

## Facile Preparation and Crystal Structure of [Bis(diphenylphosphino)amine]digold Dichloride

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Z. Naturforsch. **52b**, 769–771 (1997); received April 21, 1997

Gold(I) Complexes, Bis(diphenylphosphino)-amine Complexes, Gold(I) Chloride Complex, Phosphine Complex

Treatment of bis(diphenylphosphino)amine (dppa) with (dimethylsulfide)gold(I) chloride in the molar ratio 1:2 leads to the dinuclear complex (dppa) $Au_2Cl_2$  in 95% yield. The compound was crystallized from diethyl ether/dimethylformamide as the 1:1 solvate with dmf, the crystal structure of which has been determined. The complex features an intramolecular Au–Au contact [3.121(1) Å] and an intermolecular hydrogen bond NH–O=C.

Bis(diphenylphosphino)methane and -amine (dppm, dppa) are important difunctional ligands which are widely used for the construction of mono- and polynuclear complexes. The interplay of chelating and bridging forms arising from ring strain in four-membered rings on one hand, and from the support of metal-metal bonding by dppm/dppa on the other, leads to flexible systems with unique structures and reactivity [1,2].

Both ligands were also introduced into gold chemistry a few years ago [3–6], but dppm was by far the more favourite substrate, while dppa was used only sporadically [7–12]. Recent interest in the construction of supramolecular networks based on gold complexes with a combination of extended linear and sharply bent ligands have led to renewed activities, however, which prompt us to report the results of a structural study of the title compound as a simple prototype.

(dppa) $Au_2Cl_2$  is readily available from the reaction of the free ligand [13] with two equivalents of

(dimethylsulfide)gold(I) chloride [14] in dichloromethane at ambient temperature. A colourless crystalline product (m.p. 160 °C) is obtained in 95% yield. This preparation is superior to the one published earlier from this laboratory [5]. The analytical and spectroscopic data are in good agreement with previous data.

The product can be obtained as single crystals from a diethyl ether/dimethylformamide mixed solvent. These crystals are orthorhombic, space group  $Pbca$  with 8 formula units in the unit cell, and contain the dinuclear complex and crystal dmf in the molar ratio 1:1. The individual molecules have no crystallographically imposed symmetry, but the geometry is close to point group  $C_2$  with the twofold axis containing the N–H unit (Fig. 1).

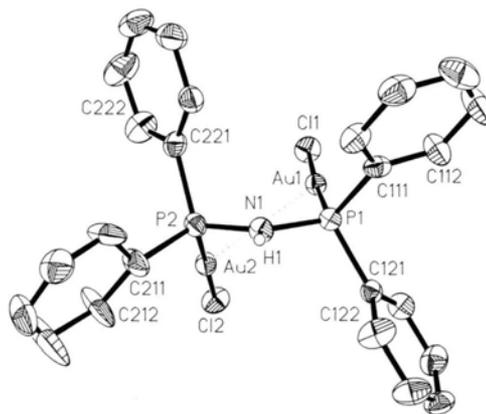


Fig. 1. Molecular structure of (dppa) $Au_2Cl_2$  with atomic numbering [ORTEP, 50% probability ellipsoids. Only one orientation of the disordered phenyl ring (CZ11–CZ16) is shown, phenyl hydrogen atoms are omitted for clarity]. Important bond lengths [Å] and angles [°] are as follows: Au1–Au2 3.121(1), Au1–P1 2.233(2), Au1–Cl1 2.293(2), Au2–P2 2.222(2), Au2–Cl2 2.277(2), P1–N1 1.670(6), P2–N1 1.670(6); P1–Au1–Cl1 176.60(7), P2–Au2–Cl2 179.05(7), P1–N1–P2 122.4(3).

The dinuclear complex has a gauche-skew conformation regarding the relative orientation of the two  $Ph_2PAuCl$  groups at the central nitrogen atom. This conformation allows for a short intramolecular Au–Au contact Au1–Au2 = 3.121(1) Å, which probably forces the molecule into this geometry.

The NH-group is engaged in hydrogen bonding with the formamide oxygen atom as judged from the NH–O distance of 1.998 Å, with an angle at the hydrogen atom N–H–O of 165.7° (Fig. 2). The

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complete molecular unit in the crystal is therefore another case where both hydrogen bonding and aurophilicity contacts determine the overall constitution of the assembly.

