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Preliminary communication

SYNTHESIS AND STRUCTURAL CHARACTERISATION OF AN UNSATURATED OSMIUM-GOLD CLUSTER $HOs_3Au(CO)_{10}(PR_3)$ (R = Et, Ph); X-RAY CRYSTAL STRUCTURES OF $HOs_3Au(CO)_{10}(PPh_3)$ AND $Os_3Au(CO)_{10}(PPh_3)(SCN)$

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Summary

The reaction of $[HOs_3(CO)_{11}]^-$ with $AuClPR_3$ (R = Et, Ph) yields the complex $HOs_3Au(CO)_{10}(PR_3)$, and the PPh_3 derivative has been characterised by an X-ray analysis; the structure is compared with that of $Os_3Au(CO)_{10}(PPh_3)$-(SCN) and is shown to contain a formally unsaturated Os—Os bond.

Mixed metal clusters are of interest since the polarity inherent in the mixed metal bonds should induce greater reactivity in these species than that observed in analogous monometallic clusters. In addition, gold complexes are of particular interest since the heterometal gold has energetically low lying, unfilled orbitals available and should be prone to nucleophilic attack. The reaction of $Os_3(CO)_{12}$ with $Au(PPh_3)X$ (X = Cl, Br, I, or SCN) to give clusters of the type $Os_3Au(CO)_{10}(PPh_3)X$ is well established [1]. These mixed-metal clusters are saturated systems with each Os atom obeying the 18-electron rule. Preliminary X-ray data on the Cl and Br derivatives has shown that the clusters consist of an Os_3 triangle one edge of which is bridged by both the $AuPPh_3$ group and the halide atom [1].

In this communication we report an alternative method for synthesising mixed Os—Au clusters. A halide may be displaced from a mononuclear halide complex by reaction with a cluster anion, or similarly by the reaction of a mononuclear cation with a cluster anion. The reaction of $[N(PPh_3)_2]$-$[HOs_3(CO)_{11}]$ with $Au(PR_3)Cl$ (R = Ph, Et) in refluxing CH_2Cl_2 yields the green complex $HOs_3Au(CO)_{10}(PR_3)$ as the sole neutral product (R = Ph: 35%, R = Et: 26%). The inclusion of $Tl^+ PF_6^-$ in the reaction increases the yield considerably by removing Cl^- from the reaction mixture.

$$[N(PPh_3)_2][HOs_3(CO)_{11}] + Au(PR_3)Cl \xrightarrow[\substack{30\ \text{min}, \\ Tl^+ PF_6^-}]{CH_2Cl_2\ \text{Reflux}} HOs_3Au(CO)_{10}(PR_3)$$

(R = Et 62%, R = Ph 64%)

Both the Et and Ph derivatives are stable green compounds, and were recrystallised from hexane. Both show one hydride resonance in their ^1H NMR spectra at τ 21.3 ($CDCl_3$). Their infrared spectra (Table 1) are consistent with the structures having a "butterfly" metal framework. A compound with the formula $HOs_3Au(CO)_{10}(PPh_3)$ and similar spectroscopic data to the complex reported here has been reported by Stone et al. from the reaction of $H_2Os_3(CO)_{10}$ with $Au(PPh_3)Me$ [2]. The molecular geometry has now been established by a single crystal X-ray analysis.

TABLE 1

INFRARED SPECTROSCOPIC DATA FOR $HOs_3Au(CO)_{10}(PR_3)$ (R = Ph, Et) (ν(CO), cm^{-1}; solvent, hexane)

PPh_3	2090w	2047s	2040m	2008s	1996m	1977m
PEt_3	2089m	2946vs	2039s	2008s	1994s	1981s

Crystal data: $C_{28}H_{16}AuO_{10}Os_3P$, *M* 1310.5, monoclinic, *a* 12.363(3), *b* 16.128(4), *c* 16.907(4) Å, β 109.16(2)°, *U* 3184.1 A^3, $Z = 4$, D_c 2.73 g cm^{-3}; $\mu(Mo\text{-}K_\alpha)$ 165.97 cm^{-1}, space group $P2_1/c$. The three Os and the Au atoms were located by multisolution Σ_2 sign expansion and the remaining non-hydrogen atoms from a subsequent electron density difference synthesis. The structure was refined by blocked-cascade least squares (Os, Au, P, O, and carbonyl C anisotropic), using 1763 unique observed intensities ($F > 3\sigma(F)$) recorded on a Stoe four-circle diffractometer with an ω/θ scan technique. The aromatic H atoms were placed in geometrically idealised positions (C—H, 1.08 A; C—C—H, 120.0°) and assigned a common isotropic temperature factor; the hydride H atom was not located. The current residuals are $R = 0.034$ and $R' = [\Sigma w^{\frac{1}{2}} \Delta / \Sigma w^{\frac{1}{2}} |F_o|] = 0.030$. The weighting scheme employed was $w = [\sigma^2(F) + 0.003 F^2]^{-1}$.

