Polynuclear Gold(I) Complexes of Functionalized Thiols and Dithiols

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Treatment of 2-mercaptoaniline with $\{[(Ph_3P)Au]_3O\}^+ BF_4^-$ leads to a regioselective auration to give the (2-aminophenyl)sulfonium complex $\{(2\text{-}H_2NC_6H_4)S[Au(PPh_3)]_2\}^+ BF_4^-$ (**1**) as the sole product. With the same reagent, 4-mercaptophenol affords the corresponding (4-hydroxyphenyl)sulfonium salt **2**, and 2-mercaptopyridine is converted into the 2-pyridylsulfonium salt **3**. Dinuclear auration of the thiol functions is thus clearly favoured over the reaction at any of the other functional groups ($-NH_2$, -py, -OH). As shown in earlier work, this is also true for HS-functional carboxylic acids. With an excess of the oxonium reagent, however, 2-mercaptosuccinic acid was now found to be converted into a tetranuclear complex with a doubly aurated sulfonium group and monoaurated carboxylate functions (**4**). Bis(2-mercaptoethyl) ether and thioether react with the oxonium salt to give tetranuclear bis(sulfonium salts) **5**, **6**, with bifurcated $\{-S[Au(PPh_3)]_2\}^+$ groups at both ends. Structural studies of compounds **1**, **5** and **6** showed the cations to be aggregated into centrosymmetrical dimers through short Au–Au contacts. Compound **5** forms one-dimensional infinite chains through a similar aggregation via the two bifurcated sulfonium end groups of each individual dicationic unit. The dications of compound **6** are associated only into centrosymmetrical dimers leaving one of the two sulfonium groups of each unit without auriophilic contacts to neighbouring dications, probably owing to an internal Au–S contact with the thioether function.

Introduction

Most current applications of gold(I) compounds are based on complexes containing sulfur ligands[1]. This is true not only for conventional "liquid golds" for the decoration of glass, chinaware and ceramics[2], but also for electrolysis systems employed for surface treatment of metals[2], and finally for gold drugs used in medicine[3]. Self-assembled monolayers (SAMs) of thiols on gold surfaces[4] are another new and promising area of research and application.

The stability, redox properties, solubility, absorption and distribution parameters of gold compounds in liquid or solid compartments and their interfaces are governed by the characteristics of the organic side-chains present in the sulfur component or in the auxiliary ligands. Recent studies have therefore focused on a tailoring of the properties of gold(I) thiolates and the gold-rich poly(gold)sulfonium salts derived therefrom through a proper choice of substituents[5–14].

As part of our own ongoing pertinent investigations we have considered functional thiols bearing ether, thioether, hydroxy, carboxylate, amino, and pyridyl substituents. The results of our preparative and structural studies are reported in the present account. Preceding papers were dedicated to (poly)thiols, hydroxythiols and a few simple carboxylic acids with thiol functions[5–10]. Owing to the growing interest in compounds with a high gold content and high solubility in polar solvents, preferentially water, the thiols were all converted into poly(gold)sulfonium salts, which are known to show greatest thermal stability and to be robust against hydrolysis and oxydative decomposition.

Results

Thiols RSH are readily converted into digold(organo)sulfonium salts $[RS(AuL)_2]^+ X^-$ by the reaction with tris[(ligand)gold(I)]oxonium salts. However, the same reagents can also be used to aurate amines, alcohols or carboxylic acids to give quaternary ammonium salts $[RN(AuL)_3]^+ X^-$ etc.[5–18].

For molecules with mixed functionalities (–SH, –OH, $-NH_2$, –COOH etc.) the relative affinity of these functional groups for AuL^+ units will determine the regioselectivity of the reactions[19]. The experiments described below have shown now that in all cases probed in this study the *thiol* group is the preferred site for coordination of not only one, but even two gold atoms before any other of the functional groups becomes involved.

