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Preliminary communication

STRUCTURE AND BONDING IN Au_2Os MIXED-METAL CARBONYL CLUSTERS: THE CRYSTAL AND MOLECULAR STRUCTURE OF $[Os(CO)_4\{AuPPh_3\}_2]$

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Summary

An X-ray analysis of $[Os(CO)_4\{AuPPh_3\}_2]$ shows that the metal atoms define an isosceles triangle in which the Au—Au distance is 2.929(1) Å, which is ca. 0.1 Å shorter than in the corresponding iron analogue $[Fe(CO)_4\{AuPPh_3\}_2]$.

Although polynuclear metal complexes containing gold-phosphine units were some of the earliest mixed-metal clusters to be studied [1], it is only within the last few years that X-ray crystallographic studies have allowed the structure and bonding in these complexes to be investigated [2,3,4]. In these systems the $AuPR_3$ units are considered to bond to two or three other metal atoms using what may be thought of as a lobe of a *sp* or *sd* hybrid orbital, the Au atom being assigned a formal oxidation state of +1. The bonding of the $AuPR_3$ group may then be considered as similar to that of a hydride atom, and, indeed, the structures of mixed-metal complexes containing one $AuPR_3$ group are very similar to their hydrido analogues [4,5]. This isolobal analogy between a hydride and a coordinated gold-phosphine has proved useful in this area of chemistry. However, when more than one $AuPR_3$ unit is present in a cluster there often appears to be an interaction between the Au atoms and the structures differ markedly from the hydrido analogues [6]. In these cases the isolobal analogy breaks down. Molecular orbital calculations [7] show that the frontier orbitals for the $AuPR_3$ fragment are comprised of an outward pointing a_1 hybrid orbital and a degenerate set of e orbitals at much higher energy. When combined these fragments have the capability of forming multicentre two-electron interactions [8].

A number of trinuclear cluster complexes containing two $AuPR_3$ groups are known, and there have been recent structural analyses on

$[Fe(CO)_4\{AuPPh_3\}_2]$ [9] and the related complexes $[Fe(CO)_4Au_2(dppm)]_2$ (dppm = $(Ph_2P)_2CH_2$) and $[Fe(CO)_4Au_2(dppe)]_2$ (dppe = $[Ph_2P)_2C_2H_4$), where the phosphine ligands act as bidentate groups [10]. The structure of $[Fe(CO)_4Au_2(dppm)]_2$ may be described as a rhomboid of Au atoms bonded with two μ_2-$Fe(CO)_4$ groups, while in the structures of $[Fe(CO)_4\{AuPPh_3\}_2]$ and $[Fe(CO)_4Au_2(dppe)]_2$ there are discrete $FeAu_2$ triangles of metal atoms. The Au—Au separation in $[Fe(CO)_4\{AuPPh_3\}_2]$ (3.028(1) Å) is longer than in $[Fe(CO)_4Au_2(dppe)]_2$ (2.977(1) Å) and it has been suggested that there is a weaker Au—Au interaction in the former, the bonding to the $Fe(CO)_4$ group having a greater contribution from 2-centre 2-electron Au—Fe bonds. The shorter distance in the latter may indicate a greater contribution from a delocalised 3-centre 2-electron Au_2Fe bond. It is of interest to compare the bonding interactions in these clusters with those in the analogous Os containing clusters, since Fe and Os clusters frequently exhibit different bonding characteristics. In this communication we report the crystal and molecular structure of $[Os(CO)_4\{AuPPh_3\}_2]$.

