Reaction of the Unsaturated Mixed Metal Cluster $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}AuPR_3)]$ (R=Ph, Et) with Carbon Monoxide and the Chemistry of the Products; the *X*-Ray Crystal Structure of $[Os_3(CO)_{10}(\mu\text{-}AuPEt_3)_2]$

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The cluster $[Os_3(CO)_{10}(AuPR_3)_2]$(R=Ph, Et) may be prepared by the decarbonylation of $[Os_3(CO)_{11}(AuPR_3)_2]$, or by the direct reaction of $[Os_3H(CO)_{11}]^-$ or $[Os_3(CO)_{11}]^{2-}$ with two equivalents of $Au(PR_3)Cl$; an *X*-ray analysis of $[Os_3(CO)_{10}(AuPR_3)_2]$ shows that both '$AuPR_3$' groups bridge the same short edge of the Os_3 triangle.

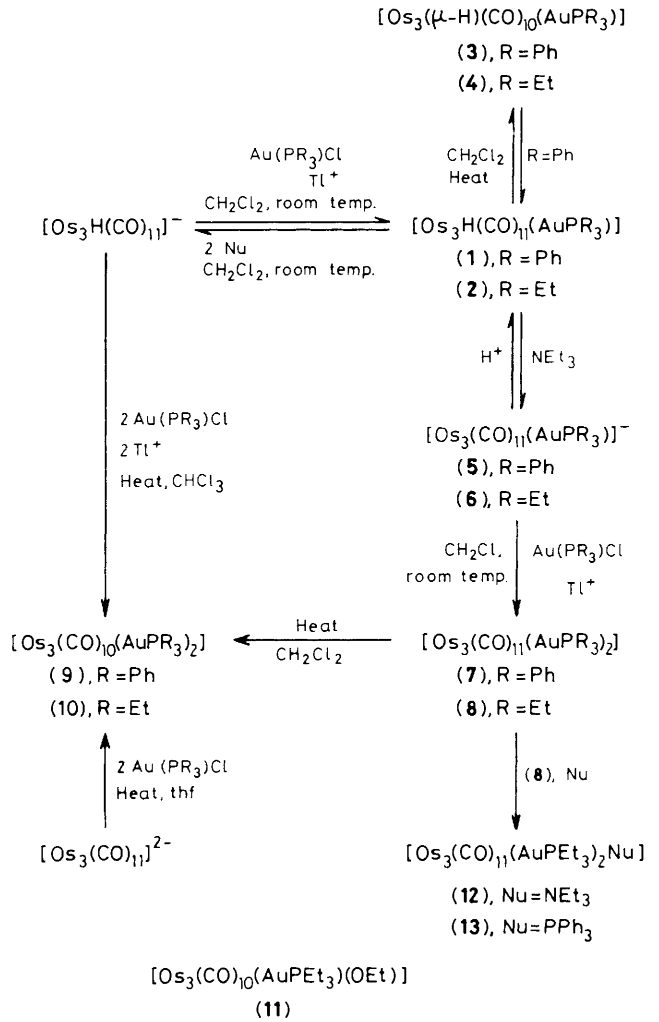
The cluster $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ has proved to be a most useful reagent in triosmium cluster chemistry, readily undergoing addition reactions with a wide range of donor species.[1] The compound is formally electron deficient having only 46 valence electrons. This 'unsaturation' is thought to be localised across one of the Os–Os bonds which is bridged by the two hydrides and is anomalously short.[2] This bond is the site of most of the reactions of the cluster. The complex $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}AuPR_3)]$ (R = Ph, Et) is also formally unsaturated and displays a geometry[3] similar to that of the dihydride. This cluster might be expected to prove a useful reagent in mixed-metal cluster chemistry, and in this communication we present an account of the chemistry of $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}AuPR_3)]$ and of some of its derivatives.

The cluster salt $[(Ph_3P)_2N][Os_3H(CO)_{11}]$ reacts with $Au(PR_3)Cl$ (R = Ph, Et) in CH_2Cl_2 in the presence of $TlPF_6$ to give quantitative yields of $[Os_3H(CO)_{11}(AuPR_3)]$ [R = Ph (**1**), Et (**2**)] which has been characterised by spectroscopic techniques.

When CH_2Cl_2 solutions of the clusters (**1**) or (**2**) are heated under reflux the previously reported[3] complexes $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}AuPR_3)]$ [R = Ph (**3**), Et (**4**)] are obtained by the loss of carbon monoxide. For complex (**3**) the reaction is reversible but for complex (**4**) a pressure of CO causes cluster fragmentation. This difference in reactivity between the two different phosphine species may reflect the smaller steric bulk of the PEt_3 group, or complex (**4**) may show a greater electronic activation of the presence of the more basic phosphine. The similarity because of the reaction of CO with (**3**) to that with $[Os_3(\mu\text{-}H)_2(CO)_{10}]$[4] indicates the similarity between a hydride and a bridging '$AuPR_3$' unit in these systems, and complexes (**3**) and (**4**) may be considered as homologues to the dihydride.

