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# UNUSUAL DEGRADATION REACTION OF ICOSAHEDRAL CLUSTER COMPOUNDS OF GOLD WITH CHELATING DIPHOSPHANES AND THE X-RAY STRUCTURE OF DI{BIS(DIPHENYLPHOSPHINO)METHANIDO}-DIGOLD(I), $\{Au(Ph_2P)_2CH\}_2$

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## Summary

Addition of $Ph_2PCH_2PPh_2$ (dppm) to icosahedral tertiary-phosphane cluster compounds of gold leads to the isolation of a mixture of the binuclear gold(I) complexes $Au_2X_2(dppm)_2$ (X = Cl or Br) and $Au_2(dppm\text{-}H)_2$ (dppm-H = $Ph_2PCHPPh_2^-$). The latter has been characterised by a single crystal X-ray structural determination, which has shown the molecule to contain an eight membered $Au_2P_4C_2$ ring, with linear coordination about the gold atoms and a gold—gold distance of 2.888(3) Å.

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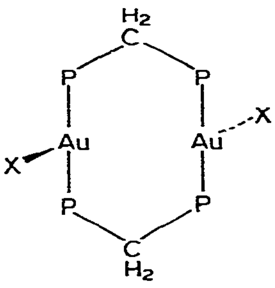
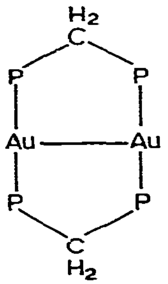
Addition of monodentate phosphanes to the newly discovered centred icosahedral gold cluster compounds [1] leads to a decrease in cluster nuclearity according to the following equation:

$$[Au_{13}Cl_2(PMe_2Ph)_{10}](PF_6)_3 + 2PMe_2Ph \rightarrow [Au_{11}(PMe_2Ph)_{10}](PF_6)_3 + 2AuCl(PMe_2Ph)$$

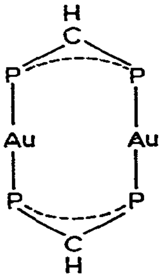
Therefore, it was of interest to determine whether the corresponding reaction with chelating diphosphanes proceeded in an analogous fashion. Addition of dppm (dppm = $Ph_2PCH_2PPh_2$) to acetone solutions of either $[Au_{13}Cl_2(PMe_2Ph)_{10}](PF_6)_3$ or $[Au_{13}Br_4(PMePh_2)_8]Br$ led to their decolourisation after a period of several hours. On standing at room temperature for approximately 24 h a mixture of colourless (Ia, X = Cl, and Ib, X = Br) and yellow (II) crystals had separated from the solution. The former were characterised as $Au_2X_2(dppm)_2$ on the basis of elemental analyses and a comparison of spectroscopic data with samples prepared by more conventional routes [2].



(I)



(IIa)

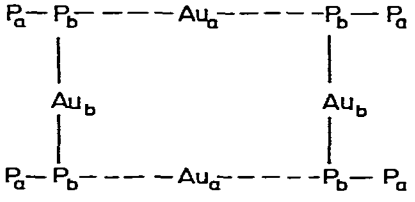


(IIb)

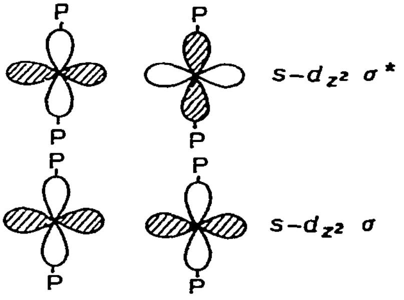
Compound II analysed correctly for $Au_2(dppm)_2$ and its mode of synthesis suggested that it might represent an unusual example of a dimeric gold(0) compound [3] (see IIa). The compound proved to be too insoluble for $^1H$ or $^{31}P$-$\{^1H\}$ NMR studies, but fortunately single crystals suitable for X-ray analysis were readily obtained from the initial reaction mixture.

*Crystal data.* The structure was determined from 2015 reflections having $I \geqslant 3\sigma(I)$ and refined to $R = 0.069$. $C_{50}H_{42}P_4Au_2$ $M = 1160.7$, triclinic $a$ 9.001(2), $b$ 11.407(5) and $c$ 11.436(6) Å, $\alpha$ 103.85(3), $\beta$ 101.89(3), and $\gamma$ 74.58(3)°, $U$ 1086 Å$^3$, $Z = 1$, $D_c$ 1.77 g cm$^{-3}$ ($D_{obs}$ 1.76 g cm$^{-3}$, by flotation), $\mu$(Mo-$K_\alpha$) 71.4 cm$^{-1}$, $F(000)$ 560, $\lambda$(Mo-$K_\alpha$) 0.71069 Å, Space Group $P\bar{1}$.

The solution of the structure was hampered by the oblate spheroidal nature of the molecule, which resulted in the crystallographic disorder illustrated in III, whereby the observed structure represents a superposition of two molecules (a) and (b) related by a rotation of 90°. The refined occupancies of the two molecules were 0.60 and 0.40.



