Isomerism of Aurated Phosphine Sulfides, Thiophosphinates, Thiophosphonates, and Thiophosphates: Structural and Quantum Chemical Studies

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The reaction of disodium phenyltrithiophosphonate with (triorganophosphine)gold(I) chlorides in the molar ratio 1:2 in dichloromethane gives high yields of the corresponding dinuclear complexes $PhP(S)[SAu(PR_3)]_2$ with R = Ph (**1**), Me, Et, *i*-Pr, and *o*-Tol. The crystal structure of complex **1** has been determined by single crystal X-ray methods. The two gold atoms are bound to separate sulfur atoms, leaving only one sulfur atom uncoordinated. The compound is stabilized by an *intra*molecular Au···Au contact. This result shows that individual auration of sulfur atoms is energetically preferred over double auration of only one sulfur atom. An analogous product is obtained from trisodium tetrathiophosphate hydrate and $(Ph_3P)AuCl$ in CH_2Cl_2/MeOH: The reaction is accompanied by partial methanolysis to give $MeOP(S)[SAu(PPh_3)]_2$. Again each gold atom is bound to a different sulfur atom. In the crystal structure of this compound, *inter*molecular Au···Au contacts lead to one-dimensional aggregates. All attempts to aurate the above products further with excess $(R_3P)AuCl$ or $\{[(R_3P)Au]_3O\}^+BF_4^-$ reagents were unsuccessful. P−S cleavage occurred instead to give tris[(triorganophosphine)gold)]sulfonium salts, $\{[(R_3P)Au]_3S\}^+X^-$. The origin of this P−S cleavage has been traced by ab initio quantum chemical calculations of the mono-, bis-, and trisauration of the model compound H_3PS (phosphine sulfide) with $[(H_3P)Au]^+$ units. Only the first step was found to be strongly exothermic (−74.5 kcal/mol), and to lead to a significant lengthening of the P−S bond. The second step has an energy balance of only −1.1 kcal/mol, but induces a further lengthening of the P−S bond, while the third step is strongly endothermic (+67.3 kcal/mol). Bond rupture probably sets in at the second auration step. Quantum chemical calculations have also confirmed the experimental finding (for **1**) that auration of the dithiophosphinate anion $[H_2PS_2]^-$ with $[(H_3P)Au]^+$ gives the cation $[H_2P(SAuPH_3)_2]^+$ (with the gold atoms bound to different sulfur atoms), the structure of which is preferred over the isomer $[H_2P(S)S(AuPH_3)_2]^+$ (with both gold atoms bound to the same sulfur atom).

Introduction

Gold monocations are known to have a high affinity for sulfide and thiolate anions.[1,2] Substrates with any sulfur functions are therefore readily aurated, and the products show high stability. The primary products, in which each sulfide group is formally saturated by one gold atom, can be aurated even further, and recent work has shown that up to four (and probably more) gold atoms can be accommodated in the coordination sphere of a sulfide dianion (Scheme 1).[3,4]

The resulting dications have an unusual square pyramidal structure[1,4] reminiscent of that of the corresponding tetragold phosphonium[5] and -arsonium[6] cations. By contrast, thiolate anions were found to form triply aurated dications $[RS(AuL)_3]^{2+}$ with a nearly tetrahedral structure.[7] The existence of the analogous triply aurated alkoxide dications $[RO(AuL)_3]^{2+}$ has not yet been confirmed, but the dication representing the quadruply aurated oxide dianion $[O(AuL)_4]^{2+}$ has been structurally characterized as a molecule with a regular tetrahedral core structure.[8]

With this background, we have recently started systematic investigations of the auration of phosphine sulfides,[9] in which the negative charge at the sulfur atom is neutralized by the neighboring phosphonium center. This should lead to a reduction of the formal charge at the aurated sulfur center and influence its acceptor properties. Surprisingly, all attempts to *poly*aurate phosphine sulfides have led to a cleavage of the P−S bond after the *mono*auration step. In the presence of a second sulfur center, as in *di*thiophosph*in*ates, auration led to stepwise auration at *each* sulfur center instead of a diauration at *one* sulfur atom.[10,11]

We have extended this work now to include *tri*thiophosph*on*ates $[RPS_3]^{2-}$ and -phosphates $[ROPS_3]^{2+}$, where there is an even greater choice of donor sites for auration. In addition, we have carried out theoretical studies (ab initio, RIMP2/MP2)

