

## Gold Coordination by Tertiary Phosphane Sulfides

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Received January 27, 1997

**Keywords:** Phosphane sulfides / Gold(I) complexes / Sulfide coordination / Phosphorus / Sulfur

Treatment of the ditertiary phosphane sulfides  $(\text{CH}_2)_n[\text{PPh}_2\text{S}]_2$ , **1a–1d**,  $n = 1–4$ , with equivalent amounts of (dimethylsulfide)gold(I) chloride  $(\text{Me}_2\text{S})\text{AuCl}$  affords the dinuclear complexes **2a–2d** with an AuCl unit attached to each sulfur atom. The chlorides can be converted into the bromides **3a–3c** by metathesis using KBr, or by reacting **1d** with (tetrahydrothiophene)gold bromide. With  $[(\text{Ph}_3\text{P})\text{Au}]^+ \text{O}_3\text{SCF}_3^-$  as the aurating agent for the diphosphane disulfides, the corresponding dicationic products are obtained:  $\{(\text{CH}_2)_n[\text{SPPh}_2\text{AuPPh}_3]_2\}^{2+} \cdot 2 \text{O}_3\text{SCF}_3^-$  (**4b–4d**,  $n = 2–4$ ). An excess of the reagents does not lead to polygold clustering at

the sulfur atoms, and P–S cleavage occurs instead to give sulfonium salts  $[\text{S}[\text{Au}(\text{PPh}_3)]_3]^+ \text{X}^-$ . The reaction of  $\text{Ph}_3\text{PS}$  with equimolar quantities of  $[(\text{Ph}_3\text{P})\text{Au}]\text{O}_3\text{SCF}_3$  leads to the cationic 1:1 complex **5**, and with an excess of the agent the P–S bond is ruptured. The structures of compounds **4b** and **4d** were determined by single-crystal X-ray diffraction. The dications have crystallographic centers of inversion, the coordination at the gold atoms is linear [4b:  $179.03(3)^\circ$ ; 4d:  $175.29(2)^\circ$ ] and the angles at the sulfur atoms are acute [4b:  $97.76(4)^\circ$ ; 4d:  $96.37(3)^\circ$ ], but there are no short Au–Au contacts.

## Introduction

Sulfide and thiolate anions are efficient clustering centers for gold(I) cations<sup>[1]</sup>. Up to four gold atoms can be accommodated at a given sulfur atom, and the resulting aggregates are stabilized through short bonding Au–Au contacts<sup>[2]</sup>.

The sulfur atoms of tertiary phosphane sulfides  $\text{R}_3\text{PS}$  should have an analogous donor potential, but it appears that this has not yet been investigated. Monoauration of phosphane sulfides appears to be readily accomplished, but no attempts to induce polyauration are documented in the literature<sup>[3–14]</sup>. We now report the results of a more systematic investigation in this area. This work is related to extensive studies in the gold coordination chemistry of phosphorus ylides  $\text{R}_3\text{PCH}_2$  and their anionic sulfur analogues  $[\text{R}_2\text{P}(\text{S})\text{CH}_2]^-$ <sup>[15]</sup>, which have provided new insight into many of the reaction pathways of bimetallic systems<sup>[16]</sup>.

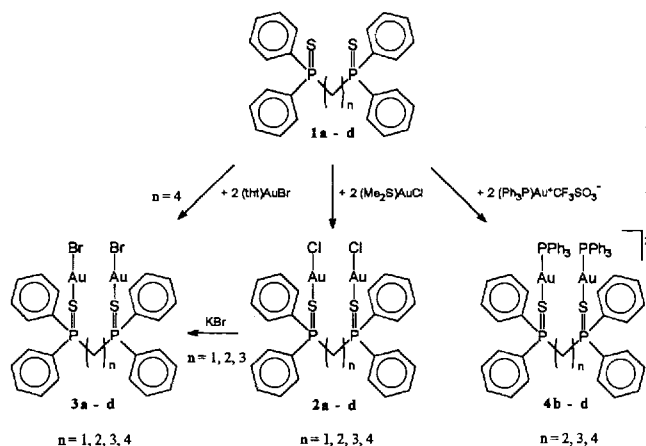
## Results

Instead of simple tertiary phosphane sulfides of the type  $\text{R}_3\text{PS}$ , which were the main targets of previous studies<sup>[3–7]</sup>, difunctional phosphane sulfides were chosen as the substrates for gold(I) complexation. These  $\alpha,\omega$ -substituted compounds offer the potential of internal stabilization through metal–metal bonding, or redistribution of the metal atoms over the two sulfur centers.

