

Preparation and Crystal Structures of Gold(I) Complexes of a Series of Benzenethiolates: Pair Formation by Gold-to-Gold Interactions of (Benzenethiolato)(triphenylphosphane)gold(I)

Masami Nakamoto^{1*}, Wolfgang Hiller, and Hubert Schmidbaur*

Anorganisch-chemisches Institut der Technischen Universität München, Lichtenbergstraße 4, W-8046 Garching, FRG

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Chloro(triphenylphosphane)gold(I) reacts readily with benzenethiol C_6H_5SH and a series of sterically hindered (2,4,6-trialkylbenzene)thiols $2,4,6-R_3C_6H_2SH$ in the presence of NEt_3 to yield stable gold(I) complexes $Ph_3PAu(S-2,4,6-C_6H_2R_3)$ [$R = H$ (1), Me (2), Et (3), *i*Pr (4)]. The crystal structures of these complexes have been determined by single-crystal X-ray diffraction analysis. In all compounds the gold atoms are linearly two-coordinate with very similar bond lengths and angles. While complexes 2–4 with bulky thiolate ligands are monomeric in the crystal lattice, complex 1 has been found to form

pairs of molecules with intermolecular gold–gold contacts of 313.5(5) pm. The Mössbauer spectra of the complexes exhibit large isomer shifts (I.S.), ranging from 3.06 to 3.72 $mm\ s^{-1}$, and quadrupole splittings (Q.S.), ranging from 7.90 to 8.68 $mm\ s^{-1}$. These data can be attributed to the strong electron-donating properties of the benzenethiolate ligands. The gold–gold contacts in complex 1 lead to I.S. and Q.S. values which are slightly smaller than those of 2–4. The Au–S distances do not show a major influence of the S–Au–P pairing in complex 1 as compared to complexes 2–4.

Recently, much attention has been paid to gold(I) complexes with a combination of phosphane (L) and thiolate ligands (SR) of the type L–Au–SR. Both extensive experimental^[1] and detailed theoretical^[2] studies have been initiated due to a variety of practical aspects including uses as antiarthritic and cancerostatic drugs^[3], but also as precursors of the thermal, chemical, or photochemical deposition of metallic gold^[4]. Surprisingly, many of the (phosphane)gold(I) thiolates are of limited stability. For example in the series $R_3PAuSPh$, the species with $R = Et$ ^[5] and Ph ^[6] are reported to be unstable, and no spectroscopic data and crystal structures are available. Only in the case of the selenolate derivatives $Ph_3PAuSePh$ ^[7] and $Ph_3PAu[Se-2,4,6-C_6H_2(tBu)_3]$ ^[8] the crystal structure of the former has recently been determined. A perpendicular arrangement of the Se–Au–P units in the molecules has been detected with a gold-gold distance of 311.8(1) pm^[7].

In many previous structural studies of gold(I) complexes with linear two-coordinate geometry convincing evidence for such intermolecular gold-gold interaction between closed d^{10} shells has been compiled^[1a,9]. Steric conditions permitting, gold(I) centers with a linear X–Au–Y structure are found in pairs, either in parallel (head-to-head or head-to-tail) or perpendicular arrangement, or in chains with a folding of the chains as they become extended^[10,11]. Tertiary and secondary phosphanes are most widely used as ligands which strongly stabilize a variety of gold(I) compounds. The bulkiness of these phosphanes R_3P or R_2PH is prohibitive for L–Au–X association in most cases. Primary phosphanes are sterically undemanding, and even ligands of the type $(2,4,6-C_6H_2R_3)PH_2$ ($R = H, Me, Et, iPr, \text{ and } tBu$) not only stabilize the gold(I) complexes $(2,4,6-C_6H_2R_3)PH_2-AuCl$ ^[11], but allow weak gold-gold contacts of 344.0(1) pm in dimers.

As part of a current program in the structural chemistry of gold(I), it appeared worthwhile to investigate gold(I) benzenethiolates with a series of substituents in 2,4,6-position. Chloro(triphenylphosphane)gold(I) was therefore allowed to react with benzenethiol and three 2,4,6-trialkylbenzenethiols $2,4,6-R_3C_6H_2SH$ ($R = Me, Et, \text{ and } iPr$) to give complexes $Ph_3PAu(S-2,4,6-C_6H_2R_3)$ [$R = H$ (1), Me (2), Et (3), *i*Pr (4)]. The crystal structures of all complexes were determined in order to delineate the steric influence on the intermolecular interactions. Structural studies were complemented by Mössbauer and NMR spectroscopic data.

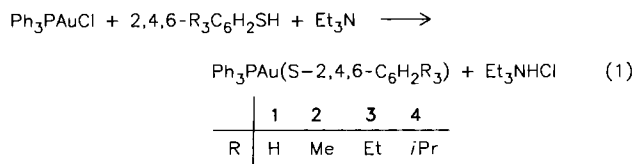
Syntheses and Properties of (Triphenylphosphane)gold(I) Complexes of a Series of Benzenethiolate Ligands

Syntheses

The reaction of bromo- or chloro(triphenylphosphane)gold(I) with various alkane- or arenethiols was reported to yield (alkanethiolato)- or (arenethiolato)(triphenylphosphane)gold(I) compounds R_3PAuSR' ($R = Ph; R' = Me, Et, nPr, nBu, PhCH_2, Ph$) as gummy solids^[6]. In most cases the products were too unstable to allow purification by recrystallization. In another study it was found that the reactions of (methylthio)- or (phenylthio)trimethylsilane with chloro(triphenylphosphane)gold(I) under reflux conditions yield the compounds $Ph_3PAuSMe$ and $Ph_3PAuSPh$, respectively^[12], but again no spectroscopic and structural investi-

^[*] On leave from the Osaka Municipal Technical Research Institute, Osaka, Japan.

gations were carried out, due to the instability of the products thus obtained. In our hands, the (triphenylphosphane)gold(I) benzenethiolates turned out to be stable compounds, which were easily characterized once available in the pure state. In an improved reaction procedure, the compounds were generated by the reaction of benzenethiol C_6H_5SH or 2,4,6- $R_3C_6H_2SH$ ($R = Me, Et, \text{ and } iPr$), with an equivalent amount of chloro(triphenylphosphane)gold(I) in THF in the presence of excess triethylamine as a base.



