Notes

Synthesis and Structure of μ-[*trans*-1,2-Bis(diphenylphosphino)ethylene]-bis[chlorogold(I)] †

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The 1 : 2 ligand: Au^I complex [ClAu(μ-*trans*-$Ph_2PCH=CHPPh_2$)AuCl] was prepared by reduction of Au^{III} to Au^I with 2,2′-thiodiethanol followed by reaction with an excess of ligand, and thus differs from the product characterized previously from direct reduction of Au^{III} with the ligand. Infrared band assignments for ν(Au–P) and ν(Au–Cl) of the present complex are 352 and 322 cm^{-1}, respectively. Assignments for ν(Au–P) and ν(Au–Cl) of 347 and 323 cm^{-1}, respectively, for the complex of the *cis* ligand, which are more consistent than present literature values, are reported also. The crystal structure of the complex has been determined from diffractometer data and refined to $R = 0.031$ based on 2 104 observed reflections [$I \geqslant 3\sigma(I)$]. The molecule sits on an inversion centre in space group $C2/c$, thus the *trans* geometry of the ligand and of the complex are rigorously reflected in the crystallographic results. The gold atom is linearly co-ordinated with normal Au–Cl and Au–P bond lengths of 2.291(2) and 2.235(2) Å, respectively. A short intermolecular Au ··· Au contact of 3.043(1) Å is observed.

In a recent paper [1] the reaction between equimolar amounts of sodium tetrachloroaurate and the potentially bidentate phosphine ligand *trans*-1,2-bis(diphenylphosphino)ethylene (*trans*-$Ph_2PCH=CHPPh_2$) was reported to lead to a 1:1 gold(I) complex (**1**) in which only one of the phosphine centres was co-ordinated instead of the expected two, as in structure (**3**). This molecular composition was proposed principally on the basis of elemental analysis and i.r. spectroscopic evidence and was distinct from other (bidentate phosphine)gold(I) complexes prepared in the same study. For example, addition of *cis*-1,2-bis(diphenylphosphino)ethylene to $AuCl_4^-$ in a 1:1 ratio led to the isolation of complex (**2**). The crystal structure of the latter was subsequently published.[2]

In our hands, reaction between tetrachloroauric acid and the *trans*-$Ph_2PCH=CHPPh_2$ ligand leads unequivocally to the digold(I) structure (**3**), when the gold is reduced first to Au^I with 2,2′-thiodiethanol.[3]

This note reports the synthesis, characterization, and *X*-ray crystal structure of complex (**3**). We also note discrepancies between i.r. band assignments reported for Au–Cl and Au–P stretches of the digold(I) complex of *cis*-$Ph_2PCH=CHPPh_2$ and those observed in our laboratories for a sample synthesized in a manner analogous to that used for complex (**3**).

Experimental

Synthesis of μ-[trans-1,2-*Bis(diphenylphosphino)ethylene*]-*bis[chlorogold(I)]* (**3**).—2,2′-Thiodiethanol (2 cm^3) was added dropwise to a solution of $HAuCl_4$ (0.90 g, 2.65 mmol) in cold water (5 cm^3). While still cold, the solution was filtered through a 2-μm filter to remove any colloidal gold that might have formed. The *trans*-1,2-bis(diphenylphosphino)ethylene ligand (0.62 g, 1.56 mmol) dissolved in ethanol (50 cm^3) was added slowly and with vigorous stirring to the cold solution of Au^I. A white precipitate appeared quickly. Stirring was continued for 45 min as the suspension was allowed to warm to room temperature. The product was filtered off, washed with water (50 cm^3) and diethyl ether (50 cm^3) and dried in air. The yield was 0.74 g (65%) based on Au. Recrystallization by slow evaporation from a 1:1 CH_2Cl_2–EtOH solution gave white needles (Found: C, 36.25; H, 2.80. Calc. for $C_{26}H_{22}Au_2Cl_2P_2$: C, 36.25; H, 2.55%), decomp. 262—264 °C; $\Lambda = 13.0$ ohm^{-1} cm^2 mol^{-1} for a 1 mmol dm^{-3} solution in nitromethane. I.r. data: ν(Au–Cl) at 322, ν(Au–P) at 352 cm^{-1}.

The digold(I) complex of *cis*-$Ph_2PCH=CHPPh_2$ ligand also may be prepared by this or similar routes.[3] Our i.r. assignments: ν(Au–Cl) at 323, ν(Au–P) at 347 cm^{-1}.

Characterization.—Elemental analyses were performed by the Analytical Laboratory of this department. The conductivity was measured on a Beckman RC-16 conductivity bridge with platinum electrodes and a cell constant of 1.00. The value found is consistent with the formulation of the substance in solution as non-ionic. Infrared spectra in the range 4 000—400 cm^{-1} of the sample pelleted in KBr were recorded on a Nicolet 20DXB spectrometer with CsI optics. Far-i.r. spectra (450—200 cm^{-1}) were recorded as CsBr pellets.

