Synthesis and Structure of a Cyclic Complex of Digold Sulfide Au_2S and of Related Compounds

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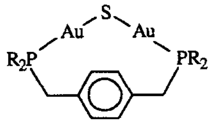
Received April 25, 1995

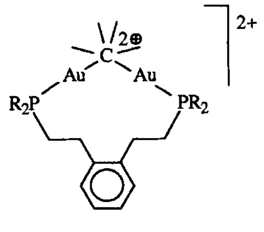
Key Words: Gold sulfide complexes / Gold thiolates / (Phosphane)gold(I) complexes / Digoldsulfonium salts / Digoldchloronium salt

1,4-Bis(diphenylphosphanylmethyl)benzene (**1**) was converted into its bis[chlorogold(I)] complex [**1** · $(AuCl)_2$] upon treatment with two equivalents of chloro(dimethyl sulfide)gold(I). The reaction of **1** · $(AuCl)_2$ with one equivalent of silver tetrafluoroborate afforded a cyclic di[gold(I)]chloronium tetrafluoroborate [**1** · Au_2Cl^+ BF_4^-]. Substitution of chloride in **1** · $(AuCl)_2$ by sodium methanethiolate in wet chloroform, gave the bis[methylthiogold(I)] complex **1** · $(AuSMe)_2$, while with sodium sulfide a cyclic complex **1** · Au_2S was obtained. Reaction of **1** · $(AuCl)_2$ with two equivalents of $AgBF_4$ followed by treatment with diphenyldisulfide or sodium methanethiolate yielded the cyclic methyl/phenylsulfonium tetrafluoroborates **1** · Au_2SPh^+ BF_4^- and **1** · $Au_2SMe^+BF_4^-$, respectively. All compounds were identified on the basis of their analytical and spectroscopic data. The crystal structures of **1** · $(AuCl)_2$, **1** · $(AuSMe)_2$, and **1** · Au_2S have been determined. The Au_2S complex has a cyclic structure with a narrow Au–S–Au angle of 86.7(1)° indicating a significant intraannular Au···Au interaction.

Many two-coordinate gold(I) complexes of the general formula L–Au–X with small neutral ligands L and simple anions X have unusual solid state structures characterized by both intra- and intermolecular contacts of gold atoms.[1,2] Supramolecular aggregations forming pairs, clusters, chains or sheets have been observed, depending on the stoichiometry, polarity and steric requirements of the complexes and their ligands, respectively.[3,4] As part of a pertinent research program we have now investigated chloro- and thiolatogold(I) complexes of a ligand specifically tailored to span two gold(I) centers bridged by a sulfur atom. The molecular geometry of *1,4-bis[(diphenylphosphanyl)-methyl]benzene* (**1**)[5] was calculated to fit the requirements of a unit [SAu_2] with an angle at S close to 90° and for a complex with linearity at the gold centers (**A**). This ligand resembles another arylidene-based ditertiary phosphane used previously for spanning edges of carbon-centered octahedra,[6] but with reduced flexibility of its framework (**B**).



A



B

Binuclear Open-Chain Complexes

Ligand **1** was prepared by published methods.[5] It reacts with two equivalents of chloro(dimethyl sulfide)gold(I) in dichloromethane at ambient temperature to give the dinuclear complex **1**·$(AuCl)_2$ in virtually quantitative yield [Eq. (1)]. Treatment of this product with sodium methanethiolate in a two-phase medium of chloroform/water afforded quantitative yields of the corresponding bis(methylthiolatogold) complex **1**·$(AuSMe)_2$, [Eq. (2)].

The molecular structures of the two binuclear open-chain compounds have been determined by single crystal X-ray diffraction methods. The complex **1**·$(AuCl)_2$ has a centrosymmetrical structure (Figure 1) with the crystallographic center of inversion located at the center of the *p*-xylene ring. The coordination geometry at the gold atoms is quasi-linear [P–Au–Cl 176.3(1)°] with unexceptional bond distances. The efficient shielding of the P–Au–Cl units by the phenyl and xylyl substituents precludes any close *inter*molecular Au···Au contacts. The *p*-xylene ring atoms are coplanar by symmetry. The absence of any distortion indicates a strain-free situation.