The alkanediyl-bis(diphenylphosphane) sulfides (**1a–1d**) are readily available through exhaustive sulfur addition to the parent phosphanes, which are commercially available. Treatment of these compounds with two mole equivalents of (dimethylsulfide)gold(I) chloride in tetrahydrofuran gives high yields of the dinuclear products **2a–2d** (Scheme 1). As investigated for the butane compound, the same reaction

with (tetrahydrothiophene)AuBr gives the analogous gold(I) bromide complex (**3d**), and metathesis of **2a–2c** with KBr in THF affords the remaining members of this series (**3a–3c**) (Scheme 1). The products are obtained as colourless crystalline solids of high melting points, soluble in polar organic solvents. Their composition is readily confirmed by microanalysis, mass spectrometry, and NMR spectroscopy (see the Experimental Section).

Scheme 1



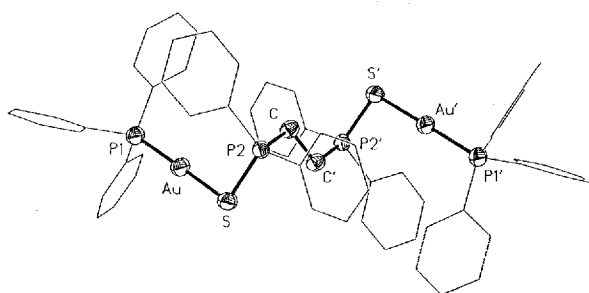
All attempts to add more than two AuX units to a ligand molecule **1** proved unsuccessful. The reactions of the ligands **1b–1d** with two equivalents of (triphenylphosphane)gold(I) trifluoromethylsulfonate in THF give dicationic 1:2 complexes (**4b–4d**) in high yield (Scheme 1). These high melting salts are stable crystalline compounds, which are soluble in polar solvents without decomposition. They are

readily identified through their analytical and spectroscopic data (see the Experimental Section).

All attempts to synthesize the corresponding complex of ligand **1a** failed. In this case the coordination of gold probably takes place through the carbon atom, as found in related experiments by Gimeno et al.<sup>[10]</sup>

The molecular structures of complexes **4b** and **4d** were determined by single-crystal X-ray diffraction studies. The crystals were grown by layering dichloromethane solutions with diethyl ether or pentane. Crystals of **4b** are triclinic, space group  $P\bar{1}$ , with  $Z = 1$  molecule per unit cell. The dication has a crystallographic center of inversion (Figure 1). Each sulfur atom bears a single  $[(\text{Ph}_3\text{P})\text{Au}]$  unit with an acute angle  $\text{P2-S-Au}$   $97.76(4)^\circ$  and linearity at the gold atom  $[\text{P1-Au-S}$   $179.03(3)^\circ$ ]. The triflate anions are noncoordinating, and there are neither intra- nor intermolecular Au-Au contacts.

Figure 1. Molecular structure of the dication of compound **4b** with atomic numbering (ORTEP<sup>[23]</sup>, hydrogen atoms omitted). Selected bond lengths (Å) and angles ( $^\circ$ ): Au-S 2.3247(8), Au-P1 2.2574(8), S-P2 2.0109(10); P1-Au-S 179.03(3), P2-S-Au 97.76(4)

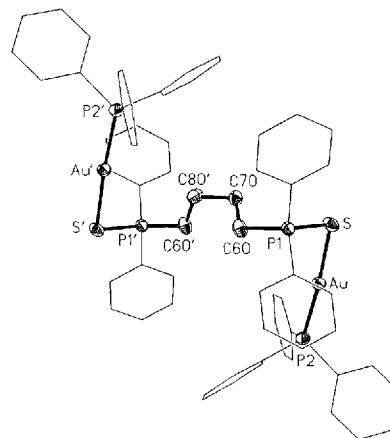


Crystals of **4d** are also triclinic, space group  $P\bar{1}$ , with  $Z = 1$  formula unit in the unit cell. The lattice contains free "triflate" anions and dications with an extended butane chain. This central part of the chain is disordered over two equivalent positions for each of the two inner carbon atoms (C70/C70' and C80/C80' in Figure 2). The configuration at the gold atoms is again linear  $[\text{P2-Au-S}$   $175.29(2)^\circ$ ], and the angle at the sulfur atoms is only  $96.37(3)^\circ$   $[\text{P2-S-Au}]$ . There is generally good agreement between all other structural parameters and those of the shorter homologue **4b**. For further details see the figure captions. Like in the reference compound, there are not even remote contacts between the gold atoms, and the triflate anions are strictly noncoordinating.

