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The Synthesis and X-Ray Structure of Trichloro-1,1,1-(diphenylphosphinomethyl)ethanetrigold(I)

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There is considerable current interest in low-valent multinuclear gold species and, in particular gold cluster compounds [1]. In an attempt to facilitate the synthesis of a centred icosohedral Au_{13} cluster of high overall symmetry we have used the ligand 1,1,1-tris(diphenylphosphinomethyl)ethane (tdme). This tridentate ligand is potentiallly capable of capping each of four tetrahedrally arranged triangular faces of the icosahedron. The structure of the gold(I) precursor to the, as yet uncrystallised, cluster species containing tdme is reported here.

X-ray analysis shows that the tripod molecule of trichloro-1,1,1-(diphenylphosphinomethyl)ethanetrigold(I) (1) has the structure illustrated in Fig. 1. Each of the three gold atoms has the normal linear coordination geometry {P–Au–Cl, 174.8–178.2°}. Chemically equivalent bonds in the three limbs of the complex are equal within experimental error. The mean Au–P bond length of 2.239 Å is considerably shorter than the mean Au–Cl length of 2.292 Å as has been found in other Au(I) compounds [2]. This shortening of the Au–P bond may be attributed to some metal to ligand back-bonding. The most interesting feature of the structure is that two legs of the tripod molecule are crossed almost orthogonally {the dihedral angle between Au(1)–P(1) and Au(2)–P( ) is 80.23°} which brings the metal atoms into very close proximity {Au(1)···Au(2) 3.091 Å}. Unusually short Au···Au contact distances are a feature of a number of Au(I) compounds and the possibility that these interactions represent significant Au–Au bonding has been the subject of considerable discussion [2, 3]. It is particularly relevant that in the structure of (1) there are no other close contacts between the atoms of the three limbs and the shortest contact involving hydrogen is between the H atom of a methylene group and a Au atom, Au(3)···H(12a) 2.485 Å. In contrast there are a number of short contacts between adjacent molecules of the complex and with the solvent benzene molecule. Therefore there seems to be no reason why the legs of the tripod should not adopt a more symmetrical configuration, and so minimise contact between the gold atoms. It seems reasonable to attribute the proximity of Au(1) to Au(2) to a bonding interaction between these atoms.

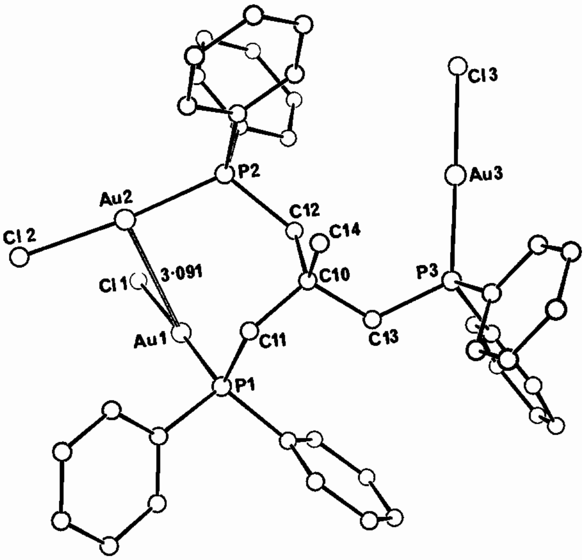

Fig. 1. The structure of the Au(1) complex of tdme, (1).

Experimental

The compound (1), $CH_3C[CH_2PPh_2AuCl]_3$, was prepared by stirring a mixture of tdme and tetrachloroauric acid in the molar ratio of 2:3 in ethanol. The resultant yellow precipitate was filtered off and recrystallised from dichloromethane/diethyl ether to form colourless hexagonal plates of (1) in approximately 50% yield. These crystals did not diffract X-rays and suitable crystals, which were cubic in shape, were obtained on slow evaporation of an acetone/benzene solution. *Crystal data* (1).- $C_{41}H_{39}Au_3Cl_3P_3 \cdot 0.5C_6H_6$, monoclinic, space group $P2_1/c$, a = 13.257(2), b = 22.018(4), c = 17.206(3) Å, β = 99.35(2)°, V = 4955.6 $Å^{-3}$, Z = 4, Mo-K_α radiation, λ = 0.71069, μ(Mo-K_α) = 87.89 cm^{-1}. The space group was unambiguously assigned from

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systematic absences in the data, h01, 1 = 2n + 1 and 0k0, k = 2n + 1. Data in the range $3 \leqslant \theta \leqslant 25^\circ$ were collected with a crystal of dimensions 0.16 × 0.16 × 0.14 mm, using a Philips PW1100 four-circle diffractometer and a scan width of 0.70°. The method of data collection, processing and absorption correction have been described previously [4]. Equivalent reflections were merged to give a total of 3776 reflections with $I/\sigma(I) > 3.0$.

The positions of the three gold atoms were located from a Patterson synthesis. The other atoms were located from subsequent difference Fourier syntheses. The phenyls rings and the benzene solvent molecule were refined as rigid groups (C–C 1.395 Å) and the hydrogen atoms were included in geometrically calculated positions (C–H 1.08 Å), with fixed thermal parameters of 0.10 Å^2. Refinement of a common population parameter for the benzene carbon atoms, with fixed thermal parameters of 0.08 Å^2, indicated a site occupancy of *ca.* 0.5 In the final stages of the refinement anisotropic thermal parameters were assigned to Au, Cl, P and the aliphatic carbon atoms. The final R was 0.0509 and R_w 0.0507.

Acknowledgement

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