The complex **1**·$(AuSMe)_2$ has no crystallographic symmetry, but the skeleton of the molecular structure (except for the orientation of the phenyl groups) is, again, close to point group C_i. The units P–Au–S are quasi-linear [174.2(1), 176.3(1)°] with standard bond lengths, and the central xylene ring system is coplanar including the carbon atoms of its CH_2 substituents. The folding of the molecules and the resulting shielding again eliminate the possibility for any *inter*molecular Au···Au contacts (Figure 2).

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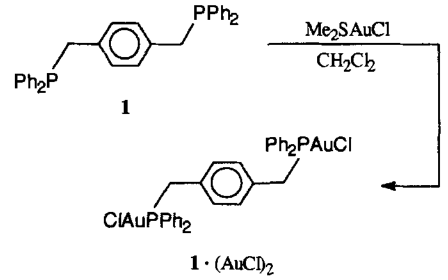
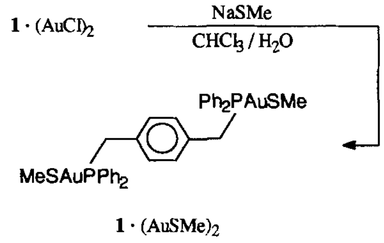
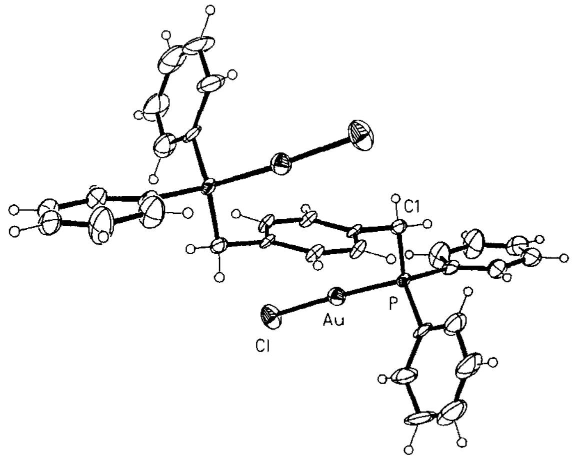


Eq. (1)



Eq. (2)

Figure 1. Molecular structure of 1,4-[(ClAu)Ph$_2$PCH$_2$]$_2$C$_6$H$_4$, **1 · (AuCl)$_2$** (ORTEP; hydrogen atoms with arbitrary radii)[a]



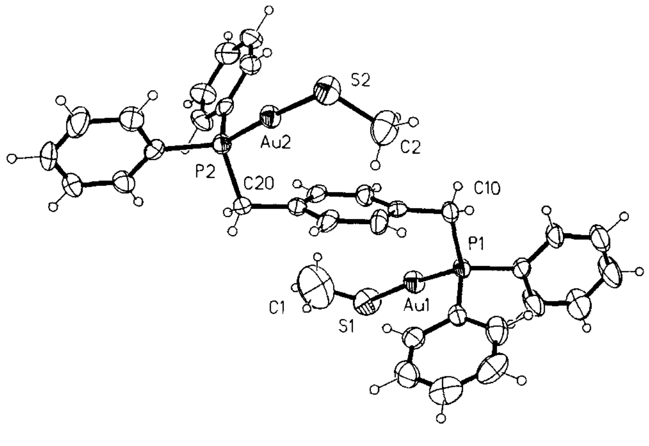
[a] Selected bond lengths [Å] and angles [°]: Au−P 2.226(2), Au−Cl 2.278(3), P−Cl 1.824(10); P−Au−Cl 176.3(1), Au−P−Cl 112.4(3).

Binuclear Cyclic Complexes

Treatment of complex **1·(AuCl)$_2$** with *one* equivalent of tetrafluoroborate in dichloromethane/tetrahydrofuran led to a AgCl precipitate and to a solution of an ionic product identified by its analytical and spectroscopic data as a salt with a cyclic digold chloronium cation **[1·Au$_2$Cl]$^+$ BF$_4$$^-$** [Eq. (3)].

^{31}P{^{1}H}-NMR spectra of solutions of the product in dichloromethane show only one singlet resonance, and the ^{1}H- and ^{13}C-NMR spectra show only one set of signals indicating equivalent phenyl rings and a symmetrically disposed xylene bridge. There is no significant change in the spectra when the temperature is lowered to −65 °C. This result eliminates the possibility for any unsymmetrical structure, for example, with the remaining chlorine atom at one gold atom and with the tetrafluoroborate unit at the other.