Treatment of triphenylphosphane sulfide  $\text{Ph}_3\text{PS}$  with  $[(\text{Ph}_3\text{P})\text{Au}]^+ \text{O}_3\text{SCF}_3^-$  gives the expected 1:1 complex **5** (Scheme 2), the data of which are useful reference values for NMR studies in this area. When this prototype was reacted with two equivalents or an excess of the same aurating agent, only the products of a P-S cleavage reaction were observed, with the sulfonium salt  $\{[\text{S}(\text{Au}(\text{PPh}_3))_3]^+ \text{O}_3\text{SCF}_3^-\}$  as the major component.

The same product also appears in analogous reactions of compounds **4b–4d** with  $[(\text{Ph}_3\text{P})\text{Au}]\text{O}_3\text{SCF}_3$ . In no case was double auration of the phosphane sulfide observed. It therefore appears that the P-S bond in phosphane sulfides

Figure 2. Molecular structure of the dication of compound **4d** with atomic numbering (ORTEP<sup>[23]</sup>, hydrogen atoms omitted); only one setting of the disordered orientations is shown. Selected bond lengths (Å) and angles ( $^\circ$ ): Au-S 2.3311(8), Au-P2 2.2560(7), S-P1 2.0201(9); P2-Au-S 175.29(2), P1-S-Au 96.37(3)



Scheme 2



is drastically weakened upon double complexation, with the immediate consequence that this bond is ruptured.

## Summary

The most important result of the present study is the failure of all attempts to generate dinuclear gold(I) complexes of phosphane sulfides. It appears that diauration of the sulfur atoms labilizes the P-S bond to such an extent that P-S bond cleavage is an immediate secondary reaction. The sulfur atom becomes the center of trigoldsulfonium cations, which are known to be highly stabilized by metal-metal interactions<sup>[1]</sup>; thus the sulfide anion is turned into a good leaving group. Analogous C-S bond cleavage processes are known to occur in the polyauration of thiols<sup>[17]</sup>.

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

## Experimental Section

All experiments were carried out under an atmosphere of dry, purified nitrogen. Glassware was dried and filled with nitrogen; solvents were distilled and kept under nitrogen. – NMR: JEOL-GX 270 (109.4 MHz), TMS as internal standard, phosphoric acid as external standard. – MS: Finnigan MAT 90. – Microanalyses: In-house analyzers (by combustion techniques). – Starting materials were either commercially available or were prepared following literature procedures:  $[(\text{Ph}_3\text{P})\text{Au}]\text{O}_3\text{BF}_4^-$ <sup>[18]</sup>,  $\text{Me}_2\text{SAuCl}$ <sup>[19]</sup>,  $(\text{tht})\text{AuBr}$ <sup>[20]</sup>,  $\text{Ph}_3\text{PAuCl}$ <sup>[21]</sup>.

1.  $(\text{CH}_2)[\text{Ph}_2\text{PSAuCl}]_2$  (**2a**): To a solution of  $\text{Me}_2\text{SAuCl}$  (131 mg, 0.45 mmol) in THF (30 ml) was added  $(\text{CH}_2)[\text{PPh}_2\text{S}]_2$  (100 mg, 0.22 mmol) dissolved in THF (20 ml). After stirring for 1 h the solvent and  $\text{Me}_2\text{S}$  were removed in vacuo and the residue was dis-

solved in dichloromethane. Addition of diethyl ether led to the precipitation of 195 mg (96%) of **2a** as a white solid. The product decomposes slowly in solution; m.p. 168°C decomp. –  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta = 7.41\text{--}7.81$  (m, 20H, ar-H), 3.45 [t,  $J = 10$  Hz, 2H,  $\text{PCH}_2$ ]. –  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta = 37.3$  (s). – MS (FAB, NBA);  $m/z$  (%): 879 (0.8)  $[\text{M}^{(37)\text{Cl}} - \text{Cl}]^+$ , 877 (2)  $[\text{M}^{(35)\text{Cl}} - \text{Cl}]^+$ , 645 (4)  $[\text{M} - \text{AuCl}_2]^+$ . –  $\text{C}_{25}\text{H}_{22}\text{Au}_2\text{Cl}_2\text{P}_2\text{S}_2$  (913.36): calcd. C 32.88, H 2.43, S 7.02; found C 32.49, H 2.51, S 6.14.

2.  $(\text{CH}_2)_2[\text{Ph}_2\text{PSAuCl}]_2$  (**2b**): Synthesis analogous to that of **2a**, with  $\text{Me}_2\text{SAuCl}$  (127 mg, 0.44 mmol) and  $(\text{CH}_2)_2[\text{Ph}_2\text{PS}]_2$  (100 mg, 0.22 mmol) giving 197 mg (98%) of **2b**; m.p. 230°C decomp. –  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta = 7.58\text{--}7.97$  (m, 20H, ar-H), 3.27 (m, 4H,  $\text{PCH}_2$ ). –  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta = 47.2$  (s). – MS (FAB, NBA);  $m/z$  (%): 659 (2)  $[\text{M} - \text{AuCl}_2]^+$ . –  $\text{C}_{26}\text{H}_{24}\text{Au}_2\text{Cl}_2\text{P}_2\text{S}_2$  (927.40): calcd. C 33.67, H 2.61, S 6.91; found C 33.55, H 2.65, S 6.45.

