The Synthesis and X-Ray Crystal Structure of the Mixed-metal Cluster [Os$_8$(CO)$_{22}$(AuPPh$_3$)$_2$]

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The bicapped octahedral dianion [Os$_8$(CO)$_{22}$]$^{2-}$ reacts with AuPPh$_3$Cl to give [Os$_8$(CO)$_{22}$(AuPPh$_3$)$_2$], the structure of which has been established by a single crystal X-ray analysis; for the first time in such reactions the anionic metal geometry has changed and the resulting Os$_8$Au$_2$ framework may be described as two octahedra sharing an edge but with one equatorial metal–metal bond missing.

The synthesis of mixed-metal carbonyl clusters containing the 'AuPR$_3$' unit has been the subject of a number of recent

studies.[1-3] This is partly because these clusters may show enhanced reactivity due to the introduction of increased

polarity in the molecule *via* the metal–gold bonds and because there are empty *p* orbitals available on the Au atoms. These clusters are also of interest because of the variety of co-ordination modes that may be adopted by the other metal atom. In complexes containing one 'AuPR$_3$' unit the gold atom has been found in edge-bridging {as in [Os$_3$(μ-H)(CO)$_{10}$-(μ-AuPPh$_3$)]}[4] or face bridging {as in [Ru$_6$C(CO)$_{15}$(NO)(μ_3-AuPPh$_3$)]}[5] positions. Molecular orbital calculations[6] indicate that the 'AuPR$_3$' fragment and a hydride have similar bonding characteristics; consequently the structures of complexes containing one Au atom may often be predicted by reference to the geometry of the analogous hydrido-derivative. When more than one 'AuPR$_3$' unit is involved in co-ordination to the cluster the situation becomes more complicated. There are examples where there is no apparent interaction beween the gold atoms, as in [Fe$_5$C(CO)$_{14}$(μ_2-AuPEt$_3$)(μ_4-AuPEt$_3$)][3] or [Ru$_6$C(CO)$_{16}$(AuPPh$_2$Me)$_2$][7], but in [Ru$_3$(CO)$_9$(μ_3-COMe)-(AuPPh$_3$)$_3$][2] and [Os$_4$(μ-H)$_2$(CO)$_{12}$(AuPPh$_3$)$_2$][8] there are direct Au–Au bonds. These observations may indicate that there is little gain in energy upon formation of Au–Au bonds. Prediction of the overall structure of products containing more than one 'AuPR$_3$' unit is therefore difficult. In all the reactions examined to date, however, no rearrangement of the anionic metal framework is observed upon the addition of '[AuPR$_3$]$^+$' groups; this is consistent with the predictions of Wade theory[9] since this cation formally donates no electrons to the cluster for skeletal bonding.
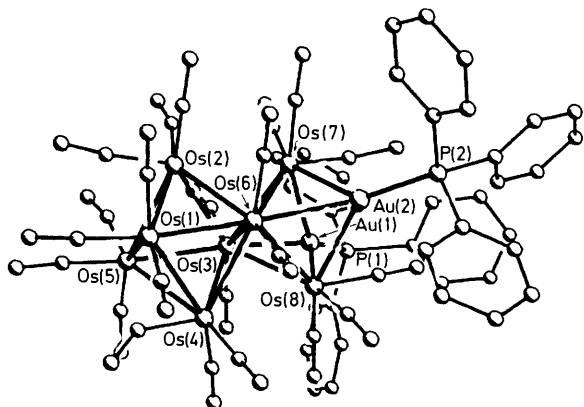

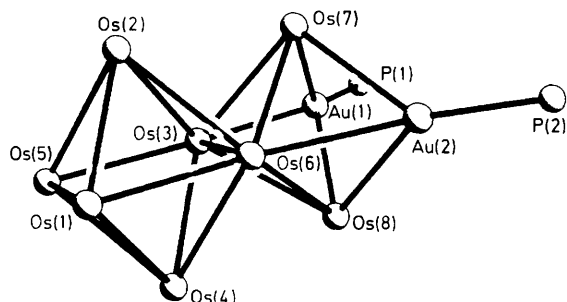**Figure 1.** The molecular structure of [Os$_8$(CO)$_{22}$(AuPPh$_3$)$_2$].

