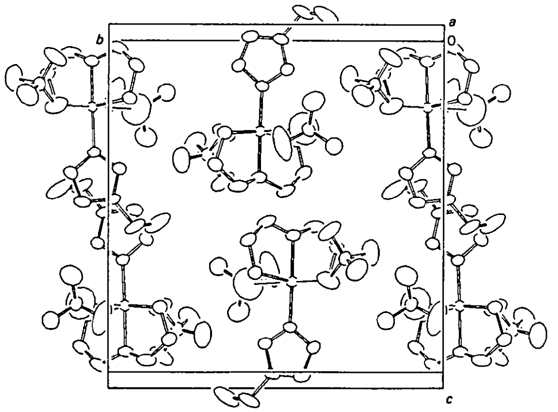

Fig. 4. *ORTEP*II drawing (Johnson, 1976) of crystal structure packing in the unit cell of (2) as viewed along the $a^*$ axis. Atoms are represented with the same conditions as in Fig. 3.

at 47·6 and 48·9° to the copper equatorial planes for (1) and (2), respectively. The Cu—N(1) bond lengths in the present complexes are slightly shorter than the corresponding Cu—N distances in the octahedral copper–imidazole complexes $[\mathrm{Cu(ImH)_4(NO_3)_2}]$ (average 2·011 Å) (McFadden, McPhail, Garner & Mabbs, 1976) and $[\mathrm{Cu(ImH)_6}](\mathrm{NO_3})_2$ (average 2·031 Å) (McFadden, McPhail, Garner & Mabbs, 1975). Bonding geometries in the imidazole ligand in each complex are essentially the same as those of the above complexes.

Crystal structures of (1) and (2) are presented in Figs. 3 and 4, respectively. No abnormally short intermolecular contacts are observed in either of the complexes. The shortest interatomic distances between non-H atoms are 3·01 (2) Å $[\mathrm{O}(23)(x,\ y,\ z)\cdots\mathrm{N}(3)(-\tfrac{1}{2}+x,\ \tfrac{1}{2}-y,\ \tfrac{1}{2}-z)]$ for (1), and 3·23 (2) Å $[\mathrm{O}(12)(x,\ y,\ z)\cdots\mathrm{C}(15)(2-x,\ -y,\ -z)]$ for (2), both of which are observed in the contacts between the cationic complex and the anion.

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# Bis-μ-[methylenebis(dimethylphosphine)]digold(I) Dichloride Dihydrate and its Comparison with the Diphenylphosphine Analogue

By Jiří Kozelka,* Hans Rudolf Oswald and Erich Dubler

*Anorganisch-Chemisches Institut der Universität Zürich, Winterthurerstrasse* 190, 8057 *Zürich, Switzerland*

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**Abstract.** $[\mathrm{Au_2(C_5H_{14}P_2)_2}]\mathrm{Cl_2.2H_2O}$, $M_r = 773{\cdot}10$, triclinic, $P\bar{1}$, $a = 7{\cdot}943\ (3)$, $b = 10{\cdot}043\ (4)$, $c = 7{\cdot}884\ (3)$ Å, $\alpha = 105{\cdot}14\ (3)$, $\beta = 109{\cdot}16\ (3)$, $\gamma = 66{\cdot}06\ (3)°$, $V = 537$ Å$^3$, $Z = 1$, $D_m = 2{\cdot}34$, $D_x = 2{\cdot}39$ g cm$^{-3}$, Mo $K\alpha$, $\lambda = 0{\cdot}7107$ Å, $\mu = 141{\cdot}7$ cm$^{-1}$, $F(000) = 360$, $T = 298$ K, $R = 0{\cdot}058$ for 2551 observed reflections. The compound was synthesized according to Ludwig & Meyer [*Helv. Chim. Acta* (1982), **65**, 934–943]. The molecule consists of dimeric units with linear coordination of the Au atoms [P—Au—P angles of 176·61 (5)°]; there is distinct metal–metal interaction [Au—Au distance = 3·010 (1) Å]. The Cl$^-$ ions are only associated, unlike in the analogous compound bis-μ-[methylenebis(diphenylphosphine)]digold(I) dichloride, where they are bound covalently. An explanation for this difference is presented.