All the complexes have readily been isolated in high yields. They show no tendency to decompose even at the stage when Et_3NHCl is removed by washing the reaction mixture with water during the workup procedure. The complexes are stable towards air and light and can be crystallized from benzene and *n*-hexane to yield colorless crystals.

NMR Spectra

Compounds **1–4** have been characterized by means of 1H -, $^{13}C\{^1H\}$ -, and $^{31}P\{^1H\}$ -NMR spectra and by elemental analysis. The analytical and NMR-spectroscopic data are summarized in the experimental section.

The 1H -NMR spectra of the present complexes measured in $CDCl_3$ at room temperature show a multiplet signal of the phosphane ligand in the range $\delta = 7.3$ to 7.6 and a singlet signal of the phenyl protons in the 3- and 5-positions of the substituted benzenethiolate ligands at $\delta = ca. 6.9$. For **1**, the thiolate protons also appear as a multiplet. In the case of the complexes **2–4**, the *o*- and *p*-alkyl substituents of the sterically hindered benzenethiolate ligands afford two sets of methyl signals for **2**, methyl and methylene signals for **3**, and methyl and methyne signals for **4**, with the relative intensities of 2:1 in each case. In the ^{13}C -NMR spectra, the phenyl carbon atoms of the phosphane ligand show coupling to phosphorus with $J(P,C)$ values of ca. 56 Hz for C-1, 7.6 to 11.5 Hz for C-2/6, 13.7 to 18.7 Hz for C-3/5, and ca. 3 Hz for C-4. A comparison with reference data suggests that the present complexes have a normal linear configuration typical for gold(I). The ^{31}P -NMR signals are observed as singlets at $\delta ca. 38$, again similar to values obtained e.g. for $Ph_3PAuSePh$ ($\delta = 39.41$)^[7].

^{197}Au -Mössbauer Spectra

The ^{197}Au nucleus is one of the most suitable to give recoil-free γ -resonances for chemical applications (Mössbauer spectroscopy)^[13]. Figure 1 shows the Mössbauer spectrum of complex **1** as a representative example.

This spectrum and the ^{197}Au -Mössbauer spectra of the other three complexes show a simple quadrupole doublet of equal intensity. The isomer shifts (I.S.) and quadrupole splittings (Q.S.) for compounds **1–4** are in the range from

3.06 to 3.72 mm s^{-1} and from 7.90 to 8.68 mm s^{-1} , respectively (see the Experimental). Compared with data for Ph_3PAuCl (I.S. = 2.96 mm s^{-1} ; Q.S. = 7.47 mm s^{-1})^[14], the present complexes show both higher I.S. and Q.S. values. Gold(I) can be considered to use sp -hybrid orbitals in the formation of normal linear complexes. With strong σ -donor and π -acceptor ligands, like phosphanes and thiols, higher s -electron density is accumulated at the gold nucleus which gives rise to higher isomer shifts^[13]. This is borne out by the present data. Furthermore, it should be pointed out that the I.S. and Q.S. values of complex **1** are significantly lower than those of the complexes **2–4**. This result can be tentatively attributed to the gold-gold interactions of complex **1** in the solid state, but the alkyl substituents at the benzene ring are assumed to be also involved in the interactions.

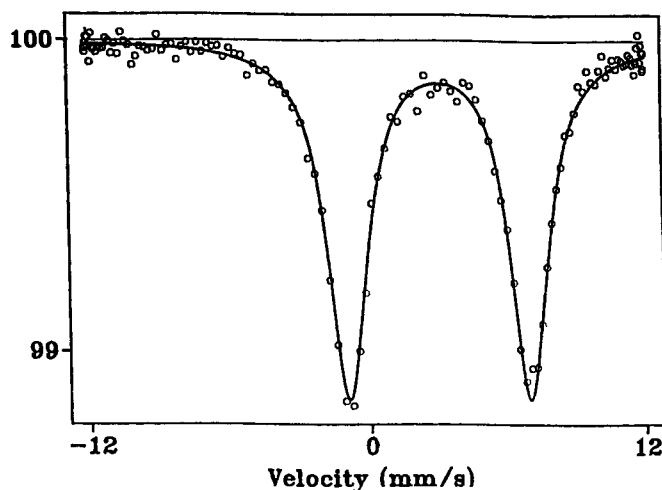


Figure 1. Mössbauer spectrum (at 4 K) of $Ph_3PAuSPh$ (**1**)