Thus the reaction of *2-mercaptoaniline* with $\{[(Ph_3P)Au]_3O\}^+ BF_4^-$ gives good yields of (2-aminophenyl)bis[(triphenylphosphane)gold(I)]sulfonium tetrafluoro borate (**1**). According to the NMR analysis, the reaction mixture contains no (2-mercaptophenyl)tris[(triphenylphosphane)gold(I)]ammonium salt, which would be the product of the selective auration of the amine group.

$$[(Ph_3P)Au]_3O^+BF_4^- + o\text{-}HS{-}C_6H_4{-}NH_2 \rightarrow \underset{\mathbf{1}}{\{[(Ph_3P)Au]_2S{-}C_6H_4{-}NH_2\text{-}o\}^+BF_4^-} \quad (1)$$

Treatment of *2-mercaptopyridine* with the same oxonium salt affords the analogous (2-pyridyl)sulfonium salt with a free pyridine function in the side chain (**2**).

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$$[(Ph_3P)Au]_3O^+BF_4^- + 2\text{-}HS\text{-}C_5H_4N \rightarrow \{2\text{-}[(Ph_3P)Au]_2S\text{-}C_5H_4N\}^+BF_4^- \quad (2)$$
2

4-Mercaptophenol is converted into (4-hydroxyphenyl)-sulfonium salt **3** following the same reaction pattern.

$$p\text{-}HO\text{-}C_6H_4\text{-}SH + 2/3\,[(Ph_3P)Au]_3O^+BF_4^- \rightarrow p\text{-}HO\text{-}C_6H_4\text{-}S[Au(PPh_3)]_2^+\,BF_4^- \quad (3)$$
3

The course of these reactions [Eq. (1)–(3)] is proof for the clear preference of –SH groups over $-NH_2$, –py and –OH functions in the auration process. The results are also of relevance for the transfer of gold(I) in biological systems, e.g. from the ligands provided in the gold drugs to functional groups of biopolymers and bioligands.

The competition of –SH and –COOH groups for $[LAu]^+$ units has been investigated in several of our earlier studies already, and again –SH groups were shown to be the favourite clustering centres[6].

It is only after the complete saturation of all thiol functions that the carboxyl groups are also accepted as donor centers by the aurating agent. An example is *2-mercaptosuccinic acid* which was now found to become quadruply aurated if an excess of the oxonium salt is employed [Eq. (4)]. Two of the gold units are first attached to the thiol function, but then both carboxylate functions become also (mono)aurated (**4**). This distribution follows from the ^{31}P chemical shifts of the phosphane ligands, which are very close to those of reference compounds.

$$HS\text{-}CH(COOH)\text{-}CH_2\text{-}COOH + 4/3\,[(Ph_3P)Au]_3O^+BF_4^- \rightarrow [(Ph_3P)Au]_2S\text{-}CH(COOAuPPh_3)\text{-}CH_2\text{-}COOAuPPh_3]^+BF_4^- \quad (4)$$
4

According to ^{31}P-NMR results there is scrambling of the two *O*-bound Ph_3PAu units in solution at ambient temperature, but at low temperature a rigid structure is observed. Details are given in the Experimental Section.

Ether and *thioether* functions are another pair of donor centres which were to be compared in this context. In order to offer virtually strain-free systems, two long-chain dithiols with central C–O–C and C–S–C units were chosen.

Treatment of *bis(2-mercaptoethyl) ether* and *thioether* with an excess of the oxonium salt gives high yields of the tetranuclear bis(sulfonium salts) **5** and **6**, respectively [Eq. (5)]. Both end groups are converted into cationic dinuclear units, while the central ether and thioether functions do not

Table 1. Crystallographic data for compounds **1**, **5** • CH_2Cl_2 and **6** • CH_2Cl_2