This chemical parallel between the clusters can be pursued further. While neither $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ nor $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}AuPR_3)]$ is acidic, the CO adducts, $[Os_3H_2(CO)_{11}]$ and $[Os_3H(CO)_{11}(AuPR_3)]$, (**1**) and (**2**), can both be deprotonated in a reversible reaction. In the case of the gold complex the product is $[Os_3(CO)_{11}(AuPR_3)]^-$ [R = Ph (**5**), Et (**6**)]. The anions (**5**) and (**6**) have only been characterised by i.r. spectroscopy and their protonation is complicated by the protonation of (**1**) and (**2**) by excess of acid.

Complex (**2**) also reacts with nucleophiles such as PPh_3 and Cl^- to give the anion $[Os_3H(CO)_{11}]^-$ in a reaction that is the reverse of the formation of (**1**) and (**2**) and is analogous to the base-induced deprotonation of a hydrido cluster.[5] The anions (**5**) and (**6**) react with excess of $Au(PR_3)Cl$ in CH_2Cl_2, in the presence of $TlPF_6$, to add a second '$AuPR_3$' unit giving the known[6] complexes $[Os_3(CO)_{11}(AuPR_3)_2]$ [R = Ph (**7**), Et (**8**)].



Scheme 1. Nu = nucleophile.

The characterisation of these species was confirmed by spectroscopic techniques.†

When CH_2Cl_2 solutions of (7) and (8) are heated under reflux carbon monoxide is readily lost and $[Os_3(CO)_{10}(AuPR_3)_2]$ [R=Ph (**9**), Et (**10**)] is obtained in 35% yield. Complexes (**9**) and (**10**) may be obtained in one step, and in 80% yield, by the reaction of $[Os_3H(CO)_{11}]^-$ with two equivalents of $Au(PR_3)Cl$ in $CHCl_3$, in the presence of $TlPF_6$. Another route to (**9**) and (**10**) is *via* the $[Os_3(CO)_{11}]^{2-}$ dianion, obtained by the reduction of $[Os_3(CO)_{12}]$ in tetrahydrofuran (thf) with potassium–benzophenone. This solution is treated with two equivalents of $Au(PR_3)Cl$, and the product obtained in 60% yield. All these reactions are summarised in Scheme 1.

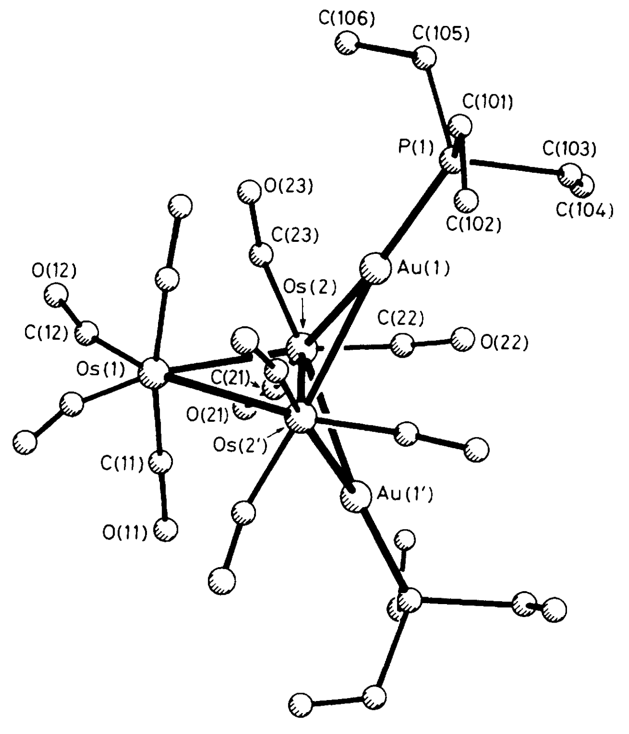


Figure 1. The molecular structure of $[Os_3(CO)_{10}(AuPEt_3)_2]$ (**10**). Bond lengths: Os(1)–Os(2), 2.830(1); Os(2)–Os(2′), 2.684(1); Os(2)–Au(1), 2.760(1); Os(2)–Au(1′), 2.762(1); Au(1)–P(1), 2.287(6) Å. Bond angles: Os(2)–Au(1)–Os(2′), 58.2(1); Os(2)–Os(1)–Os(2′), 56.6(1); Os(2)–Au(1)–P(1), 151.3(2)°.

Under the same conditions $[Os_3H(CO)_{10}(COCH_2Ph)]$ gives (**10**) in 22% yield but when $[Os_3(CO)_{10}(OEt)_2]$ is used the major product is the cluster $[Os_3(CO)_{10}(AuPEt_3)(OEt)]$ (**11**). These complexes were characterised by spectroscopic techniques.†