Crystal Structures of the Complexes

The complexes crystallize from benzene and *n*-hexane at room temperature as colorless crystals. Their crystal structures have been determined by single-crystal X-ray diffraction analysis. Crystal data are compiled in Table 1. Crystals of complex **1** contain two independent molecules in the asymmetric unit, which form pairs by gold-gold interactions, as shown in Figure 2. Selected bond distances and angles of complex **1** are listed in Table 2, together with those of the other complexes. Each monomer unit features a linear coordination of the gold atoms with angles $S1-Au1-P1 = 179.12(7)$ and $S2-Au2-P2 = 175.79(6)^\circ$. The two independent Au-S bond lengths are very similar [$229.6(2)$ and $230.2(2) \text{ pm}$], but longer than the Au-P bond lengths [$225.9(2)$ and $225.8(2) \text{ pm}$]. The latter are thus significantly shorter than in $Ph_3PAuSePh$ [$226.7(1)$ and $226.7(2) \text{ pm}$]^[7]. This result may be explained by the difference of the donor ability of thiolate and selenolate ligands, which leads to a different *trans* influence. The Au1-Au2 contact in the dimer of **1** amounts to $313.55(3) \text{ pm}$, similar to the value found in the $Ph_3PAuSePh$ dimer (311.8 pm)^[7]. Intermolecular Au-Au contacts of this type are very common and are observed also for other gold(I) complexes with sulfur-

containing ligands such as $\text{Au}_2(\text{CH}_2\text{PPh}_2\text{S})_2$ ^[15], $\text{Au}_2[\text{S}_2\text{-P}(i\text{Pr})_2]_2$ ^[16], and $\text{Au}_2[\text{S}_2\text{CN}(n\text{Pr})_2]_2$ ^[17]. The distances observed range from 290.0 to 350.0 pm^[18] and are attributed to relativistic effects in the valence orbitals of gold atoms^[19].

The X-ray analyses of complexes 2–4 gave very similar results regarding the basic Ph_3PAuS moieties and the con-

figuration of the SR' ligands ($\text{R}' = 2,4,6\text{-R}_3\text{C}_6\text{H}_2$, $\text{R} = \text{Me}$, Et , $i\text{Pr}$) (Table 2). As representative examples, the molecular structures of the complexes 3 and 4 are shown in Figures 3

Table 1. Crystal data for the compounds 1–4

Compound	1	2	3	4
Formula	$\text{C}_{24}\text{H}_{20}\text{AuPS}$	$\text{C}_{27}\text{H}_{26}\text{AuPS}$	$\text{C}_{30}\text{H}_{32}\text{AuPS}$	$\text{C}_{33}\text{H}_{38}\text{AuPS}$
M	568.43	610.51	652.59	694.68
Crystal system	triclinic	monoclinic	orthorhombic	monoclinic
Space group	$\text{P}\bar{1}$	$\text{P}2_1/\text{n}$	$\text{P}2_12_12_1$	$\text{P}2_1/\text{n}$
a [pm]	1100.1(1)	1233.4(1)	876.2(1)	1352.4(1)
b [pm]	1152.6(1)	1540.6(1)	1597.9(1)	1694.5(2)
c [pm]	1671.0(1)	1309.0(1)	1937.2(1)	1437.2(2)
α [°]	97.00(1)			
β [°]	93.45(1)	102.77(1)		110.09(1)
γ [°]	93.18(1)			
V [pm ³ × 10 ⁶]	2095.0	2425.9	2712.2	3093.1
Z	4	4	4	4
ρ_{calc} [Mg m ⁻³]	1.802	1.311	1.598	1.492
μ [mm ⁻¹]	71.86	48.72	55.61	48.81
min. abs. corr.	0.831	0.591	0.108	0.766
max. abs. corr.	1.131	1.361	1.164	1.194
av. abs. corr.	0.997	1.004	0.791	1.004
θ max. [°]	27	28	32	26
no. reflections:				
measured	8282	6317	10105	6545
unique	7801	5787	(Friedel pairs)	6011
observed [$I \geq 3\sigma(I)$]	5614	3821	3565	4433
R	0.025	0.034	0.046 (0.056)	0.028
wR	0.028	0.039	0.048	0.030
Parameters	488	272	149	326
max. height in final ΔF map	0.784	0.267	0.987	0.344
Database*	CSD-56261	CSD-56232	CSD-56214	CSD-56050

* Further details of the crystal structure determinations have been deposited with the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, W-7514 Eggenstein-Leopoldshafen 2. The data are available on request with the CSD numbers given above.

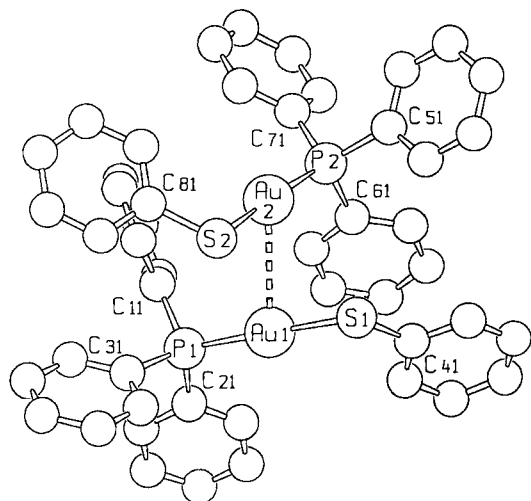


Figure 2. Pairs of molecules of Ph_3PAuSPh (1) in the crystal with atomic numbering

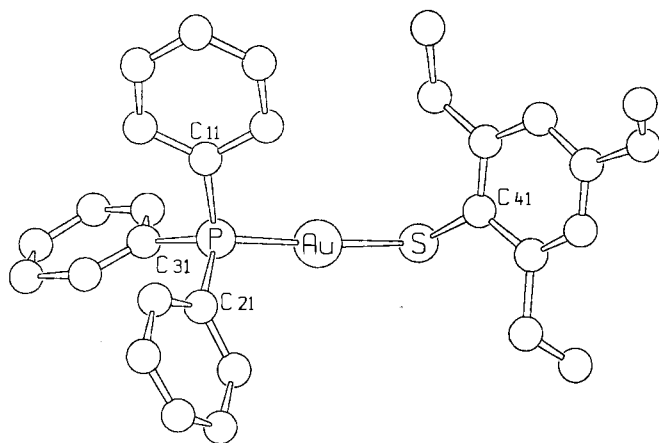


Figure 3. Molecular structure of $\text{Ph}_3\text{PAu}(\text{S}-2,4,6\text{-C}_6\text{H}_2\text{Et}_3)$ (3)

