

## Preparation and Crystal Structure of the First Phosphido-bridged Gold(I) Complex: Tetra(n-butyl)ammonium Diphenylphosphidobis[bromogold(I)]

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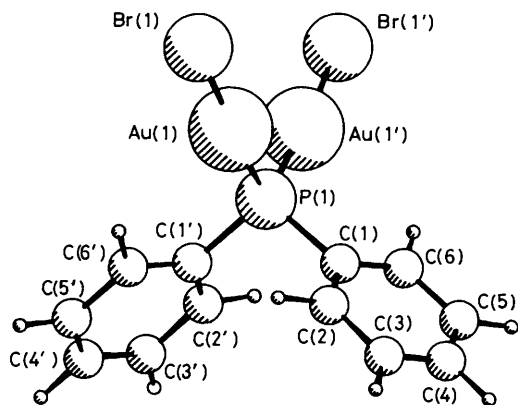
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The first authenticated gold(I) complex containing a bridging phosphido ligand,  $\text{Bu}_4\text{N}[(\text{AuBr})_2(\mu\text{-PPh}_2)]$ , has been characterised by X-ray crystallography.

Tertiary phosphines have an extensive and well understood co-ordination chemistry with gold(I), and large numbers of two-, three-, and four-co-ordinate complexes have been characterised. In sharp contrast, there appears to be only a single report of the interaction of a gold(I) complex with a secondary phosphine.<sup>1</sup> Diphenylphosphine was found to react with  $[\text{AuMe}(\text{PMe}_2\text{Ph})]$  to give a material of empirical composition  $\text{AuPPh}_2$ , presumably polymeric, but characterised only by elemental analysis. We were interested in this

substance, since it is iso-electronic with the gold(I) thiolates  $[\text{AuSR}]_n$ ,<sup>2</sup> and we have investigated the reactions of  $\text{Ar}_2\text{PH}$  ( $\text{Ar} = \text{Ph}, p\text{-MeC}_6\text{H}_4, p\text{-Bu}^t\text{C}_6\text{H}_4$ ) with gold(I) complexes under a variety of conditions. We report now on a novel product obtained from  $[\text{AuBr}_2]^-$  and  $\text{PPh}_2\text{H}$ .

When  $\text{Et}_4\text{N}[\text{AuBr}_2]$  was treated with  $\text{PPh}_2\text{H}$  (1 mol. equiv.) in dichloromethane, a white precipitate of  $\text{Et}_4\text{NBr}$  was obtained, together with a colourless, gold-containing oil which could not be solidified. When the reaction was repeated with



**Figure 1.** Structure of the anion  $[(\text{AuBr})_2(\mu\text{-PPh}_2)]^-$  (PLUTO<sup>4-</sup>). Note that the phosphorus atom lies on a crystallographic two-fold axis. Selected bond lengths (Å) and angles (°) are: Au(1)–P(1), 2.243(3); Au(1)–Br(1), 2.401(2); P(1)–C(1), 1.83(1); Au(1)–Au(1'), 3.722; Au(1)–P(1)–Au(1'), 112.1(2); Br(1)–Au(1)–P(1), 176.6(1); Au(1)–P(1)–C(1), 108.1(5); C(1)–P(1)–C(1'), 102.4(8) (' denotes an atom generated by  $1-x, y, 3/2-z$ ).

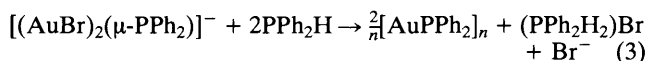
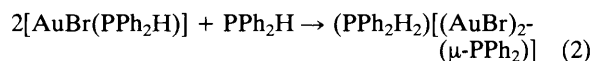
$\text{Bu}_4\text{N}[\text{AuBr}_2]$ , white, gold-containing crystals were obtained, which were characterised by X-ray crystallography.† They proved to be the first authenticated example of a phosphido-bridged gold(I) complex,  $\text{Bu}_4\text{N}[(\text{AuBr})_2(\mu\text{-PPh}_2)]^-$ .

The structure of the anion is shown in Figure 1, together with selected bond lengths and angles. The co-ordination of the gold(I) atoms is linear ( $\angle \text{P-Au-Br } 176.6^\circ$ ) with normal

† *Crystal data:*  $\text{C}_{28}\text{H}_{46}\text{Au}_2\text{Br}_2\text{NP}$ .  $M = 981.40$ , monoclinic, space group  $C2/c$ ,  $a = 25.170(1)$ ,  $b = 12.1218(8)$ ,  $c = 15.3480(9)$  Å,  $\beta = 135.330(4)^\circ$ ,  $U = 3292.1$  Å<sup>3</sup>,  $Z = 4$  (molecular ions positioned on a crystallographic two-fold axis),  $D_c = 1.98$  g cm<sup>-3</sup>,  $\mu(\text{Mo-K}\alpha) = 110.03$  cm<sup>-1</sup>. Data were measured on a CAD4 diffractometer with graphite-monochromated Mo-K $\alpha$  radiation using  $\omega/2\theta$  scans. Lorentz polarisation and absorption corrections were applied. Structure solution was by normal heavy-atom techniques followed by full matrix least-squares refinement (SHELX<sup>3</sup>). The  $\text{Bu}_4\text{N}^+$  cation was disordered, and required several atoms to be represented by pairs of semi-occupied sites. A final  $R = 0.042$  and  $R_w = 0.045$  was attained for 1393 observed independent reflexions [ $|F_o| \geq 3\sigma(|F_o|)$ ,  $\theta \geq 25^\circ$ ] with the anion being refined anisotropically, except for its hydrogen atoms, which were placed in chemically reasonable positions with a common overall temperature factor. The disordered cation was treated isotropically, with hydrogen atoms omitted. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

bond lengths. The novel feature is the bridging phosphido group, with an Au–P–Au angle of  $112.1(2)^\circ$ . The Au–Au distance is large (3.722 Å), indicating the absence of any significant metal–metal interaction. The phosphorus atom is close to tetrahedral, with the Au–P–Au angle slightly expanded at the expense of C–P–C. The P–Au distance is similar to those reported for  $\text{Ph}_3\text{P-Au}$  complexes.<sup>5</sup> Thus, the  $\text{Ph}_2\text{PAu}_2$  phosphorus atom has very similar hybridisation to  $\text{Ph}_3\text{PAu}$ , i.e. the second AuBr group acts as a 'soft' ligand towards phosphorus, and is electronically equivalent to a phenyl group (cf. ref. 6).

The reaction presumably occurs in two stages, with intermediate formation of  $[\text{AuBr}(\text{PPh}_2\text{H})]$ . In separate experiments, with different starting materials, we have n.m.r. and Mössbauer spectroscopic evidence<sup>7</sup> for the formation of the corresponding chloro-complex,  $[\text{AuCl}(\text{PPh}_2\text{H})]$ , the first-known complex of gold(I) with a secondary phosphine, but this has not yet been isolated in a pure state. Reaction of the intermediate with a second mole of the phosphine could lead to deprotonation and the formation of the observed product. It is likely that  $[(\text{AuBr})_2(\mu\text{-PPh}_2)]^-$  is a precursor of the polymer  $[\text{AuPPh}_2]_n$  [reactions (1)–(3)].



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