Polynuclear Gold(I) Complexes of Mercaptocarboxylic Acids

Alexander Sladek, Wolfgang Schneider, Klaus Angermaier, Andreas Bauer, Hubert Schmidbaur*

Anorganisch-chemisches Institut der Technischen Universität München, Lichtenbergstrasse 4, D-85747 Garching, Germany

Dedicated to Professor Kurt Dehnicke on the occasion of his 65th birthday

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 $Gold(I)\ Thiolates,\ (Benzylthiolato)gold(I)\ Complexes,\ Gold(I)\ Mercaptocarboxylates,\ Polynuclear\ Gold(I)\ Complexes$

In a search for air-stable and water-soluble mercapto compounds of gold with a high gold content, benzylthiol, α -mercapto-acetic acid, β -mercapto-propionic acid, and thiosalicylic acid were converted into aurated sulfonium salts by treatment with reagents of the type $[(R_3P)Au]_3O^+$ BF₄⁻ or $[(R_3P)Au]^+$ BF₄⁻. - BzSH served as a mono-functional model thiol, which was converted into BzS[Au(PMe_3)]_2^+ BF_4^- (1). The small tertiary phosphine was chosen in order to minimize steric effects. In the crystal the cations are associated into centrosymmetrical dimers through short Au–Au contacts (auriophilicity). - The two carboxylic acids with thiol functions, HSCH₂COOH and HSCH₂CH₂COOH, gave triply aurated species of the type {[(Ph₃P)Au]₂S(CH₂)_nCOOAu(PPh₃)}⁺ BF₄⁻ (2: *n* = 2, 3: *n* = 3). The crystal structure analysis of the representative compound **2** showed again the presence of centrosymmetrical cation dimers with geometrical details of the sulfonium part of the molecules very similar to those of the reference compound **1**. In addition, the carboxyl groups in **2** and **3** bear a (phosphine)gold unit mono-hapto bound at one of the oxygen atoms. - 2-HS-C₆H₄-COOH was converted into a sulfonium salt {[(Ph₃P)Au]₂S-C₆H₄-COOH}⁺ BF₄⁻ (4), which crystallizes free of solvent from dry dichloromethane, and as a monohydrate with one mole of dichloromethane (**4a** = **4**·H₂O·CH₂Cl₂) from hydrous CH₂Cl₂. In the solvent-free crystalline phase (**4**) the cations are associated into dimers with the usual intermolecular double Au–Au contacts, but in **4a** there are monomeric cations with the water molecule hydrogen-bonded to the carboxylic acid function.

Introduction

Gold metal surfaces [1] and gold cations (Au⁺ or LAu⁺) have a high affinity for thioether (RSR), thiol (RSH) and thiolate (RS⁻) functions [2]. Gold complexes based on these functions are the most important classes of compounds for all aspects of gold usage [3]. Gold thiolates in particular have been the main ingredients of all gold pastes (liquid golds) for gilding in arts, handicraft and technology, and of virtually all drugs that appeared in the long history of gold therapy in medicine [4, 5].

Most of these compounds are neutral gold(I) thiolates (LAuSR) with or without an auxiliary ligand L [6-18]. Both L and R may carry functional groups, however, and recent interest has focused on the potential offered by such variations, *e. g.* for improved solubility or resorption properties, respectively. Current studies also include phosphine-free

* Reprint requests to Prof. Dr. H. Schmidbaur.

formulations like *e. g.* anionic species derived from thiomalonic [19] or thiosalicylic acid [20].

In an important extension of this chemistry, work carried out in the 1970ies has shown that the sulfur atoms in thiol(ate)s can accept more than one LAu⁺ group with the formation of thiolato-bridged dinuclear cations [21 - 26] of the type $[RS(AuL)_2]^+$. The structures of salts of such cations have been determined [14, 25, 26] and were found to show interesting intramolecular Au-Au interactions and intermolecular association phenomena. The individual cations feature extremely small Au-S-Au angles (ca. 85°) and, correspondingly, short Au-Au contacts (of ca. 3.1 Å), and two of these cations undergo aggregation through generation of an almost perfect square of gold atoms (A). This structural pattern is similar to the findings for the $[S(AuL)_3]^+$ cations (B).