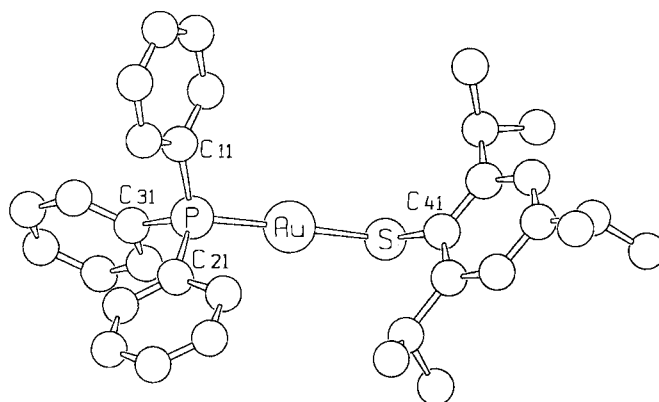


Figure 4. Molecular structure of $\text{Ph}_3\text{PAu}[\text{S}-2,4,6\text{-C}_6\text{H}_2(i\text{Pr})_3]$ (4)

Table 2. Selected bond distances [pm] and angles [°]

Compound	1	2	3	4
Au1–Au2	313.55(3)			
Au1–S1	229.6(2)	228.4(2)	228.8(4)	228.4(2)
Au1–P1	225.9(2)	225.5(2)	226.0(3)	225.5(2)
Au2–S2	230.2(2)			
Au2–P2	225.8(2)			
Au2–Au1–S1	77.44(4)			
Au1–Au2–S2	75.83(4)			
Au1–Au2–P2	103.52(4)			
Au2–Au1–P1	103.31(4)			
S1–Au1–P1	179.12(7)	175.24(7)	176.2(1)	176.35(5)
S2–Au2–P2	175.79(6)			
Au1–S1–C41	107.8(2)	110.8(3)	101.7(5)	105.9(2)
Au2–S2–C81	107.8(2)			

and 4. The Au–S bond length of complex 4 is 228.4(2) pm, only slightly shorter than that of 1 [229.6(2) pm] in spite of the presence of bulky alkyl substituents in the 2- and 6-positions of the benzenethiolate ligand. The Au–P bond length [225.5(2) pm] is quite similar to those of the complex 1. Again, the S–Au–P unit is quasi-linear [176.35(5)°] in complex 4. The dihedral angles S–Au1–Au2–S2 and P1–Au1–Au2–P2 are found to be 96.1(1) and 100.8(1)°, respectively, indicating that in complex 1 the two S–Au–P groups are quasi-perpendicular, not parallel (head-to-head or head-to-tail)^[1a].

In conclusion, the present work has shown that (*tert*-phosphane)gold(I) benzenethiolates can be obtained in good yields as stable monomeric compounds, which are easily characterized by standard techniques. In the solid state an association of the monomers by intermolecular metal-metal interactions is only observed for the unsubstituted benzenethiolate. It appears therefore that even minor steric effects, as present in the substituted benzenethiolates, preclude the intermolecular approach necessary for the weak Au(I)⋯Au(I) interactions, which quite obviously are easily overruled. This is particularly true for solvation in solution, which also leads to complete separation of the monomers. In the absence of steric hindrance or solvent molecules, however, LAuX complexes (with L a neutral donor ligand and X an anionic group) are generally found as aggregates with close Au⋯Au contacts regardless of the nature of L and X.

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Experimental

All experiments were carried out under dry and purified nitrogen. Solvents were distilled over drying agents under nitrogen. — NMR: solvent CDCl₃, reference compounds tetramethylsilane and phosphoric acid, Jeol JNM GX 400 spectrometer. — Mössbauer spectra (crystalline powders at 4 K) were measured at the Physics Department, Technische Universität München.

2,4,6-Triethylbenzenesulfonyl chloride was prepared following a literature method^[20]. 2,4,6-Trimethyl-, 2,4,6-triethyl-, and 2,4,6-triisopropylbenzenethiol were synthesized from the corresponding 2,4,6-trialkylbenzenesulfonyl chlorides by LiAlH₄ reduction according to a literature procedure^[21]. Chloro(triphenylphosphane)gold(I) was obtained as described previously^[22]. All other reagents were obtained commercially.

(*Benzenethiolato*)(*triphenylphosphane*)gold(I) (1): To a solution of chloro(triphenylphosphane)gold(I) (0.98 g, 1.98 mmol) in 40 ml of tetrahydrofuran (THF) a mixture of benzenethiol (0.22 g, 2.0 mmol) and triethylamine (0.20 g, 2.0 mmol) in the same solvent (15 ml) was added dropwise at room temp. The reaction mixture was stirred for 1 h to give a white precipitate. The solvent was evaporated under reduced pressure and the white residue triturated with water (25 ml) to remove Et₃NHCl. After 30 min a white solid was collected by filtration, washed with water (2 × 5 ml) and a minimum amount of methanol, and finally dried in vacuo. Recrystallization from benzene/*n*-hexane yielded 0.60 g of colorless crystals of 1 (53%), m.p. 155–167 °C (ref.^[5] 161–163 °C). — ¹H NMR: δ = 6.97 (dd, 1H, SPh *p*-H), 7.09 (dd, 2H, SPh *m*-H), 7.34–7.61