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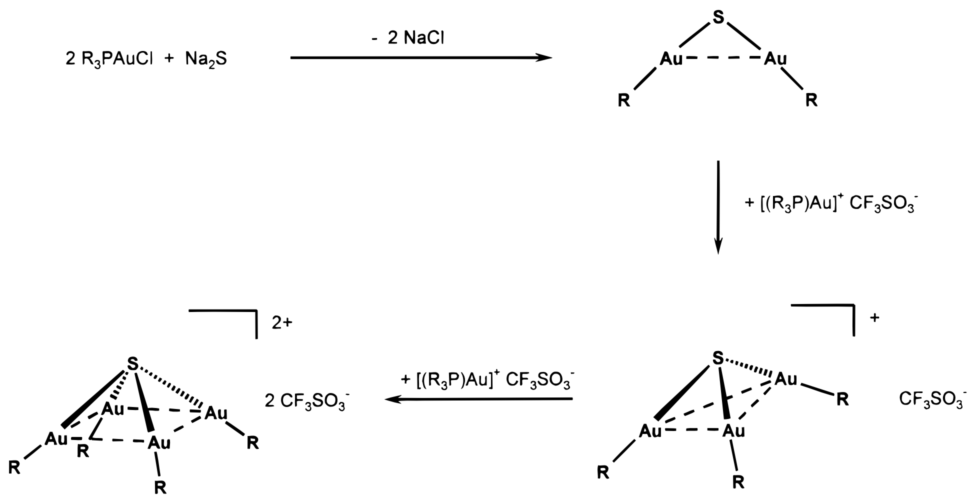
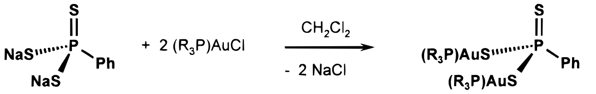
Scheme 1



of the diauration of the $[H_2PS_2]^-$ anion and of the stepwise triauration of phosphine sulfide H_3P-S as a model substrate. $[H_3P-Au]^+$ cations were introduced as the acceptor units in each case.

Preparative Results

Treatment of a solution of a (phosphine)gold chloride in moist dichloromethane with disodium phenyltrithiophosphonate in the molar ratio 2:1 leads in a metathesis reaction to the corresponding dinuclear trithiophosphonate complexes (eq 1). Crystals of the triphenylphosphine complex **1** can be obtained by crystallization from dichloromethane/pentane at 0 °C (yield 78%, mp 157 °C with decomposition). The complexes with other tertiary phosphines are also colorless, air-stable solids, soluble in di- and trichloromethane (yield 65−86%). All compounds **1**−**5** have been characterized by their analytical and spectroscopic data (Experimental Section); their $^{31}P\{^1H\}$ NMR spectra show two singlet signals of relative intensity 1:2 and prove the proposed stoichiometry. A reaction route affording the trinuclear complexes starting with phenyltrithiophosphonic acid bis(trimethylsilyl)ester has recently been published.[10]

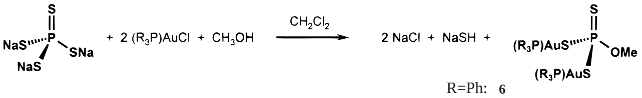


R = Ph, Me, Et, *i*-Pr, *o*-Tol

1 2 3 4 5

(1)

All attempts to accomplish a metathesis reaction leading to the formation of polyaurated tetrathiophosphate failed. Treatment of several (phosphine)gold chlorides in dichloromethane with trisodium tetrathiophosphate in methanol led to the corresponding dinuclear trithiophosphate complex as a methanolysis product (eq 2). It was not possible to find a solvent system in which both educts and products were stable.

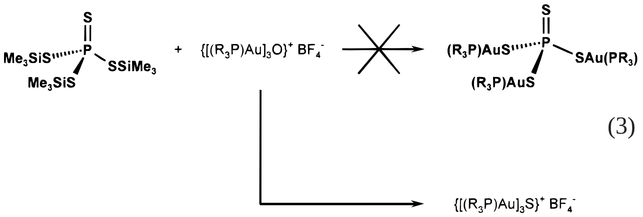


R=Ph: **6**

(2)

The neutral triphenylphosphine complex **6** was isolated by crystallization from CH_2Cl_2/pentane (yield 73%) as a colorless, air-stable solid, soluble in di- and trichloromethane, but insoluble in pentane and diethyl ether. Its composition was confirmed by elemental analysis. The ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were instrumental in showing that in chloroform solution the $AuPPh_3$ units are structurally equivalent.

Tris(trimethylsilyl)tetrathiophosphate was also probed as starting material, but its reaction with 1 equiv of tris[(phosphine)gold(I)]oxonium tetrafluoroborate in dichloromethane at −40 °C led to P−S bond cleavage and formation of tris[(phosphine)gold(I)]sulfonium tetrafluoroborate (eq 3). No (phosphine)gold(I) tetrathiophosphate could be detected or isolated.



(3)

Structural Studies

S,*S*′-Bis[(triphenylphosphine)gold(I)] phenyltrithiophosphonate, **1**, crystallizes in the monoclinic space group $P2_1/c$ with $Z = 4$ formula units in the unit cell. The lattice contains independent molecular units with no crystallographically imposed symmetry (Figure 1). Two of the three sulfur atoms (S1, S2) are aurated with angles S1−Au1−P1/S2−Au2−P3 [(168.15(6)/171.91(5)°] significantly bent away from the 180° standard to allow an intramolecular Au···Au contact of 3.1793(4) Å. The coordination at the phosphorus atom is distorted tetrahedral with one short [P3=S3 = 1.932(2) Å] and two long [P3−S1 and P3−S2 = 2.070(2) Å] P−S bond lengths, the former clearly representing a double bond. There are no sub-van der Waals intermolecular contacts (neither Au···Au nor Au···S).