Advanced theoretical calculations of the bonding situation in the compounds of the type $[S(AuL)_3]^+$ have demonstrated that relativistic and correlation

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effects are essential for a description of the electronic situation in the new clusters [27].

Digold(organo)sulfonium salts $[RS(AuL)_2]^+ X^$ may also be involved in the *in vivo* degradation and metabolism of gold drugs. Spectroscopic evidence has been accumulated which justifies this assumption [5].

Following earlier contributions from this laboratory [21,26] we now present the results of synthetic and structural work on another example of type **A** with the smallest tertiary phosphine (PMe₃), and on related compounds derived from mercaptocarboxylic acids HS(CH₂)_nCOOH (n = 1, 2) and



Fig. 1. Molecular structure of the cation dimer of compound **1** with atomic numbering. The monomer components are related by a center of inversion. (ORTEP, 50% probability ellipsoids; hydrogen atoms omitted for clarity.) - Selected distances [Å] and angles [°]: Au1– Au2 3.060(1), Au1–Au2' 3.078(1), Au1-S 2.331(3), Au2-S 2.345(3), Au1–P1 2.262(3), Au2-P2 2.258(4), S-C1 1.85(1); Au1-S-Au2 81.7(1), Au1-S-C1 110.6(4), Au2-S-C1 101.0(5), Au2-Au1-Au2' 78.5(1).

2-HS-C₆H₄-COOH. These compounds were expected to be water-soluble gold thiolates with a high gold content, as required for a number of applications in advanced technology and medicine.

Results

S,*S*-*Bis*[(trimethylphosphine)gold(I)]benzylsulfonium tetrafluoroborate (1)

Benzylthiol is readily converted into the digoldsulfonium salt (1) by reaction with two equivalents of (trimethylphosphine)gold(I) tetrafluoroborate [28] in dichloromethane/tetrahydrofuran. The product is obtained (in 74% yield) as an air-stable, colourless, crystalline solid, m.p. 179°C, which is easily characterized by its analytical and spectroscopic data.

$$BzSH + 2 [(Me_3P)Au]^+ BF_4^- \rightarrow [HBF_4] + BzS[Au(PMe_3)]_2^+ BF_4^-$$
(1)
1

Compound 1 crystallizes in the monoclinic space group P2₁/n with four formula units in the unit cell (Table I). The lattice contains tetrafluoroborate anions and dimeric cations $\{[(Me_3P)Au]_2SBz\}_2^{2+}$ (Fig. 1). In the monomeric unit, the benzyl sulfur atom is bridging the two gold atoms with a sharp angle Au1-S-Au2 of only 81.7(1)° and a short Au1–Au2 contact of 3.060(1) Å. The two C-S-Au angles are much larger [101.0(4) and 101.5(1)°] and may be taken as standard angles at sulfonium centers.

The dimers are formed through an approach of two monomers in a head-to-tail fashion with Au1– Au2'/Au1'–Au2 distances of 3.078(1) Å as the closest intermolecular contacts. The dimers have a crystallographic center of inversion in the center of the square of gold atoms formed in the association process. The structure is analogous to literature data