Crystal data: $C_{40}H_{30}Au_2O_4OsP_2$, M 1220.72, orthorhombic, a 13.039(3), b 15.851(2), c 18.499(3) Å, U 3823.39 Å^3, $Z = 4$, D_c 2.120 g cm^{-3}, $F(000)$ 2264, λ(Mo-K_α) 0.71069 Å, μ(Mo-K_α) 110.39 cm^{-1}, space group $Pc2_1n$ (non-standard setting of $Pna2_1$, No. 33). The Os and Au atoms were located by random tangent expansion and the remaining non-hydrogen atoms from subsequent electron density difference syntheses. The structure was refined by full-matrix least squares (Os, Au, P, and carbonyl C, O anisotropic). The phenyl rings were refined as rigid groups (C—C, 1.395 Å; C—C—C, 120.0°) with individual isotropic temperature factors, and the phenyl H atoms were placed in idealised positions (C—H, 1.08 Å; C—C—H, 120.0°) and constrained to ride on the relevant C atom; the H atoms were assigned a common isotropic temperature factor. 7517 profile fitted reflections were recorded on a Stoe four-sircle diffractometer with an ω/θ scan technique. The current residuals for the 2923 observed reflections $[F > 4\sigma(F)]$ are $R = 0.047$ and $R' = [\Sigma\omega^{\frac{1}{2}}\Delta/\Sigma\omega^{\frac{1}{2}}|F_o|] = 0.048$. The weighting scheme employed was $\omega = 2.343/[\sigma^2(F) + 0.00087F^2]$.

The molecular structure of $[Os(CO)_4\{AuPPh_3\}_2]$ is shown in Fig. 1, together with some important bond parameters. The three metal atoms lie at the vertices of an approximately isosceles triangle in which the long edge is defined by the Au—Au vector. The Au_2Os triangle is essentially coplanar with the two equatorial carbonyl groups bonded to Os(1) and the P atoms or the triphenylphosphine groups (maximum deviation is 0.15 Å for Au(2)). There are no particularly short intramolecular contacts within the structure, the shortest is 2.88 Å between C(221) and H(106) on adjacent phenyl rings; the dihedral angle between the rings C(101)—C(106) and C(221)—C(226) is 58.6°. The P(1)...P(2) distance is 5.82 Å. Neither are there intermolecular contacts which are significantly shorter than the sum of the Van der Waals radii, the shortest being 2.76 Å between C(205) and H(126) where the second atom is related by the symmetry operation $(x - \frac{1}{2};\ y + \frac{1}{2}, \frac{1}{2} - z)$. It is apparent from an analysis of the non-bonded contacts within the crystal structure that the observed geometry is more likely to be a result of electronic rather than steric factors.