	1	**5** • CH_2Cl_2	**6** • CH_2Cl_2
empirical formula	$C_{42}H_{36}Au_2BF_4NP_2S$	$C_{76}H_{68}Au_4B_2F_8OP_4S_2$ • CH_2Cl_2	$C_{76}H_{68}Au_4B_2F_8P_4S_3$ • CH_2Cl_2
formula weight	1129.46	2231.72	2247.78
crystal system	monoclinic	monoclinic	triclinic
space group (No.)	$P2_1/c$ (No.14)	$P2_1/c$ (14)	$P\bar{1}$ (2)
a [Å]	12.151(1)	26.125 (2)	14.349 (1)
b [Å]	18.195(1)	14.921 (1)	15.208 (1)
c [Å]	18.536(2)	19.720 (2)	19.955 (1)
α [°]	90	90	80.70 (1)
β [°]	108.05(1)	95.96 (1)	87.22 (1)
γ [°]	90	90	71.54 (1)
V [Å^3]	3896.5(8)	7645 (1)	4076.0 (5)
$\rho_{calcd.}$ [gcm^{-3}]	1.925	1.939	1.831
Z	4	4	2
μ(Mo-K_α) [cm^{-1}]	77.09	79.23	74.55
T [°C]	–68	–68	–68
radiation	Mo-K_α	Mo-K_α	Mo-K_α
scan	Θ-Θ	ω	Θ-Θ
hkl range	±14/+22/+22	±33/+19/–24	±18/±19/+25
measured reflections	7208	14616	16160
unique reflections	6991	14184	16107
observed reflections [with $F_o \geq 4\sigma(F_o)$]	6094	10681	13787
refined parameters	483	898	861
$wR2$[a]	0.0654	0.0931	0.1151
R(based on F) (OMIT4)[b]	0.0268	0.0394	0.0387
ρ_{fin}(max/min) [eÅ^{-3}][c]	+0.84/–0.83	+1.94/–1.07	+3.82/–1.17
absorption corr.: T_{min}/T_{max}	empirical 0.7667/0.9989	empirical 0.3553/0.9997	empirical 0.5604/0.9987
weighting scheme[d]	$l = 0.0235/k = 9.4313$	$l = 0.0489/k = 4.0088$	$l = 0.0532/k = 21.3890$

[a] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$. – [b] $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. – [c] Residual electron densities located at gold atoms. – [d] $w = q/\sigma^2(F_o^2) + (l \cdot p)^2 + k \cdot p$; $p = \max(F_o^2, 0) + 2 \cdot F_c^2/3$.

become engaged in dative bonding to an additional gold acceptor. The products are analogous to the gold complexes of the related α,ω-dimercaptoalkanes.

$$HS(CH_2)_2X(CH_2)_2SH + 4/3\ [(PPh_3)Au]_3O^+BF_4^- + NaBF_4 \rightarrow \{[(PPh_3)Au]_2S(CH_2)_2X(CH_2)_2S[Au(PPh_3)]_2\}^{2+}(BF_4^-)_2 \quad (5)$$

5: X = O; **6**: X = S

All compounds have been characterized by their analytical and spectroscopic data (Experimental Section), and the crystal and molecular structures of three representative examples (**1**, **5** and **6**) have been determined.

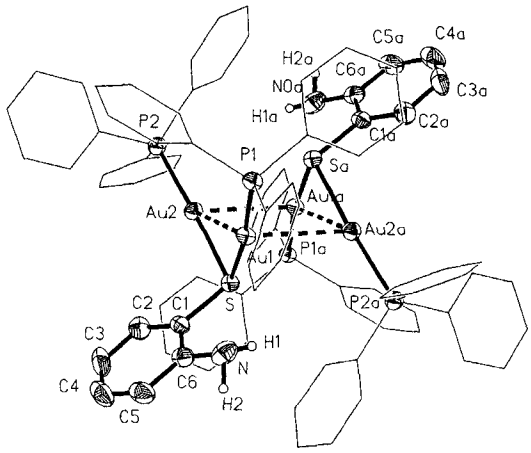
Crystal and Molecular Structures

The *aniline derivative* **1** (Figure 1) crystallizes in the monoclinic space group $P2_1/c$ with $Z = 4$ formula units in the unit cell. The lattice is composed of tetrafluoroborate anions and dimeric cations $[\{[(Ph_3P)Au]_2S-C_6H_4-NH_2-2\}_2]^{2+}$. In this dication the monomeric units are related by a center of inversion (Figure 1). In each monomer the sulfur atom is bridging the two gold atoms with an acute angle Au1–S–Au2 of only 83.34(4)° and a short distance Au1–Au2 of 3.1236(4) Å. The two C–S–Au angles are much larger [104.0(2) and 107.4(2)°, respectively]. The dimerization of the cations occurs via the bifurcated sulfonium end groups and affords an almost regular square of gold atoms [Au1–Au2′/Au2–Au1′ 3.1969(3) Å]. This structural pattern resembles very closely that of numerous other aggregated digold(organo)sulfonium salts, and the underlying type of bonding has been discussed repeatedly in previous papers[5–13].