The molecular structure of $HOs_3Au(CO)_{10}(PPh_3)$ is shown in Fig. 1. together with some important bond parameters. The three Os atoms define the vertices of a distorted isosceles triangle, the short edge of which is bridged by the Au atom to give a "butterfly" arrangement of metal atoms. The dihedral angle between the Os(1)Os(2)Os(3) and the Os(1)Os(2)Au(1) planes is 109.8°. The hydride ligand was not located directly but the distribution of the carbonyl ligands around the short Os—Os bond indicates that it also bridges this edge; *cis* Os—Os—C angle for the short bond is 116° compared to that of 91° for the other two Os—Os edges. The dimensions of the carbonyl groups and of the phosphine group are similar to those reported in other cluster complexes. There is a weak bonding interaction across the cluster with a distance of 3.22 Å between C(34) the C atom of an axial carbonyl on Os(3) and the gold atom Au(1).

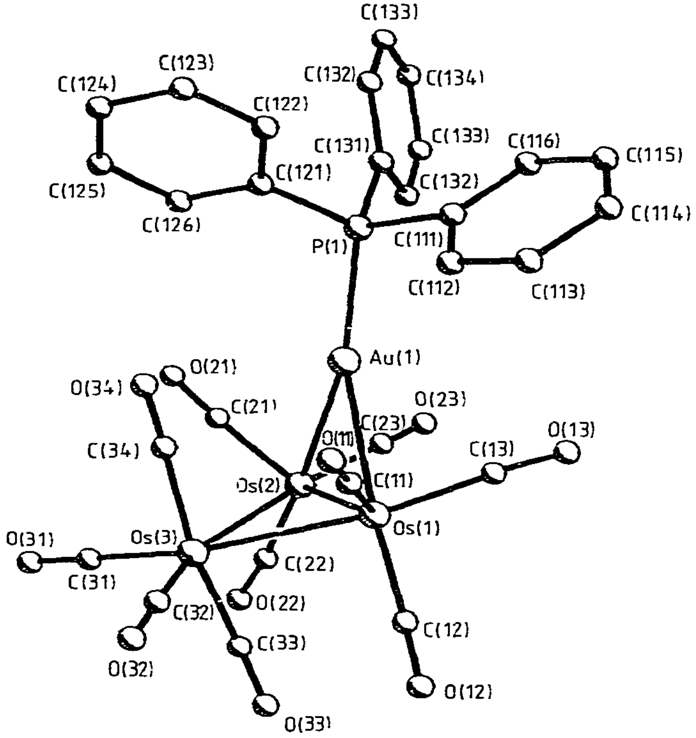

Fig. 1. The molecular structure of $HOs_3Au(CO)_{10}(PPh_3)$. Bond lengths: Os(1)—Os(2), 2.699(1); Os(1)—Os(3), 2.824(1); Os(2)—Os(3), 2.844(1); Au(1)—Os(1), 2.772(2); Au(1)—Os(2), 2.738(1); Au(1)—P(1), 2.320(7) Å. Bond angles: Os(1)—Au(1)—Os(2), 58.7(1); Os(1)—Au(1)—P(1), 141.8(2); Os(2)—Au(1)—P(1), 159.4(2)°.

In terms of electron counting $HOs_3Au(CO)_{10}(PPh_3)$ is a 58 electron system since both the gold and the hydride ligands act as one electron donors. This cluster has two electrons fewer than in the species $Os_3Au(CO)_{10}(PPh_3)X$ (X = Cl, Br, I, or SCN), where X acts as a three electron donor, and may be considered as unsaturated. In the clusters $H_2Os_3(CO)_{10}$ [3] and $HOs_5(CO)_{13}(PhNC_6H_4N)$ [4] the unsaturation is consistent with the short Os—Os bonds which are of similar length to the Os(1)—Os(2) edge in $HOs_3Au(CO)_{10}(PPh_3)$. To confirm that the short Os—Os bond did not occur in the saturated Os—Au species the molecular structure of $Os_3Au(CO)_{10}$-$(PPh_3)(SCN)$ was determined; the X-ray structures of the Cl and Br derivatives have not been published in full.

$Os_3Au(CO)_{10}(PPh_3)(SCN)$ was prepared by the reaction of $Au(PPh_3)$-(SCN) with $Os_3(CO)_{12}$ in refluxing toluene [1] and orange crystals were obtained from hexane.

Crystal data: $C_{29}H_{15}AuNO_{10}Os_3PS$, M 1368.02, monoclinic, a 15.240(5), b 8.962(4), c 26.008(9) Å, β 106.75(2)°, U 3401.48 A^3, $Z = 4$, D_c 2.67 g cm^{-3}; $\mu(Mo\text{-}K_\alpha)$ 155.97 cm^{-1}, space group $P2_1/n$. 3192 reflections were recorded on a Stoe four-circle diffractometer and corrected for absorption. 2800 unique, observed reflections ($F > 3\sigma(F)$) were used in the solution and refinement of the structure by the same techniques as for $HOs_3Au(CO)_{10}$-