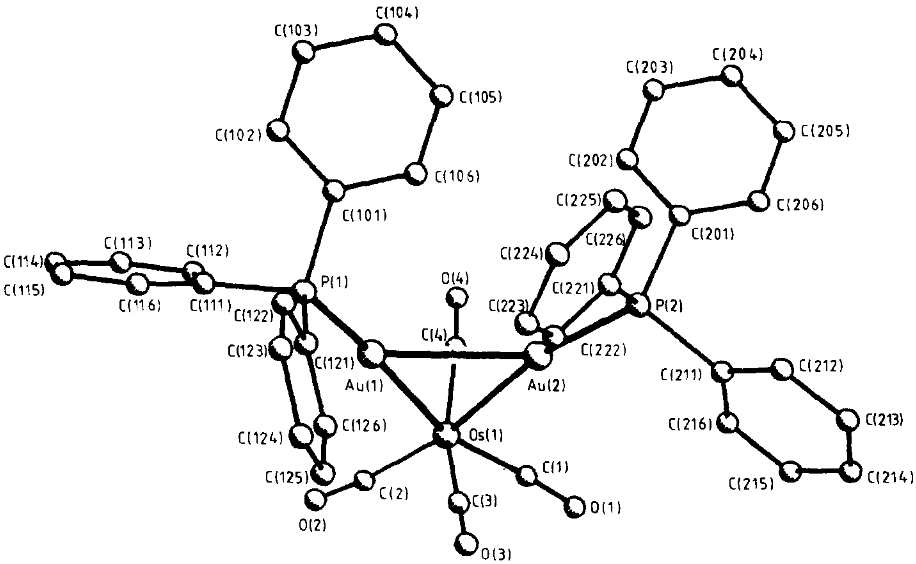

Fig. 1. The molecular structure of $[Os(CO)_4\{AuPPh_3\}_2]$. Bond lengths: Au(1)—Au(2), 2.929(1); Au(1)—Os(1), 2.667(1); Au(2)—Os(1), 2.646(1); Au(1)—P(1), 2.226(6); Au(2)—P(2), 2.324(6); Os(1)—C(1), 1.91(4); Os(1)—C(2), 1.96(4) Å. Bond angles: Au(1)—Os(1)—Au(2), 66.9(1); Os(1)—Au(1)—Au(2), 56.2(1); Os(1)—Au(2)—Au(1), 56.9(1); P(1)—Au(1)—Os(1), 174.1(1); P(1)—Au(1)—Au(2), 124.5(2); P(2)—Au(2)—Os(1), 168.2(2); P(2)—Au(2)—Au(1), 131.3(3); C(1)—Os(1)—C(2), 101(2)°.

The Au(1)—Au(2) distance in $[Os(CO)_4\{AuPPh_3\}_2]$ is ca. 0.1 Å shorter than the equivalent distance in the Fe analogue [9], and the Au—Os—Au angle is reduced by ca. 6° when compared to the equivalent Au—Fe—Au angle of 73°. The C(1)—Os—C(2) angle, however, is not significantly different from the C—Fe—C angle of 102° in $[Fe(CO)_4\{AuPPh_3\}_2]$. The Au(1)—Au(2) distance in $[Os(CO)_4\{AuPPh_3\}_2]$ is also ca. 0.05 Å shorter than the equivalent distance in $[Fe(CO)_4Au_2(dppe)]_2$ [10]. The acute Au—Os—Au and Au—Fe—Au angles in these systems are indicative of an interaction between the Au atoms, and may be contrasted, for example, with the I—Ru—I angle of 92.9° in *cis*-$[Ru(CO)_4I_2]$ where the Ru—I distances (2.72 Å) are similar to the Os—Au distances under discussion and there is no direct interaction between the iodine atoms [11]. If there is, indeed, a correlation with Au—Au distance and Au—M—Au angle it would appear that there is a stronger interaction between the Au atoms in $[Os(CO)_4\{AuPPh_3\}_2]$ than in the Fe analogue. This may indicate a greater contribution of a 3-centre 2-electron interaction to the bonding scheme, as proposed for $[Fe(CO)_4Au_2(dppe)]_2$ [10], than occurs in $[Fe(CO)_4\{AuPPh_3\}_2]$.

The Au(1)—Os(1) and Au(2)—Os(1) bond lengths in $[Os(CO)_4\{AuPPh_3\}_2]$ are also significantly shorter than the average distances of 2.755(4) and 2.762(4) Å for the Au—Os bonds in the tetranuclear complexes $[Os_3H(CO)_{10}(AuPPh_3)]$ and $[Os_3(SCN)(CO)_{10}(AuPPh_3)]$ [3], respectively. As with the $Fe(CO)_4$ unit in $[Fe(CO)_4Au_2(dppe)]_2$ [10] the $Os(CO)_4$ unit exhibits a coordination geometry which is intermediate between tetrahedral and C_{2v} *cis*-divalent octahedral with C—Fe—C angles between 91(1) and 157(1)°.

A simple view of the bonding in [$Os(CO)_4\{AuPPh_3\}_2$] might invoke the use of *sp* or *sd* hybridized orbitals on the formally gold(I) atoms interacting with each other and with an orbital on the Os atom to form a "closed" three centre bonding molecular orbital. The inclusion of *d* orbitals [12] in the bonding scheme results in hybrid orbitals which are tangential [13] with respect to the Os—Au vectors and permits direct bonding orbital overlap between the Au atoms strengthening the Au—Au bonding.

Atomic coordinates and bond parameter data for [$Os(CO)_4\{AuPPh_3\}_2$] 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.

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