For the present case it is important to note that the *ortho*-amino group appears not to be involved in significant gold coordination. The Au–N distance of 2.882(3) Å is well beyond the bonding region and may represent only a dipole orientation of the two neighbouring units fixed in close proximity through the *ortho* positioning. Apparently, the angle S–Au1–P1 of 173.72(4)° is not affected by this contact. The interaction between the BF_4^- anion and the $-NH_2$ group, which may represent a hydrogen bond, is crystallographically ill-defined because of the disorder of the anion in the crystal. It appears, however, that this hydrogen bonding is more significant for the orientation of the amino group than the gold coordination.

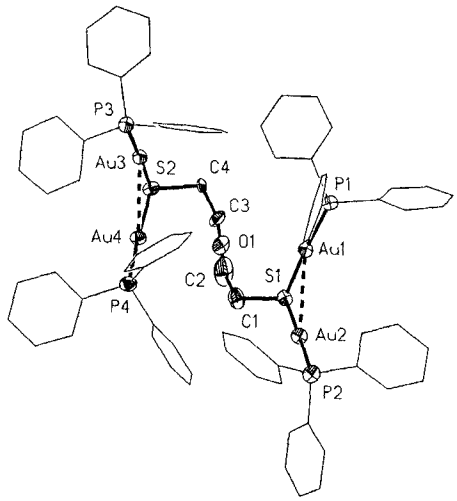
Crystals of the *ether-functional compound* **5** (Figures 2–4), obtained from dichloromethane solution, are monoclinic, space group $P2_1/c$, with $Z = 4$ formula units in the unit cell and one mole-equivalent of CH_2Cl_2. The lattice is composed of independent tetrafluoroborate anions, solvent molecules and one-dimensional chains of dications. Each individual dication has two bifurcated $\{-S[Au(PPh_3)]_2\}^+$ end groups which are paired up with the equivalent end groups of neighbouring dications at either end. The intra- and intermolecular contacts between the gold atoms, which are the basis for the aggregation of the dications into chains, resemble those of other digold(organo)sulfonium salts, including the representative example **1** (above)[5–13]. The gold atoms at the corners of the resulting parallelograms of metal atoms and their ligands are related by centres of inversion. Details are given in the figure captions.

Figure 1. Molecular structure of compound **1** with atomic numbering; the dication has a crystallographic center of inversion (ORTEP, 50% probability ellipsoids; arene hydrogen atoms omitted for clarity)[a]



[a] Selected bond lengths [Å] and angles [°]: Au1–Au2 3.1236(4), Au2–Au1′ 3.1969(3), Au1–S 2.3454(12), Au2–S 2.3528(13), Au1–P1 2.2637(13), Au2–P2 2.2762(13), S–C1 1.796(5), N–C6 1.419(8); Au1–S–Au2 83.34(4), Au1–S–C1 104.0(2), Au2–S–C1 107.4(2), P1–Au1–S 173.72(4), P2–Au2–S 176.61(5).

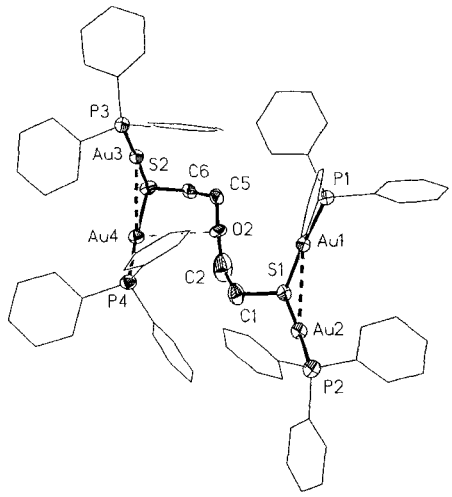
Figure 2. Structure of the dication in the crystal of $\{[(Ph_3P)Au]_2S(CH_2)_2O(CH_2)_2S[Au(PPh_3)]_2\}^{2+}(BF_4^-)_2$ (**5**) (ORTEP, except for phenyl carbon atoms; hydrogen atoms omitted for clarity; SOF = 0.5 for O1, C3, C4)[a]