**Introduction.** Binuclear gold(I) phosphine complexes are interesting primarily for two reasons: (i) the various coordination numbers and geometries found in them; (ii) the frequently observed metal–metal interactions (Schmidbaur, Wohlleben, Schubert, Frank & Huttner,

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* Present address to which correspondence should be directed: Université René Descartes, Laboratoire de Chimie et Biochimie Pharmacologiques et Toxicologiques, 45, rue des Saints-Pères, 75270 Paris Cédex 06, France.

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1977; Schmidbaur, Mandl, Bassett, Blaschke & Zimmer-Gasser, 1981; Ludwig & Meyer, 1982). The additional importance of gold(I) phosphines arises from their potential use in chemotherapy of arthritis (Sutton, McGusty, Walz & DiMartino, 1972; Sutton, 1983).

Table 1. *Atomic parameters and their estimated standard deviations (in parentheses)*

Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $B_{eq} = \frac{4}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

| | $x$ | $y$ | $z$ | $B_{eq}$(Å$^2$) |
|---|---|---|---|---|
| Au | 0·12309 (4) | 0·01618 (3) | 0·40224 (4) | 2·276 (6) |
| Cl | 0·1000 (5) | 0·2451 (4) | 0·8134 (4) | 4·84 (8) |
| P(1) | 0·3791 (3) | −0·1683 (2) | 0·5405 (3) | 1·91 (4) |
| P(2) | −0·1223 (3) | 0·2094 (2) | 0·2714 (3) | 1·86 (3) |
| O | 0·269 (1) | 0·471 (1) | 1·137 (1) | 5·7 (3) |
| C | 0·304 (1) | −0·2935 (8) | 0·604 (1) | 2·2 (1) |
| C(11) | 0·546 (1) | −0·292 (1) | 0·409 (1) | 2·9 (2) |
| C(12) | 0·520 (1) | −0·095 (1) | 0·744 (1) | 2·9 (2) |
| C(21) | −0·239 (2) | 0·162 (2) | 0·038 (1) | 4·6 (3) |
| C(22) | −0·057 (1) | 0·360 (1) | 0·270 (2) | 3·9 (2) |

Table 2. *Important interatomic distances* (Å) *and bond angles* (°)

Primed labels refer to relative coordinates ($-x$, $-y$, $1-z$).

| | | | |
|---|---|---|---|
| Au–Au′ | 3·010 (1) | P(1)–C | 1·823 (7) |
| Au–P(1) | 2·302 (2) | P(1)–C(11) | 1·805 (7) |
| Au–P(2) | 2·299 (2) | P(1)–C(12) | 1·799 (7) |
| Au–Cl | 3·462 (2) | P(2)–C′ | 1·807 (7) |
| Au–Cl′ | 3·519 (3) | P(2)–C(21) | 1·802 (8) |
| | | P(2)–C(22) | 1·792 (8) |
| P(1)–Au–P(2) | 176·61 (5) | | |
| Au–P(1)–C | 111·8 (2) | Au–P(2)–C′ | 111·3 (2) |
| Au–P(1)–C(11) | 117·4 (3) | Au–P(2)–C(21) | 114·9 (4) |
| Au–P(1)–C(12) | 111·5 (3) | Au–P(2)–C(22) | 114·9 (3) |
| O–Cl | 3·263 (8) | | |
| O–Cl($-x$,$1-y$,$2-z$) | 3·204 (9) | | |
| Cl–O–Cl($-x$,$1-y$,$2-z$) | 104·1 (2) | | |

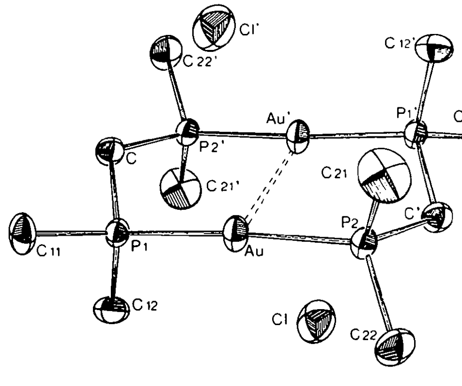

Fig. 1. *ORTEP* (Johnson, 1976) drawing of compound (1) with 50% probability ellipsoids.