Table 3. Atomic positional and equivalent isotropic displacement B_{eq} [pm² · 10⁴] parameters of compound 1. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3) \cdot [B_{11}a^2 + B_{22}b^2 + B_{33}c^2 + B_{12}ab(\cos \gamma) + B_{13}ac(\cos \beta) + B_{23}bc(\cos \alpha)]$

Atom	x	y	z	B(eq)
Au1	0.23487(2)	0.40759(2)	0.32196(1)	3.468(5)
Au2	0.07409(2)	0.27038(2)	0.17569(1)	3.406(5)
S1	0.2013(2)	0.5500(2)	0.2398(1)	4.44(4)
S2	-0.0635(2)	0.3212(2)	0.2703(1)	4.25(4)
P1	0.2680(2)	0.2696(2)	0.4044(1)	3.67(4)
P2	0.2085(2)	0.2338(1)	0.08017(9)	3.26(3)
C11	0.2539(6)	0.1229(6)	0.3512(4)	3.8(1)
C12	0.1406(7)	0.0779(6)	0.3200(4)	4.4(2)
C13	0.1240(8)	-0.0311(6)	0.2743(5)	5.6(2)
C14	0.2207(9)	-0.0952(7)	0.2583(6)	6.9(2)
C15	0.3342(8)	-0.0513(7)	0.2862(6)	7.0(2)
C16	0.3544(7)	0.0574(7)	0.3340(5)	5.5(2)
C21	0.4190(7)	0.2858(8)	0.4547(4)	5.2(2)
C22	0.5035(8)	0.3604(8)	0.4304(7)	7.0(2)
C23	0.6222(9)	0.3737(9)	0.4681(9)	10.1(3)
C24	0.650(1)	0.315(1)	0.5294(7)	12.0(3)
C25	0.570(1)	0.242(2)	0.5546(6)	14.9(5)
C26	0.452(1)	0.226(1)	0.5174(6)	10.5(4)
C31	0.1632(6)	0.2683(6)	0.4839(4)	3.8(1)
C32	0.1267(8)	0.1680(7)	0.5147(5)	5.9(2)
C33	0.0500(9)	0.1708(8)	0.5771(5)	7.1(2)
C34	0.0070(8)	0.2760(8)	0.6083(5)	6.1(2)
C35	0.0412(8)	0.3771(8)	0.5776(5)	6.2(2)
C36	0.1175(7)	0.3734(7)	0.5161(5)	5.2(2)
C41	0.3439(6)	0.6066(5)	0.2154(4)	4.0(1)
C42	0.3468(8)	0.6671(7)	0.1482(5)	5.5(2)
C43	0.4534(9)	0.7177(8)	0.1271(5)	7.1(2)
C44	0.5578(8)	0.7089(8)	0.1718(6)	7.7(2)
C45	0.5607(8)	0.6503(8)	0.2377(7)	7.5(3)
C46	0.4514(8)	0.5997(7)	0.2590(5)	5.6(2)
C51	0.1688(5)	0.3030(5)	-0.0085(4)	3.4(1)
C52	0.1585(7)	0.4250(7)	0.0019(5)	4.9(2)
C53	0.1265(7)	0.4817(7)	-0.0636(5)	5.8(2)
C54	0.1027(7)	0.4193(7)	-0.1394(5)	6.0(2)
C55	0.1110(8)	0.3007(7)	-0.1490(4)	5.6(2)
C56	0.1442(7)	0.2427(6)	-0.0842(4)	4.4(2)
C61	0.3650(6)	0.2843(5)	0.1131(4)	3.3(1)
C62	0.4350(6)	0.3595(6)	0.0743(4)	4.3(2)
C63	0.5550(7)	0.3900(7)	0.1024(5)	5.3(2)
C64	0.6055(7)	0.3447(7)	0.1678(5)	5.3(2)
C65	0.5366(7)	0.2706(7)	0.2069(4)	5.3(2)
C66	0.4166(7)	0.2396(7)	0.1791(4)	4.6(2)
C71	0.2223(6)	0.0808(5)	0.0431(4)	3.5(1)
C72	0.1371(6)	-0.0040(6)	0.0594(4)	4.4(2)
C73	0.1473(7)	-0.1209(6)	0.0300(5)	5.2(2)
C74	0.2420(7)	-0.1532(6)	-0.0144(5)	5.2(2)
C75	0.3287(7)	-0.0702(7)	-0.0299(5)	5.3(2)
C76	0.3189(6)	0.0468(6)	-0.0020(4)	4.3(2)
C81	-0.1467(6)	0.1913(6)	0.2874(4)	3.8(1)
C82	-0.1827(8)	0.1824(8)	0.3643(5)	5.8(2)
C83	-0.2538(9)	0.0856(9)	0.3790(5)	7.2(2)
C84	-0.2882(9)	-0.0031(7)	0.3194(6)	7.1(2)
C85	-0.2532(9)	0.0047(8)	0.2442(6)	7.0(2)
C86	-0.1821(7)	0.1018(7)	0.2277(5)	5.1(2)

(m, 17H, SPh *o*-H and PPh₃). — ¹³C{¹H} NMR: δ = 123.41 (s, SPh C-4), 128.01 (s, SPh C-3/5), 128.30 (s, SPh C-1), 129.3 [d, ¹J(P,C) = 58 Hz, PPh₃ C-1], 129.2 [d, ³J(P,C) = 11.4 Hz, PPh₃ C-3/5], 131.76 [d, ⁴J(P,C) = 2.3 Hz, PPh₃ C-4], 132.53 (s, SPh C-2/6), 134.2 [d, ²J(P,C) = 13.7 Hz, PPh₃ C-2/6]. — ³¹P{¹H} NMR: δ = 37.7 (s). — Mössbauer spectrum: I.S. = 3.06 mm s⁻¹, Q.S. = 7.90 mm s⁻¹.

