of synthesis is to treat a cluster anion with a mononuclear metal halide or cation.² We have recently reported that the reaction

of $[\text{Os}_3\text{H}(\text{CO})_{11}]^-$ with $[\text{PR}_3\text{AuCl}]$ (R = Ph, Et) gives the mixed-metal cluster $[\text{Os}_3\text{AuH}(\text{CO})_{10}(\text{PR}_3)]$ in high yield.³ In this communication we report an extension of this mode of synthesis to give the clusters $[\text{Os}_4\text{AuH}(\text{CO})_{13}(\text{PR}_3)]$ (1),



Scheme 1. i, Ti^+ , CH_2Cl_2 , room temp.; 10 min.



Scheme 2. i, Refluxing octane, 4 h, under N_2 .

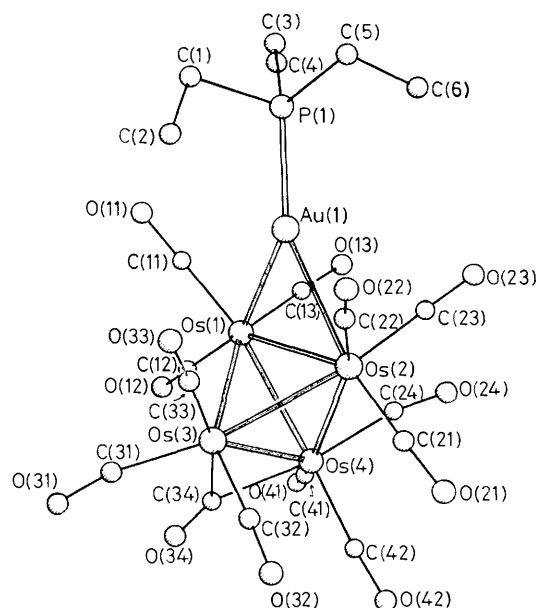


Figure 1. The molecular structure of $[\text{Os}_4\text{Au}(\mu\text{-H})(\text{CO})_{13}(\text{PEt}_3)]$, (1). Bond lengths: Os(1)–Os(2), 2.929(2); Os(1)–Os(3), 2.952(2); Os(1)–Os(4), 2.820(2); Os(2)–Os(3), 2.832(2); Os(2)–Os(4), 2.813(2); Os(3)–Os(4), 2.812(2); Au(1)–Os(1), 2.745(2); Au(1)–Os(2), 2.799(2); Au(1)–P(1), 2.288(12); Os(3)–C(34), 2.25(5); Os(4)–C(34), 2.06(5); Os(2) \cdots C(24), 2.69(5); Os(4)–C(24), 1.92(5); Os(1)–C(11), 1.80(4) Å. Bond angles: Os(1)–Au(1)–Os(2), 63.8(1); Os(1)–Au(1)–P(1), 149.9(3); Os(1)–Au(1)–P(2), 146.4(3); Os(3)–C(34)–Os(4), 81(1); Os(4)–C(24)–O(24), 160(4)°.

$[\text{Os}_3\text{FeAuH}(\text{CO})_{13}(\text{PR}_3)]$ (2), $[\text{Os}_4\text{AuH}_3(\text{CO})_{12}(\text{PR}_3)]$ (3), $[\text{Ru}_4\text{AuH}_3(\text{CO})_{12}(\text{PEt}_3)]$ (4), and $[\text{Os}_5\text{AuH}(\text{CO})_{15}(\text{PR}_3)]$ (5) in high yield (Scheme 1). The inclusion of $\text{Ti}[\text{PF}_6]$ in the reaction increases the yield considerably by removing Cl^- from the reaction mixture.

The clusters (1), (3), and (5) may also be isolated from the product mixture when $[\text{Os}_3\text{AuH}(\text{CO})_{10}(\text{PR}_3)]$ is thermolysed in refluxing octane (Scheme 2).