[a] Selected distances [Å] and angles [°]: Au1–Au2 3.2139(5), Au1–S1 2.320(2), Au1–P1 2.266(2), Au2–S1 2.334(2), Au2–P2 2.276(2), Au3–Au4 3.0891(5), Au3–S2 2.343(2), Au3–P3 2.282(2), Au4–S2 2.336(2), Au4–P4 2.267(2); Au1–S1–Au2 87.35(7), Au1–S1–C1 110.4(3), Au2–S1–C1 104.9(3), P1–Au1–S1 176.39(7), P2–Au2–S1 176.24(7), Au3–S2–Au4 82.64(6), Au3–S2–C4 97.8(7), Au4–S2–C4 104.3(7), P3–Au3–S2 178.20(7), P4–Au4–S2 171.27(8).

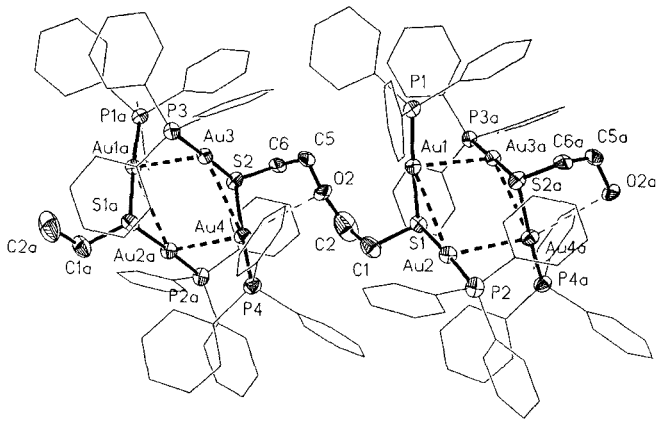
The diethylether chain $(-CH_2CH_2OCH_2CH_2-)$ connecting the two sulfonium ends is unfolded and was found to be disordered in the crystal. This disorder was resolved in the structure solution to give two positions for the oxy-

Figure 3. Structure of the dication in the crystal of $\{[(Ph_3P)Au]_2S(CH_2)_2O(CH_2)_2S[Au(PPh_3)]_2\}^{2+}(BF_4^-)_2$ (**5**) (ORTEP, except for phenyl carbon atoms; hydrogen atoms omitted for clarity; SOF = 0.5 for O2, C5, C6)[a]



[a] Selected distances [Å] and angles [°]: O2–Au4 3.136; Au3–S2–C6 118.5(7), Au4–S2–C6 107.2(7).

Figure 4. Part of a chain of $\{[(Ph_3P)Au]_2S(CH_2)_2O(CH_2)_2S[Au(PPh_3)]_2\}^{2+}$ dications in the lattice of **5** (ORTEP, except for carbon atoms; hydrogen atoms omitted for clarity; SOF = 0.5 for O2, C5, C6)[a]



[a] Selected distances [Å] and angles [°]: Au1–Au3a 3.2337(5), Au2–Au4a 3.1737(5); Au2–Au1–Au3a 82.631(13), Au4–Au1a 96.238(13).

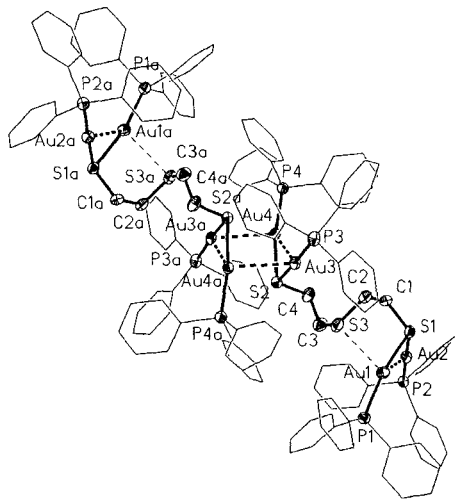
gen atom (Figures 2, 3), only one of which has a distant contact to one of the gold atoms [Au4–O2 3.136(1) Å].