C₂₄H₂₀AuPS (568.4)

Calcd. C 50.71 H 3.55 P 5.45 S 5.64

Found C 50.50 H 3.56 P 5.76 S 5.90

Table 4. Atomic positional and equivalent isotropic displacement B_{eq} [pm² · 10⁴] parameters of compound 2

Atom	x	y	z	B(eq)
Au	0.02030(2)	0.56245(2)	0.76746(2)	3.751(5)
S	0.1934(2)	0.5624(2)	0.7317(2)	5.56(4)
P	-0.1546(1)	0.5541(1)	0.7922(1)	3.38(3)
C11	-0.2607(6)	0.5687(5)	0.6735(5)	3.7(1)
C12	-0.2393(7)	0.5396(5)	0.5803(6)	4.4(2)
C13	-0.3208(8)	0.5472(6)	0.4885(6)	5.8(2)
C14	-0.4196(9)	0.5842(6)	0.4901(7)	6.3(2)
C15	-0.4425(8)	0.6145(6)	0.5808(7)	5.8(2)
C16	-0.3626(7)	0.6056(6)	0.6741(6)	4.7(2)
C21	-0.1831(6)	0.6375(5)	0.8813(5)	3.6(1)
C22	-0.1973(7)	0.6169(6)	0.9812(6)	4.8(2)
C23	-0.2112(8)	0.6817(7)	1.0475(7)	6.3(2)
C24	-0.2143(8)	0.7675(7)	1.0167(7)	6.3(2)
C25	-0.2019(8)	0.7878(6)	0.9187(8)	6.2(2)
C26	-0.1849(7)	0.7238(5)	0.8506(6)	4.9(2)
C31	-0.1868(6)	0.4530(4)	0.8480(5)	3.6(1)
C32	-0.2944(6)	0.4259(5)	0.8426(6)	4.8(2)
C33	-0.3152(8)	0.3511(6)	0.8941(7)	5.8(2)
C34	-0.2283(9)	0.3033(6)	0.9518(6)	5.9(2)
C35	-0.1226(9)	0.3305(6)	0.9576(8)	6.3(2)
C36	-0.0992(7)	0.4046(6)	0.9055(7)	5.2(2)
C41	0.2738(6)	0.6519(5)	0.7941(5)	3.7(1)
C42	0.2334(6)	0.7373(5)	0.7856(5)	4.0(2)
C43	0.3056(7)	0.8039(5)	0.8267(6)	4.5(2)
C44	0.4166(7)	0.7892(5)	0.8762(6)	4.7(2)
C45	0.4517(7)	0.7043(6)	0.8831(6)	4.9(2)
C46	0.3848(6)	0.6353(5)	0.8439(6)	4.1(2)
C421	0.1145(7)	0.7607(6)	0.7333(8)	5.8(2)
C441	0.4918(9)	0.8650(6)	0.9192(8)	6.9(3)
C461	0.4299(8)	0.5424(6)	0.8545(8)	6.5(2)

(2,4,6-Trimethylbenzenethiolato)(triphenylphosphane)gold(I) (2): To a solution of chloro(triphenylphosphane)gold(I) (0.70 g, 1.41 mmol) in 25 ml of THF a mixture of 2,4,6-trimethylbenzenethiol (0.23 g, 1.51 mmol) and triethylamine (0.16 g, 1.58 mmol) in the same solvent was added dropwise at room temp. In the same manner as described above, colorless crystals of 2 (0.65 g, 77%) were obtained by recrystallization from benzene/*n*-hexane, m.p. 166–167°C. — ¹H NMR: δ = 2.14 (s, 3H, *p*-CH₃), 2.54 (s, 6H, *o*-CH₃), 6.79 (s, 2H, SPh 3/5-H), 7.33–7.36 (m, 15H, PPh₃). — ¹³C{¹H} NMR: δ = 20.69 (s, *p*-CH₃), 24.44 (s, *o*-CH₃), 128.01 (s, SPh C-3/5), 129.05 [d, ³J(P,C) = 7.6 Hz, PPh₃ C-3/5], 129.72 [d, ¹J(P,C) = 55.7 Hz, PPh₃ C-1], 131.47 [d, ⁴J(P,C) = 2.3 Hz, PPh₃ C-4], 133.21 (s, SPh C-1), 134.11 [d, ²J(P,C) = 13.7 Hz, PPh₃ C-2/6], 135.63 (s, SPh C-4), 140.80 (s, SPh C-2/6). — ³¹P{¹H} NMR:

δ = 38.05 (s). — Mössbauer spectrum: I.S. = 3.50 mm s⁻¹, Q.S. = 8.44 mm s⁻¹.

