The Synthesis and X-Ray Structure Analysis of Dichloro{1,3-bis(diphenylphosphino)propane}digold(I)

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In an attempt to facilitate the synthesis of high nuclearity gold cluster compounds we have been studying reactions of gold(I) derivatives of the bidentate ligand 1,3-bis(diphenylphosphino)propane (prophos) [1]. Hexa- and undecagold cluster compounds have previously been obtained by van der Welden [2] and Vollenbroek [3] respectively using this ligand. The structure of the potential cluster precursor prophos$(AuCl)_2$ is reported here.

Dichloro {1,3-bis(diphenylphosphino)propane}digold(I), (*1*) prophos$(AuCl)_2$, was prepared in dichloromethane solution from the reaction of a 2:1 molar ratio of chlorocarbonylgold(I) and prophos. After evaporation of the solvent the product was recrystallized from dichloromethane/benzene as colourless crystal (yield, 90%; mp, 268 °C; ν(Au–Cl), 340 cm^{-1}). Crystals suitable for X-ray analysis were grown from a cooled dichloromethane solution layered with benzene.

X-ray analysis shows that the molecule has the structure shown in Fig. 1. The two Au atoms each have approximately linear coordination {P–Au–Cl 173.6(3) and 175.7(3)°}. Chemically equivalent bonds in the two limbs of the compound are equivalent within experimental error. The mean Au–P bond length of 2.234 Å is considerably shorter than the mean Au–Cl length of 2.300 Å. The shortening of Au–P bonds, which is possibly due to some gold to ligand back bonding, is characteristic of a number of Au(I) species [4] including the related tripod molecule 1,1,1-(diphenylphosphinomethyl)ethanetrigold, $CH_3C(CH_2PPh_2AuCl)_3$ (*2*), in which the corresponding Au–P and Au–Cl lengths average 2.239 and 2.292 Å respectively [5].

The two limbs of the prophos$(AuCl)_2$ molecule point away from each other so that the two gold atoms are well separated. This contrasts with the structure [6] in an unusual trinuclear cationic complex of the related diphenylphosphinomethane (dppm) ligand $[ClAu(dppm)Au(dppm)AuCl]^+$, in which the configuration allows two short Au···Au contacts of 3.067 and 3.1644 Å. The tripod molecule (*2*) also has a short intramolecular Au···Au distance of 3.091 Å which is thought to be due to some bonding interaction [5]. It is interesting that there are short Au(1)···Au(2) distances in the crystal structure of prophos$(AuCl)_2$ but these occur between adjacent molecules related by the *b*-glide. If this short contact distance is due to a weak bonding interaction the overall structure may be regarded as being composed of polymeric chains as illustrated in Fig. 2.

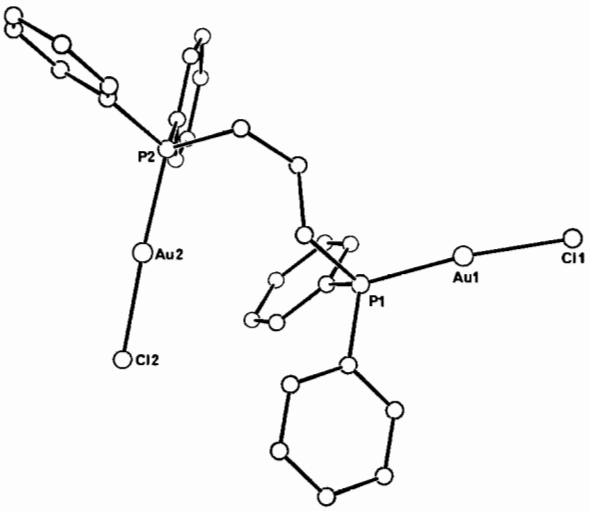

Fig. 1. The structure of the dinuclear molecule prophos(Au-Cl)$_2$ (*1*). Important bond lengths (Å) are Au(1)–Cl(1) 2.305(6), Au(2)–Cl(2) 2.296(7), Au(1)–P(1) 2.231(6), Au(2)–P(2) 2.237(7), P(1)–C(1) 1.80(2), P(2)–C(3) 1.80-(2), P(1)–C(111) 1.81(2), P(2)–C(211) 1.82(2), P(1)–C-(121) 1.81(2), P(2)–C(221) 1.81(2), C(1)–C(2) 1.55(3), C(2)–C(3) 1.55(3).

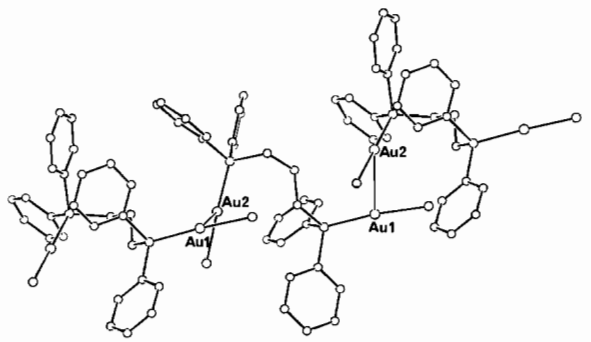

Fig. 2. The 'polymeric' chain structure of (*1*); the Au(1)··· Au(2) (0.5 – x, 0.5 + y, z) distance is 3.316 Å.

Crystal data (*1*): $C_{27}H_{26}Au_2Cl_2P_2$, orthorhombic, space group Pbcn, $a = 19.507(4)$, $b = 14.404(3)$, $c = 19.827(4)$ Å, $V = 5571.0$ Å^3, $Z = 8$, Mo-Kα radiation $\lambda = 0.71069$ Å, μ(Mo-Kα) = 104.2 cm^{-1}.

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The X-ray structure determination was undertaken using 2341 reflections with $I \geqslant \sigma(I)$ measured with a Philips PW1100 four-circle diffractometer. Refinement used full matrix least squares procedures [7] with anisotropic thermal parameters assigned to the Au, Cl and P atoms, and converged at a final R of 0.062. The phenyl rings were treated as rigid groups (C–C 1.395, C–H 1.08 Å and C–C–C 120°), and the hydrogen atoms were assigned thermal parameters of 0.10 $Å^2$ which were not refined.

The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K. Any request should be accompanied by the full literature citation for this letter.

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