Crystals of the *thioether-bridged compound* **6** (Figure 5), obtained from dichloromethane, are triclinic, space group $P\bar{1}$, with two formula units and two solvent molecules in the unit cell. Apart from independent tetrafluoroborate anions and solvent molecules, the crystals are built from *dimeric* dications instead of extended chains as found in the oxygen analogue **5** (above). Only one of the bifurcated ends of each dication is associated with the corresponding end group of a neighbouring dication, while the other is not involved in any intermolecular contacts. The dimers have a crystallographically imposed center of inversion (Figure 4). The dimensions of the individual units are again similar to those of related model systems[7], including compounds **1** and **5**. Details are given in the figure captions.

The reason for a chain termination after the formation of a dimer only may be the consequence of the intramolecular contacts of the thioether sulfur atoms S3, S3′ with the gold atoms Au1, Au1′, respectively [Au1–S3 3.019(1) Å]. This contact causes a compression of the angle S1–Au1–P1 to 168.37(7)° and probably diminishes the acceptor properties of Au1 to such an extent that intermolecular auriophilic contacts become redundant. Note that the corresponding contact Au4–O2 in compound **5**, which occurs only in one of two disordered conformations, is longer [3.136(1) Å] and is associated with a larger angle S2–Au4–P4 [171.27(8)°]

The three structures presented here provide further examples for the rapidly expanding supramolecular chemistry of gold(I)–sulfur compounds. The details are evidence for the delicate interplay of weak contacts that govern the arrangement of the individual units in the solid state. The situation is complicated even further in solution, where the solvation of the ion pairs or larger aggregates may become the dominating effect.

Figure 5. A pair of dications $\{[(PPh_3)Au]_2S(CH_2)_2S(CH_2)_2S[Au(PPh_3)]_2\}^{2+}$ in the tetrafluoroborate salt **6** (ORTEP, except for phenyl carbon atoms; hydrogen atoms omitted for clarity)[a]



[a] Selected distances [Å] and angles [°]: Au1–Au2 3.0433(5), Au1–S1 2.349(2), Au1–P1 2.270(2), Au2–S1 2.326(2), Au2–P2 2.264(2), Au3–Au4 3.1595(5), Au3–S2 2.345(2), Au3–P3 2.279(2), Au4–S2 2.337(2), Au4–P4 2.269(2), Au3–Au4a 3.0623(5), Au1–S3 3.019(1); Au1–S1–Au2 81.23(6), Au1–S1–C1 108.5(3), Au2–S1–C1 106.9(3), P1–Au1–S1 168.37(7), P2–Au2–S1 178.20(6), Au3–S2–Au4 84.88(6), Au3–S2–C4 105.9(3), Au4–S2–C4 100.1(3), P3–Au3–S2 174.37(7), P4–Au4–S2 169.98(6), Au3–Au4–Au3a 94.941(13).

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Experimental Section

All experiments were carried out routinely under dry and pure nitrogen. Glassware and solvents were dried and filled/saturated with nitrogen. – NMR: Jeol 400 spectrometer, deuterated solvents with the usual standards. – MS: Varian MAT 311A instrument (FD, dichloromethane solvent). – The thiols were commercially available; $[(Ph_3P)Au_3]O^+BF_4^-$ was prepared according to a literature procedure[20].

(2-Aminophenyl)bis[(triphenylphosphane)gold(I)]sulfonium Tetrafluoroborate (**1**): To a solution of 2-mercaptoaniline (0.025 g, 0.20 mmol) in dichloromethane (15 ml) were added $[(Ph_3P)Au]_3O^+BF_4^-$ (0.197 g, 0.13 mmol) and $NaBF_4$ (0.100 g, 0.91 mmol) at room temperature. After 2 h, the solution was filtered and the solvent was removed in a vacuum. The white residue was taken up again in dichloromethane and layered with pentane. After one week, colourless crystals were obtained (0.148 g, 65.5%), m.p. 218°C. – ^1H NMR ($CDCl_3$): δ = 7.73–6.80 (m, 19H, Ph–H), 6.62 (br. s, 2H, NH_2). – ^{31}P NMR ($CDCl_3$): δ = 34.3, (s, PPh_3). – $C_{41}H_{36}Au_2BF_4NP_2S$ (1129.46): calcd. C 44.66, H 3.21, N 1.24; found C 44.54, H 3.32, N 1.06.