All the compounds have been isolated as air-stable solids although (2) is mildly light sensitive. The mass and i.r. spectra are consistent with the proposed molecular formulae. The n.m.r. spectra exhibit hydride resonances in the range τ 25.5–29.3 which may be assigned to μ_2 -bridging hydrides. In order to establish the geometries of these complexes the molecular structures of (1) and (3) have been determined by single-crystal X-ray analyses. Complex (1) was recrystallised from hexane to yield red crystals.†‡

† Crystal data for (1): $\text{C}_{19}\text{H}_{16}\text{AuO}_{15}\text{Os}_4\text{P}$, $M = 1441.06$, orthorhombic, space group $P2_12_12_1$, $a = 23.503(11)$, $b = 14.100(6)$, $c = 9.012(4)$ Å, $U = 2986.5$ Å³, $Z = 4$, $D_c = 3.20$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 219.35$ cm⁻¹. Final $R = 0.053$, ($R_w = 0.050$) for 2341 unique observed diffractometer data (blocked-cascade least squares with Os, Au, P anisotropic, C, O isotropic).

‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

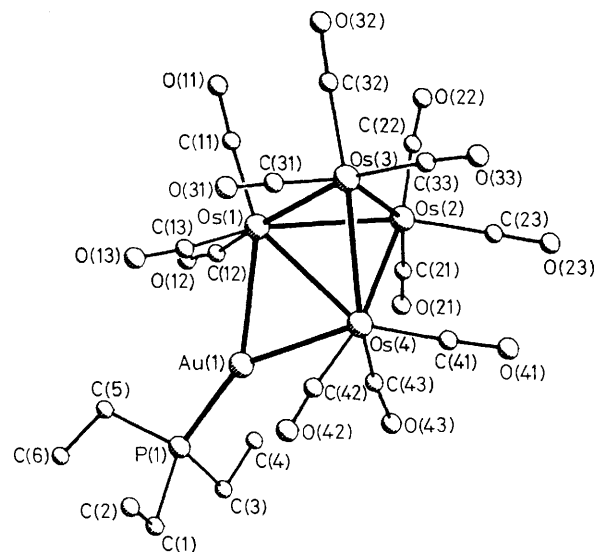


Figure 2. The molecular structure of $[\text{Os}_4\text{Au}(\mu\text{-H})_3(\text{CO})_{12}(\text{PEt}_3)]$, (3). Bond lengths: Os(1)–Os(2), 2.944(1); Os(1)–Os(3), 2.823(2); Os(1)–Os(4), 2.960(1); Os(2)–Os(3), 2.982(2); Os(2)–Os(4), 2.816(2); Os(3)–Os(4), 2.962(2); Au(1)–Os(1), 2.783(2); Au(1)–Os(4), 2.803(2); Au(1)–P(1), 2.297(12); Os(1)–C(12), 1.87(3); Au(1) \cdots C(12), 2.64(3); Os(4)–C(43), 1.69(6); Au(1) \cdots C(43), 2.65(4) Å. Bond angles: Os(1)–Au(1)–Os(4), 64.0(1); Os(1)–Au(1)–P(1), 146.2(2); Os(4)–Au(1)–P(1), 149.8(2); Os(1)–C(12)–O(12), 168(3); Os(4)–C(43)–O(43), 175(5)°.