(III)



(IV)

It proved possible to satisfactorily delineate the phosphorus and carbon atoms of the two distinct molecules. The molecular structure of one of the molecules is illustrated in Fig. 1. The dimeric gold molecule lies on a crystallographically imposed centre of symmetry with the gold atoms separated by an average distance of 2.888(3) Å, close to the interatomic separation in metallic gold (2.884 Å), and therefore consistent with the proposed gold(0) structure IIa. The phosphorus and gold atoms are coplanar and lie within ±0.03 Å of the best least squares plane passing through these atoms. The carbon atoms of the ring also lie close to this plane (±0.25 Å) leading overall to a chair con-

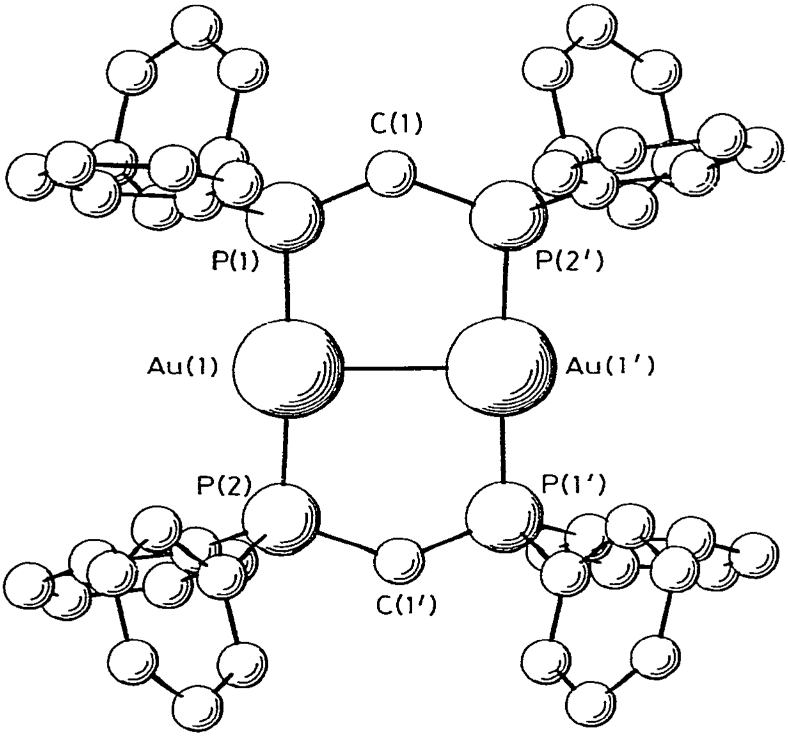


Fig. 1. Molecular structure of $Au_2(dppm\text{-}H)_2$. For reasons of clarity the hydrogen atoms have been omitted, and only one of the molecules which represent the total crystallographically disordered situation has been illustrated. The following bond lengths and angles have been averaged for both molecules: Au(1)—Au(1') 2.883(3), Au(1)—P(1) 2.290(7), Au(1)—P(2) 2.290(7), P(1)—C(1) 1.62(4), P(2')—C(1) 1.74(4) Å; P(1)—Au(1)—P(2) 176.0(3), Au(1')—Au(1)—P(1) 90.8(2), Au(1')—Au(1)—P(2) 92.6(2), P(1)—C(1)—P(2') 129(2), C(1)—P(1)—Au(1) 115(1) and C(1)—P(2')—Au(1') 111(1)°. The atoms X and X' refer to atoms related by the centre of symmetry.

formation for the eight-membered ring. However, the envelope conformation defined by the $Au_2P_2C$ rings is less pronounced than that commonly observed in A-frame complexes of the dppm ligand [4]. Furthermore, the average P—C bond lengths for the two distinct molecules of 1.62(3) and 1.74(4) Å are shorter than those commonly associated with the dppm ligand (1.84 Å), and the average P(1)—C(1)—P(2') bond angle of 129(2)° is larger than that in dppm complexes (110—117°) [4]. The bond lengths and angles are more consistent with the ylid or bis(diphenylphosphido)methanido (dppm-H) structure illustrated in IIb than the dppm structure illustrated in IIa. The corresponding average bond lengths in the related complex $Au_2(dppm\text{-}H)(CH_2PBu_2CH_2)$ are 1.74 Å and 123° respectively [5]. The formulation IIb was confirmed by infrared studies, which demonstrated the absence of bands at ca. 2900 $cm^{-1}$ that could be attributed to the $\nu(CH_2)$ stretching modes and the synthesis of a sample of IIb with identical physical and chemical properties by the following route developed by Schmidbaur [5]:

$$2AuCl(PR_3) + 2LiCH(PPh_2)_2 \rightarrow IIb + 2LiCl$$

The formation of the phosphane ylid complex IIb in preference to the dppm complex IIa from the mixed valence gold(0)—gold(I) icosahedral cluster is a tribute to the remarkable stability of the eight-membered ring system in the former and perhaps reflects a degree of cyclic delocalisation. It is interesting to note that the addition of dppm to polynuclear alkylcopper(I) compounds leads to the formation of a trinuclear complex $[Cu(dppm\text{-}H)]_3$ [6].

The linear coordination about the $d^{10}$ gold(I) atoms in IIb suggests according to the model developed by Orgel [7] that the gold—gold interactions in the compound occur primarily through the ($d_{z^2}$—$s$) hybrid orbitals illustrated in IV. However, since these orbitals are filled their interaction can only result in a 4-electron repulsive interaction. Therefore, the short Au—Au interatomic distance in IIb and related gold(I) complexes must originate from the mixing-in of virtual 6*p* orbitals on the metal [8].

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