(2-Pyridyl)bis[(triphenylphosphane)gold(I)]sulfonium Tetrafluoroborate (**2**): To a solution of 2-mercaptopyridine (0.017 g, 0.15 mmol) in dichloromethane (10 ml) were added $[(Ph_3P)Au]_3O^+BF_4^-$ (0.150 g, 0.10 mmol) and $NaBF_4$ (0.016 g, 0.15 mmol) at room temperature. After 1 h, a small residue was filtered off and the volume of the solvent was reduced in a vacuum to ca. 5 ml. Addition of diethyl ether (20 ml) gave **2** as a white solid (0.10 g, 60%), m.p. 135°C (dec.). – ^1H NMR ($CDCl_3$): δ = 8.37–7.28 (m, Ph–H, pyr–H). – ^{31}P NMR ($CDCl_3$): δ = 33.5 (s, PPh_3). – $C_{41}H_{34}Au_2BF_4NP_2S$ (1115.48): calcd. C 44.14, H 3.16, N 1.26, S 2.87; found C 44.03, H 2.93, N 1.07, S 2.77.

(4-Hydroxyphenyl)bis[(triphenylphosphane)gold(I)]sulfonium Tetrafluoroborate (**3**): To a solution of 4-mercaptophenol (0.035 g, 0.25 mmol) in dichloromethane (20 ml) were added $[(Ph_3P)Au]_3O^+BF_4^-$ (0.250 g, 0.17 mmol) and $NaBF_4$ (0.027 g, 0.25 mmol) at room temperature. The suspension formed after 1 h was filtered off. Evaporation of the solvent to ca. 5 ml and addition of diethyl ether (20 ml) gave **3** as a bright yellow solid (0.18 g, 65%), m.p. 126°C. – ^1H NMR ($CDCl_3$): δ = 7.52–6.84 (m, Ph–H). – ^{31}P NMR ($CDCl_3$): δ = 36.7 (s, PPh_3). – $C_{42}H_{35}Au_2BF_4OP_2S \cdot 1/2\ C_4H_{10}O$ (1241.67): calcd. C 46.43, H 4.05, S 2.58; found C 46.50, H 3.4, S 2.38.

α,ω-O,O,S,S-Tetrakis[(triphenylphosphane)gold(I)]-2-mercaptosuccinate Tetrafluoroborate (**4**): A solution of $[(Ph_3P)Au]_3OBF_4$ (0.15 g, 0.10 mmol) in dichloromethane (15 ml) was treated with thiosuccinic acid (0.01 g, 0.07 mmol). The resulting clear solution was stirred for 1 h. Evaporation of the solvent to ca. 5 ml and addition of diethyl ether (20 ml) gave a precipitate of complex **4** as a white solid (0.06 g, 40%), m.p. 140°C (dec.). – ^1H NMR ($CDCl_3$): δ = 7.6–7.2 (m, 72H, Ph–H), 4.85 ("t", $1H_X$, CH), 3.35 (dd, $1H_A$, $^3J(H_A,H_X)$ = 6.7 Hz, $^2J(H_A,H_B)$ = 16.5 Hz, CH_2), 2.98 (dd, $1H_B$, $^3J(H_B,H_X)$ = 7.3 Hz, $^2J(H_A,H_X)$ = 16.5 Hz, CH_2). – ^{31}P NMR ($CDCl_3$, 25°C): δ = 34.3 (s, 2P, PPh_3–S), 27.7 (m, 2P, PPh_3–O); ($CDCl_3$, –60°C) 34.3 (s, 2P, PPh_3–S), 27.4 (s, 1P, PPh_3–O1), 26.8 (s, 1P, PPh_3–O2). – $C_{75}H_{63}Au_4BF_4O_4P_4S$ (2070.96): calcd. C 44.07, H 3.06, S 1.54; found C 43.96, H 2.77, S 1.64.