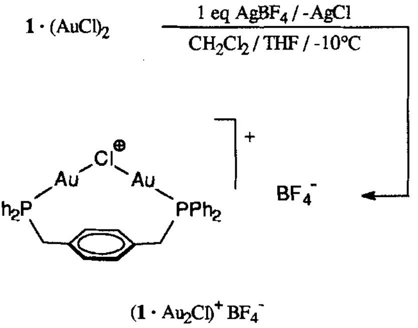
Figure 2. Molecular structure of 1,4-[(H$_3$CSAu)Ph$_2$PCH$_2$]$_2$C$_6$H$_4$, **1 · (AuSMe)$_2$** (ORTEP; hydrogen atoms with arbitrary radii)[a]



[a] Selected bond lengths [Å] and angles [°]: Au1−S1 2.277(3), Au1−P1 2.245(2), S1−C1 1.76(2), Au2−P2 2.252(2), Au2−S2 2.282(3), S2−C2 1.80(1), P1−C10 1.825(8), P2−C20 1.843(7); P1−Au1−S1 174.1(1), P2−Au2−S2 176.3(1), Au1−S1−C1 101.4(6), C2−S2−Au2 102.0(4), Au1−P1−C10 114.6(3), Au2−P2−C20 110.3(3).

Most importantly, the FAB mass spectrum has the molecular mass of the cation **[1·Au$_2$Cl]$^+$** as the parent ion, followed by a fragment originating from a loss of AuCl.

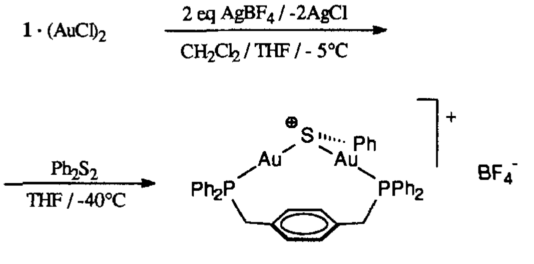
There is precedent in the literature for compounds with bis[(phosphane)gold(I)]chloronium cations.[7] This earlier work also includes a study of the crystal structure of [(Ph$_3$PAu)$_2$Cl]$^+$ BF$_4$$^-$, which revealed a heavy atom skeleton bent at a chlorine atom bridging the two gold atoms. The formula with a cyclic cation, proposed in Eq. (3), is based on this analogy, but it represents a unique case of a *cyclic* chloronium salt with low-valent, low-coordinate metal atoms. Chlorine bridging is also present in the electroneutral zig-zag chains of crystalline AuCl.[8,9]



Eq. (3)

The reaction of complex **1·(AuCl)$_2$** with *two* equivalents of AgBF$_4$ in CH$_2$Cl$_2$/THF at −5 °C afforded a precipitate of AgCl and a solution of a strongly nucleophilic binuclear gold compound. This was tentatively assigned the structure of the bis(tetrafluoroborate), and was found to react with diphenyl disulfide at −40 °C to give good yields of a cyclic digold(phenyl)sulfonium salt [Eq. (4)]. The product was identified unequivocally on the basis of its analytical and spectroscopic data.

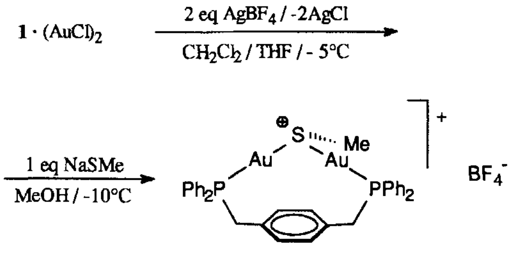
Reaction of the bis(tetrafluoroborate) with one equivalent of sodium methanethiolate in methanol gives the digold(methyl)sulfonium salt [Eq. (5)]. This methyl homologue was characterized only by its NMR and FAB-MS data.



Eq. (4)

$(\mathbf{1}\cdot Au_2SPh)^+BF_4^-$

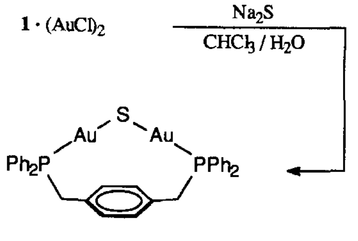
Digold(alkyl/aryl)sulfonium salts are quite well known,[10–13] including structural data,[12,13] and therefore a discussion of the stoichiometry and structure is not necessary. It is only the large ring structure of the cation which is of specific interest regarding the ligand properties of **1**.



