Synthesis and *X*-Ray Crystal and Molecular Structure of the Mixed-metal Cluster Anion $[Os_6Au(CO)_{20}H_2]^-$

By BRIAN F. G. JOHNSON, DAVID A. KANER, JACK LEWIS,* and PAUL R. RAITHBY
(*University Chemical Laboratory, Lensfield Road, Cambridge* CB2 1EW)

Summary The unsaturated mixed-metal cluster anion $[Os_6Au(CO)_{20}H_2]^-$ has been prepared as its $[N(PPh_3)_2]^+$ salt by the reaction of $[Os_3Au(CO)_{10}(PR_3)H]$ (R = Ph, Et) with $[N(PPh_3)_2]Cl$; its *X*-ray crystal structure shows that the Au^I atom links two '$Os_3(CO)_{10}H$' units *via* co-ordination to two short Os–Os bonds.

A HIGH-YIELD synthesis of the mixed-metal clusters $[Os_3Au(CO)_{10}(PR_3)H]$ (R = Ph, Et) has been developed recently.[1] These 'butterfly' clusters have two electrons fewer than the related saturated cluster $[Os_3Au(CO)_{10}(PPh_3)(SCN)]$ and the electronic unsaturation is thought to be localised on the short [2·699(1) Å] Os–Os 'hinge' bond.[1]

The clusters $[Os_3Au(CO)_{10}(PR_3)H]$ are expected to be reactive for several reasons. They have an unsaturated centre at the short Os–Os bond and might be expected to show reactivity similar to that of $[Os_3(CO)_{10}H_2]$.[2] The gold centre is sterically less hindered than metal centres in many carbonyl clusters and may have energetically low-lying orbitals available so that it may undergo nucleophilic attack. The polarity in the Os–Au bonds may induce reactivity greater than that of monometal clusters.

The clusters $[Os_3Au(CO)_{10}(PR_3)H]$ (R = Ph, Et) undergo no reaction when refluxed alone in CH_2Cl_2 under N_2 and can be recovered quantitatively at the end of the experiment. When the experiment is repeated with a two-fold excess of $[N(PPh_3)_2]Cl$ present a reaction occurs in $\frac{1}{2}$ h to give $[N(PPh_3)_2][Os_6Au(CO)_{20}H_2]$ which is precipitated by addition of hexane and purified by fractional recrystallisation from CH_2Cl_2–hexane. A single hydride resonance is observed in the ^1H n.m.r. spectrum at τ 21·26 ($CDCl_3$) which is very similar to the value of τ 21·3 for $[Os_3Au(CO)_{10}(PR_3)H]$.[1] The i.r. spectrum in the carbonyl region closely resembles that of $[Os_3Au(CO)_{10}(PR_3)H]$ which suggests a similar carbonyl symmetry: $[N(PPh_3)_2][Os_6Au(CO)_{20}H_2]$: ν_{CO} 2090vw, 2074m, 2044vs, 2029w sh, 1991s, 1978s sh, and 1957s sh cm^{-1}. Crystals suitable for an X-ray analysis were obtained as dark green rectangular blocks by recrystallisation from CH_2Cl_2–hexane.

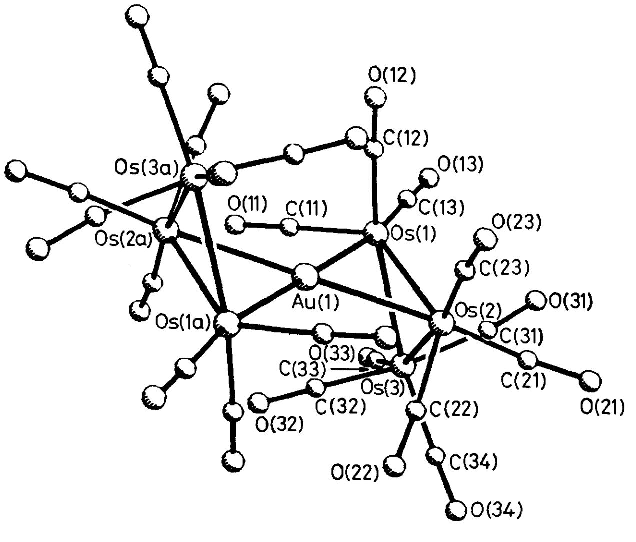

FIGURE. The molecular structure of the $[Os_6Au(CO)_{20}H_2]^-$ anion. Bond lengths: Au(1)–Os(1), 2·806(1) [2·809(1)]; Au(1)–Os(2), 2·802(1) [2·814(1)]; Os(1)–Os(2), 2·698(1) [2·689(1)]; Os(1)–Os(3), 2·830(1) [2·840(2)]; Os(2)–Os(3), 2·826(1) [2·828(2)] Å; bond angles: Os(1)–Au(1)–Os(2), 57·5(1) [57·1(1)]°. The dihedral angle between the Os(1)Os(2)Os(3) and Os(1)Os(2)Au(1) planes is 113·8 [112·2]°.

