A Novel Three-co-ordinate Di-gold(I) Diphosphine Complex [Au$_2$(Me$_2$PCH$_2$PMe$_2$)$_3$](BF$_4$)$_2$ 0.5C$_7$H$_8$: X-Ray Crystal and Molecular Structure

Wolfgang Bensch,* Mario Prelati, and Werner Ludwig

Institute for Inorganic Chemistry, University of Zürich, Winterthurerstrasse 190, CH-8057 Zürich, Switzerland

The crystal structure determination of [Au$_2$(dmpm)$_3$](BF$_4$)$_2$ 0.5C$_7$H$_8$ (dmpm = Me$_2$PCH$_2$PMe$_2$) has shown that the compound is a dimer composed of two bridged trigonal planar three-co-ordinate gold atoms; two independent cations per asymmetric unit are found in the crystal.

The co-ordination geometry in gold(I)-tertiary phosphine complexes is determined by the steric and electronic properties of the ligand. Structures exhibiting three-co-ordinate gold(I) atoms are dominated by arylphosphines, e.g. [(Ph$_3$P)$_2$AuCl],[1] [(Ph$_3$P)$_3$Au]$^+$.[2] Our attempts to synthesize monomeric three-co-ordinate gold(I) complexes with tertiary alkylphosphines failed. Such three-co-ordinate species with tertiary alkylphosphines have been identified in solution using ^{31}P n.m.r. spectroscopy, e.g. [Au(PBu$_3$)$_3$]$^+$.[3] The molecular structure reported here provides a basis for the spectroscopic investigation[4] of the Van der Waals gold–gold interaction between neighbouring complex moieties, which will be continued in the near future. This contribution deals with the preparation and a crystal structure, which is similar to the bicyclo[3.3.3]undecane structure, already known for Pd^0 and crystallographically determined for Pt^0.[5]

By reacting [Pr$^i_3$PAuCl] with bis(dimethylphosphino)-methane (dmpm, 1.6 equiv.) in dry acetone under nitrogen for 1 h at 40 °C a yellow product was obtained in high yield. The powder was recrystallized in MeCN/acetone. The chemical analysis was in agreement with the stoicheiometry [Au$_2$(dmpm)$_3$]Cl$_2$. The tetrafluoroborate salt was precipitated from a concentrated aqueous solution of the chloride by adding a saturated aqueous solution of NH$_4$BF$_4$. A suitable crystal for the X-ray crystal structure determination with dimensions 0.15 × 0.10 × 0.065 mm^3 was obtained within six days by open evaporation from a solution of toluene, acetonitrile, and ethanol (3 : 1 : 1 by volume).†

In contrast to [Au$_2$(dmpm)$_2$]Cl$_2$ 2H$_2$O^6 which consists of dimers of nearly linearly co-ordinated gold atoms the complex
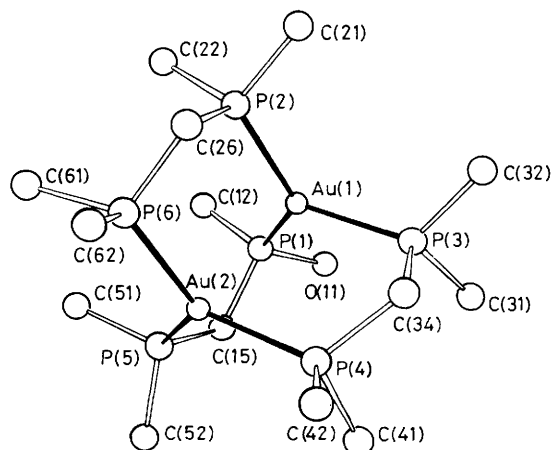

Figure 1. The structure of one of the molecules in the gold complex [Au$_2$(Me$_3$PCH$_2$PMe$_3$)$_3$](BF$_4$)$_2$.

presented here is made up by two nearly trigonal planar co-ordinated gold atoms. The two planes in each molecule are connected by P–C–P bridges with Au–P distances lying between 2.344(7) and 2.384(7) Å. The P–Au–P angles are slightly distorted from the ideal 120°.

The environment of the gold atoms is displayed in Figure 1. The geometry is close to ideal trigonal planar with P–Au–P angles ranging from 114.7 to 124.9° for Au(1), from 117.7 to 121.5° for Au(2), from 117.6 to 122.4° for Au(1') and from 115.7 to 127.3° for Au(2'). The Au(1) atom is 0.034 Å out of the least-squares plane through the P atoms, the Au(2') atom is 0.021 Å out of the plane, whereas the other two gold atoms are situated nearly within the least-squares plane of the P atoms. Such deviations from the ideal 120° angle and small deviations from planarity are also observed in other trigonal planar co-ordinated gold complexes.[9] In each molecule two of these trigonal planar co-ordinated gold atoms are connected *via* P–C–P bridges. The planes in molecule 1 [gold atoms Au(1) and Au(2)] are tilted by a dihedral angle of 15.9°, whereas the corresponding planes of the other molecule are nearly parallel with a dihedral angle of 1.1°. As a consequence of this connection, short Au · · · Au contacts are observed [3.040(1) Å for Au(1)–Au(2) and 3.050(1) Å for Au(1')–Au(2')]. Such short contacts are frequently observed in Au[I] derivatives, even when the Au atoms are in separate molecules.[10,13]

The Au–P distances are situated in the range from 2.344(7) to 2.384(7) Å (average: 2.358 Å) and are in the same region as in many other Au–P bond-containing gold complexes.[9—12,14] It should be noted that for the more usual two-co-ordination the Au–P bond length is markedly shorter (typically *ca.* 2.25 Å). The solvent molecules (toluene) are situated in interstices between the gold-clusters.

References

1 N. C. Baenziger, K. M. Dittemore, and J. R. Doyle, *Inorg. Chem.*, 1974, **13**, 805.

2 L. J. Guggenberger, *J. Organomet. Chem.*, 1974, **81**, 271.

3 C. B. Colburn, W. E. Hill, C. A. McAuliffe, and R. V. Parish, *J. Chem. Soc., Chem. Commun.*, 1979, 218.

4 W. Ludwig and W. Meyer, *Helv. Chim. Acta*, 1983, **65**, 934.

5 Lj. Manojlovic-Muir and K. W. Muir, *J. Chem. Soc., Chem. Commun.*, 1982, 1155, and references therein.

6 J. Kozelka, H. R. Oswald, and E. Dubler, *Acta Crystallogr., Sect. C*, 1986, **42**, 1002.

7 G. M. Sheldrick, SHELXS-84, Crystal Structure Solution, University of Göttingen, 1984.

8 G. M. Sheldrick, SHELX-76, Program for Crystal Structure Determination, University of Cambridge, 1976.

9 J. A. Muir, M. M. Muir, and S. Arias, *Acta Crystallogr., Sect B*, 1982, **38**, 1318.

10 P. G. Jones, G. M. Sheldrick, R. Uson, and A. Laguna, *Acta Crystallogr., Sect. B*, 1980, **36**, 1486.

11 J. A. Muir, M. M. Muir, and S. Arias, *Acta Crystallogr., Sect. B*, 1982, **38**, 2047.

12 H. Schmidbauer, A. Wohlleben, F. Wagner, O. Orama, and G. Hüttner, *Chem. Ber.*, 1977, **110**, 1748.

13 V. Jiang, S. Alvarez, and R. Hoffmann, *Inorg. Chem.*, 1985, **24**, 749.

14 P. G. Jones, *Gold Bull.*, 1981, **14**, 102; 1981, **14**, 159; 1983, **16**, 114; 1986, **19**, 46.