Eq. (5)

$(\mathbf{1}\cdot Au_2SMe)^+BF_4^-$

Treatment of **1·(AuCl)₂** with sodium sulfide hydrate $Na_2S_{(aq)}$ in chloroform at room temperature gave quantitative yields of the di[gold(I)]sulfide complex **1·Au₂S** [Eq. (6)]. The product is soluble in chlorocarbon solvents. Its FAB mass spectrum shows the parent ion $(M)^+$ in high intensity, accompanied by the ions $(M + Au)^+$ and $(M - AuS)^+$. The NMR spectra (in $CDCl_3$) have a singlet ^{31}P resonance and one set of ^1H and ^{13}C signals for a symmetrically disposed bidentate ligand. There is no indication of a lowering of the D_{2h} or C_{2v} symmetry of the xylene ring in solution. Considering the folding of the macrocycle detected in the solid state structure (Figure 3), these NMR results prove that a rapid ring inversion occurs in solution.

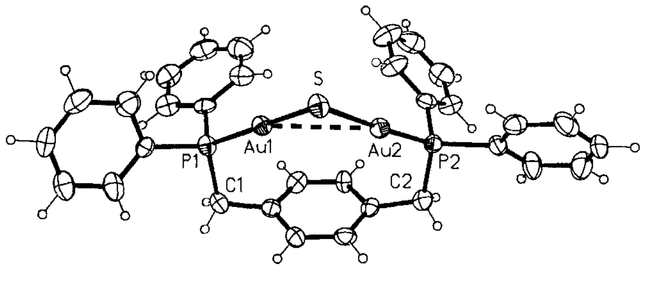


Eq. (6)

$\mathbf{1}\cdot Au_2S$

The compound crystallizes from $CHCl_3$ with two molecules of solvent to produce **1·Au₂S 2 CHCl₃**. In the crystal, the molecule has no crystallographically-imposed symmetry, but its structure closely approaches mirror symmetry (Figure 3). The macrocycle has a narrow Au–S–Au angle of only 86.7(1)°, associated with a short intraannular Au···Au distance of 3.147(1) Å. The S–Au–P linkages are not quite linear [175.7(1) and 175.9(1)°, respectively], and the bending is such that the gold atoms approach each other.

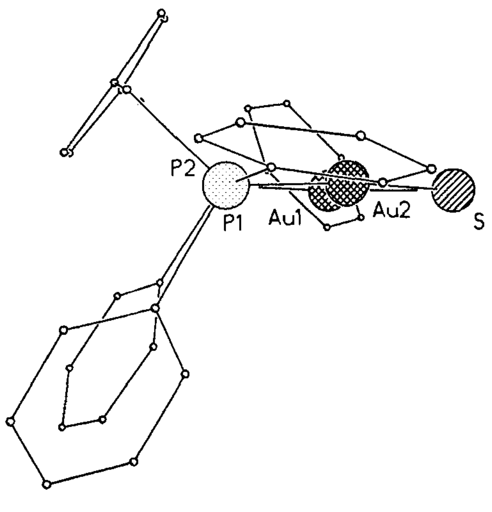
Figure 3. Molecular structure of $\{1,4\text{-}[Ph_2PCH_2]_2C_6H_4\}Au_2S$, **1 · (Au₂S)** (ORTEP; hydrogen atoms with arbitrary radii)[a]



[a] Selected bond lengths [Å] and angles [°]: Au1–S 2.298(2), Au2–S 2.283(2), Au1–P1 2.260(2), Au2–P2 2.260(2), Au1–Au2 3.146(1), P1–C1 1.844(9), P2–C2 1.824(9); Au1–S–Au2 86.7(1), P1–Au1–S 175.7(1), P2–Au2–S 175.9(1), Au1–P1–C1 113.6(3), Au2–P2–C2 114.2(3).