3.  $(\text{CH}_2)_3[\text{Ph}_2\text{PSAuCl}]_2$  (**2c**): Synthesis analogous to that of **2a**, with  $\text{Me}_2\text{SAuCl}$  (124 mg, 0.42 mmol) and  $(\text{CH}_2)_3[\text{Ph}_2\text{PS}]_2$  (100 mg, 0.21 mmol) giving 192 mg (97%) of **2c**; m.p. 187°C decomp. –  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 7.54\text{--}7.85$  (m, 20H, ar-H), 3.13 (m, 4H,  $\text{PCH}_2\text{CH}_2$ ), 2.04 (m, 2H,  $\text{PCH}_2\text{CH}_2$ ). –  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 45.5$  (s). – MS (FAB, NBA);  $m/z$  (%): 905 (0.1)  $[\text{M}^{(35)\text{Cl}} - \text{Cl}]^+$ , 673 (7)  $[\text{M} - \text{AuCl}_2]^+$ . –  $\text{C}_{27}\text{H}_{26}\text{Au}_2\text{Cl}_2\text{P}_2\text{S}_2$  (941.42): calcd. C 34.44, H 2.78, S 6.81; found C 34.52, H 2.87, S 6.63.

4.  $(\text{CH}_2)_4[\text{Ph}_2\text{PSAuCl}]_2$  (**2d**): Synthesis analogous to that of **2a**, with  $\text{Me}_2\text{SAuCl}$  (132 mg, 0.45 mmol) and  $(\text{CH}_2)_4[\text{Ph}_2\text{PS}]_2$  (110 mg, 0.22 mmol) giving 205 mg (96%) of **2d**. The compound is stable in air and in solution, soluble in dichloromethane and chloroform, but insoluble in pentane and diethyl ether. Crystals were obtained from dichloromethane solution by layering with diethyl ether; m.p. 144°C decomp. –  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 7.21\text{--}7.89$  (m, 20H, ar-H), 2.84 (m, 4H,  $\text{PCH}_2\text{CH}_2$ ), 2.01 (m, 4H,  $\text{PCH}_2\text{CH}_2$ ). –  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 45.1$  (s). – MS (FAB, NBA);  $m/z$  (%): 921 (8)  $[\text{M}^{(37)\text{Cl}} - \text{Cl}]^+$ , 919 (18)  $[\text{M}^{(35)\text{Cl}} - \text{Cl}]^+$ , 687 (100)  $[\text{M} - \text{AuCl}_2]^+$ . –  $\text{C}_{28}\text{H}_{28}\text{Au}_2\text{Cl}_2\text{P}_2\text{S}_2$  (955.44): calcd. C 35.52, H 2.95, S 6.71; found C 35.94, H 3.06, S 6.96.

5.  $(\text{CH}_2)_2[\text{Ph}_2\text{PSAuBr}]_2$  (**3a**): To a solution of **2a** (78 mg, 0.09 mmol) in THF (100 ml) was added an excess of KBr (300 mg, 1.90 mmol) in  $\text{H}_2\text{O}$  (20 ml). After stirring for 5 h the THF was removed in vacuo and the precipitated product was extracted with dichloromethane and dried with  $\text{Na}_2\text{SO}_4$ . Addition of pentane led to the precipitation of 71 mg (84%) of **3a** as a white solid. The product decomposes slowly in solution; m.p. 181°C decomp. –  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 7.48\text{--}7.82$  (m, 20H, ar-H), 3.47 [t,  $J = 10$  Hz, 2H,  $\text{PCH}_2$ ]. –  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 36.9$  (s). – MS (FAB, NBA);  $m/z$  (%): 923 (2)  $[\text{M}^{(81)\text{Br}} - \text{Br}]^+$ , 921 (1)  $[\text{M}^{(79)\text{Br}} - \text{Br}]^+$ , 645 (18)  $[\text{M} - \text{AuBr}_2]^+$ .

6.  $(\text{CH}_2)_2[\text{Ph}_2\text{PSAuBr}]_2$  (**3b**): Synthesis analogous to that of **3a**, with **2b** (95 mg, 0.10 mmol) and KBr (300 mg, 1.90 mmol) giving 88 mg (87%) of **3b**; m.p. 245°C decomp. –  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 7.52\text{--}7.86$  (m, 20H, ar-H), 3.22 (m, 4H,  $\text{PCH}_2$ ). –  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 45.7$  (s). – MS (FAB, NBA);  $m/z$  (%): 659 (0.32)  $[\text{M} - \text{AuBr}_2]^+$ .