Bis[(triphenylphosphine)gold(I)] *O*-methyltrithiophosphate, **6**, crystallizes in the monoclinic space group $P2_1/n$ with $Z = 4$ molecules in the unit cell. The lattice is composed of equivalent molecular units, one of which is shown in Figure 2. These molecules are aggregated into strings through short intermolecular Au···Au contacts (Figure 3). The two P−Au−S units are close to linear with standard Au−P and Au−S distances. The geometry at the central phosphorus atom is distorted tetrahedral.

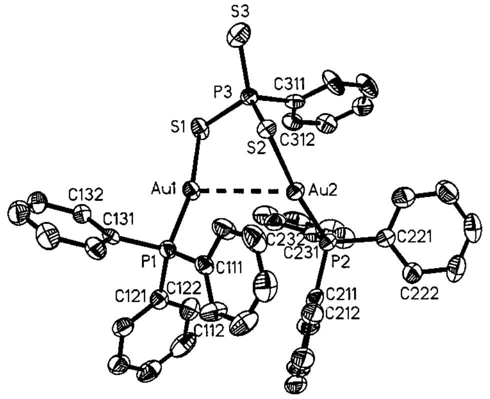


Figure 1. Molecular structure of compound **1** (ORTEP drawing with 50% probability ellipsoids; H-atoms omitted for clarity). Selected bond lengths (Å) and angles (deg): Au1−P1 = 2.257(2), Au1−S1 = 2.329(2), Au2−P2 = 2.256(2), Au2−S2 =- 2.321(1), P2−S1 = 2.070(2), P3−S2 = 2.070(2), P3−S3 = 1.932(2), P3−C311 = 1.815(6), Au1···Au2 = 3.1793(4); P1−Au1−S1 = 168.15(6), P2−Au2−S2 = 171.91(5), S1−P3−S2 = 109.82(9), S1−P3−S3 = 115.21(10), S1−P3−C311 = 106.2(2), S2−P3−S3 = 109.66(10), S2−P3−C311 = 106.3(2), S3−P3−C311 = 109.2(2).

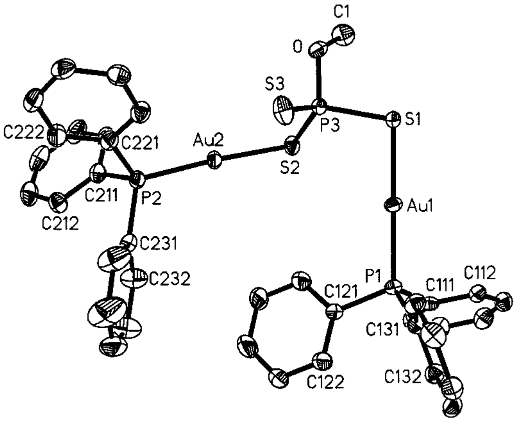


Figure 2. Molecular structure of compound **6** (ORTEP drawing with 50% probability ellipsoids; H-atoms omitted for clarity). Selected bond lengths (Å) and angles (deg): Au1−P1 = 2.310(2), Au1−S1 = 2.371(2), Au2−P2 = 2.288(2), Au2−S2 = 2.351(1) P3−S1 = 2.059(2), P3−S2 = 2.061(2), P3−S3 = 1.961(2), P3−O = 1.663(4), O−C1 = 1.459(7); P1−Au1−S1 = 178.96(5), P2−Au2−S2 = 176.01(6), S1−P3−S2 = 107.06(9), S1−P3−S3 = 116.57(9), S1−P3−O = 101.5(2), S2−P3−S3 = 116.08(9), S2−P3−O = 106.7(2), S3−P3−O = 107.6(2), P3−O−C1 = 122.7(4).

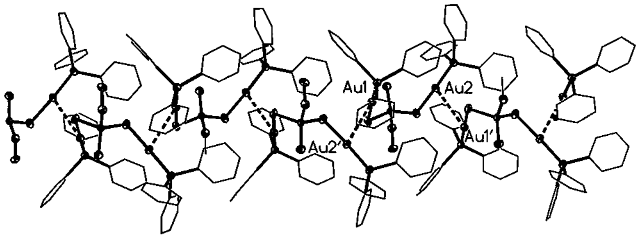
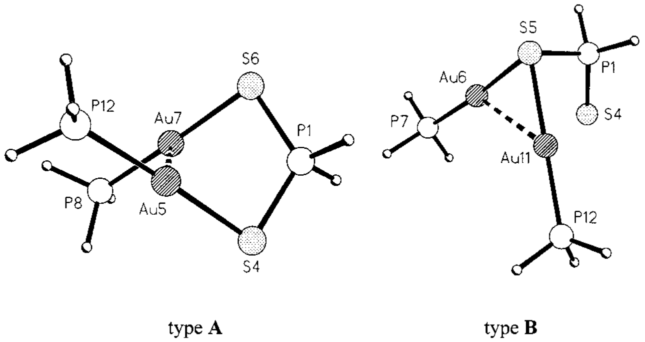


Figure 3. Chain formation of the monomers of compound **6** through Au···Au contacts [Au1···Au2′ = 3.3464(5)].



type **A** type **B**

Figure 4. Isomeric structures **A** and **B** of bis[(phosphine)gold(I)] dithiophosphinate.