	1	$2 \cdot CH_2Cl_2$	4	4a
Empirical formula	$C_{13}H_{25}Au_2BF_4P_2S$	$\begin{array}{c} C_{56}H_{47}Au_3BF_4O_2P_3S\\ \cdot CH_2Cl_2 \end{array}$	$C_{43}H_{35}Au_2BF_4O_2P_2S$	$C_{44}H_{39}Au_{2}BCl_{2}F_{4}O_{3}P_{2}S$
Formula weight	756.03	1639.54	1158.45	1261.46
Crystal system	monoclinic	triclinic	triclinic	monoclinic
Space group (No.)	$P2_1/n$ (14)	P1 (2)	P1 (2)	$P2_1(4)$
a [Å]	12.375(1)	13.157 (1)	11.321(1)	12.517(1)
b [Å]	9.259(1)	14.378 (2)	13.400(1)	12.530(1)
c [Å]	18.763 (3)	15.325 (2)	14.578(1)	14.264(1)
α [°]	90	80.67 (1)	71.03(1)	90
β [°]	96.63 (1)	80.50(1)	88.64(1)	102.63(1)
γ [°]	90	79.17 (1)	72.67(1)	90
$V[Å^3]$	2135.6 (5)	2782.3 (6)	1989.9 (3)	2183.0 (2)
$\rho_{\rm calc} [\rm g cm^{-3}]$	2.35	1.96	1.93	1.76
Z	4	2	2	2
μ (Mo-K _{α}) [cm ⁻¹]	140.00	81.6	75.5	70.1
T [°C]	- 59	- 68	- 62	- 68
Radiation	$Mo-K_{\alpha}$	$Mo-K_{\alpha}$	$Mo-K_{\alpha}$	Mo-K $_{\alpha}$
Scan	$\Theta - \Theta$	$\Theta - \Theta$	ω	$\theta - \theta$
hkl Range	\pm 23 / + 15 / + 11	\pm 16 / \pm 17 / + 18	\pm 13 / \pm 16 / + 17	\pm 15 / \pm 15 / + 17
Measured / unique reflections	5152/4210	10888 / 10228	7800 / 7794	8560 / 8401
Observed reflections [with $F_0 > 4\sigma(F_0)$]	3583	9082	6779	8072
Refined parameters	209	652	500	537
R^*	0.0520	0.0299	0.0213	0.0254
$wR2^{**} / R_w^{***}$	- / 0.0730	-/0.0339	0.0580 / -	- / 0.0388
$\rho_{\rm fin}({\rm max/min}) [{\rm e}{\rm \AA}^{-3}]$	+ 4.49 / - 3.90	+ 1.36 / - 1.57	+ 0.96 / - 0.73	+ 2.17 / - 0.98
Absorption corr.:	no	empirical	empirical	empirical
T _{min} / T _{max}		0.7321 / 0.9998	0.5738 / 0.9990	0.6308 / 0.9990
Weighting scheme				
$(a / b)^{****}$	l = 1.0000 /	l = 1.0000 /	a = 0.0191 /	l = 1.0000 /
or $(l / k)^{*****}$	k = 0.006289	k = 0.000176	b = 2.5950	k = 0.005947

Table I. Crystallographic data for compounds 1, 2·CH₂Cl₂, 4 and 4a.

* $R = \sum (|F_0| - |F_c|) / \sum |F_0|$; ** $wR2 = [\sum (F_0^2 - F_c^2)^2 / \sum [w(F_0^2)^2]^{1/2}$; *** $R_w = [w(|F_0| - |F_c|)^2 / \sum wF_0^2]^{1/2}$; **** $w = q/[\sigma^2(F_0)^2 + (ap)^2 + bp]$; $p = [Max(F_0^2, 0) + 2F_c^2]/3$; ***** $w = 1/[\sigma^2(F_0) + k(F_0)^2]$.

recorded for other RS[Au(PR'₃)]₂⁺ salts: R = Bz, R' = Ph [14]; R = 'Bu, R' = Ph [26]. Except for cases with severe steric hindrance, the structure shown in Fig. 1 should thus be taken as the common configuration of this type of cations.

Similar results were also obtained with α , ω dithiols, which can give rise to one-dimensional aggregates through contacts between the bifurcated groups at either end of the molecules [29]. Tri- and polythiols behave accordingly [26, 29]. O,S,S-Tris[(triphenylphosphine)gold(1)]- α mercaptoacetate and - β -mercaptopropionate tetrafluoroborate (**2**, **3**)

Treatment of mercaptoacetic acid with equimolar quantities of tris[(triphenylphosphine)gold(I)]oxonium tetrafluoroborate [30] in dichloromethane at room temperature gives high yields of the triply aurated mercaptocarboxylate tetrafluoroborates **2** and **3**. Compound **2** is an air-stable, colourless, crystalline material, m.p. 168° C with decomposition, while compound **3** is an off-white powder, difficult to purify, which could not be crystallized. Both compounds are not soluble in acidic or alcaline water, but are stable under these conditions.

$$HS(CH_{2})_{n}COOH + [(Ph_{3}P)Au]_{3}O^{+} BF_{4}^{-}$$

$$\rightarrow [H_{2}O] + \{[(Ph_{3}P)Au]_{2}S(CH_{2})_{n}C(O)OAu(PPh_{3})\}^{+} BF_{4}^{-}$$

$$2 (n = 1)$$

$$3 (n = 2)$$
(2)

Analytical and spectroscopic data of both compounds are in full agreement with the proposed composition and structure (Experimental Part).