7.  $(\text{CH}_2)_3[\text{Ph}_2\text{PSAuBr}]_2$  (**3c**): Synthesis analogous to that of **3a**, with **2c** (74 mg, 0.08 mmol) and KBr (300 mg, 1.90 mmol) giving 69 mg (85%) of **3c**. The compound shows low solubility in common solvents; m.p. 195°C decomp. –  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 7.51\text{--}7.87$  (m, 20H, ar-H), 2.83 (m, 4H,  $\text{PCH}_2\text{CH}_2$ ), 2.40 (m, 2H,  $\text{PCH}_2\text{CH}_2$ ). –  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 45.2$  (s). – MS (FAB, NBA);  $m/z$  (%): 951 (0.1)  $[\text{M}^{(81)\text{Br}} - \text{Br}]^+$ , 673 (2)  $[\text{M} - \text{AuBr}_2]^+$ .

8.  $(\text{CH}_2)_4[\text{Ph}_2\text{PSAuBr}]_2$  (**3d**): To a solution of (tht)AuBr (186 mg, 0.51 mmol) in THF (30 ml) was added  $(\text{CH}_2)_4[\text{PPh}_2\text{S}]_2$  (119

mg, 0.25 mmol) dissolved in THF (50 ml). After stirring for 30 min the solvent and tht were removed in vacuo and the residue was dissolved in dichloromethane. Addition of pentane led to the precipitation of 248 mg (93%) of **3d** as a white solid. The compound is stable in air and in solution, soluble in dichloromethane and chloroform, but insoluble in pentane and diethyl ether. Crystals were obtained from dichloromethane solution by layering with pentane; m.p. 151°C decomp. –  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 7.52\text{--}7.85$  (m, 20H, ar-H), 2.80 (m, 4H,  $\text{PCH}_2\text{CH}_2$ ), 2.11 (m, 4H,  $\text{PCH}_2\text{CH}_2$ ). –  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 45.8$  (s). – MS (FAB, NBA);  $m/z$  (%): 965 (3)  $[\text{M}^{(81)\text{Br}} - \text{Br}]^+$ , 963 (3)  $[\text{M}^{(79)\text{Br}} - \text{Br}]^+$ , 687 (34)  $[\text{M} - \text{AuBr}_2]^+$ . –  $\text{C}_{28}\text{H}_{28}\text{Au}_2\text{Br}_2\text{P}_2\text{S}_2$  (1044.34): calcd. C 32.20, H 2.70, S 6.14; found C 32.31, H 2.82, S 6.47.

9.  $(\text{CH}_2)_2[\text{Ph}_2\text{PSAuPPh}_3]_2^{2+} \cdot 2 \text{CF}_3\text{SO}_3^-$  (**4b**):  $\text{Ph}_3\text{PAuCl}$  (107 mg, 0.22 mmol) dissolved in THF (10 ml) was added to a solution of  $\text{AgCF}_3\text{SO}_3$  (56 mg, 0.22 mmol) in THF (30 ml) at 0°C. After stirring for 15 min the solution was filtered and added to  $(\text{CH}_2)_4[\text{Ph}_2\text{PS}]_2$  (50 mg, 0.11 mmol) dissolved in THF (50 ml). The solution was stirred for 2 h at room temperature. Evaporation of the solvent in vacuo to a volume of ca. 5 ml and subsequent addition of pentane led to the precipitation of 166 mg (92%) of **4b** as a white solid. Crystals of **4b** suitable for X-ray studies were obtained from dichloromethane solution by layering with diethyl ether; m.p. 247°C decomp. –  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta = 7.12\text{--}7.88$  (m, 50H, ar-H), 3.27 (m, 4H,  $\text{PCH}_2$ ). –  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 134.3$  (s), 130.1 (m, AXX'), 131.7 (m, AXX'), 126.8 (d,  $J = 74$  Hz, C-*para*, -*meta*, -*ortho*, -*ipso* in  $\text{Ph}_2\text{P}$ ), 132.7 (s), 129.8 (d,  $J = 12$  Hz), 133.7 (d,  $J = 14$  Hz), 127.1 (d,  $J = 61$  Hz, C-*para*, -*meta*, -*ortho*, -*ipso* in  $\text{Ph}_3\text{PAu}$ ), 23.9 (s,  $\text{PCH}_2$ ). –  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 52.2$  (s, 2 P,  $\text{Ph}_2\text{PS}$ ), 39.9 (s, 2 P,  $\text{Ph}_3\text{PAu}$ ). – MS (FD,  $\text{CH}_2\text{Cl}_2$ );  $m/z$  (%): 921 (40)  $[\text{M} - \text{AuPPh}_3]^+$ , 690 (67)  $[\text{M}]^{2+}/2$ . –  $\text{C}_{64}\text{H}_{54}\text{Au}_2\text{F}_6\text{O}_6\text{P}_4\text{S}_4$  (1679.19): calcd. C 45.78, H 3.24; found C 45.98, H 3.41.