Crystallography.—*Crystal data.* $C_{26}H_{22}Au_2Cl_2P_2$, $M = 861.25$, monoclinic, space group $C2/c$, $a = 16.620(3)$, $b = 15.082(2)$, $c = 11.373(2)$ Å, $\beta = 117.31(1)°$, $U = 2\,533.0$ Å^3, $Z = 4$, $D_c = 2.258$ g cm^{-3}, $F(000) = 1\,600$, μ(Mo-K_α) = 119.02 cm^{-1}, λ(Mo-K_α) = 0.710 73 Å, $T = 298$ K, minimum and maximum transmission factors 64.81 and 99.99%.

Data collection and refinement. A single crystal of approximate dimensions 0.15 × 0.20 × 0.15 mm was mounted with epoxy on a glass fibre for data collection. Cell dimensions were determined by least-squares refinement of the setting angles for 25 reflections ($15 \leqslant \theta \leqslant 17.5°$). Intensity data were collected on an Enraf–Nonius CAD4 diffractometer at room temperature using an ω—θ scan technique and variable scan speeds. Data absent by virtue of the centring condition were not collected. Otherwise a unique quadrant of data $2 \leqslant 2\theta \leqslant 56°$ ($\pm h$, $+k$, $+l$) was collected.

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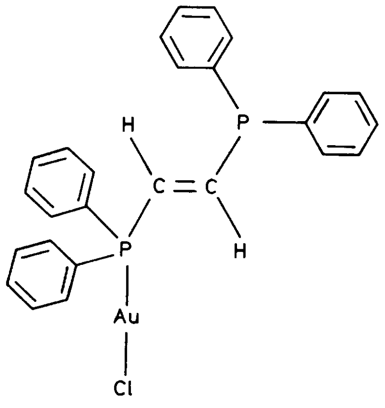
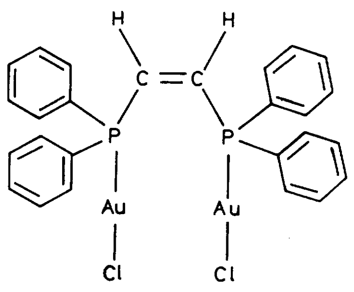
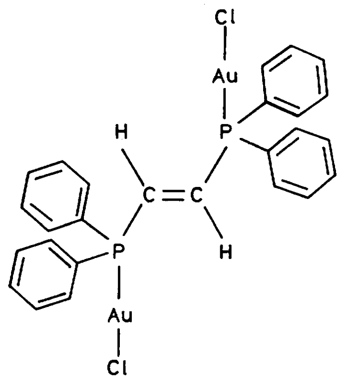
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.



(1)



(2)



(3)

Table 1. Positional parameters and their estimated standard deviations for complex (3)

Atom	x	y	z
Au	0.398 03(2)	0.160 05(2)	0.200 85(2)
Cl	0.396 1(1)	0.240 4(2)	0.028 7(2)
P	0.383 1(1)	0.084 8(1)	0.359 0(2)
C(1)	0.468 2(4)	0.000 1(5)	0.438 8(6)
C(2)	0.277 1(4)	0.026 1(5)	0.292 9(6)
C(3)	0.205 6(5)	0.057 0(6)	0.179 1(8)
C(4)	0.120 9(6)	0.019 1(7)	0.135(1)
C(5)	0.107 3(6)	−0.051 5(7)	0.201 1(9)
C(6)	0.177 9(6)	−0.082 8(6)	0.312 6(9)
C(7)	0.263 2(6)	−0.045 0(6)	0.358 5(8)
C(8)	0.383 3(4)	0.154 8(5)	0.487 5(6)
C(9)	0.394 5(5)	0.245 9(6)	0.481 2(8)
C(10)	0.389 6(7)	0.301 0(6)	0.574 1(9)
C(11)	0.372 6(6)	0.267 8(7)	0.671 0(8)
C(12)	0.360 3(7)	0.180 6(7)	0.676 8(8)
C(13)	0.364 7(6)	0.122 7(6)	0.586 3(7)

Table 2. Principal bond distances (Å) and angles (°)

Au–Cl	2.291(2)	P–C(2)	1.800(8)
Au–P	2.235(2)	P–C(8)	1.802(7)
P–C(1)	1.810(7)	C(1)–C(1′)	1.31(1)
P–Au–Cl	173.5(1)	C(1)–P–C(2)	104.6(3)
Au–P–C(1)	114.4(3)	C(1)–P–C(8)	107.3(3)
Au–P–C(2)	111.3(2)	C(2)–P–C(8)	105.3(3)
Au–P–C(8)	113.3(3)	P–C(1)–C(1′)	126.9(8)