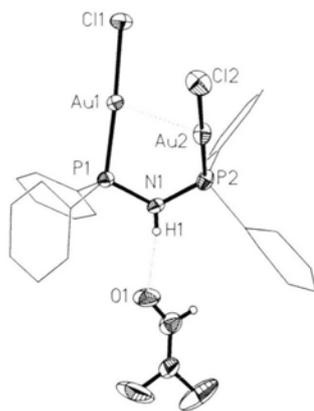


Fig. 2. The complete molecular unit of  $(\text{dppa})\text{Au}_2\text{Cl}_2 \times \text{dmf}$  showing the hydrogen bonding between both components:  $\text{N1-H1}$  0.784 Å,  $\text{H1}\cdots\text{O1}^*$  1.998 Å,  $\text{N1-H1}\cdots\text{O1}$  165.7°. \*Symmetry position of O1:  $x-1$ ;  $0.5-y$ ;  $z-0.5$ .

## Experimental

All experiments were routinely carried out in an atmosphere of dry nitrogen. Solvents and glassware were also dried and filled/saturated with nitrogen. Standard equipment was used throughout.

**Preparation:** A solution of dppa (0.36 g, 0.93 mmol) in  $\text{CH}_2\text{Cl}_2$  (20 ml) is slowly added to a solution of  $(\text{Me}_2\text{S})\text{AuCl}$  (0.55 g, 1.86 mmol) in the same solvent (25 ml) at 0 °C with stirring. After 2 h the product is precipitated from the solution by addition of diethyl ether (25 ml). The colourless product is collected and dried in a vacuum (yield 0.75 g, 95%, m.p. 160 °C). For analytical and spectroscopic data see Ref. [5].

**Structure determination:** A suitable crystal was mounted in a glass capillary and used for measurements of precise cell constants and intensity data collection. During data collection, three standard reflections were measured periodically as a general check of crystal and instrument stability. No significant changes were observed. Diffraction intensities were corrected for Lp and absorption effects (psi-scans). The structure was solved by di-

rect methods and refined by full matrix least-squares calculations against  $F^2$ . The thermal motion of all non hydrogen atoms was treated anisotropically. One of the phenyl rings (CZ11–CZ16) was slightly disordered and refined in split positions. All hydrogen atoms of the complex except for the N–H atom were placed in idealized calculated positions and allowed to ride on their corresponding carbon atom with fixed isotropic contributions ( $U_{\text{iso}(\text{fix})} = 1.5 \times U_{\text{eq}}$  of the attached C atom). The N–H atom was found and included with fixed isotropic contributions ( $U_{\text{iso}(\text{fix})} = 1.5 \times U_{\text{eq}}$  of the N atom). The H atoms of the solvent dmf molecule were also placed in idealized calculated positions and allowed to ride on their corresponding carbon atom with fixed isotropic contributions ( $U_{\text{iso}(\text{fix})} = 0.15 \text{ \AA}^2$ ). Important interatomic distances and angles are summarized in the corresponding figure caption.

**Crystal data:**  $\text{C}_{27}\text{H}_{28}\text{Au}_2\text{Cl}_2\text{N}_2\text{OP}_2$ ,  $M_r = 923.29$ , orthorhombic,  $a = 14.593(1)$ ,  $b = 10.328(2)$ ,  $c = 20.010(2)$  Å, space group  $\text{Pbca}$ ,  $Z = 8$ ,  $V = 5935.9(9)$  Å<sup>3</sup>,  $D_c = 2.066$  g cm<sup>-3</sup>,  $F(000) = 3472$ ; Enraf Nonius CAD4 diffractometer, Mo- $K_\alpha$  radiation ( $\lambda = 0.71073$  Å),  $T = -68$  °C,  $\mu(\text{Mo-}K_\alpha) = 101.86$  cm<sup>-1</sup>,  $T_{\text{min}} = 0.452$ ,  $T_{\text{max}} = 0.998$ ; 6440 reflections measured, 6379 reflections were used for refinement of 355 parameters,  $R1$  ( $wR2$ ) = 0.0371 (0.0644),  $\rho_{\text{fin}} = +0.89/-0.84$  eÅ<sup>-3</sup>. The function minimized was  $wR2 = \{[\sum w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$ , with  $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$  and  $p = (F_o^2 + 2F_c^2)/3$ ;  $a = 0.0190$ ,  $b = 23.18$ . Anisotropic thermal parameters, tables of distances and angles, and atomic coordinates have been deposited with Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen. The data are available on request on quoting CSD-406870.

## Acknowledgements

This work was supported by Deutsche Forschungsgemeinschaft, by Fonds der Chemischen Industrie, and – through the donation of chemicals – by Degussa AG and Heraeus GmbH. The authors thank Mr. J. Riede for establishing the X-ray data set.

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