# Gold Coordination by a Tertiary Phosphine with Three Thioether Functions

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The reaction of tris(phenylthiomethyl)phosphine with equimolecular amounts of  $[AuPPh_3]^+[BF_4]^-$  affords the complex (tris(phenylthiomethyl)phosphine)(triphenylphosphine)-gold(I) tetrafluoroborate **1** in good yield. The X-ray diffraction analysis of this product shows an unusual conformation with the three CH<sub>2</sub>SPh arms of the phosphine folded back towards the metal atom shielding the P-Au-P' unit. The reaction of the same substrate with Bis(tetrahydrothiophene)gold(I) perchlorate in a 1:1 molar ratio leads to the displacement of both weakly coordinated tht ligands, and a dimeric product  $[AuP(CH_2SPh)_3]_2(ClO_4)_2$  **2** is obtained.

# Introduction

The majority of gold compounds used in modern technology and medicine are based on systems where the metal is coordinated by phosphorus and/or sulfur ligands [1]. This is true in particular for "liquid golds" used for gilding [2] and for the drugs successfully applied for the treatment of rheumatoid arthritis and even cancer [3]. Tertiary phosphines are clearly superior to all other ligands in gold chemistry, but sulfur containing ligands are more versatile owing the better leaving group properties of thiol and thioether functions and to their useful redox properties.

A combination of two independent ligands with P- and S-donor functionality at a common metal center may often be the configuration of choice to secure both stability and reactivity for a given substrate. The same combination can be achieved if the phosphine and thioether functionalities are present in the same ligand. We have therefore initiated preparative and structural studies on compounds based on the P-Au-S moiety [4], including those where ambidentate ligands contain mixed functions and offer polyfunctionality [5].

In the present paper we report our results with the ligand tris(phenylthiomethyl)phosphine [6] as a multi/mixed-functional donor for gold(I). This ligand is readily prepared from phenylthiomethyllithium and triphenylphosphite. Its ligand properties have not been probed to date, but the corresponding phosphine sulfide has recently been applied successfully in the coordination chemistry of the low-valent coinage metals [7].

## **Results and Dicussion**

The reaction between a freshly prepared solution of  $[AuPPh_3]^+[BF_4]^-$  and an equimolecular amount of  $(PhSCH_2)_3P$  in tetrahydrofuran at 0°C for 1 h affords the cationic complex **1** formulated in equation 1 in high yield. The product is a stable, colorless crystalline solid, soluble in common polar organic solvents.



The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of complex 1 at room temperature in CDCl<sub>3</sub> shows only one broad signal at  $\delta = 42.5$  ppm. However, this resonance splits into the expected AB system as the temperature is lowered to -60 °C (see Experimental Section). This behaviour suggests a rapid ligand exchange in solution, which is slowed down at low

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Table I. Crystallographic data for compound 1.

	1
Empirical formula	$C_{39}H_{26}AuBF_4P_2S_3$
Formula weight	936.49
Crystal system	orthorhombic
Space group (No.)	Pbca (No.61)
a [Å]	19.978(2)
<i>b</i> [Å]	15.610(2)
<i>c</i> [Å]	24.526(3)
$V[Å^3]$	7649(1)
$\rho_{\rm calc}  [\rm g cm^{-3}]$	1.627
Z	8
$\mu$ (Mo-K <sub><math>\alpha</math></sub> ) [cm <sup>-1</sup> ]	41.41
T [°C]	-74
Radiation	Mo-K $_{\alpha}$
Scan	ω
hkl Range	-25, -19, +30
Measured reflections	7064
Unique reflections	7064
Observed reflections	5373
(with $F_o \ge 4\sigma(F_o)$ )	
Refined parameters	487
wR2 *	0.0792
$R_{based on F}$ (OMIT4) **	0.0371
$\rho_{\text{fin}}(\text{max/min}) [\text{e}\text{\AA}^{-3}]^{***}$	+1.22 / -1.78
Absorption corr.:	empirical
$T_{min}/T_{max}$	0.7440 / 0.9984
Weighting scheme ****	l = 0.0385, k = 1.4403

\*  $wR2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2};$ 

\*\*  $R = \Sigma (||F_o| - |F_c||) / \Sigma |F_o|;$ 

\*\*\* Residual electron densities located at the gold atom; \*\*\*\*  $w = 1/(\sigma^2(F_o^2) + (1 \cdot p)^2 + k \cdot p), p = Max(F_o^2, 0) + 2 \cdot F_c^2/3.$ 

temperature. The <sup>1</sup>H NMR spectrum is less sensitive to changes in temperature. It exhibits a multiplet for the phenyl groups and a singlet ( $\delta = 3.8$  ppm) for the methylene groups. The coupling constant <sup>2</sup>J(PH) appears to be accidentally zero.