The ³¹P{¹H} NMR spectra (in CDCl₃) show only one broad singlet at room temperature, but at -60°C these signals are split consistently into two peaks of relative intensity 1:2. This result rules out an isomeric structure with triply aurated sulfur centers and free carboxylate groups, instead of the O,S,Saurated alternative formulated in Eq. (2), or the less likely S,O,O-aurated isomer.

Crystals of compound **2**, grown from CH₂Cl₂ by layering with diethyl ether, are triclinic, space group PI, with two formula units and two dichloromethane solvent molecules in the unit cell (Table I). The lattice contains independent solvent molecules,



Fig. 2. Molecular structure of the cation dimer of compound **2** with atomic numbering. The monomer components are related by a center of inversion. (OR-TEP, 50% probability ellipsoids; hydrogen atoms omitted for clarity.) - Selected distances [Å] and angles [°]: Au1–Au2 3.042(1), Au1–Au2' 3.079(1), Au1-S 2.337(1), Au2-S 2.341(1), Au1-P1 2.269(1), Au2-P2 2.259(1), S-C1 1.846(7), Au3-O 2.057(4), Au3-P3 2.215(2), O1-C2 1.277(7), O2-C2 1.213(7), C1-C2 1.516(7); Au1-S-Au2 81.1(1), Au1-S-C1103.6(2), Au2-S-C1 105.4(2), Au2-Au1-Au2' 93.5(1), P1-Au1-S 172.0(1), P2-Au2-S 173.4(1), P3-Au3-O 172.6(1).

tetrafluoroborate anions, and dimeric cations which are shown in Fig. 2. The sulfur atom of each monomeric unit is doubly aurated and thus converted into a sulfonium center, while the carboxylate group is mono-aurated at one of the oxygen atoms. As in the model compound **1**, the pyramid with the sulfur apex is very steep, with an Au1-S-Au2 angle of only 81.1(1)° and a distance Au1–Au2 of 3.042(1) Å. The remaining two angles at sulfur [Au1-S-C1 103.6(2)°, Au2-S-C1 105.4(2)°] are larger and closer to a pseudo-tetrahedral standard. The third gold atom (Au3) is attached to one carboxylate oxygen atom [Au3-O1 2.057(4) Å], with the usual linear coordination at the metal atom.

The aggregation of the cation into dimers occurs via the bifurcated sulfonium end groups and affords an almost regular square of gold atoms (with the crystallographic center of inversion in its center) with distances Au1–Au2'/Au2–Au1' 3.079(1) Å. The structural similarity of compounds **1** and **2** is immediately obvious from Figures 1 and 2.

It is interesting to note that no further aggregation (into chains or larger rings) takes place through intermolecular contacts between the carboxylatebound gold atoms. This may have steric reasons.

Compound **3** is believed to have a structure similar to that of the lighter homologue **2**, but except for the analogies in the spectral data, there is no proof for this suggestion.

S,*S*-*Bis*[(*triphenylphosphine*)gold(*I*)]*hydrogenthiosalicylate tetrafluoroborate* (**4**)

Thiosalicylic acid is aurated regioselectively at its sulfur atom on treatment of the compound with two equivalents of $[(Ph_3P)Au]BF_4$ in tetrahydrofuran at 0°C. The product **4** is obtained as a colourless, air- and water-stable solid in 75 % yield, m.p. 220°C with decomposition. The behaviour in acidic or alcaline water is analogous to compounds **2** and **3**.

The analytical data and the NMR spectra of the compound are in good agreement with the proposed formula (Experimental Section).