Recently, Ludwig & Meyer (1982) synthesized the binuclear complex bis-$\mu$-[methylenebis(dimethylphosphine)]digold(I) dichloride (1) and found complete dissociation in water up to 0·01 $M$ concentration. This is interesting since in the analogous compound bis-$\mu$-[methylenebis(diphenylphosphine)]digold(I) dichloride (2), there is coordinative Au–Cl bonding in the solid state and only slight dissociation in polar solvents has been found (Schmidbaur, Wohlleben, Schubert, Frank & Huttner, 1977). In order to understand this difference, we prepared single crystals of (1), determined the crystal structure, and compared it with that of (2).

**Experimental.** Colorless plates obtained from hot acetonitrile solutions by slow cooling; crystal used: 0·4 × 0·26 × 0·08 mm; $D_m$ determined by flotation method; Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$; cell parameters by least squares on setting angles for 25 reflections, $15·8 \leq 2\theta \leq 38·1°$; $\omega$–$2\theta$ scans, range of $hkl$: $-11 \leq h \leq 11$, $-13 \leq k \leq 13$, $-10 \leq l \leq 10$, $\sin\theta/\lambda < 0·70$ Å$^{-1}$; standards 410, $\bar{3}21$, $\bar{3}\bar{1}1$, $\bar{2}1\bar{3}$, 203, $2\bar{3}2$, remeasured every 100 reflections, exhibited no systematic variations in intensity (total loss of intensity 0·3%); 6216 reflections measured, 3109 unique, 2551 observed above $3\sigma(I)$, $\sigma(I)$ based on counting statistics, $\sigma(F) = 0·5\sigma(I)/F_o$, $R_{int} = 0·038$. Lp, absorption (data numerically corrected, based on crystal shape, 8 × 8 × 8 grid size, transmission coefficient 0·07–0·41) and secondary extinction ($g = 1·5 \times 10^{-6}$) corrections. Patterson and Fourier methods, full-matrix least-squares refinement, anisotropic for all atoms, H atoms not included. $\sum w(\Delta F)^2$ minimized, $w = 1/[\sigma^2(F_o) + (p^2/4)F_o^2]$, $p = 0·08$; atomic scattering factors from *International Tables for X-ray Crystallography* (1974); final $R = 0·058$, $wR = 0·070$ including all observed $[I > 3\sigma(I)]$ reflections, $S = 1·62$, $(\Delta/\sigma) < 0·01$. Final difference Fourier map showed several peaks up to 6·6 e Å$^{-3}$ in the vicinity of the Au atom, most probably due to incompleteness of absorption correction. Max. height of peaks not associated with the Au atom 1·7 e Å$^{-3}$; some of these peaks attributable to H atoms (but not included in the refinement). All programs taken from the *Structure Determination Package* (Enraf–Nonius, Delft, Holland).

**Discussion.** Final positional parameters are given in Table 1, important bond lengths and bond angles are listed in Table 2. Fig. 1 displays an *ORTEP* drawing of the molecule.*

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42937 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