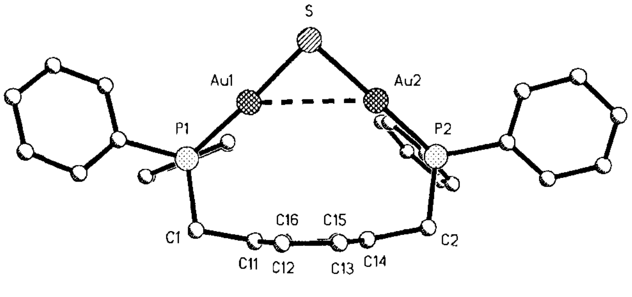
As can be seen from a different projection of the compound shown in Figure 4, the large ring is folded at the phosporus atoms, but the skeleton of the heavy elements (P_2Au_2S) is almost planar (Figure 4). The geometry of the bridging p-xylene unit is indicative of some ring strain. The phenylene ring is not planar with folding angles of the planes C12–C11–C16 and C13–C14–C15 versus C12–C13–C15–C16 of 3.8 and 4.3°, respectively, and a bending of C1 away from the C12–C11–C16 plane (6.8°) and of C2 from the C13–C14–C15 plane (6.1°) (Figure 5). These distortions appear to be necessary in order to secure a small Au–S–Au angle and to preserve linearity at the gold atoms as much as possible. The structure is therefore another example of the influence of Au···Au interactions on

Figure 4. Side projection of the molecule **1 · (Au₂S)** (Figure 3). (Arbitrary radii for all atoms; hydrogen atoms omitted for clarity.)



the molecular configurations and conformations of multinuclear gold(I) complexes.

Figure 5. Projection of the molecule **1 · (Au$_2$S)** (Figure 3), parallel to the *p*-xylene group (C1, C11–C16, C2), showing the non-planarity of this group. (SCHAKAL, arbitrary radii for all atoms; hydrogen atoms omitted for clarity.)



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 are grateful to Mr. *J. Riede* for carefully establishing the X-ray data sets.

Experimental

All experiments were carried out under dry, purified nitrogen. Samples and solutions were protected against direct incandescent light. Solvents were dried, distilled and saturated with nitrogen. Glassware was oven-dried and filled with nitrogen. 1,4-Bis[(diphenylphosphanyl)methyl)]benzene was prepared according to literature method[5]. MS: Finnigan MAT 90; NMR: Jeol GX 400 spectrometer with TMS as an internal standard and CDCl$_3$ as solvent, unless stated otherwise.

Bis[chlorogold(I)] Complex **1·(AuCl)$_2$**: A solution of 949 mg (2 mmol) of 1,4-C$_6$H$_4$(CH$_2$PPh$_2$)$_2$ in 120 ml of dichloromethane is added dropwise to a solution of 1.18 g (4 mmol) of Me$_2$SAuCl in 70 ml of dichloromethane at ambient temperature. After stirring for 30 min the clear solution is concentrated under vacuum. Addition of pentane leads to precipitation of the white product, which is filtered off, washed with pentane and dried under vacuum. Yield 1.77 g (94%), m.p. 327°C. – ^{1}H NMR: δ = 3.73 (d, $^2J_{HP}$ = 11 Hz, C*H*$_2$), 6.88 (s, C$_6$*H*$_4$), 7.27–7.64 (m, Ph-*H*). – ^{13}C{^{1}H} NMR: δ = 35.5 (d, $^1J_{CP}$ = 43 Hz, *C*H$_2$), 128.4 (d, $^1J_{CP}$ = 58 Hz, Ph-*ipso-C*), 129.2 (m, Ph-*meta-C*), 130.6 (s, C$_6$H$_4$-*C*H), 131.1 (s, C$_6$H$_4$-*ipso-C*), 132.4 (m, Ph-*para-C*), 133.4 (m, Ph-*ortho-C*). – ^{31}P{^{1}H} NMR: δ = 34.3 (s). – MS (FAB): *m/z* (%) = 903.5 (1) [M$^+$-Cl]. – C$_{32}$H$_{28}$Au$_2$Cl$_2$P$_2$ (939.40): calcd. C 40.92, H 3.00, Au 41.94; found C 40.94, H 3.09, Au 41.59.