Single crystals obtained from *anhydrous* dichloromethane/pentane (triclinic, space group $P\bar{1}$, Z = 2) are free of solvent (Table I). The lattice contains centrosymmetrical *dimeric* cations with the same basic skeleton [CS(AuL)₂]₂ as present in compounds **1** and **2** (Fig. 3). The distorted square of gold atoms formed in the dimerisation has edges Au1–Au2 = 3.1270(5) Å and Au1–Au2'/ Au1'–Au2 3.1628(4) Å, with Au–Au–Au angles of 91.84(1)° at Au1 and 88.16(1)° at Au2. The Au1-S-Au2 angle is small [83.44(3)°], while the Au1-S-C1 and Au2-S-C1 angles are larger at 107.2(1)° and 111.7(1)°, respectively.

There is a sub-van der Waals contact between one of the gold atoms and one of the carboxylate oxygen atoms (Au2–O1 2.778 Å), but very surprisingly there are no hydrogen bonds between the two carboxylic acid functions. The distance between a fluorine atom of the anion and the hydroxyl oxygen atom, as well as the angle at the hydrogen atom $[O2-F1 2.721 \text{ Å}, O2-H-F1 161.3^\circ]$ can be taken as indicative of a hydrogen bond between these units, however.



Fig. 4. Molecular structure of the monomeric cation in phase **4a** (**4**·H₂O·CH₂Cl₂) with atomic numbering. (OR-TEP, 50% probability ellipsoids, arene hydrogen atoms omitted for clarity; the water molecule is hydrogenbonded to the carboxylic acid function and to the BF4⁻ anion.) - Selected distances [Å] and angles [°]: Au1–Au2 3.107(1), Au1-S 2.332(1), Au2-S 2.340(1), Au1-P1 2.269(1), Au2-P2 2.258(1), Au2–O2 3.079, S-C1 1.793(7), O1-C7 1.19(1), O2-C7 1.302(9), C7-C2 1.520(9), O2-H 0.950, H–O3 2.612, O3–O2 2.612, O3–H1 1.045, H1–F1 1.721, O3–F1 2.766; Au1-S-Au2 83.4(1), Au1-S-C1 109.6(2), Au2-S-C1 104.8(2), P1-Au1-S 177.2(1), P2-Au2-S 168.8(1), O1-C7-O2 124.5(6), O1-C7-C2 120.6(7), O2-C7-C2 114.8(6), O2-H-O3 164.0, O3-H1-F1 167.1. Symmetry positions of O3: *x*, *y*, *z*; F1: *x*, *y*, *z*+1.

The structure of compound **4** is thus an unprecedented example where auriophilic bonding (Au– Au) is overruling hydrogen bonding (between carboxylic acid groups). It is unlikely that steric effects are responsible for this preference, since the thiosalicylic acid group of the monomeric cations in particular would be free to be rotated in positions suitable for hydrogen bonding of the type present e. g. in acetic acid. The compensation of the loss of packing energy through hydrogen bonding to the BF₄⁻ anions helps to save the cation dimerization via Au–Au contacts.

Single crystals obtained from *hydrous* dichloromethane upon layering with pentane contain one mole of CH₂Cl₂ and one mole of H₂O per formula unit (**4a**). The monoclinic unit cell, space group P2₁, comprises Z = 2 of these formula units and two solvent molecules (Table I). The lattice is built from independent tetrafluoroborate anions, dichloromethane molecules, and *monomeric* cations which form a hydrogen bond with the water molecule through their carboxylic acid function (Fig. 4).

In the cation, the two gold atoms are attached to the mercaptide sulfur atom converting it into a pyramidal sulfonium center. The Au-S-Au angle of only $83.4(1)^{\circ}$ is associated with a short Au–Au contact of 3.107(1) Å. Together with the angles C1-S-Au1 $[109.6(2)^{\circ}]$ and C1-S-Au2 $[104.8(2)^{\circ}]$, these data of the monomeric cations are very similar to those in the dimeric cations in crystals of compound 4 (above). It appears that the dimerization is associated with only very minor structural changes. The crystal structures of compounds 4 and 4a, which were obtained serendipitously by using hydrous and anhydrous solvents, respectively, have offered a unique chance to compare monomers and dimers of the same species of this type in virtually strainfree lattices. It is very important to know that the formation of supramolecular structures through auriophilic bonding is not associated with significant changes in the basic structures of the components.