Two of the three sulfur atoms (S1, S2) are engaged in coordinative bonding, each carrying only one gold atom. The distances P3−S1 = 2.059(2) Å and P3−S2 = 2.061(2) Å clearly represent P−S single bonds, and this is also reflected by the angles P3−S1−Au1 = 100.65(7)° and P3−S2−Au2 = 102.08(7)°. The third sulfur atom (S3) and the methoxy group have no structurally discernible donor/acceptor interactions and show standard P═S and P—O—Me bonding characteristics [P3−S3 = 1.961(2) Å, P3—O = 1.663(4) Å, C1—O—P3 = 122.7(4)°].

These structural results demonstrate that two monoaurations of sulfur centers are preferred over a diauration at only one sulfur center. It is unlikely that the opportunities for aurophilic bonding are of significance for this preference, because it is known that aurophilic bonding is as common for [RS−Au−L] molecules as it is for $[R-S(AuL)_2]^+$ units.[12,13] It should be noted that the two bulky Ph_3P ligands are not preventing aurophilic contacts between gold atoms within the same molecule or between different molecules, although the mutual approach is clearly not an optimum [Au1−Au2 = 3.1793(4) Å in **1**, Au1−Au2′ = 3.3464(5) Å in **6**], even though neighboring P−Au−S axes are "crossed" to reduce congestion.

Quantum Chemical Studies

For dinuclear complexes of dithiophosphinate ligands we have recently shown that there is also a structural type realized in the solid state, in which the gold atoms are equally bonded to different sulfur atoms (type **A**, Figure 4).[10] In contrast, NMR data suggest the existence of an equilibrium in solution with both gold(I) atoms attached to the same sulfur (type **B**, Figure 4). The energy difference associated with this ligand exchange is expected to be very small, but there are no calculations to support this assumption.

To analyze this equilibrium, a geometrical optimization was performed for both structure types on reduced integral second-order Møller−Plesset (RIMP2) level[14] using Turbomole[15] and 19 valence-electron (19 VE) pseudopotentials,[16] followed by a single-point MP2[17] energy calculation with the resulting structures. C_2 symmetry was assumed for structure **A**, C_s symmetry for structure **B**. H atoms were used in the calculations instead of the phenyl groups present in the experimental counterparts, a widely accepted model.[18,19] At the ab initio MP2 level, PMe_3 gives the same interaction depth, but larger R_e than for PH_3.[19]

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Table 1. Calculated Bond Distances and Angles of the Two Isomers of Bis[(phosphine)gold(I)] Dithiophosphinate in Comparison with Known Crystal Structure Data

	$\{H_2P[SAu(PH_3)]_2\}^+$ type **A** MP2	$\{Ph_2P[SAu(PPh_3)]_2{}^+BF_4{}^-$ type **A** XRD		$\{H_2P(S)S[Au(PH_3)]_2\}^+$ type **B** MP2
P1−S4	2.07 Å	2.04 Å	P1−S4	1.98 Å
S4−Au5	2.34 Å	2.34 Å	P1−S5	2.16 Å
Au5−P12	2.28 Å	2.25 Å	S5−Au6	2.37 Å
Au5−Au7	2.93 Å	3.24 Å	Au6−P7	2.28 Å
P1−S4−Au5	93.8°	101.9°	Au6−Au11	2.92 Å
S4−Au5−P12	174.4°	173.3°	Au6−S4	3.25 Å
S6−P1−S4	117.0°	115.3°	P1−S5−Au6	89.7°
			S5−Au6−P7	175.5°
			Au6−S5−Au11	76.0°

Table 2. Calculated Bond Distances and Angles in $\{H_3PS[Au(PH_3)]_n\}^{n+}$ (n = 1, 2, 3)

	n = 1		n = 2		n = 3
P2−S3	2.03 Å	P2−S3	2.11 Å	P1-S5	2.14 Å
S3−Au4	2.33 Å	S3−Au4	2.36 Å	S5−Au6	2.37 Å
Au4−P5	2.29 Å	Au4−P5	2.30 Å	Au6−P7	2.31 Å
P2−S3−Au4	96.8°	Au4−Au11	3.03 Å	Au6−Au11	3.94 Å
S3−Au4−P5	176.3°	P2−S3−Au4	101.1°	P1−S5−Au6	105.9°
		S3−Au4−P5	175.1°	S5−Au6−P7	177.9°
		Au4−S3−Au11	79.7°	Au6−S5−Au11	112.8°