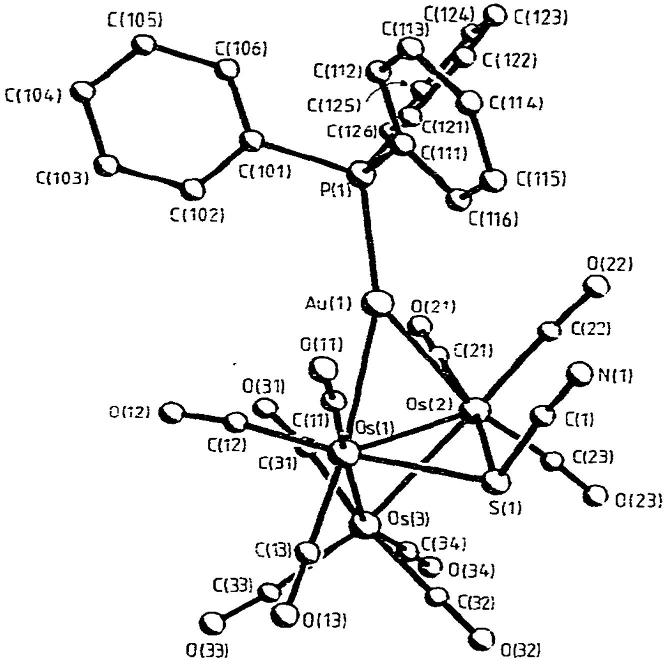

Fig. 2. The molecular structure of $Os_3Au(CO)_{10}(PPh_3)(SCN)$. Bond lengths: Os(1)—Os(2), 2.899(1); Os(1)—Os(3), 2.863(1); Os(2)—Os(3), 2.863(1); Au(1)—Os(1), 2.768(1); Au(1)—Os(2), 2.755(1); Au(1)—P(1), 2.310(4); Os(1)—S(1), 2.435(6); Os(2)—S(2), 2.421(6); S(1)—C(1), 1.73(2); C(1)—N(1), 1.12(2) Å. Bond angles: Os(1)—Au(1)—Os(2), 63.1(1); Os(1)—S(1)—Os(2), 73.3(2); Os(1)—Au(1)—P(1), 148.1(2); Os(2)—Au(1)—P(1), 146.5(1)°.

(PPh_3). The structure was refined (Os,Au,N,O,P,S, carbonyl and thiocyanate C anisotropic, phenyl H in idealised positions, C—H 1.08 Å, C—C—H 120.0°) to $R = 0.040$ and $R' = [\Sigma w^{\frac{1}{2}}\Delta/\Sigma w^{\frac{1}{2}}|F_o|] = 0.039$; the weighting scheme was $w = [\sigma^2(F) + 0.0005F^2]^{-1}$ *.

The structure of $Os_3Au(CO)_{10}(PPh_3)(SCN)$ is shown in Fig. 2, which includes some important bond parameters. The Os_3Au "butterfly" framework is observed again, but the Os_3 triangle is more nearly equilateral and it is now the longest edge which is bridged by the $Au(PPh_3)$ group and the SCN ligand. The dihedral angle between the Os(1)Os(2)Os(3) and Os(1)Os(2)Au(1) planes has widened to 133.8° and there is no longer an interaction between the Au(1) atom and an axial carbonyl on Os(3). The dimensions of the carbonyl, phosphine, and thiocyanate ligands do not deviate significantly from the expected values, and the S—C—N bond angle is 175(2)°.

The bond parameters for $H_2Os_3(CO)_{10}$ [3], $HOs_3Au(CO)_{10}(PPh_3)$, and $Os_3Au(CO)_{10}(PPh_3)(SCN)$ are shown in Table 2. The unbridged edges in all three complexes have similar bond lengths and are best considered as single bonds. The Os—Au distances in the two tetranuclear clusters are also similar

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*Atomic coordinates and bond parameter data for both compounds have been deposited with the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. They may be obtained on request from the Director if the full literature citation for the communication is given.

TABLE 2

SELECTED BOND LENGTHS AND ANGLES

	$H_2Os_3(CO)_{10}$	$HOs_3Au(CO)_{10}(PPh_3)$	$Os_3Au(CO)_{10}(PPh_3)(SCN)$
Bridged Os—Os (Å)	2.683(1)	2.699(1)	2.899(1)
unbridged Os—Os (Å)	2.815(1) [a]	2.834(1) [a]	2.863(1) [a]
Os—Au (Å)		2.755(2) [a]	2.772(2) [a]
Os—Au—Os (°)		58.7(1)	63.1(1)

[a] Average of two distances.

which indicates that any delocalisation of electron density in the hydrido complex is not centred on the Au atom. This leaves the bridged edges in the three clusters. In the two unsaturated species the bond lengths are significantly shorter than single bond values while the bridged edge in the thiocyanate complex is similar to the other Os—Os bond lengths in the cluster. The unsaturation in $HOs_3Au(CO)_{10}(PPh_3)$ appears to be localised on the bridged Os—Os bond and the $Au(PPh_3)$ coordinates to the cluster in a similar manner to a hydride in $H_2Os_3(CO)_{10}$. The molecule therefore contains two potential acceptor centres, the gold and the unsaturated Os—Os link. Preliminary experiments indicate a facile adding of nucleophiles to the molecule including the reversible uptake of carbon monoxide.

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