Is Regular Tetrahedral Geometry Possible in Gold(I)–Phosphine Complexes? *X*-Ray Crystal Structures of Three Modifications of $(PPh_3)_4Au^+BPh_4^-$

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Summary *X*-Ray crystal structures of three modifications of tetrakis(triphenylphosphine)gold(I) tetraphenylborate have been determined, one at −150 °C, none shows the expected simple tetrahedral geometry

THE archetypal co-ordination geometry for gold(I) is linear two-co-ordination Trigonal planar co-ordination has been demonstrated by *X*-ray structure determinations of *e g* L_2AuCl[1] and $L_3Au^+B_9H_{19}S^-$[2] ($L = Ph_3P$ throughout this paper) Four-co-ordination is, however, less well established Crystal structures have been determined only for the chelates $[o\text{-}C_6H_4(AsR_2)_2]_2Au^+$ ($R = Et$,[3] Me[4]), the existence of four-co-ordinate, presumably tetrahedral, species with monodentate ligands has been deduced in solution from n m r data[5,6] and in the solid state by Mossbauer spectroscopy[7] This paper reports attempts to establish four-co-ordination in L_4Au^+ by *X*-ray crystallography †

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW Any request should be accompanied by the full literature citation for this communication

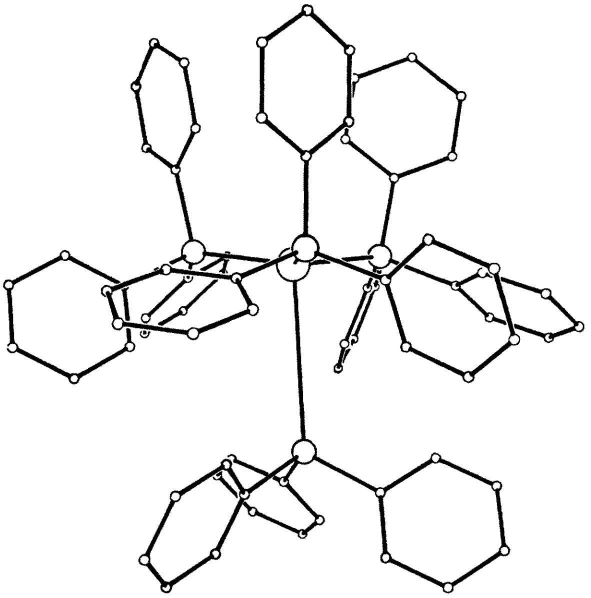

FIGURE 1. Modification (I). Key: large circle Au, medium circles P, small circles C. The view direction is in the plane of the three strongly bonded P atoms.

$L_4Au^+BPh_4^-$ was obtained as a white powder by Malatesta *et al.*[8] Recrystallisation from chloroform of a sample obtained by their method afforded colourless crystals [modification(I)]. The crystal structure (Figure 1) shows that (I) contains an $L_3Au\ldots L$ unit with a very long Au . . . P contact (3·946 Å). The gold atom is displaced 0·25 Å out of the plane of the other three P atoms towards this distant P, which implies a very weak Au . . . P interaction. The L_3Au unit shows trigonal planar geometry [Au–P 2·392, 2·406, and 2·408(4) Å; P–Au–P 116·0, 119·3, and 121·4(2)°]. In $L_3Au^+B_9H_{19}S^-$ [2] the Au–P bonds are significantly shorter (2·345, 2·384, and 2·389 Å).‡

Further attempts to recrystallise $L_4Au^+BPh_4^-$ proved unsuccessful; benzene yielded twinned crystals, acetonitrile mostly $L_3Au^+BPh_4^-$.[9] Eventually small, weakly diffracting, colourless crystals [modification (II)] were obtained by diffusion of an ethanolic solution of $NaBPh_4$ into one of LAuCl + 3L. Attempts to solve this structure showed unrealistic thermal parameters for Au, and disorder of this atom was suspected. This was resolved into two components; one Au site, lying on a twofold axis, is tetrahedrally co-ordinated while the other, on a general position, is trigonally co-ordinated (Figure 2). The ratio of site occupation factors refined to 1 within 1 e.s.d. The Au–P bond lengths are 2·602 and 2·610(9) Å (tetrahedral site), and 2·434, 2·445, and 2·461(12) Å (trigonal site). The extremely long bond lengths of the tetrahedral component cannot be attributed to steric repulsions of the bulky phosphine ligands, since L_4Pd shows Pd–P bond lengths of 2·427 and 2·458(5) Å.[10]