Single crystals of compound **1** suitable for Xray diffraction studies were obtained by layering a dichloromethane solution of this complex with diethyl ether at room temperature for 48 h. The crystals are orthorhombic, space group Pbca, with Z=8 formula units in the unit cell (Table I). The lattice is built of independent monomeric complex cations and anions, and no unusual sub-van der Waals contacts are observed between these components. The structure of the cation is shown in Fig. 1. It has no crystallographically imposed symmetry, but approaches closely the symmetry requirements of point group C<sub>3</sub>. The PPh<sub>3</sub> and P(CH<sub>2</sub>SPh)<sub>3</sub> units are in a staggered conformation (Fig. 2) and the angle P1-Au-P2 of 174.37(5)° is close to the



Fig. 1. Molecular structure of the cation complex 1 with atomic numbering (ORTEP, hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): Au-P(1) 2.2923(13), Au-P(2) 2.3036(13), S(1)-C(2) 1.797(6), S(2)-C(1) 1.805(6), S(3)-C(3) 1.790(6), P(1)-Au-P(2) 174.37(5), S(2)-C(1)-P(1) 115.7(3), S(1)-C(2)-P(1) 115.6(3), S(3)-C(3)-P(1) 113.6(3).



Fig. 2. A view of the cation complex 1 along the axis P(1)-Au-P(2) (ORTEP, hydrogen atoms omitted).

ideal value for a linear geometry. Very surprisingly the three  $CH_2SPh$  arms are folded back towards the metal atom, thus shielding the P1-Au-P2 unit very effectively. The S…Au contacts are found to be rather long, however, and are not indicative of any significant Au $\cdots$ S bonding [Au-S1 = 3.908(1). Au-S2 = 4.255(1), Au-S3 = 3.862(1) Å].

The reaction of the free phosphine with  $[Au(tht)_2]^+ClO_4^-$  in a 1:1 molar ratio in dichloromethane at room temperature leads to the displacement of both weakly coordinated tetrahydrothiophene ligands, and the dinuclear product formulated in eq. (2) is obtained.



Its  ${}^{31}P{}^{1}H$  NMR spectrum shows only one singlet at  $\delta = 29.1$  ppm, and the resonances due to the methylene protons in the <sup>1</sup>H NMR spectrum appear also as a singlet. Both spectra are not temperaturedependent, which suggests a rapid site exchange of the gold atom between the sulfur atoms, which is rapid on the NMR time scale even at -60°C.

#### **Experimental Part**

All experiments were carried out routinely under an atmosphere of dry, pure nitrogen. Standard equipment was used throughout. [AuPPh3][BF4] was prepared in situ by reaction of AgBF4 and AuClPPh3 in THF according to a standard procedure, and [Au(tht)<sub>2</sub>]ClO<sub>4</sub> [8] and (PhSCH<sub>2</sub>)<sub>3</sub>P [6] according to the literature. The NMR spectra were recorded in CDCl<sub>3</sub> with SiMe<sub>4</sub> as internal standard for <sup>1</sup>H, and  $H_3PO_4$  (85%) as external standard for <sup>31</sup>P{<sup>1</sup>H} on a JEOL GX 400 spectrometer. Mass spectra were obtained on a Varian MAT 311A spectrometer.

Caution: Perchlorate salts are potentially dangerous.

## [Tris(phenylthiomethyl)phosphine](triphenylphosphine)gold(I) tetrafluoroborate (1)

To a freshly prepared solution of [AuPPh<sub>3</sub>]<sup>+</sup>[BF<sub>4</sub>]<sup>-</sup> (0.10 mmol) in 15 mL of thf was added tris(phenylthiomethyl)phosphine (0.04 g, 0.10 mmol) and the mixture was stirred for 30 min. Evaporation of the solvent to a residual volume of ca. 5 ml and addition of diethyl ether (20 ml) afforded complex 1 as a white solid (yield 0.06 g, 65%).

C<sub>39</sub>H<sub>36</sub>AuBF<sub>4</sub>P<sub>2</sub>S<sub>3</sub>

Calcd C 49.5 H 3.83 S 10.16%,

Found C 48.9 H 3.61 S 10.08%.