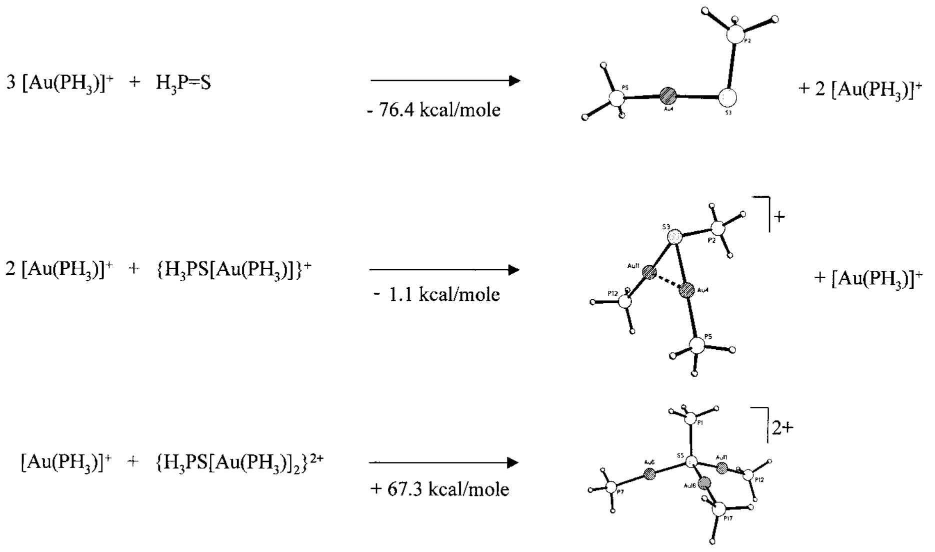

Figure 5. Energy balance of a stepwise auration of phosphine sulfide.

Selected distances and angles of the calculated structures are summarized in Table 1 and compared with the values from the crystal structure of $[Ph_2P(SAuPh_3)_2]^+BF_4^-$.[10] For type **A** an energy minimum fully consistent with the solid-state structure was found. However, due to the absence of significant sterical effects the Au−Au distance (2.93 Å) is smaller by about 0.3 Å as compared with the experimental value. As well-known,[19] the MP2 level exaggerates the aurophilic interaction for large enough basis sets (2f). The calculated structural type **B** also shows strong gold···gold interactions with a distance of 2.92 Å, but no interactions of the gold atoms with the noncoordinated sulfur atom. A comparison of the calculated MP2 energies (ΔE = 8 kcal/mol) confirms that in the gas phase type **A** is favored, which is in good agreement with the result of the experimental work. However, considering the small energy difference, type **B** cannot be excluded totally for certain solvents or for combinations with other anions.

While thiols can easily be converted into di- or trinuclear complexes,[7] for the related phosphine sulfides only monoauration has been observed.[9] Attempts of polyauration have failed and resulted in the formation of triaurosulfonium salts by cleavage of the phosphorus−sulfur bond, probably owing to a drastic lengthening and weakening of the P−S bond.

In pertinent calculations again only hydrogen atoms were used instead of phenyl groups to give model systems $H_3PS(AuPH_3)_n{}^{n+}$ (n = 1, 2, 3). Standard MP2 geometry optimization and energy calculation methods were applied: For n = 1 (C_s symmetry) the Gaussian94[20] program package was used, and for n = 2 (C_s) and n = 3 (C_{3v}) Turbomole was used.[15] Selected distances and angles of the cations are summarized in Table 2. The energetic balance is given in Figure 5.

The structure obtained for the monoaurated product is fully consistent with known related solid-state structures.[9] Coordination of a $AuPH_3$ group to H_3PS leads to a lengthening of the phosphorus−sulfur bond from 1.97 Å in H_3PS to 2.03 Å in the adduct. The energy gain for this step amounts to −76.4 kcal/mol. By contrast, coordination of a second [(phosphine)gold]$^+$

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unit has an only slightly exothermic character ($\Delta E = -1.1$ kcal/mol), even though the two metal atoms can approach each other quite closely at Au4−Au11 = 3.03 Å. In the second auration step a further significant weakening of the phosphorus−sulfur bond shows in a lengthening to P2−S3 = 2.11 Å. It is probably at this stage that rupture of the P−S bond occurs to give triaurosulfonium salts. A third auration step has only a minor influence on the P−S bond (P1−S5 = 2.14 Å), and the four groups surround the sulfur atom in a tetrahedral geometry similar to that of $MeS[Au(PPh_3)]_3^{2+}$.[7] In this model the gold−gold distances become too long to allow metal−metal interactions. This step is strongly endothermic, $\Delta E = +67.3$ kcal/mol. The SAu_3 pyramid can only revert to a geometry with short Au⋯Au contacts by a cleavage of the P−S bond.

In conclusion this short theoretical study has shown that auration of tertiary phosphine sulfides affords a very stable mononuclear product, while di- and triauration lead to a weakening of the P−S bond and are associated with an only weakly exothermic or strongly endothermic energy balance, respectively. The experimentally observed cleavage of the PS bond at the second auration step opens up a pathway to the much more stable trigoldsulfonium cations.