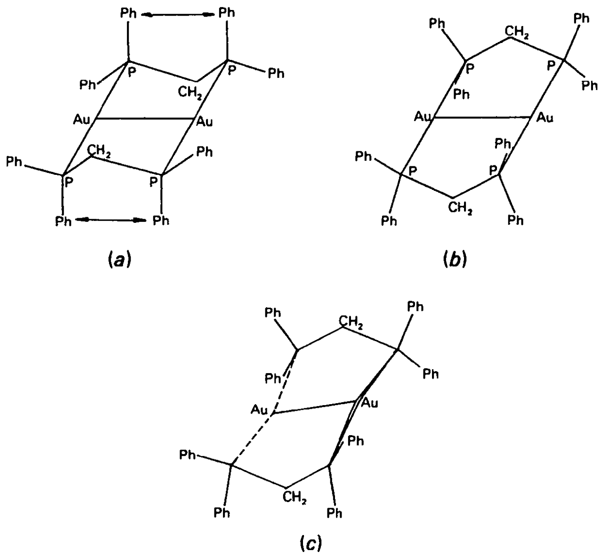

Fig. 2. Schematic drawings of compound (2), Ph=phenyl, (*a*) in a 'chair' conformation as found for (1) (the arrows indicate the close phenyl–phenyl contact which would arise), (*b*) in a conformation with planar Au—Au—P—C—P rings, (*c*) with non-linear P—Au—P angles as actually occurring in crystals.

The Au—P and Au—Au distances are very similar to those found in (2) (Schmidbaur, Wohlleben, Schubert, Frank & Huttner, 1977). The main differences from (2) are: (i) the almost linear P—Au—P angle [176·6°, as opposed to 155·9° in (2)], (ii) the very well maintained planarity of the $Au_2P_4$ unit [maximum deviations from the least-squares plane are 0·04 Å, as opposed to 0·38 Å in (2)], (iii) the large Au—Cl distances of 3·49 (3) Å which show that the $Cl^-$ ions are not bound covalently [as in (2), where the Au—Cl distance is 2·77 Å] but only associated.

Each of the two water molecules forms two hydrogen bonds to chloride ions of two neighboring unit cells.

If in (2) the Au and P atoms were coplanar as in (1), a close non-bonding contact of approximately 3·0 Å between the axial phenyl rings of the ligands would arise (Fig. 2*a*). The phenyl rings would come further apart when the methylene C atoms moved into the $Au_2P_4$ plane (Fig. 2*b*). This would create, on the other hand, strain in the Au—Au—P—C—P five-membered rings; this strain could be removed upon decreasing the P—Au—P angles (Fig. 2*c*). Such geometry is actually found for (2). A non-linear P—Au—P structure, of course, is much more susceptible to additional coordination than a linear one. Thus, the structure and bonding in (2) can be explained in terms of steric repulsion. The crystal structure of (1) demonstrates that the linear P—Au—P unit does not have an *a priori* tendency to bend and to bind a chloride ligand. We cannot exclude, however, that the electron-withdrawing effect of the phenyl rings slightly favors the $Cl^-$ coordination in (2), in addition to the steric effect.

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# Structure of the Tetrahydrofuran Adduct of Mono-*N*-lithiohexamethylcyclotrisilazane

BY MARTIN HAASE AND GEORGE M. SHELDRICK

*Institut für Anorganische Chemie der Universität, Tammannstrasse* 4, *D*-3400 *Göttingen, Federal Republic of Germany*

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**Abstract.** Bis-$\mu$-(2,2,4,4,6,6-hexamethylcyclotrisilazanato)-bis[(tetrahydrofuran)lithium(I)], $C_6H_{20}LiN_3Si_3.C_4H_8O$, $M_r = 297{\cdot}55$, triclinic, $P\bar{1}$, $a = 9{\cdot}037\ (1)$, $b = 12{\cdot}063\ (1)$, $c = 17{\cdot}779\ (2)$ Å, $\alpha = 89{\cdot}77\ (1)$, $\beta = 88{\cdot}62\ (1)$, $\gamma = 72{\cdot}22\ (1)°$, $U = 1845$ Å$^3$, $Z = 4$, $D_x = 1{\cdot}071$ Mg m$^{-3}$, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}244$ mm$^{-1}$, $F(000) = 648$, $T = 290$ K, $R = 0{\cdot}053$ for 4450 observed reflections. There are two crystallographically independent dimers, each lying on an inversion centre. The $Si_3N_3$ ring has a distorted boat

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