Figure 2. The cluster core geometry in [Os$_8$(CO)$_{22}$(AuPPh$_3$)$_2$]. Bond lengths: Os(1)–Os(2), 2.904(3); Os(1)–Os(4), 2.896(3); Os(1)–Os(5), 2.990(3); Os(1)–Os(6), 2.786(3); Os(2)–Os(3), 2.882-(3); Os(2)–Os(5), 2.893(3); Os(2)–Os(6), 2.864(3); Os(2) ... Os(7), 3.142(3); Os(3)–Os(4), 2.858(3); Os(3)–Os(5), 2.774(3); Os(3)–Os(6), 2.859(2); Os(3)–Os(7), 2.781(3); Os(3)–Os(8), 2.802(3); Os(4)–Os(5), 2.901(3); Os(4)–Os(6), 2.878(3); Os(4) . . . . Os(8), 3.108(3); Os(6)–Os(7), 2.806(3); Os(6)–Os(8), 2.785(3); Os(7) . . . Os(8), 3.373(3); Au(1)–Os(3), 2.740(3); Au(1)–Os(7), 3.003(3); Au(1)–Os(8), 2.952(3); Au(2)–Os(6), 2.765(3); Au(2)–Os(7), 2.976(3); Au(2)–Os(8), 2.948(3); Au(1)–P(1), 2.276(14); Au(2)–P(2), 2.303(15) Å.

We now report the reaction of the dianion [Os$_8$(CO)$_{22}$]$^{2-}$ (**1**) with 2 equiv. of '[AuPR$_3$]$^+$' to give the neutral complex [Os$_8$(CO)$_{22}$(AuPPh$_3$)$_2$] (**2**) during which a major rearrangement of the Os$_8$ skeleton occurs.

Reaction of the salt [PPh$_3$Me]$_2$[Os$_8$(CO)$_{22}$] with 2 equiv. of [AuPPh$_3$]Cl in the presence of [Tl][PF$_6$] (which acts as a chloride acceptor) in CH$_2$Cl$_2$, gives the neutral cluster [Os$_8$-(CO)$_{22}$(AuPPh$_3$)$_2$] (**2**) as the only product. The complex (**2**), which exhibits ν_{CO} stretching frequencies at 2091w, 2086m, 2050vs, 2042s(sh), 2022w, and 2002w cm^{-1} in CH$_2$Cl$_2$, was purified by t.l.c. using CH$_2$Cl$_2$–hexane (4:1) as eluant and obtained in 65% yield by recrystallisation from CH$_2$Cl$_2$–hexane. No parent ion was detected in the mass spectrum of (**2**), but fragments consistent with the above formulation were observed. Dark brown crystals of (**2**) suitable for *X*-ray analysis were obtained.

Crystal data: C$_{58}$H$_{30}$Au$_2$O$_{22}$Os$_8$P$_2$, M = 3055.6, orthorhombic, space group *Pna*2$_1$, a = 26.192(6), b = 25.030(6), c = 10.404(3) Å^3, Z = 4, D_C = 2.97 g cm^{-3}, $F(000)$ = 4534, μ(Mo-K_α) = 170.48 cm^{-1}. 4166 intensities in the range $5 < 2\theta < 45°$ were recorded on a Syntex *P*2$_1$ diffractometer using graphite-monochromated Mo-K_α radiation. 2979 absorption-corrected data with $F > 4\sigma$ (F) were used to solve (direct methods and Fourier difference syntheses) and refine (blocked full matrix) the structure. The Os and Au atoms were assigned anisotropic thermal parameters; the phenyl rings were refined as rigid bodies with phenyl H atoms in idealised positions. The final residuals were R = 0.053 and R^1 = $[\Sigma w^{\frac{1}{2}}\Delta/\Sigma w^{\frac{1}{2}}|F_o|]$ = 0.053.†

The overall molecular structure of (**2**) is illustrated in Figure 1, while the cluster core together with selected bond parameters is shown in Figure 2. The geometry of the ten-metal-atom framework resembles that observed in the [Ru$_{10}$C$_2$(CO)$_{24}$]$^{2-}$ dianion,[10] although there are significant distortions from this geometry which are related to the introduction of the 'AuPPh$_3$' units. The metal framework in (**2**) may be described as an octahedron of Os atoms [Os(1)–Os(6)] with one edge bridged by two more Os atoms [Os(7) and Os-(8)] in such a manner as to produce a pseudo Os$_4$ 'butterfly' arrangement [Os(3),Os(6),Os(7),Os(8)] on the side of the octahedron. The distance between the two bridging atoms, Os(7) and Os(8), is 3.373(4) Å, and is rather too long to indicate a significant bonding interaction. The distances between the bridging Os atoms and the apical Os atoms of the octahedron are somewhat shorter [Os(2) ... Os(7), 3.142(3) Å; Os(4) ... Os(8), 3.108(3) Å] and are similar to the equivalent distances in [Ru$_{10}$C$_2$(CO)$_{24}$]$^{2-}$.[10] The Au atoms of the 'AuPPh$_3$' groups cap the open sides of the 'butterfly' [Os(3),Os(7),Os(8) and Os(6),Os(7),Os(8)] to give a distorted edge-fused diocta-hedral metal arrangement; the Au(1) . . . Au(2) distance of 4.534(1) Å is non-bonding. This distortion from an octa-hedral arrangement is probably in part due to the bonding requirements of these fragments.[6] All 22 carbonyl groups are terminally co-ordinated to the cluster, two each being bonded to Os(3) and Os(6), and three each to the remaining Os atoms.