Bis[methanethiolatogold(I)] Complex **1·(AuSMe)$_2$**: 188 mg (0.2 mmol) of 1,4-C$_6$H$_4$(CH$_2$PPh$_2$AuCl)$_2$ is dissolved in 15 ml of chloroform and 5 ml of an aqueous solution of 70 mg (1 mmol) of NaSMe is added to the solution. The resulting two-phase system is stirred vigorously for 2 h. The aqueous layer is separated from the organic layer and washed twice with 5 ml of chloroform. The chloroform layers are combined and dried with Na$_2$SO$_4$ and the solvent evaporated under vacuum. Yield 189 mg (98%), m.p. 291°C. – ^{1}H NMR: δ = 2.38 (s, C*H*$_3$), 3.66 (d, $^2J_{HP}$ = 10 Hz, C*H*$_2$), 6.89 (s, C$_6$*H*$_4$), 7.24–7.59 (m, Ph-*H*). – ^{13}C{^{1}H} NMR: δ = 10.7 (s, *C*H$_3$), 35.6 (d, $^1J_{CP}$ = 28 Hz, *C*H$_2$), 129.0 (d, $^3J_{CP}$ = 11 Hz, Ph-*meta-C*), 129.8 (d, $^1J_{CP}$ = 50 Hz, Ph-*ipso-C*), 130.4 (d, $^3J_{CP}$ = 3 Hz, C$_6$H$_4$-*C*H), 131.6 (s, C$_6$H$_4$-*ipso-C*), 132.4 (d, $^4J_{CP}$ = 2 Hz, Ph-*para-C*), 133.4 (d, $^2J_{CP}$ = 13 Hz, Ph-*ortho-C*). – ^{31}P{^{1}H} NMR: δ = 37.4 (s). – C$_{34}$H$_{34}$Au$_2$P$_2$S$_2$ (962.65): calcd. C 42.38, H 3.56, S 6.66; found C 41.81, H 3.47, S 6.28.

μ-Chloroniumdigold(I) Tetrafluoroborate (**[1·Au$_2$Cl]$^+$BF$_4^-$**): 188 mg (0.2 mmol) of 1,4-C$_6$H$_4$(CH$_2$PPh$_2$AuCl)$_2$ is dissolved in 60 ml of dichloromethane and the solution is cooled to –7°C. A solution of 39 mg (0.2 mmol) of AgBF$_4$ in 10 ml of THF is added dropwise. A precipitate of AgCl is filtered off and the volume of the resulting clear solution is reduced under vacuum. Addition of pentane affords the product as a white precipitate, which is filtered, washed with pentane and dried in a vacuum. Yield 196 mg (99%), d.p. 152°C, m.p. 167°C. – ^{1}H NMR (CD$_2$Cl$_2$): δ = 3.82 (d, $^2J_{HP}$ = 11 Hz, C*H*$_2$), 6.89 (s, C$_6$*H*$_4$), 7.46–7.64 (m, Ph-*H*). – ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ = 35.4 (d, $^1J_{CP}$ = 33 Hz, *C*H$_2$), 127.5 (d, $^1J_{CP}$ = 61 Hz, Ph-*ipso-C*), 129.6 (m, Ph-*meta-C*), 130.6 (s, C$_6$H$_4$-*C*H), 132.9 (s, Ph-*para-C*), 133.5 (m, Ph-*ortho-C*), 134.1 (s, C$_6$H$_4$-*ipso-C*). – ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ = 47.6 (s). – MS (FAB): *m/z* (%) = 903.3 (19) [M$^+$], 671.3 (3) [M$^+$ – AuCl]. – C$_{32}$H$_{28}$Au$_2$BClF$_4$P$_2$ (990.72): calcd. C 38.79, H 2.85, Au 39.76; found C 38.51, H 2.80, Au 39.12.

μ-Phenylsulfoniumdigold(I) Tetrafluoroborate (**[1·Au$_2$SPh]$^+$BF$_4^-$**): 94 mg (0.1 mmol) of 1,4-C$_6$H$_4$(CH$_2$PPh$_2$AuCl)$_2$ is dissolved in 40 ml of dichlormethane and the solution is cooled to –7°C. A solution of 39 mg (0.2 mmol) of AgBF$_4$ in 10 ml of THF is added dropwise to give a precipitate of AgCl, which is filtered off. The clear solution is cooled to –40°C and then treated with a solution of 22 mg (0.1 mmol) of Ph$_2$S$_2$ in 10 ml of THF. After stirring for 20 min at this temperature, the mixture is allowed to warm to room temperature. The solvent is evaporated to dryness under vacuum and the residue extracted with 35 ml of dichloromethane. Addition of diethyl ether to the filtrate produces a white precipitate, which is filtered off, washed with ether and dried in vacuo. Yield 78 mg (73%), m.p. 148°C (dec). – ^{1}H NMR (CD$_2$Cl$_2$): δ = 3.91 (d, $^2J_{HP}$ = 10 Hz, C*H*$_2$), 6.95 (s, C$_6$*H*$_4$), 7.31–7.35 (s, SPh-*H*), 7.46–7.64 (m, PPh-*H*). – ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ = 36.4 (d, $^1J_{CP}$ = 21 Hz, *C*H$_2$), 127.6 (s, SPh-*para-C*), 127.9 (s, SPh-*ortho-C*), 128.7 (d, $^1J_{CP}$ = 52 Hz, PPh-*ipso-C*), 129.4 (s, SPh-*meta-C*), 129.8 (s, SPh-*ipso-C*), 130.0 (m, PPh-*meta-C*), 130.8 (s, C$_6$H$_4$-*C*H), 133.1 (s, PPh-*para-C*), 133.4 (s, C$_6$H$_4$-*ipso-C*), 133.8 (m, PPh-*ortho-C*). – ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ = 49.2 (s). – MS (FAB): *m/z* (%) = 976.8 (100) [M$^+$], 900.7 (5) [M$^+$ – Ph], 868.8 (4) [M$^+$ – SPh]. – C$_{38}$H$_{33}$Au$_2$BF$_4$P$_2$S (1064.43): calcd. C 42.88, H 3.12, Au 37.01; found C 42.53, H 3.00, Au 36.12.