Experimental Part

General: All experiments were routinely 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 400, TMS as internal standard, phosphoric acid as external standard. MS: Finnigan MAT 90. Starting materials were either commercially available or were prepared following literature procedures: $[(Ph_3P)Au]_3O^+ BF_4^- [30], [(Me_3P)Au]^+BF_4^- [28], (Me_3P)AuCl [31].$

S,*S*-*Bis*[(*trimethylphosphine*)gold(1)]-benzylsulfonium tetrafluoroborate (1)

(Trimethylphosphine)gold(I) tetrafluoroborate (0.25 g, 0.5 mmol) was freshly prepared from the chloride and AgBF₄ in tetrahydrofuran (20 mL) at 0°C and treated with thiobenzylalcohol BzSH (0.03 mL, 0.25 mmol) for 4 h. The volume of the reaction mixture is reduced to 10 mL in a vacuum and mixed with diethyl ether (10 mL). The colourless, crystalline precipitate is recrystallized from dichloromethane/ diethyl ether; 74 % yield (0.19 g), m.p. 179°C, soluble in CH₂Cl₂ and CHCl₃, insoluble in pentane and diethyl ether, air- and moisture-stable both in solution and as a solid.

¹H NMR (CDCl₃, 23°C): δ = 1.60 ppm, d, J(P,H) = 9.9 Hz, 18H, Me; 4.30, s, 2H, CH₂; 7.2 - 7.5, m, 5H, Ph. ³¹P{1H} NMR (CDCl₃): δ = -3.2, s. MS (FAB, nitrobenzylalcohol): m/z = 669, M⁺ (17 %). C₁₃H₂₅Au₂BF₄P₂S (756.03) Calcd C 20.64, H 3.33, S 4.24%, Found C 20.11, H 3.09, S 4.18%.

O,S,S-Tris[(triphenylphosphine)gold(I)]- α mercaptoacetate tetrafluoroborate (2)

A solution of $[(Ph_3P)Au]_3O^+$ BF₄⁻ (0.43 g, 0.29 mmol) in dichloromethane (10 mL) is treated with α -mercaptoacetic acid (0.02 mL, 0.29 mmol) at RT. After 4 h the reaction mixture is filtered and the product is precipitated from the filtrate by addition of diethyl ether; colourless, crystalline solid; 76 % yield (0.34 g), m.p. 168°C with decomposition, soluble in CH₂Cl₂, CHCl₃ and tetrahydrofuran, insoluble in pentane and diethyl ether, air- and moisture-stable in solution and as a solid.

¹H NMR (CDCl₃, -60°C): δ = 7.00 - 7.50, m, 45H, Ph; 3.83, s, 2H, CH₂. ¹³C{¹H} NMR (CDCl₃, -60°C): δ = 36.5, s, CH₂; 126.9, br d, J(P,C) = 65.3 Hz, and 127.4, br d, J(P,C) = 58.8 Hz, C(ipso); 129.2, br s, C(meta); 132.2, br s, C(para); 133.7, br s, C(ortho); 175.8, s, CO₂. ³¹P{¹H} NMR (CDCl₃, -60°C): δ = 27.0, s, 1P, PAuO; 34.1, s, 2P, PAuS.

 $\begin{array}{c} C_{56}H_{47}Au_3BF_4O_2P_3S\cdot 0.9\ CH_2Cl_2\ (1635.38)\\ Calcd \ C\ 41.83,\ H\ 3.01,\ Au\ 36.13,\ Cl\ 4.12\%,\\ Found \ C\ 41.38,\ H\ 3.05,\ Au\ 35.80,\ Cl\ 4.12\%. \end{array}$

O,S,S-Tris[(triphenylphosphine)gold(I)]- β mercaptopropionate tetrafluoroborate (**3**)