It can be seen that (**9**) and (**10**) represent the next members of the homologous series $[Os_3(CO)_{10}(X)_2]$ (X=H, 'AuPR$_3$'). In order to determine the molecular geometry of the digold species a single-crystal *X*-ray diffraction study of (**10**) was undertaken.‡ The molecular structure is illustrated in Figure 1 together with some important bond parameters. The three Os atoms define an isosceles triangle the shorter edge of which is bridged on both sides of the Os_3 plane by the two 'AuPEt$_3$' units. The molecule exhibits crystallographic C_2 symmetry, with the two-fold axis passing through Os(1) and bisecting the Os(2)–Os(2′) bond. The dihedral angle between the Os(1)Os(2)-Os(2′) and the Os(2)Os(2′)Au(1) planes is 116.9°, while that between Os(2)Os(2′)Au(1) and Os(2)Os(2′)Au(1′) is 53.8°. There is no direct Au–Au interaction, and the interatomic separation of 4.304(2) Å is in marked contrast to the related

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† Selected spectroscopic data: ^1H n.m.r. ($CHCl_3$): (**1**), δ −4.48 (d, J_{H-P} 15.6 Hz); (**2**), δ −4.49 (d, J_{H-P} 15.7 Hz); (**9**) δ 7.78—7.64 (m); (**10**), δ 1.80—1.51 (m, 6H) and 1.30—0.95 (m, 9H); (**11**), δ 3.53 (q, *J* 7 Hz, 2H), 2.05—1.81 (m, 6H), and 1.41—1.03 (m, 12H); i.r. ν_{CO}/cm^{-1} (CH_2Cl_2): (**1**) 2108(w), 2057(m), 2039(m), 2024(s), 2000(m), and 1973(m,br); (**5**) 2067(w), 2044(w), 2002(sh), 1993(s), 1981(sh), 1924(w), and 1595(w); (**7**) 2111(m), 2067(m), 2031(s), 2020(sh), 2000(m), 1978(sh), 1955(sh), and 1931(sh); (**9**) 2067(w), 2012(s), 1977(m), 1965(w), and 1937(m); (**11**) 2093(m), 2039(s), 2013(s), 2004(s), 1983(w), 1971(m), and 1957(s); (**12**) 2093(m), 2044(s), 2012(vs), 1972(w), 1956(w), and 1910(w); *m/z*: (**2**), 1172; (**8**), 1485; (**10**), 1486; (**11**), 1216; (**12**), 1480.

‡ *Crystal data:* $C_{22}H_{30}Au_2O_{10}Os_3$, M = 1419.0, monoclinic, space group $I2/c$, a = 13.701(3), b = 14.982(4), c = 17.512(5) Å, β = 103.47(2)°, U = 3495.8 Å^3, Z = 4, D_c = 2.695 g cm^{-3}, $F(000)$ = 2632, graphite-monochromated Mo-K_α radiation, λ = 0.71069 Å, μ(Mo-K_α) = 193.21 cm^{-1}. 3523 Intensities were recorded ($3.0 < 2\theta \leqslant 50.0°$) on a Syntex $P2_1$ diffractometer and were corrected for absorption. 2663 Reflections [$F > 5\sigma(F)$] were used to solve (direct methods and Fourier difference techniques) the structure which was refined by full-matrix least-squares (Au, Os, P, O, and carbonyl C anisotropic; ethyl C common isotropic; these atoms are disordered and were refined with partial occupancies) to R = 0.076 and R_w = 0.078. 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.

species $[Os_3(CO)_{11}(AuPPh_3)_2]$[6] and $[Os_4H_2(CO)_{12}(AuPPh_3)_2]$[7] where the Au–Au distances are 2.845(1) and 2.793(4) Å, respectively. The structure of (**10**) is closely related to that of the dihydride, $[Os_3(\mu\text{-}H)_2(CO)_{10}]$,[2] where the length of the hydride-bridged Os–Os bond [2.681(1) Å] is not significantly different from that in (**10**). The average unbridged Os–Os distance of 2.815(2) Å in the dihydride is only marginally shorter than the value in (**10**). The two Au atoms symmetrically bridge the Os(2)–Os(2′) bond, and the Os–Au distances in (**10**) are similar to the average value of 2.76(1) Å in $[Os_3H(CO)_{10}(AuPPh_3)]$.[3] In the latter complex the Au atom is considered to be sp hybridized. In this way one lobe of the sp hybrid orbital points towards the mid-point of the bridged Os–Os bond and the '$AuPPh_3$' unit donates one electron to the cluster in a manner similar to a hydride. The bonding of the two '$AuPPh_3$' groups to the cluster in (**10**) may be described in an analogous manner. The Os(2)Os(2′)Au(1)Au(1′) unit may then be thought of as a four-centre four-electron system. An essentially similar bonding scheme has been used to describe the Os_2H_2 unit in $[Os_3(\mu\text{-}H)_2(CO)_{10}]$.[8]

In the case of (**10**) the structural similarity to the dihydride is not reflected in the chemistry of the CO adduct. The reaction of (**8**) with nucleophiles might be expected to yield the anion $[Os_3(CO)_{11}(AuPEt_3)]^-$, but, in fact, it results in the formation of an adduct, $[Os_3(CO)_{11}(AuPEt_3)_2(Nu)]$ [Nu = NEt_3 (**12**), PPh_3 (**13**)]. This reaction is reversible for Nu = NEt_3. The difference between the behaviour of this species and that of the other CO adduct may reflect the greater steric crowding around the Au centres, in this case, which would prevent dissociation since a double nucleophilic attack would be required to give a stable gold cation.

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