It was then noticed that the acetonitrile recrystallisation had yielded, besides $L_3Au^+BPh_4^-$, a few large crystals [modification (III)] very similar in habit to those of (II). One of these was used to collect data at −150 °C, in the hope of obtaining better-resolution data and of resolving the disorder into one component favoured at low temperature. Structure analysis of (III) showed that the gold atom remains disordered at low temperature, but with a site ratio tetrahedral: trigonal of 7: 1. The Au–P bond lengths are considerably lower than at room temperature, the tetrahedral component showing a twofold distortion: 2·504 and 2·561(2) Å (tetrahedral), and 2·359, 2·389, and 2·401(6) Å (trigonal).

The tetrahedral site is thus preferred at low temperature and must be of marginally lower energy than the trigonal site. This is consistent with the singlet Mössbauer spectrum at 4 K;[7] any residual trigonal component at 4 K would, however, be difficult to detect using Mössbauer spectroscopy,

TABLE. *Crystal Data*

Modification	(I)	(II)	(III)
Formula[a]	$L_3Au^+X^-.L.CHCl_3$	$L_4Au^+X^-.EtOH$	$L_4Au^+X^-.MeCN$
M_r	1684·75	1611.44	1606·42
Space group	*P*2$_1$/*n*	*Ibca*	*Ibca*
T/°C	20	20	−150
a/Å	16·009(6)	22·161(10)	21·657(10)
b/Å	30·025(12)	23·111(11)	22·917(15)
c/Å	16·893(6)	30·651(14)	30·652(15)
β/deg.	90·84(2)		
U/Å^3	8119	15,698	15,213
Z	4	8	8
D_x/g cm^{-3}	1·378	1·364	1·403
μ(Mo-K_α) cm^{-1}	20	20	21
Diffractometer	Stoe 4-circle	Stoe 4-circle	Stoe 2-circle
2θ range/deg.	7—50	7—40	3—50
Reflexions	11,789	3283	8819 (*h*0—24*l*)
Unique refl.	11,255	3271	6711
Observed refl.	8499 > 4σ(*F*)	1872 > 3σ(*F*)	4995>4σ(*F*)
Crystal size/mm	0·4 × 0·3 × 0·3	0·1 × 0·1 × 0·15	0·7 × 0·7 × 0·6
Absorption corr.	No	No	Yes
Final *R*	0·073	0·112	0·051
Final R_w	0·076	0·084	0·055

[a] X = BPh_4; L = PPh_3

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‡ The first of these bond lengths was reported as 2·373 Å,[2] but this is not consistent with co-ordinates and cell constants.

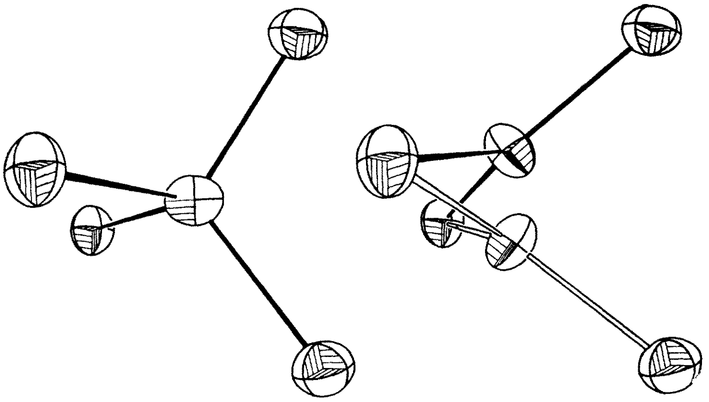

FIGURE 2. Modification (II). Left: the AuP_4 core of the tetrahedral component. Right: the trigonal component (full bonds) and its symmetry-generated equivalent (open bonds). All atoms are represented as 50% probability ellipsoids.

since quadrupole split peaks of the trigonal site would possess at most 1/14 the intensity of the singlet tetrahedral site peak (assuming a site ratio $\geqslant$ the 7 : 1 found at −150 °C).

It may be concluded that the assumption of tetrahedral coordination in gold(I) complexes at room temperature is not justified, at least in the solid state.

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