Experimental Section

General Procedures. All experiments were carried out under an atmosphere of dry, purified nitrogen. Glassware was dried and filled with nitrogen. If not otherwise stated, solvents were dried, distilled, and kept under nitrogen. NMR: JEOL-GX 270 (109.4 MHz), $SiMe_4$ as internal standard, phosphoric acid as external standard. MS: Finnigan MAT 90. Microanalyses: Elementar (by combustion techniques). Starting materials were either commercially available or prepared following literature procedures: $PhP(S)(SNa)_2$,[21] $Na_3PS_4{\cdot}9H_2O$,[22] $P(S)(SSiMe_3)_3$,[23] $(Me_3P)AuCl$,[24] $(Et_3P)AuCl$,[25] $(i\text{-}Pr_3P)AuCl$,[26] $(Ph_3P)AuCl$,[27] $(o\text{-}Tol_3P)AuCl$,[28] $\{[(Ph_3P)Au]_3O\}^+BF_4^-$.[29]

Syntheses. $PhP(S)[SAu(PPh_3)]_2$, 1. To a solution of $(Ph_3P)AuCl$ (231 mg, 0.470 mmol) in moist dichloromethane (20 mL) was added $PhP(S)(SNa)_2$ (58 mg, 0.230 mmol). After the solution was stirred for 2 h, the solvent was removed totally in vacuo, and the remaining precipitate was extracted with 10 mL of dry dichloromethane. After filtration the solvent was again removed in vacuo, and the remaining colorless solid was washed with diethyl ether and pentane. Crystals suitable for X-ray studies of complex **1** could be obtained from a dichloromethane solution layered with pentane by cooling to 0 °C (yield 201 mg, 78%). The compound is air-stable and stable in solution, soluble in dichloromethane and chloroform, but insoluble in pentane and diethyl ether. Mp 157 °C dec. Anal. Calcd for $C_{42}H_{35}Au_2P_3S_3$: C, 44.93; H, 3.14. Found: C, 44.58; H, 3.54. ^1H NMR ($CDCl_3$): δ 7.26−8.44 (m, Ph). $^{31}P\{^1H\}$ NMR: δ 84.6 (s, 1 P, $PhPS_3$), 35.4 (s, 2 P, $AuPPh_3$). $^{13}C\{^1H\}$ NMR: δ 134.1 (d, $J_{CP} = 15$ Hz), 129.2 (d, $J_{CP} = 12$ Hz), 131.7 (s), 127.8 (d, $J_{CP} = 60$ Hz) (*o*-, *m*-, *p*-, *ipso*-C of $AuPPh_3$), 128.9 (d, $J_{CP} = 12$ Hz), 127.1 (d, $J_{CP} = 13$ Hz), 129.6 (s) (*o*-, *m*-, *p* -C of $PhPS_3$), *ipso*-C atoms of $PhPS_3$ were not observed with certainty. MS (FAB): *m*/*z* (rel intens) 1123 (7, $[M + 1]^+$).

Table 3. Crystal Data, Data Collection, and Structure Refinement for Compounds **1** and **6**[a]

	1	**6**
	Crystal Data	
empirical formula	$C_{42}H_{35}Au_2P_3S_3$	$C_{37}H_{33}Au_2OP_3S_3$
M_r	1122.72	1076.66
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$
a (Å)	12.134(1)	12.694(3)
b (Å)	13.134(1)	12.895(1)
c (Å)	24.428(3)	22.895(3)
β (deg)	94.83(1)	94.25(1)
V (Å^3)	3879.2(6)	3737.4(11)
ρ_{calcd} (g cm^{-3})	1.922	1.913
Z	4	4
F(000)	2152	2056
μ(Mo Kα)	78.71	81.67
	Data Collection	
T (°C)	−78	−110
scan mode	$\omega-\theta$	ω
hkl range	$-14 \rightarrow +10$, $0 \rightarrow 16$, $-30 \rightarrow +30$	$0 \rightarrow 16$, $0 \rightarrow 16$, $-28 \rightarrow 28$
$\sin(\theta/\lambda)_{max}$	0.62	0.64
no. of measured reflns	11 542	8188
no. of unique reflns	7600 [R_{int} = 0.0396]	7846 [R_{int} = 0.0208]
no. of reflns used for refinement	6701	7789
abs correction	DIFABS	ψ-scans
	Refinement	
no. of refined params	451	415
final R values [$I > 2\sigma(I)$]		
$R1^a$	0.0296	0.0324
wR2^b	0.0540	0.0764
(shift/error)$_{max}$	<0.001	<0.001
ρ_{fin}(max/min) (e Å^{-3})	0.819/−0.759	1.705/−1.948

[a] $R = \sum(||F_o| - |F_c||)/\sum|F_o|$. [b] $wR2 = \{[\sum w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) = (ap)^2 + bp]$; $p = (F_o^2 + 2F_c^2)/3$; $a = 0.0240$ (**1**), 0.0376 (**6**); $b = 14.05$ (**1**), 4.01 (**6**).