μ-Methylsulfoniumdigold(I) Tetrafluoroborate (**[1·Au$_2$SMe]$^+$BF$_4^-$**): 188 mg (0.2 mmol) of 1,4-C$_6$H$_4$(CH$_2$PPh$_2$AuCl)$_2$ is dissolved in 60 ml of dichloromethane and the solution is cooled to –7°C. A solution of 39 mg (0.2 mmol) of AgBF$_4$ in 10 ml of THF is added dropwise to give a precipitate of AgCl, which is filtered off. After addition of 14 mg (0.2 mmol) of NaSMe in 15 ml of THF/methanol (1:3) to the filtrate, the resulting colourless solution is stirred for 1 h, and the solvent removed under vacuum. Yield 178 mg (89%), dec. 190°C. – ^{1}H NMR (CD$_2$Cl$_2$): δ = 2.70 (s, C*H*$_3$), 3.90 (d, $^2J_{HP}$ = 10 Hz, C*H*$_2$), 6.94 (s, C$_6$*H*$_4$), 7.50–7.75 (m, PPh-*H*). – ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ = 30.0 (s, *C*H$_3$), 36.1 (d, $^1J_{CP}$ = 28 Hz, *C*H$_2$), 127.0 (d, $^1J_{CP}$ = 58 Hz, Ph-*ipso-C*), 129.9 (m, Ph-*meta-C*), 130.7 (s, C$_6$H$_4$-*C*H), 131.4 (s, C$_6$H$_4$-*ipso-C*), 133.0 (s, Ph-*para-C*), 133.9 (m, Ph-*ortho-C*). – ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ = 48.5 (s). – MS (FAB): *m/z* (%) = 915.9 (37) [M$^+$], 900.7 (3) [M$^+$ – Me], 671.7 (9) [M$^+$ – AuSMe].

μ-Digold(I)sulfide Complex **1·Au$_2$S**: 188 mg (0.2 mmol) of 1,4-C$_6$H$_4$(CH$_2$PPh$_2$AuCl)$_2$ is dissolved in 15 ml of chloroform and 7 ml of an aqueous solution of 120 mg (0.5 mmol) of Na$_2$S·9 H$_2$O

Table 1. Crystallographic Data for **1 · (AuCl)$_2$ · CHCl$_3$**, **1 · (AuSMe)$_2$**, **1 · Au$_2$S · 2 CHCl$_3$**[a]