10.  $(\text{CH}_2)_3[\text{Ph}_2\text{PSAuPPh}_3]_2^{2+} \cdot 2 \text{CF}_3\text{SO}_3^-$  (**4c**): Synthesis analogous to that of **4b**, with  $\text{Ph}_3\text{PAuCl}$  (104 mg, 0.21 mmol),  $\text{AgCF}_3\text{SO}_3$  (54 mg, 0.21 mmol) and  $(\text{CH}_2)_3[\text{Ph}_2\text{PS}]_2$  (50 mg, 0.11 mmol) giving 156 mg (88%) of **4c**; m.p. 148°C decomp. –  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta = 7.13\text{--}7.88$  (m, 50H, ar-H), 3.22 (m, 4H,  $\text{PCH}_2\text{CH}_2$ ), 2.04 (m, 2H,  $\text{PCH}_2\text{CH}_2$ ). –  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta = 131.9$  (s), 130.1 (d,  $J = 13$  Hz), 131.9 (d,  $J = 11$  Hz), 127.7 (d,  $J = 83$  Hz, C-*para*, -*meta*, -*ortho*, -*ipso* in  $\text{Ph}_2\text{P}$ ), 132.9 (d,  $J = 3$  Hz), 130.0 (d,  $J = 12$  Hz), 134.2 (d,  $J = 14$  Hz), 127.6 (d,  $J = 61$  Hz, C-*para*, -*meta*, -*ortho*, -*ipso* in  $\text{Ph}_3\text{PAu}$ ), 30.7 [dd,  $^1\text{J}(\text{CP}) = 53$  Hz,  $^2\text{J}(\text{CP}) = 16$  Hz,  $\text{PCH}_2\text{CH}_2$ ], 16.2 (m,  $\text{PCH}_2\text{CH}_2$ ). –  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 49.0$  (s, 2 P,  $\text{Ph}_2\text{PS}$ ), 37.5 (s, 2 P,  $\text{Ph}_3\text{PAu}$ ). – MS (FD,  $\text{CH}_2\text{Cl}_2$ );  $m/z$  (%): 697 (100)  $[\text{M}]^{2+}/2$ .

11.  $(\text{CH}_2)_4[\text{Ph}_2\text{SAuPPh}_3]_2^{2+} \cdot 2 \text{CF}_3\text{SO}_3^-$  (**4d**): Synthesis analogous to that of **4b**, with  $\text{Ph}_3\text{PAuCl}$  (110 mg, 0.22 mmol),  $\text{AgCF}_3\text{SO}_3$  (58 mg, 0.22 mmol) and  $(\text{CH}_2)_4[\text{Ph}_2\text{PS}]_2$  (54 mg, 0.11 mmol) giving 169 mg (89%) of **4d**. Crystals of **4d** suitable for X-ray studies were obtained from dichloromethane solution by layering with pentane; m.p. 212°C decomp. –  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta = 7.18\text{--}7.95$  (m, 50H, ar-H), 2.89 (m, 4H,  $\text{PCH}_2\text{CH}_2$ ), 1.83 (m, 4H,  $\text{PCH}_2\text{CH}_2$ ). –  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta = 134.2$  (d,  $J = 3$  Hz), 130.1 (d,  $J = 13$  Hz), 132.1 (d,  $J = 11$  Hz), 128.0 (d,  $J = 82$  Hz, C-*para*, -*meta*, -*ortho*, -*ipso* in  $\text{Ph}_2\text{P}$ ), 132.9 (d,  $J = 3$  Hz), 129.9 (d,  $J = 12$  Hz), 134.2 (d,  $J = 14$  Hz), 127.7 (d,  $J = 61$  Hz, C-*para*, -*meta*, -*ortho*, -*ipso* in  $\text{Ph}_3\text{PAu}$ ), 30.6 (d,  $J = 55$  Hz,  $\text{PCH}_2\text{CH}_2$ ), 23.5 (d,  $J = 22$  Hz,  $\text{PCH}_2\text{CH}_2$ ). –  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta = 49.6$  (s, 2 P,  $\text{Ph}_2\text{PS}$ ), 37.7 (s, 2 P,  $\text{Ph}_3\text{PAu}$ ). – MS (FAB, NBA);  $m/z$  (%): 1410 (2)  $[\text{M} + 1]^+$ , 949 (2)  $[\text{M} - \text{AuPPh}_3]^+$ , 687 (58)  $[\text{M} - \text{Au}(\text{PPh}_3)_2]^+$ . –  $\text{C}_{66}\text{H}_{58}\text{Au}_2\text{F}_6\text{O}_6\text{P}_4\text{S}_4$  (1707.25): calcd. C 46.43, H 3.42; found C 45.98, H 3.41.