The structure of (**2**) shows that a gross overall change in the Os$_8$ polyhedron from the bicapped octahedral arrangement in [Os$_8$(CO)$_{22}$]$^{2-}$ (**1**)[11] has occurred upon the reaction with '[AuPR$_3$]$^+$' and demonstrates another facile structural transformation in Os$_8$ cluster chemistry. Previously we have shown that the metal frameworks in large clusters, especially those containing eight Os atoms, are flexible and undergo extensive
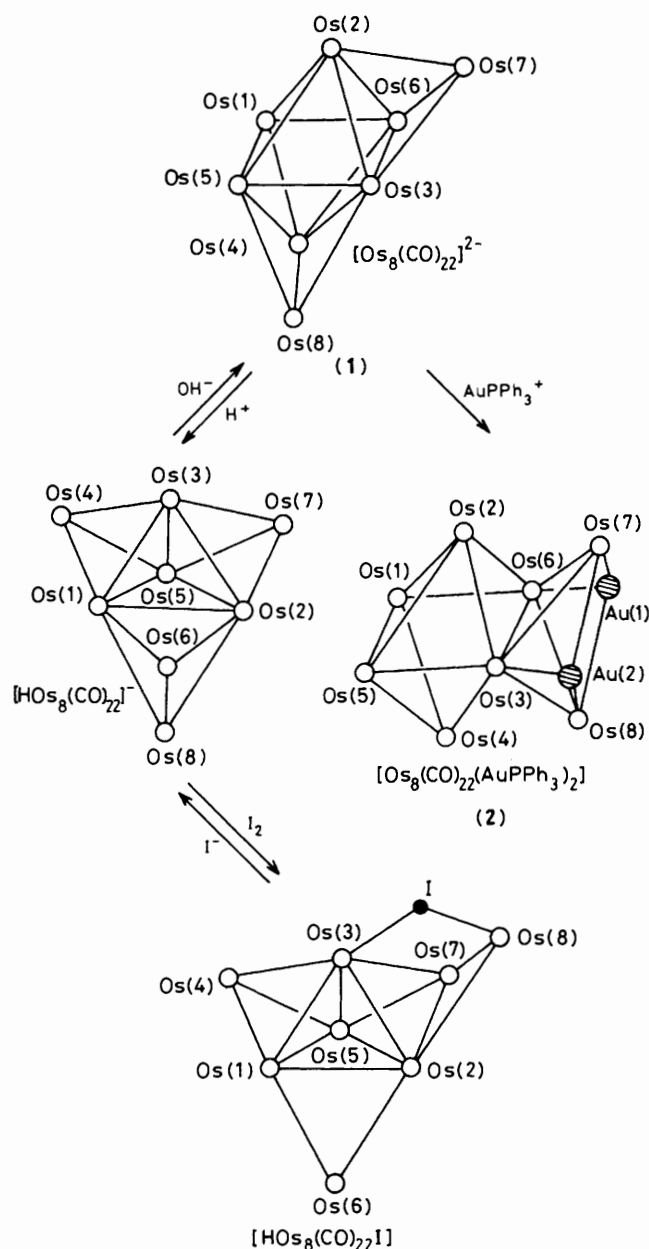
Scheme 1. Transformations in Os_8 cluster frameworks.

rearrangement upon protonation[12] or addition of I^+ (from I_2)[13] (see Scheme 1). In fact all the crystallographically character-ised M_8 clusters exhibit different metal core geometries.

This work emphasizes the suggestion that the energy differences between various Os_8 structures is small.[12] This, coupled with the fact that there is no interstitial atom to 'bind' the metals together, means that polyhedral rearrangements can readily occur. In this respect it is interesting to note that in the formation of $[Fe_5C(CO)_{14}(\mu_2\text{-}AuPEt_3)(\mu_4\text{-}AuPEt_3)]^3$ and $[Ru_6C(CO)_{16}(AuPPh_2Me)_2]^7$ from their respective dianions the carbido-atom is believed to play an important role in anchor-ing the cluster together.

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