C₂₇H₂₆AuPS (610.5)

Calcd. C 53.12 H 4.29 P 5.07 S 5.25

Found C 53.17 H 4.36 P 4.70 S 5.53

(2,4,6-Triethylbenzenethiolato)(triphenylphosphane)gold(I) (3): To a solution of chloro(triphenylphosphane)gold(I) (0.88 g, 1.80 mmol) in 40 ml of THF a mixture of 2,4,6-triethylbenzenethiol (0.35 g, 1.80 mmol) and triethylamine (0.19 g, 1.88 mmol) in the same solvent was added dropwise at room temp. Colorless crystals of 3 (0.78 g, 66%) were obtained by recrystallization from benzene/*n*-hexane, m.p. 114–115°C. — ¹H NMR: δ = 1.22 [t, 3H, J(H,H) = 7.6 Hz, *p*-CH₂CH₃], 1.33 [t, 6H, J(H,H) = 7.3 Hz, *o*-CH₂CH₃], 2.59 [q, 2H, J(H,H) = 7.3 Hz, *p*-CH₂], 3.20 [q, 4H, J(H,H) = 7.3 Hz, *o*-CH₂], 6.92 (s, 2H, SPh 3/5-H), 7.38–7.49 (m, 15H, PPh₃). — ¹³C{¹H} NMR: δ = 15.05 (s, *o*-CH₂CH₃), 15.63 (s, *p*-CH₂CH₃), 28.43 (s, *p*-CH₂), 29.84 (s, *o*-CH₂), 125.00 (s, SPh C-3/5), 129.05 [d, ³J(P,C) = 11.4 Hz, PPh₃ C-3/5], 129.80 [d, ¹J(P,C) = 55.7 Hz, PPh₃ C-1], 131.49 [d, ⁴J(P,C) = 3.0 Hz, PPh₃ C-4], 134.16 [d, ²J(P,C) = 13.7 Hz, PPh₃ C-2/6], 140.29 (s, SPh C-4), 146.83 (s, SPh C-2/6). —

Table 5. Atomic positional and equivalent isotropic displacement B_{eq} [pm² · 10⁴] parameters of compound 3. Starred atoms were refined isotropically

Atom	x	y	z	B(eq)
Au	0.81682(6)	0.04251(3)	0.14609(3)	5.523(8)
S	0.8987(5)	0.0562(3)	0.2577(2)	8.9(1)
P	0.7416(4)	0.0199(2)	0.0360(2)	4.54(7)
C11	0.900(1)	0.0050(7)	-0.0225(5)	4.2(2)*
C12	0.891(1)	-0.0490(9)	-0.0793(6)	5.7(3)*
C13	1.018(2)	-0.0569(9)	-0.1214(7)	7.0(3)*
C14	1.150(2)	-0.0167(8)	-0.1079(7)	7.0(3)*
C15	1.160(2)	0.0345(9)	-0.0526(7)	7.6(3)*
C16	1.037(1)	0.0465(9)	-0.0069(6)	6.3(3)*
C21	0.628(1)	0.1017(7)	-0.0033(5)	4.3(2)*
C22	0.546(2)	0.1531(8)	0.0395(6)	5.8(3)*
C23	0.448(2)	0.217(1)	0.0087(9)	9.2(5)*
C24	0.447(2)	0.224(1)	-0.0594(9)	8.7(4)*
C25	0.521(2)	0.174(1)	-0.1012(9)	9.1(5)*
C26	0.614(2)	0.1104(9)	-0.0728(7)	6.5(3)*
C31	0.631(1)	-0.0741(6)	0.0304(5)	3.8(2)*
C32	0.667(2)	-0.1422(7)	0.0711(6)	5.3(2)*
C33	0.588(2)	-0.2152(8)	0.0678(7)	5.9(3)*
C34	0.465(2)	-0.2217(9)	0.0268(7)	7.5(4)*
C35	0.424(2)	-0.157(1)	-0.0171(9)	10.3(5)*
C36	0.513(2)	-0.0809(9)	-0.0124(8)	7.7(4)*
C41	1.050(2)	0.1257(8)	0.2485(7)	6.2(3)*
C42	1.193(2)	0.1034(9)	0.2240(7)	7.6(3)*
C43	1.313(2)	0.161(1)	0.2239(8)	8.5(4)*
C44	1.292(2)	0.243(1)	0.2437(8)	8.5(4)*
C45	1.157(2)	0.265(1)	0.2665(8)	8.0(4)*
C46	1.037(2)	0.2091(9)	0.2726(7)	7.2(4)*
C421	1.207(3)	0.017(1)	0.202(1)	12.3(6)*
C422	1.337(4)	0.000(2)	0.160(2)	20(1)*
C441	1.415(3)	0.316(2)	0.236(2)	20(1)*
C442	1.503(5)	0.319(2)	0.198(2)	25(2)*
C461	0.887(4)	0.250(2)	0.289(1)	19(1)*
C462	0.872(4)	0.278(2)	0.347(2)	25(1)*

$^{31}\text{P}\{^1\text{H}\}$ NMR: $\delta = 37.98$ (s). — Mössbauer spectrum: I.S. = 3.56 mm s $^{-1}$, Q.S. = 8.43 mm s $^{-1}$.

$\text{C}_{30}\text{H}_{32}\text{AuPS}$ (652.6)