$PhP(S)[SAu(PMe_3)]_2$, 2. The synthesis was analogous to that of **1** with $(Me_3P)AuCl$ (143 mg, 0.464 mmol) and $PhP(S)(SNa)_2$ (58 mg, 0.232 mmol) to give 113 mg (65%) of **2**. Mp 139 °C dec. Anal. Calcd for $C_{12}H_{23}Au_2P_3S_3$: C, 19.21; H, 3.09; S, 12.82. Found: C, 18.98; H, 3.25; S, 13.30. ^1H NMR ($CDCl_3$): δ 7.85−8.24 (m, 5 H, $PhPS_3$), 1.72 (d, $J_{HP} = 11$ Hz, 18 H, $AuPMe_3$). $^{31}P\{^1H\}$ NMR: δ 85.6 (s, 1 P, $PhPS_3$), −6.3 (s, 2 P, $AuPMe_3$). $^{13}C\{^1H\}$ NMR: δ 128.4 (d, $J_{CP} = 11$ Hz), 127.2 (d, $J_{CP} = 12$ Hz), 129.7 (d, $J_{CP} = 3$ Hz), (*o*-, *m*-, *p*-C of $PhPS_3$), *ipso*-C atoms of $PhPS_3$ were not observed with certainty, 17.1 (d, $J_{CP} = 32$ Hz, $AuPMe_3$). MS (FAB): *m*/*z* (rel intens) 751 (11, $[M + 1]^+$).

$PhP(S)[SAu(PEt_3)]_2$, 3. The synthesis was analogous to that of **1** with $(Et_3P)AuCl$ (131 mg, 0.370 mmol) and $PhP(S)(SNa)_2$ (47 mg, 0.180 mmol) to give 101 mg (78%) of **3**. Mp 159 °C dec. Anal. Calcd for $C_{18}H_{35}Au_2P_3S_3$: C, 25.91; H, 4.23. Found: C, 25.36; H, 3.98. ^1H NMR ($CDCl_3$): δ 7.25−8.52 (m, 5 H, $PhPS_3$), 1.81 (m, 12 H, $AuP(CH_2CH_3)_3$), 1.10 (m, 18 H, $AuP(CH_2CH_3)_3$). $^{31}P\{^1H\}$ NMR: δ 86.0 (s, 1 P, $PhPS_3$), 36.6 (s, 2 P, $AuPEt_3$). $^{13}C\{^1H\}$ NMR: δ 129.2 (d, $J_{CP} = 12$ Hz), 127.0 (d, $J_{CP} = 13$ Hz), 128.6 (d, $J_{CP} = 3$ Hz), (*o*-, *m*-, *p*-C of $PhPS_3$), *ipso*-C atoms of $PhPS_3$ were not observed with certainty, 18.0 (d, $J_{CP} = 32$ Hz, $AuP(CH_2CH_3)_3$), 9.0 (d, $J_{CP} = 6$ Hz, $AuP(CH_2CH_3)_3$). MS (FAB): *m*/*z* (rel intens) 835 (10, $[M + 1]^+$).

$PhP(S)[SAu(P\text{-}i\text{-}Pr_3)]_2$, 4. The synthesis was analogous to that of **1** with $(i\text{-}Pr_3P)AuCl$ (145 mg, 0.370 mmol) and $PhP(S)(SNa)_2$ (47 mg, 0.180 mmol) to give 150 mg (86%) of **4** as a yellow viscous liquid. ^1H NMR ($CDCl_3$): δ 7.29−8.57 (m, 5 H, $PhPS_3$), 2.23 (m, 6 H, $AuP[CH(CH_3)_2]_3$), 1.23 (m, 36 H, $AuP[CH(CH_3)_2]_3$). $^{31}P\{^1H\}$ NMR: δ 84.5 (s, 1 P, $PhPS_3$), 67.3 (s, 2 P, $AuP\text{-}i\text{-}Pr_3$). $^{13}C\{^1H\}$ NMR: δ 129.3 (d, $J_{CP} = 12$ Hz), 127.1 (d, $J_{CP} = 14$ Hz), 128.9 (s), (*o*-, *m*-, *p*-C of $PhPS_3$), *ipso*-C atoms of $PhPS_3$ were not observed with certainty, 23.9 (d, $J_{CP} = 29$ Hz, $AuP[CH(CH_3)_2]_3$), 20.3 (d, $J_{CP} = 3$ Hz, $AuP[CH(CH_3)_2]_3$). MS (FAB): *m*/*z* (rel intens) 1276 (3, $[M + AuP\text{-}i\text{-}Pr_3]^+$), 1117 (40, $[M + Au]^+$, 919 (2, $[M + 1]^+$).