Crystal data: $C_{56}H_{32}AuNO_{20}Os_6P_2$, M = 2438·94, monoclinic, space group $C2/c$, a = 27·777(12), b = 18·273(8), c = 26·540(11) Å, β = 111·42(3)°, U = 12 540·4 Å^3, Z = 8, D_c = 2·58 g cm^{-3}, μ(Mo-K_α) = 145·33 cm^{-1}. 8107 Intensities ($2\theta_{max}$ = 47·5°) were collected on a Stoe four-circle diffractometer using graphite-monochromated Mo-K_α radiation and an ω–θ scan technique. The data were corrected for absorption and averaged to give 5455 unique observed reflections [$F > 4\sigma(F)$]. The structure was solved by a combination of direct methods (location of Os and Au atoms) and Fourier difference techniques, and refined by blocked-cascade least squares (Os, Au, and P anisotropic) to R = 0·052 and $R' = [\Sigma w^{\frac{1}{2}}\Delta/\Sigma w^{\frac{1}{2}}|F_o|]$ = 0·056. The phenyl rings were refined as rigid bodies with the H atoms placed in idealised positions (C–H, 1·08 Å; C–C–H, 120°) and assigned a common isotropic temperature factor.†

The asymmetric unit in the unit cell of this structure contains two half molecules of the cluster anion, each with the Au atom sitting on a crystallographic centre of symmetry, and two half molecules of the cation, each with the N atom lying on a two-fold axis. One complete molecule $[Os_6Au(CO)_{20}H_2]^-$ is shown in the Figure which includes some important bond parameters; the parameters in square brackets refer to the second molecule. The anion consists of two centrosymmetrically related isosceles Os_3 triangles linked through a gold(I) atom. The metal framework may be described as two 'butterfly' fragments sharing a common 'wing-tip' vertex. The structure of each '$Os_3(CO)_{10}H$' unit is closely related to that of $[Os_3(CO)_{10}H_2]^3$ because it is the short Os(1)–Os(2) bond that is symmetrically bridged by the Au atom in place of one of the μ_2-hydrides. From the distribution of the carbonyl ligands which bend away from the short edge (average *cis* Os–Os–C angle of 116·6°) the second hydride also bridges this bond. The metal–metal distances in this anion are similar to the unbridged [mean 2·815(1) Å] and bridged [2·683(1) Å] bond lengths in $[Os_3(CO)_{10}H_2]$[3] and, as in the case of the dihydride, the unsaturation is presumably localised in the short Os(1)–Os(2) bond. The arrangement of the carbonyls in the Os_3 fragments of the anion is similar to that in $[Os_3(CO)_{10}H_2]$[3] except that four carbonyl groups, C(11)O(11) and C(32)O(32) and their symmetry equivalents, surround the Au(1) atom [Au(1)···C(11), 3·24 Å; Au(1)···C(32), 3·39 Å]. However, these carbonyls do not show significant deviations from linearity [Os(1)–C(11)–O(11), 177(2)°; Os(3)–C(32)–O(32), 176(2)°] and there does not seem to be a significant bonding interaction to the Au atom.

The Au(1) atom displays a square-planar co-ordination geometry as does the central metal atom in the other mixed-metal clusters $[Fe_4Pd(CO)_{16}]^{2-}$ and $[Fe_4Pt(CO)_{16}]^{2-}$.[4] However, in $[Os_6Au(CO)_{20}H_2]^-$ the central Au atom is in oxidation state +1 which normally exhibits linear bivalent co-ordination geometry. The bonding may then be viewed as Au^I co-ordinating to the two Os_3 units in the same manner as does a hydride in $[Os_3(CO)_{10}H_2]$.[3] The unsaturation is not delocalised over the 'Os_4Au' core since the Au–Os bond lengths are in good agreement with the single bond values of 2·755 and 2·772 Å in $[Os_3Au(CO)_{10}H(PPh_3)]$ and $[Os_3Au(CO)_{10}(PPh_3)(SCN)]$,[1] respectively.

The reaction to produce the $[Os_6Au(CO)_{20}H_2]^-$ anion is unusual because it seems to require the fission of the gold–phosphine bond in $[Os_3Au(CO)_{10}(PPh_3)H]$. It appears that

---

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

the formation of a second Os–Au linkage more than compensates for the Au–P bond cleavage and stabilises the cluster.

We thank the S.R.C. for financial support.

(*Received*, 11*th May* 1981; *Com.* 557.)

---

[1] B. F. G. Johnson, D. A. Kaner, J. Lewis, and P. R. Raithby, *J. Organomet. Chem.*, submitted for publication.

[2] A. J. Deeming and S. Hasso, *J. Organomet. Chem.*, 1976, **114**, 313; J. R. Shapley, J. B. Keister, M. R. Churchill, and B. G. DeBoer, *J. Am. Chem. Soc.*, 1975, **97**, 4145.

[3] R. W. Broach and J. M. Williams, *Inorg. Chem.*, 1979, **18**, 314.

[4] G. Longoni, M. Manassero, and M. Sansoni, *J. Am. Chem. Soc.*, 1980, **102**, 3242.