12.  $[Ph_3PSAuPPh_3]^+ CF_3SO_3^-$  (**5**): Synthesis analogous to that of **4b**, with  $Ph_3PAuCl$  (100 mg, 0.20 mmol),  $AgCF_3SO_3$  (52 mg, 0.20 mmol) and  $Ph_3PS$  (59 mg, 0.20 mmol) giving 164 mg (90%) of **5**. Crystals were obtained from THF solution by layering with pentane; m.p. 225°C decomp. –  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  = 7.12–7.77 (m, ar-H). –  $^{13}C$   $\{^1H\}$  NMR ( $CDCl_3$ ):  $\delta$  = 134.1 (d,  $J$  = 3 Hz), 129.9 (d,  $J$  = 13 Hz), 132.6 (d,  $J$  = 12 Hz), 127.3 (d,  $J$  = 86 Hz, C-*para*, -*meta*, -*ortho*, -*ipso* in  $Ph_3P$ ), 132.7 (s), 129.7 (d,  $J$  = 11 Hz), 133.7 (d,  $J$  = 14 Hz), 128.0 (d,  $J$  = 55 Hz, C-*para*, -*meta*, -*ortho*, -*ipso* in  $Ph_3PAu$ ). –  $^{31}P$   $\{^1H\}$  NMR ( $CDCl_3$ ):  $\delta$  = 46.1 (s, 1 P,  $Ph_3PS$ ), 37.5 (s, 1 P,  $Ph_3PAu$ ). – MS (FAB, NBA);  $m/z$  (%): 753 (100)  $[M^+]$ . –  $C_{37}H_{30}AuF_3O_3P_2S_2$  (902.67): calcd. C 49.23, H 3.35, S 7.10; found C 49.04, H 3.42, S 6.81.

**Crystal Structure Determinations:** Suitable single crystals of **4b** and **4d** were sealed into glass capillaries and used for measurement

Table 1. Crystal data, data collection, and structure refinement for compounds **4b** and **4d**

	<b>4b</b>	<b>4d</b>
<b>Crystal data</b>		
Formula	$C_{64}H_{54}Au_2F_6O_6P_4S_4$	$C_{66}H_{58}Au_2F_6O_6P_4S_4$
$M_r$	1679.12	1707.18
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Cryst. dim. (mm)	$0.20 \times 0.25 \times 0.45$	$0.17 \times 0.25 \times 0.50$
$a$ (Å)	10.777(1)	10.658(1)
$b$ (Å)	12.898(1)	12.770(1)
$c$ (Å)	13.055(1)	13.306(1)
$\alpha$ (°)	69.64(1)	111.31(1)
$\beta$ (°)	76.92(1)	102.52(1)
$\gamma$ (°)	71.36(1)	96.19(1)
$V$ (Å <sup>3</sup> )	1598.3(3)	1612.0(2)
$\rho_{calc}$ (g cm <sup>-3</sup> )	1.744	1.759
$Z$	1	1
$F(000)$ (e)	822	838
$\mu$ (Mo- $K_\alpha$ ) (cm <sup>-1</sup> )	48.8	48.4
<b>Data collection</b>		
Diffractionmeter	Enraf Nonius CAD4	
Radiation	Mo- $K_\alpha$ , 0.71073 Å, graphite monochromator	
$T$ (°C)	23	-68
Scan mode	$\omega$	$\omega$
$hkl$ range	$\pm 13/\pm 16/\pm 16$	$\pm 13/\pm 16/\pm 16$
Measured refl.	6600	6856
Unique refl.	6599	6846
Used refl.	6591	6846
Absorption corr.	empirical	empirical
$T_{min}/T_{max}$ (%)	0.6954/0.9998	0.6357/0.9990
<b>Refinement</b>		
Refined parameters	388	406
H atoms (found/calcd.)	0/54	0/58
$R1^{[a]}$	0.0227	0.0195
$wR2^{[a]}$	0.0564	0.0513
$\rho_{fin}(\max/\min)$ (e Å <sup>-3</sup> ) <sup>[b]</sup>	+0.79/-0.63	+1.57/-0.87

[a]  $R1 = \sum (|F_o| - |F_c|) / \sum |F_o|$ ,  $wR2 = [\sum w(F_o^2 - F_c^2)^2] / [\sum w(F_o^2)^2]^{1/2}$ ,  $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$ ,  $p = (F_o^2 + 2F_c^2)/3$ ,  $a = 0.0305$ ,  $b = 0.0271$  (**4b**, **4d**);  $b = 0.7539$ ,  $1.7043$  (**4b**, **4d**). – [b] Residual electron densities located close to the Au atoms.

