Nearly Regular Tetrahedral Geometry in a Gold(I)–Phosphine Complex. *X*-Ray Crystal Structure of Tetrakis(methyldiphenylphosphine)gold(I) Hexafluorophosphate

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Summary An *X*-ray crystal structure determination shows the gold(I) complex with four methyldiphenylphosphine ligands to have $\bar{4}$ symmetry with all Au–P bond lengths equal and nearly tetrahedral angles; further, ^{31}P n.m.r. spectroscopy at -80 °C indicates that the nearly tetrahedral species persists in solution.

GOLD(I) complexes are stabilised by sulphur and phosphorus ligands with linear, two-co-ordinate geometry most frequently found, although three-co-ordinate species are known as well. The only four-co-ordinate structure characterised by a full *X*-ray analysis[1] is that with the bidentate, chelating ligand, *o*-phenylenebis(dimethylarsine) (diars), $[Au(diars)_2][Au(C_6F_5)_2]$. Recent investigations[2] of three different crystalline modifications of $[Au(PPh_3)_4]BPh_4$ have shown highly distorted complexes and led to the suggestion that with monodentate ligands, 'the assumption of tetrahedral co-ordination in gold(I) complexes at room temperature is not justified, at least in the solid state.' We have synthesised, characterised, and determined the single crystal structure of the nearly tetrahedral tetrakis(methyldiphenylphosphine)gold(I) hexafluorophosphate which we report here.

Reaction of potassium tetrabromogold(III) with 5 equiv. of methyldiphenylphosphine in ethanol at room temperature gave a nearly colourless solution within minutes. Addition of a saturated solution of sodium hexafluorophosphate then yielded colourless crystals which analysed in agreement with the formulation $[Au(PPh_2Me)_4]PF_6$. Presumably the fifth equivalent of the phosphine ligand serves as a reducing agent for the gold(III) starting material. Recrystallisation from CH_2Cl_2–Et_2O gave tetragonal crystals.

Crystal data: $C_{52}H_{52}AuF_6P_5$, $M_r = 1142{\cdot}82$, space group $P4/ncc$ with $a = 14{\cdot}797(1)$, $c = 22{\cdot}184(3)$ Å, $U = 4857$ Å^3, $Z = 4$, $D_c = 1{\cdot}563$, $D_m = 1{\cdot}561$ g cm^{-3}. Intensity data [1776 reflexions, 1449 with $I > 2\sigma(I)$, $2{\cdot}5° < 2\theta < 46{\cdot}8°$, measured at $20(\pm 3)$ °C] were obtained using a Syntex P$\bar{1}$ diffractometer equipped with a graphite monochromater and Mo-K_α radiation. Empirical absorption corrections were applied ($\mu = 32{\cdot}4$ cm^{-1}) and the structure was solved using heavy atom methods. The gold atom occupies a site of $\bar{4}$ symmetry and the phosphorus atom of the counter-ion is situated on a four-fold axis. Positional parameters were refined for all atoms. Anisotropic thermal parameters were used for all non-H atoms, and fixed (4·0 Å^2) isotropic thermal parameters for H atoms. Final convergence in the refinement of 183 parameters was reached with $R = 0{\cdot}029$ and $R_w = 0{\cdot}023$.†

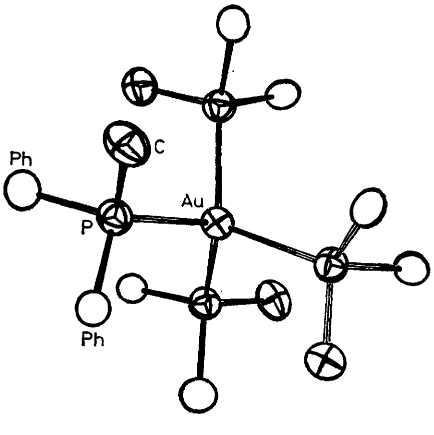

FIGURE. The co-ordination geometry about gold(I) in $(PPh_2Me)_4$-Au$^+$. Phenyl ring positions are indicated by open ellipses for the carbon atom bound to phosphorus.

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† The atomic co-ordinates for this work are available 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.

The co-ordination environment about gold (Figure) is nearly that of a regular tetrahedron. The Au–P bonds, which are all equivalent by the $\bar{4}$ symmetry, are 2·449(1) Å in length and the two independent P–Au–P angles are 105·24(4) and 118·32(4)° yielding a slightly 'flattened' tetrahedron. The Au–P bonds are much longer than those found in the bismethyldiphenylphosphine analogue,[3] $[Au(PPh_2Me)_2]PF_6$, 2·316(4) Å, and somewhat longer than the three short Au–P bonds found in modification (I) of $[Au(PPh_3)_4]BPh_4$ (average, 2·402 Å). However, they are in the range of those reported for the trigonal site (average, 2·447 Å) and much less than those of the tetrahedral site (average, 2·606 Å) of modification (II) of $[Au(PPh_3)_4]BPh_4$. Clearly Au–P bonds are subject to considerable variation in length, as one might expect for a bond between a 'soft' ligand and a low-valent metal ion such as gold(I). For methyldiphenylphosphine there appears no great difficulty in attaining nearly regular tetrahedral co-ordination, whereas in the case of the more bulky triphenylphosphine steric factors force a great elongation of the Au–P bonds. In the latter case there is presumably a rather close energy balance between a trigonal, essentially, three-co-ordinate form with three reasonably strong Au–P bonds and a tetrahedral form with four, individually, much weaker, Au–P bonds. All other structural details of the complex are as would be expected.

The solution ^{31}P n.m.r. spectrum of a pure sample of $[Au(PPh_2Me)_4]PF_6$ at −80 °C in CH_2Cl_2 gives a single sharp peak at 5·4 p.p.m. as well as the PF_6^- heptet centred at 144·3 p.p.m. (relative to an external H_3PO_4 standard) establishing that the four-co-ordinate complex is maintained in solution and is the same as that previously characterised by Parish and his co-workers.[4] To date, we have been unable to crystallise a sample of the three-co-ordinate complex $[Au(PPh_2Me)_3]PF_6$.

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