NMR:  ${}^{31}P{}^{1}H{}(CDCl_3, 25^{\circ}C): \delta 42.4 (br); -60^{\circ}C: \delta_A 42.2$ (1P),  $\delta_{\rm B}$  38.9 (1P) [<sup>2</sup>J(A-B) = 331.3 Hz]; <sup>1</sup>H (CDCl<sub>3</sub>, 25°C): 8 3.8 (CH<sub>2</sub>, s, 6H), 6.8-7.5 (Ph, m, 30H). FAB mass spectrum:  $m/z = 858.8 (M^+, 100\%)$ .

### Bis[tris(phenylthiomethyl)phosphine]gold(I) perchlorate (2)

To a solution of tris(phenylthiomethyl)phosphine (0.12 g, 0.30 mmol) in 20 ml of dichloromethane was added bis(tetrahydrothiophene)gold(I) perchlorate (0.14 g, 0.30 mmol) and the mixture was stirred for 1 h. Evaporation of the solvent to ca. 5 ml and addition of diethyl ether gave complex 2 as a white solid (yield 0.15 g, 72%).

C42H42Au2Cl2O8P2S6

Calcd C 36.2 H 3.03 S 13.1%, Found C 36.8 H 3.44 S 13.45%.

NMR:<sup>31</sup>P{<sup>1</sup>H} (CDCl<sub>3</sub>, 25°C):  $\delta$  29.1, (s); <sup>1</sup>H (CDCl<sub>3</sub>, 25°C): 8 3.7 (CH<sub>2</sub>, s, 12H), 7.2-7.4 (Ph, m, 30H). FD mass spectrum:  $m/z = 597 [M^{2+}, 3.5\%], 1293 [(M+ClO_4)^+,$ 100%1.

#### Crystal Structure Determination

A suitable crystal of compound 1 was sealed under argon at dry ice temperature into a glass capillary and examined directly on the diffractometer. Data were corrected for Lorentz polarization and absorption effects. The structure was solved by direct methods and refined by full-matrix least-squares calculations. The thermal motion was treated anisotropically for all non-hydrogen atoms. All hydrogen atoms were treated isotropically. Further information on the structure determinations may be obtained from Fachinformationszentrum Karlsruhe. Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the CSD number 406499.

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- [1] W. S. Rapson, T. Groenewald, Gold Usage, Acad. Press, London (1978).
- [2] P. J. Sadler, Gold Bull. 9, 110 (1976).
- [3] a) J. Weinstock, B. M. Sutton, G. Y. Kuo, D. T. Walz, M. J. DiMartino, J. Med. Chem. **17**, 139 (1974);
  b) A. Lorber, T. M. Simon, Gold Bull. **12**, 97 (1979);
  c) B. M. Sutton, Gold Bull. **19**, 15 (1986);

d) Abstracts, Second International Conference on Gold and Silver in Medicine, J. Inorg. Biochem. **42**, 289 (1991);

e) P. J. Sadler, in A. V. Xavier (ed.), Frontiers in Bioinorganic Chemistry, p. 376, VCH-Verlag, Weinheim (1986);

f) C. K. Mirabelli, D. T. Hill, L. F. Faucette, F. L. McCabe, G. R. Girard, D. B. Bryan, B. M. Sutton, J. O'Leary Bartus, S. T. Crooke, R. K. Johnson, J. Med. Chem. **30**, 2181 (1987);

g) K. C. Dash, H. Schmidbaur, in H. Sigel (ed.): Metal Ions in Biological Systems, p. 179, Marcel Dekker, New York and Basel (1982).

[4] a) A. Sladek, H. Schmidbaur, Chem. Ber. 128, 907 (1995); b) A. Sladek, W. Schneider, K. Angermaier, A. Bauer, H. Schmidbaur, Z. Naturforsch. **51b**, 765 (1996);

c) A. Sladek, H. Schmidbaur, Inorg. Chem. **35**, 3268 (1996);

d) A. Sladek, K. Angermaier, H. Schmidbaur, J. Chem. Soc. Chem. Commun. **1996**, 1959;

e) A. Sladek, H. Schmidbaur, Z. Naturforsch., in press;

f) J. M. López-de-Luzuriaga, A. Sladek, H. Schmidbaur, J. Chem. Soc. Dalton Trans., in press.

- [5] E. Olmos, A. Schier, H. Schmidbaur unpublished results.
- [6] S. Fuchs, Doctoral Thesis, Technical University of Munich (1996).
- [7] S. Fuchs, K. Angermaier, A. Bauer, H. Schmidbaur, Chem. Ber. / Recueil 130, 105 (1997).
- [8] R. Usón, A. Laguna, M. Laguna, J. Jiménez, M. P. Gómez, A. Sainz, J. Chem. Soc., Dalton Trans. 1990, 3457.