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PhP(S)[SAu(P-*o*-Tol$_3$)]$_2$, 5. The synthesis was analogous to that of **1** with (*o*-Tol$_3$P)AuCl (193 mg, 0.360 mmol) and PhP(S)(SNa)$_2$ (45 mg, 0.180 mmol) to give 165 mg (76%) of **5**. Mp 167 °C dec. Anal. Calcd for $C_{48}H_{47}Au_2P_3S_3$: C, 47.77; H, 3.92; S, 7.97. Found: C, 47.42; H, 3.98; S, 7.68. ^{1}H NMR (CDCl$_3$): δ 6.91−8.63 (m, 29 H, aryl), 2.52 (s, 18 H, CH$_3$). ^{31}P{^{1}H} NMR: δ 82.2 (s, 1 P, PhPS$_3$), 17.6 (s, 2 P, AuP-*o*-Tol$_3$). MS (FAB): *m/z* (rel intens) 835 (10%, $[M + 1]^+$).

MeOP(S)[SAu(PPh$_3$)]$_2$, 6. To a solution of (Ph$_3$P)AuCl (267 mg, 0.540 mmol) in 20 mL of dichloromethane was added $Na_3PS_4 \cdot 9H_2O$ (71 mg, 0.27 mmol) in 5 mL of methanol. After the solution was stirred for 2 h, the solvents were removed in vacuo, and the remaining precipitate was extracted with 10 mL of dry dichloromethane. After filtration the solvent was again removed in vacuo, and the remaining colorless solid was washed with diethyl ether and pentane. Crystals suitable for X-ray studies of complex **6** could be obtained from a dichloromethane solution layered with pentane by cooling to 0 °C (yield 212 mg, 73%). The compound is air-stable and stable in solution, soluble in dichloromethane and chloroform, but insoluble in pentane and diethyl ether. Mp 178 °C dec. Anal. Calcd for $C_{37}H_{33}Au_2OP_3S_3$: C, 41.27; H, 3.09. Found: C, 40.99; H, 3.14. ^{1}H NMR (CDCl$_3$): δ 7.48−8.25 (m, 30 H, AuPPh$_3$), 3.74 [d, $J_{HP} = 13$ Hz, 3 H, OMe]. ^{31}P{^{1}H} NMR: δ 122.3 (s, 1 P, MeOPS$_3$), 34.5 (s, 2 P, AuPPh$_3$). ^{13}C{^{1}H} NMR: δ 134.0 (d, $J_{CP} = 13$ Hz), 129.0 (d, $J_{CP} = 11$ Hz), 131.5 (s), 126.9 (d, $J_{CP} = 58$ Hz) (*o*-, *m*-, *p*-, *ipso*-C of AuPPh$_3$), 53.3 [d, *J*(CP), 17 Hz].

{[(Ph$_3$P)Au]$_3$S}$^+$BF$_4^-$. To a solution of P(S)(SSiMe$_3$)$_3$ (45 mg, 0.119 mmol) in 5 mL of dichloromethane were added at −78 °C {[(Ph$_3$P)-Au]$_3$O}$^+$BF$_4^-$ (235 mg, 0.158 mmol) in 5 mL of dichloromethane and NaBF$_4$ (100 mg, 0.91 mmol). After being stirred for 2 h at −40 °C the solution was filtered and the solvent removed in vacuo. The main product of the colorless precipitate was identified as {[(Ph$_3$P)Au]$_3$S}$^+$BF$_4^-$ (yield 126 mg, 71%). ^{1}H NMR (CDCl$_3$): δ 7.72−8.41 (m). ^{31}P{^{1}H} NMR: δ 33.4 (s); ^{13}C{^{1}H} NMR: δ 133.8 (d, $J_{CP} = 14$ Hz), 129.3 (d, $J_{CP} = 12$ Hz), 132.0 (s), 127.2 (d, $J_{CP} = 59$ Hz) (*o*-, *m*-, *p*-, *ipso*-C of AuPPh$_3$). MS (FAB): *m/z* (rel intens) 1409 (100, $[M]^+$).

Crystal Structure Determinations. Specimens of suitable quality and size of compounds **1** and **6** were mounted in glass capillaries and used for measurements of precise cell constants and intensity data collection on an Enraf Nonius CAD4 diffractometer (Mo Kα radiation, λ(Mo Kα) = 0.710 73 Å). During data collection, three standard reflections were measured periodically as a general check of crystal and instrument stability. No significant changes were observed. Lp correction was applied, and intensity data were corrected for absorption effects. The structures were solved by direct methods (SHELXS-86) and completed by full-matrix least-squares techniques against F^2 (SHELXL-93). The thermal motion of all non-hydrogen atoms was treated anisotropically. All hydrogen atoms were placed in idealized calculated positions and allowed to ride on their corresponding carbon atoms with fixed isotropic contributions ($U_{iso(fix)} = 1.5U_{eq}$ of the attached C atom). Further information on crystal data, data collection, and structure refinement is summarized in Table 3. Important interatomic distances and angles are shown in the corresponding figure captions.

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Supporting Information Available: Tables of data collection and refinement parameters, atomic coordinates, thermal parameters including those for hydrogen, complete bond distances and angles, and anisotropic displacement parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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