The molecular structure of (1) is shown in Figure 1 together with some important bond parameters. The structure is similar to that of $[\text{Ru}_4\text{H}_2(\text{CO})_{13}]^4$ with one of the bridging hydrides replaced by the μ_2 -AuPEt₃ group. The co-ordination geometry at Au(1) suggests that the metal atom may best be described as linear sp hybridized Au^I with one lobe of the sp orbital pointing at the mid-point of the Os(1)–Os(2) bond. The P(1)–Au(1)–midpoint-[Os(1)–Os(2)] angle of 177.9° is consistent with this hypothesis. This interaction is similar to that of a bridging hydride and both species act as one-electron donors. Although the hydride in (1) was not located directly the carbonyl groups C(11)O(11) and C(31)O(31) bend away from the Os(1)–Os(3) edge with an average *cis* Os–Os–C (carbonyl) angle of 111° indicating that the hydride bridges this edge. Three of the Os atoms each have three terminal carbonyl groups bonded to them while the fourth metal atom, Os(4), has two terminal and two asymmetrically bridging carbonyl groups; the deviation from linearity of the bridging carbonyl groups is illustrated by the Os(4)–C(24)–O(24) and Os(4)–C(34)–O(34) angles of 160(4) and 143(4)°, respectively. The two carbonyl-bridged Os–Os bonds are significantly shorter than those bridged by the Au or H atoms. There is a short contact of 2.54(4) Å between Au(1) and the carbonyl carbon C(11); however there does not seem to be a significant interaction since the carbonyl ligand retains its linearity with an Os(1)–C(11)–O(11) angle of 172(4)°.

The similarity between a bridging hydride and the bridging AuPEt₃ group is also illustrated by the structure of $[\text{Os}_4\text{Au}(\mu\text{-H})_3(\text{CO})_{12}(\text{PEt}_3)]$ (3) which is shown in Figure 2, including some important bond parameters.‡§ The structure closely resembles that of $[\text{Os}_4(\mu\text{-H})_4(\text{CO})_{12}]^5$ and the Os₄

§ Crystal data for (3): $\text{C}_{18}\text{H}_{18}\text{AuO}_{12}\text{Os}_4\text{P}$, $M = 1415.06$, triclinic, space group $P\bar{1}$, $a = 9.737(4)$, $b = 10.041(5)$, $c = 16.256(8)$ Å, $\alpha = 73.40(2)$, $\beta = 74.02(2)$, $\gamma = 89.56(2)$ °, $U = 1459.89$ Å³, $Z = 2$, $D_c = 3.22$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 224.29$ cm⁻¹. Final $R = 0.061$ ($R_w = 0.059$) for 2763 unique observed diffractometer data (blocked cascade least squares with Os, Au, P, and ethyl C anisotropic, carbonyl C, O isotropic).

tetrahedron in both clusters exhibits idealised D_{2d} symmetry. Again one of the bridging hydrides has been replaced by the AuPEt₃ unit in (3). The average value of 2.964 Å for the four long bridged bonds in [Os₄(μ-H)₄(CO)₁₂] is very similar to that of the four long bonds in (3) regardless of whether they are bridged by a hydride or the Au atom. The geometry around the Au(1) atom indicates that it should be considered as sp hybridized {P(1)–Au(1)–midpoint–[Os(1)–Os(4)] 177.7°}, and that it donates one electron to an Os–Os fragment to form a delocalised three-centre Os–Au–Os bond. It has been shown previously that an sp hybridized Au atom will co-ordinate in a similar manner to a hydride with an unsaturated Os–Os bond.^{3,6} The linearity of the carbonyls C(12)O(12) and C(43)O(43) suggests that there is no interaction between these ligands and Au(1) despite the fairly short Au...C distances.

In both the structures (1) and (3) the Au–P distance is similar to the value of 2.279(8) Å in [Ph₃PAuMe]⁷ where the Au^I atom is sp hybridized. Au–P bond lengths in regular three-co-ordinate Au^I complexes are slightly longer, lying in the range 2.32–2.40 Å.⁸ This observation is consistent with the assignment of the Au^I atom in (1) and (3) as sp hybridized.

By analogy with the structures of (1) and (3) it is probable that (2), (4), and (5) also contain μ-AuPR₃ groups. These may replace bridging hydride ligands so that the structures

might be expected to be closely related to those of [Os₃FeH₂(CO)₁₃], [Ru₄H₄(CO)₁₂],⁹ and [Os₅H₂(CO)₁₅], respectively.

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