The preparative method was the same as described for **2**, with 0.02 mL (0.23 mmol) of β -mercaptopropionic acid. The product (0.27 g, 75% yield) is a stable, off-white powder. ¹H NMR (here and in the following as for **2**): $\delta = 2.73$, s, 2H, CH₂S; 3.50, s, 2H, CH₂; 7.05 - 7.45, m, 45H, Ph. ¹³C{¹H} NMR: $\delta = 29.0$, s, CH₂S; 43.2, s, CH₂; 127.1, d, J(P,C) = 60.7 Hz, and 127.1, d, J(P,C) = 65.3 Hz, C(ipso); 129.0, d, J(P,C) = 11.9 Hz, and 129.4, d, J(P,C) = 12.9 Hz, C(meta); 132.0, s, and 132.3, s, C(para); 133.6, d, J(P,C) = 13.8 Hz, and 133.7, d, J(P,C) = 12.9 Hz, C(ortho); 175.5, s, CO₂. ³¹P{¹H} NMR: $\delta = 27.3$, s, 1P, PAuO; 34.3, s, 2P, PAuS.

C₅₇H₄₉Au₃BF₄O₂P₃S·0.8 CH₂Cl₂ (1636.67) Calcd C 42.42, H 3.12, Au 36.10, Cl 3.47%, Found C 41.81, H 3.20, Au 35.80, Cl 3.39%.

S,*S*-*Bis*[(*triphenylphosphine*)gold(1)]-(*hydrogen*)thiosalicylate tetrafluoroborate (**4**, **4a**)

(Ph₃P)AuCl (0.122 g, 0.247 mmol) is treated with AgBF₄ (0.048 g, 0.247 mmol) in tetrahydrofuran (20 mL) at 0°C to give a solution of $[(Ph_3P)Au]BF_4$. To the filtrate is added a solution of thiosalicylic acid (0.019 g, 0.123 mmol) in 5 mL of THF and allowed to react for 30 min at 0°C with stirring. The solvent is removed in a vacuum

and the oily residue taken up in dichloromethane. Layering of the solution with pentane gives a small amount of colourless crystals (5 mg, **4**) and a violet oil, which is again taken up in CH₂Cl₂, filtered to remove colloidal gold particles, and reprecipitated, now as a colourless solid, with pentane. This crop (**4a**, 0.117 g, 75 % yield) contains dichloromethane and water. The crystals loose solvent at 129°C and decompose above 220°C.

¹H NMR (**4a**, CHCl₃, 23°C): δ = 5.24, s, CH₂Cl₂; 5.37, br s, H₃O⁺; 7.26 - 7.46, m, C₆H_{5/4}; 7.85, d, J(H,H) = 7.3 Hz, H(ortho-S); 7.90, d, J(H,H) = 8.5 Hz, H(ortho-CO₂). ¹³C{¹H} NMR (CDCl₃, 23°C): δ = 127.6, d, J(P,C) = 61 Hz, C(ipso)Ph; 129.6, d, J(P,C) = 12 Hz, C(meta)Ph; 132.5, d, J(P,C) = 2 Hz, C(para)Ph; 133.8, d, J(P,C) = 14 Hz, C(ortho)Ph; 128.5, 130.0, 132.0, 132.9, 134.0, 136.6, not assigned (C₆H₄); 168.4, s, COOH. ³¹P{¹H} NMR (CDCl₃, -60°C): δ = 33.1, s.

 $\begin{array}{l} \mbox{4a: } C_{43}H_{35}Au_2BF_4O_2P_2S\cdot H_2O\cdot CH_2Cl_2 \ (1261.46) \\ Calcd \ C \ 41.89, \ H \ 3.12\%, \\ Found \ C \ 41.92, \ H \ 3.04\%. \end{array}$

Crystal Structure Determination

Suitable crystals of compounds 1, 2, 4 and 4a were sealed under argon at dry ice temperature into glass capillaries and examined directly on the diffractometer. Data were corrected for Lorentz, polarisation and absorption effects. Structures were solved by direct methods and refined by full-matrix least-squares calculations. The thermal motion was treated anisotropically for all nonhydrogen atoms, and isotropically for all hydrogen atoms. Details of the X-ray structure determinations have been deposited at Fachinformationszentrum Karlsruhe GmbH, D-76344 Eggenstein-Leopoldshafen, Germany, and may be obtained by quoting the CSD number 59244.

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