The data were corrected for background and for Lorentz-polarization effects. An empirical absorption correction based on ψ scans of nine reflections with $80 \leqslant \chi \leqslant 90°$ was applied. There was no evidence of crystal decay from standard reflections monitored every 3 h of exposure time. Symmetry-equivalent reflections were averaged; the agreement factors were 3.0% on F_o and 2.5% on I. A total of 3 043 unique observations were measured, of which 2 104 were considered observed [$I \geqslant 3\sigma(I)$]. The position of one unique gold atom was located from a Patterson map and the remaining non-hydrogen atoms from Fourier difference maps. In the later stages, hydrogen atoms were added as fixed contributions in positions calculated from geometric considerations and with fixed isotropic thermal parameters. Non-hydrogen atoms were refined with anisotropic librational amplitudes; in all, there were 145 variables. The function minimized in all full-matrix least-squares calculations was $\Sigma w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F)$. Refinement converged (max. $\Delta/\sigma = 0.09$) to values of the conventional residuals R = 0.031 and R' = 0.038. A final Fourier difference synthesis showed one peak of height 0.962 e Å^{-3} within 1 Å of the gold atom, but was otherwise featureless. Refinement in the non-centrosymmetric alternative space group C_c failed to converge and led to physically unrealistic bond distances. All calculations were performed on a VAX 11/785 computer using the Enraf–Nonius structure-determination package as modified locally. Values of neutral atom scattering factors from ref. 4 were used.

Results

Reduction of Au^{III} to Au^{I} with 2,2′-thiodiethanol followed by reaction with a slight excess of the bidentate ligand *trans*-1,2-

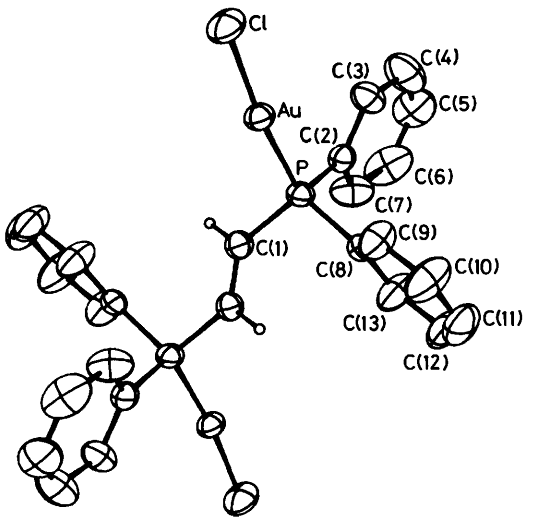


Figure. View of complex (3). Probability ellipsoids are drawn at the 50% level. Hydrogens on the phenyl rings are omitted for clarity

bis(diphenylphosphino)ethylene produced the 1:2 ligand:gold(I) complex (3) shown in the Figure. The product of this route differs from that characterized from the direct reduction of Au^{III} with the ligand.[1] For the digold complex of *trans*-$Ph_2PCH=CHPPh_2$ the Au–Cl and Au–P stretches are 322 and 352 cm^{-1}, respectively, contrasting sharply to the values of 331 and 360 cm^{-1}, respectively, reported for the 1:1 complex (**1**) and also to the values of 329 and 371 cm^{-1} reported for the digold complex (**2**) of *cis*-$Ph_2PCH=CHPPh_2$. The latter observation was disturbing to us as there is no apparent reason for such large differences between ν(Au–P) for the complexes of the *trans* and *cis* ligands. Our own investigations of complex (**2**) showed ν(Au–Cl) at 323 cm^{-1} and ν(Au–P) at 347 cm^{-1}; these band assignments are certainly closer to those for complex (**3**) and are more realistic numbers.

Crystallographically, the molecule sits on an inversion centre in the centrosymmetric space group *C*2/*c* with the inversion centre at the midpoint of the ethylene bridge. The *trans* geometry of the ligand and of the complex thus are reflected rigorously by the crystallographic results and only one half of the molecule is crystallographically unique. The gold atom is linearly co-ordinated with a P–Au–Cl angle of 173.5(1)°. The Au–Cl and Au–P bond distances of 2.291(2) and 2.235(2) Å, respectively, are within normal ranges for gold(I) complexes.[5] The C–C distance in the ethylene bridge is 1.31(1) Å, which is equivalent to the value of 1.33(2) Å reported for the *cis*-ethylene bridged structure.[2]

A notable feature of the crystal structure is the very short intermolecular contact of 3.043(1) Å between gold atoms related by a two-fold rotation. Short intermolecular Au ••• Au contacts are common to gold(I) compounds[6] and, as noted by others,[7] may be indicative of weak binding interactions which stabilize the structures in the form of polymeric chains. The intramolecular Au ••• Au distance is 7.742(1) Å. There are no other significant short contacts within the crystal structure.

References

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