Calcd. C 55.21 H 4.94 P 4.75 S 4.91

Found C 55.24 H 5.06 P 4.48 S 4.98

(2,4,6-Triisopropylbenzenethiolato)(triphenylphosphane)gold(I) (4): To a solution of chloro(triphenylphosphane)gold(I) (0.73 g, 1.48 mmol) in 30 ml of THF a mixture of 2,4,6-triisopropylbenzenethiol (0.35 g, 1.48 mmol) and triethylamine (0.15 g, 1.48 mmol) in the same solvent was added dropwise at room temp. Colorless crystals of 4 (0.67 g, 65%) were obtained by recrystallization from benzene/*n*-hexane, m.p. 175–176°C. — ^1H NMR: $\delta = 1.23$ [d, 6H, $J(\text{H,H}) = 6.7$ Hz, *p*-CH(CH $_3$) $_2$], 1.28 [d, 12H, $J(\text{H,H}) = 6.7$ Hz, *o*-CH(CH $_3$) $_2$], 2.86 (sept, 1H, *p*-CH), 4.46 (sept, 1H, *o*-CH), 6.96 (s, 2H, SPh 3/5-H), 7.40–7.50 (m, 15H, PPh $_3$). — $^{13}\text{C}\{^1\text{H}\}$ NMR: $\delta = 23.81$ [s, *o*-CH(CH $_3$) $_2$], 24.15 [s, *p*-CH(CH $_3$) $_2$], 31.93 (s, *o*-CH), 33.94 (s, *p*-CH), 120.47 (s, SPh C-3/5), 129.0 [d, $^3J(\text{P,C}) = 11.45$ Hz, PPh $_3$ C-3/5], 129.79 [d, $^4J(\text{P,C}) = 55.7$ Hz, PPh $_3$ C-1], 131.45 [d, $^4J(\text{P,C})$

= 2.3 Hz, PPh $_3$ C-4], 133.02 (s, SPh C-1), 134.16 [d, $^2J(\text{P,C}) = 18.7$ Hz, PPh $_3$ C-2/6], 145.04 (s, SPh C-4), 150.95 (s, SPh C-2/6). — $^{31}\text{P}\{^1\text{H}\}$ NMR: $\delta = 38.12$ (s). — Mössbauer spectrum: I.S. = 3.72 mm s $^{-1}$, Q.S. = 8.68 mm s $^{-1}$.

$\text{C}_{33}\text{H}_{38}\text{AuPS}$ (694.6)

Calcd. C 57.06 H 5.51 P 4.46 S 4.61

Found C 57.10 H 5.53 P 4.13 S 4.99

Crystal Structure Determination of 1–4: All crystallographic investigations were performed on the automated four-circle diffractometer CAD4 (Enraf-Nonius) with Mo- K_α radiation at T = 293 K. The structures were solved by Patterson synthesis^[23]. In the final refinement all non-H atoms were assigned anisotropic displacement parameters, the idealized H positions were included in the structure factor calculations. A summary of the crystal data is given in Table 1; Table 2 contains selected bond distances and angles, Tables 3–6 positional parameters. Figures 2–4 show the structures of compounds 1, 3, and 4 along with the numbering scheme^[24]. The structure of complex 2 is very similar to those of 3 and 4 and hence no Figure is given.

Table 6. Atomic positional and equivalent isotropic displacement B_{eq} [pm $^2 \cdot 10^4$] parameters of compound 4

Atom	x	y	z	B(eq)
Au	0.22297(2)	0.73413(1)	0.34424(1)	3.321(4)
S	0.1783(1)	0.70530(9)	0.4800(1)	4.07(3)
P	0.2574(1)	0.75896(9)	0.2042(1)	3.55(3)
C11	0.3942(4)	0.7432(4)	0.2156(4)	4.1(1)
C12	0.4452(4)	0.7919(4)	0.1688(5)	5.3(1)
C13	0.5497(5)	0.7768(5)	0.1803(5)	6.6(2)
C14	0.6030(5)	0.7159(5)	0.2358(5)	6.9(2)
C15	0.5530(5)	0.6690(5)	0.2818(6)	6.6(2)
C16	0.4484(5)	0.6817(4)	0.2721(5)	5.5(2)
C21	0.2302(4)	0.8607(3)	0.1622(4)	4.1(1)
C22	0.1857(7)	0.8812(4)	0.0662(5)	7.1(2)
C23	0.1689(8)	0.9593(5)	0.0392(6)	9.3(3)
C24	0.1962(7)	0.8068(5)	0.1071(6)	8.3(2)
C25	0.2378(7)	0.9975(5)	0.2036(7)	8.0(3)
C26	0.2558(6)	0.9190(4)	0.2339(6)	6.1(2)
C31	0.1778(4)	0.6989(3)	0.1009(4)	3.8(1)
C32	0.2104(5)	0.6791(4)	0.0224(4)	5.1(2)
C33	0.1423(6)	0.6374(5)	-0.0575(5)	6.3(2)
C34	0.0448(6)	0.6156(5)	-0.0584(6)	7.4(2)
C35	0.0132(6)	0.6344(6)	0.0184(6)	8.0(2)
C36	0.0785(5)	0.6763(5)	0.0986(5)	5.6(2)
C41	0.2592(3)	0.7680(3)	0.5777(3)	3.3(1)
C42	0.3348(4)	0.7330(4)	0.6594(4)	3.6(1)
C43	0.3913(4)	0.7806(4)	0.7386(4)	4.1(1)
C44	0.3763(4)	0.8602(4)	0.7392(4)	4.2(1)
C45	0.3019(4)	0.8949(4)	0.6571(4)	4.3(1)
C46	0.2422(4)	0.8496(3)	0.5763(4)	3.6(1)
C421	0.3579(5)	0.6450(4)	0.6662(5)	5.0(2)
C422	0.3303(9)	0.6068(6)	0.7477(9)	12.0(4)
C423	0.4679(6)	0.6258(5)	0.6775(9)	10.5(3)
C441	0.4364(5)	0.9097(5)	0.8290(5)	6.0(2)
C442	0.380(1)	0.9175(8)	0.8964(6)	14.1(4)
C443	0.4813(8)	0.9813(6)	0.8079(7)	10.7(3)
C461	0.1572(5)	0.8894(4)	0.4900(5)	5.3(2)
C462	0.0546(6)	0.8900(7)	0.5111(7)	9.8(3)
C463	0.1855(8)	0.9712(5)	0.4672(6)	8.6(3)

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