empirical formula	$C_{33}H_{29}Au_2Cl_5P_2$	$C_{34}H_{34}Au_2P_2S_2$	$C_{34}H_{30}Au_2Cl_6P_2S$
formula weight	1058.69	962.67	1139.21
crystal system	monoclinic	monoclinic	monoclinic
space group (No.)	C2/c (No.15)	$P2_1/n$ (No.14)	$P2_1/c$ (No.14)
a [Å]	15.679(2)	15.528(2)	17.542(2)
b [Å]	9.357(2)	9.689(1)	14.913(1)
c [Å]	24.550(7)	22.478(3)	14.618(1)
α [°]	90	90	90
β [°]	104.53(1)	106.38(1)	98.06(1)
γ [°]	90	90	90
V [Å^3]	3486.5(1)	3244.6(1)	3786.3(6)
ρ_{calc} [gcm^{-3}]	2.017	1.982	1.998
Z	4	4	4
F(000) [e]	2000	1832	2160
μ(Mo-K_α) [cm^{-1}]	89.04	92.8	83.28
cryst. dim. [mm]	0.25 / 0.35 / 0.50	0.20 / 0.25 / 0.30	0.15 / 0.35 / 0.35
T [°C]	-71	-62	-62
hkl range	$-18 \le h \le 19$	$0 \le h \le 19$	$0 \le h \le 22$
	$-1 \le k \le 11$	$0 \le k \le 12$	$0 \le k \le 18$
	$-18 \le l \le 31$	$-28 \le l \le 27$	$-18 \le l \le 18$
measured reflections	3999	7736	8744
unique reflections (R_{int})	3785 (0.047)	5988 (0.0134)	7229 (0.0174)
observed reflections	3785	4535	5922
	$F_o^2 \ge -3\sigma F_o^2$	$F_o \ge 4\sigma F_o$	$F_o \ge 4\sigma F_o$
refined parameters	186	361	406
absorption corr.:	-	empirical	empirical
T_{min} / T_{max}	- / -	0.5146 / 0.9984	0.2355 / 0.9987
R *	0.056	0.039	0.046
	$wR_2 = 0.134$	$R_w = 0.036$	$R_w = 0.044$
weighting scheme	a = 0.0493	l = 1.0000	l = 1.0000
	b = 120.969	k = 0.001718	k = 0.000548
ρ_{fin}(max/min) [eÅ^{-3}]	+2.027 / -1.950	+1.982 / -1.257	+2.175 / -2.045

[a] $$*R = \frac{\Sigma \left||F_o| - |F_c|\right|}{\Sigma |F_o|} \qquad R_w = \sqrt{\frac{\Sigma w(|F_o| - |F_c|)^2}{\Sigma w F_o^2}} \qquad w = \frac{l}{\sigma^2(F_o) + kF_o^2}$$

$$wR_2 = \sqrt{\frac{\Sigma w(F_o^2 - F_c^2)^2}{\Sigma w(F_o^2)^2}} \qquad w = \frac{1}{\sigma^2(F_o^2) + a^2p^2 + bp} \qquad p = \frac{\mathrm{Max}(F_o^2, 0) + 2F_c^2}{3}$$

is added to the solution. The resulting two-phase system is stirred vigorously for 2 h. The aqueous layer is separated from the organic layer and washed twice with 5 ml of chloroform. The organic solution is dried with Na_2SO_4 and the solvents evaporated in vacuo. Yield 180 mg (100%), m.p. 287 °C (dec.). – ^1H NMR: $\delta = 3.69$ (d, $^2J_{HP} = 10$ Hz, CH_2), 6.85 (s, C_6H_4), 7.24–7.83 (m, PPh-*H*). – $^{13}C\{^1H\}$ NMR (CD_2Cl_2): $\delta = 36.5$ (d, $^1J_{CP} = 22$ Hz, CH_2), 129.2 (d, $^1J_{CP} = 50$ Hz, Ph-*ipso-C*), 129.3 (m, Ph-*meta-C*), 130.8 (s, C_6H_4-*C*H), 131.6 (s, Ph-*para-C*), 132.5 (s, C_6H_4-*ipso-C*), 133.4 (m, Ph-*ortho-C*). – $^{31}P\{^1H\}$ NMR: $\delta = 42.5$ (s). – MS (FAB): *m/z* (%) = 1096.6 (23) [M + Au$^+$], 900.8 (8) [M$^+$], 671.5 (5) [M$^+$ – SAu]. – $C_{32}H_{28}Au_2P_2S$ (900.52): calcd. C 42.72, H 3.13, S 3.56; found C 42.23, H 3.30, S 3.35.

Crystal Structure Determination: The samples were mounted in glass capillaries. An Enraf Nonius CAD4 diffractometer with graphite-monochromated Mo-K_α radiation was used. The structures were solved by direct methods (SHELXTL-PC), and all H atoms were placed in calculated positions. The chloroform molecule in the structure of **1 · (AuCl)$_2$ · CHCl$_3$** is disordered. The final cell parameters and specific data collection parameters are summarized in Table 1. Further details of the X-ray structure determinations may be obtained from Fachinformationszentrum Karlsruhe GmbH, D-76344 Eggenstein-Leopoldshafen, Germany on quoting the depository number CSD-58971, the names of the authors and the journal citation.

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