2,2'-Bis{bis[(triphenylphosphane)gold(I)]sulfonio}diethyl Ether Bis(tetrafluoroborate) (**5**): A solution of $[(Ph_3P)Au]_3O^+BF_4^-$ (0.250 g, 0.17 mmol) in dichloromethane (20 ml) was treated with $NaBF_4$ (0.05 g, 0.45 mmol) and then with bis(2-mercaptoethyl) ether (0.016 ml, 0.12 mmol) at ambient temperature with stirring. After 1 h, a white flaky precipitate was removed by filtration and the solvent evaporated from the filtrate in a vacuum. Addition of diethyl ether (20 ml) gave **5** as a white solid (0.130 g, 50%). A dichloromethane solution (5 ml) of this product was layered with diethyl ether (30 ml) at room temperature. After 24 h, colourless crystals were isolated. – MS; *m/z* (%): 986.7 (14.06) $[M^{2+}/2]$, 1410.7 (100) $[S(AuPPh_3)_3^+]$. – ^{31}P NMR ($CDCl_3$, 25°C): δ = 37.3 (s, 4P). – ^1H NMR ($CDCl_3$): δ = 3.27 (t, 4H, $J_{H,H}$ = 6.1 Hz, CH_2S), 3.77 (t, 4H, $J_{H,H}$ = 6.1 Hz, CH_2O), 7.40–7.49 (m, 60H, Ph–H). – ^{13}C NMR ($CDCl_3$): δ = 31.4 (s, CH_2S), 73.6 (s, CH_2O), 128.1 (d, C_{ipso}, $J_{P,C}$ = 59.74 Hz), 129.52 (d, C_{meta}, $J_{P,C}$ = 11.95 Hz), 132.29 (s, C_{para}), 134.02 (d, C_{ortho}, $J_{P,C}$ = 13.79 Hz). – $C_{76}H_{68}Au_4B_2F_8OP_4S_2 \cdot 2\ CH_2Cl_2$ (2316.75): calcd. C 40.36, H 3.07, S 2.97; found C 40.43, H 3.13, S 2.76.

2,2'-Bis{bis[(triphenylphosphane)gold(I)]sulfonio}diethyl Sulfide Bis(tetrafluoroborate) (**6**): To a solution of $[(Ph_3P)Au]_3O^+BF_4^-$ (0.30 g, 0.20 mmol) in 10 ml of dichloromethane were added $NaBF_4$ (0.10 g, 0.91 mmol) and bis(2-mercaptoethyl) sulfide (0.02 ml, 0.15 mmol) at ambient temperature. After stirring for 1 h, a brown precipitate was filtered off and the filtrate layered with diethyl ether (30 ml). After 12 h, colourless crystals were obtained (0.170 g, 40%). – MS; *m/z* (%): 994.5 (45) $[M^{2+}/2]$, 1410.7 (100) $[S(AuPPh_3)_3^+]$. – ^1H NMR (CD_2Cl_2): δ = 2.65 (m, 4H, CH_2S), 3.37 (m, 4H, CH_2SAu), 7.17–7.41 (m, 60H, Ph–H). – ^{13}C NMR ($CDCl_3$): δ = 31.57 (s, CH_2S), 35.72 (s, CH_2SAu), 127.64 (d, C_{ipso}, $J_{P,C}$ = 59.75 Hz), 129.19 (d, C_{meta}, $J_{P,C}$ = 11.03 Hz), 132.08 (s, C_{para}), 133.62 (d, C_{ortho}, $J_{P,C}$ = 13.79 Hz). – ^{31}P NMR (CD_2Cl_2): δ = 36.7 (s, PPh_3). – $C_{76}H_{68}Au_4B_2F_8P_4S_3 \cdot 0.5\ CH_2Cl_2$ (2205.39): calcd. C 41.66, H 3.15, Au 35.72; found C 41.53, H 3.20, Au 36.30.

Crystal-Structure Determinations: Suitable crystals of compounds **1**, **5** and **6** were sealed under argon at dry-ice temperature into glass capillaries and examined directly on the diffractometer (Table 1). Data were corrected for Lorentz polarization and absorption effects. Structures were solved by direct methods and refined by full-matrix least-squares calculations against F^2. The thermal motion was treated anisotropically for all non-hydrogen atoms. All calculated hydrogen atoms were treated isotropically. High residual electron density is always close to the gold atoms. 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 depository numbers CSD-406146 (**1**), -406147 (**5**), and -406148 (**6**).

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