of precise cell constants and collection of intensity data. During data collection, three standard reflections were measured periodically as a general check of crystal and instrument stability. No significant changes were observed for the compounds. Diffraction intensities were corrected for Lorentz polarization and absorption effects. The structures were solved by direct methods for **4d** and by the Heavy Atom Method for **4b**, and were refined by full matrix least-squares calculations against  $F^2$ [22]. The thermal motion of all non-hydrogen atoms was treated anisotropically. The hydrogen atoms of the compounds were calculated in idealized positions and their isotropic thermal parameters were tied to that of the adjacent carbon atom by a factor of 1.5. Details of the crystal data, data collection and structure refinement are summarized in Table 1. Selected interatomic distances and angles are given in the corresponding figure captions. Further information may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository numbers CSD-406430 (**4b**) and CSD-406429 (**4d**), the names of the authors, and the full journal citation.

- [1] H. Schmidbaur, *Chem. Soc. Rev.* **1995**, 24, 391–400.
- [2] F. Canales, M. C. Gimeno, P. G. Jones, A. Laguna, *Angew. Chem., Int. Ed. Engl.* **1994**, 33, 769–770.
- [3] I. M. Keen, *J. Chem. Soc.* **1965**, 5751–5752.
- [4] M. S. Hussain, E. O. Schlemper, *Acta Crystallogr. C* **1987**, 43, 450–453.
- [5] P. G. Jones, E. Bembenek, *J. Cryst. Spectrosc.* **1992**, 22, 397–401.
- [6] M. G. King, G. P. McQuillan, *J. Chem. Soc. A* **1967**, 898–901.
- [7] P. G. Jones, A. F. Williams, *J. Chem. Soc., Dalton Trans.* **1977**, 1430–1434.
- [8] E. Fritsch, K. Polborn, K. Sünkel, W. Beck, *Z. Anorg. Allg. Chem.* **1992**, 617, 110–115.
- [9] A. Laguna, M. Laguna, A. Royo, M. N. Fraile, *J. Organomet. Chem.* **1986**, 315, 269–276.
- [10] M. C. Gimeno, A. Laguna, M. Laguna, F. Sanmartin, P. G. Jones, *Organometallics* **1993**, 12, 3984–3991.
- [11] R. J. Staples, S. Wang, J. P. Fackler, Jr., S. O. Grim, E. de Laubenfels, *Acta Crystallogr. C* **1994**, 50, 1242–1244.
- [12] R. M. Dávila, A. E. Elduque, T. Grant, R. J. Staples, J. P. Fackler, Jr., *Inorg. Chem.* **1993**, 43, 1749–1755.
- [13] O. Crespo, M. C. Gimeno, P. G. Jones, A. Laguna, *Inorg. Chem.* **1994**, 33, 6128–6131.
- [14] R. Usón, A. Laguna, M. Laguna, J. Jimenez, M. P. Gomez, A. Sainz, P. G. Jones, *J. Chem. Soc., Dalton Trans.* **1990**, 333–338.
- [15] [15a] H. Schmidbaur, *Acc. Chem. Res.* **1975**, 8, 62–70. – [15b] H. Schmidbaur, "Organogold Compounds"; *Gmelin Handbook of Inorganic Chemistry*, Springer-Verlag, Berlin **1980**. – [15c] A. Grohmann, H. Schmidbaur, *Comprehensive Organometallic Chemistry II* (Eds.: J. Wardell, E. W. Abel, F. G. A. Stone, G. Wilkinson), vol. 3, Pergamon Press, Oxford **1995**.
- [16] J. P. Fackler, Jr., *Polyhedron* **1997**, 16, 1, and references therein.
- [17] A. Sladek, H. Schmidbaur, unpublished results, **1996**.
- [18] A. N. Nesmeyanov, E. G. Perevalova, Y. T. Struchkov, M. Y. Antipin, K. I. Grandberg, V. P. Dyadchenko, *J. Organomet. Chem.* **1980**, 201, 343.
- [19] K. C. Dash, H. Schmidbaur, *Chem. Ber.* **1973**, 106, 1221–1225.
- [20] G. E. Coates, C. Parkin, *J. Chem. Soc.* **1963**, 421–429.
- [21] N. C. Baenziger, W. E. Bennet, D. M. Soboroff, *Acta Crystallogr. B* **1976**, 32, 962–963.
- [22] G. M. Sheldrick, *SHELXL-93*, Universität Göttingen, **1993**.
- [23] C. K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.

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