Dithiolates as Bridging Ligands in Di- and Trinuclear Gold Complexes. X-ray Structures of $[Au_2(3,4\text{-}S_2C_6H_3CH_3)(PPh_3)_2]$, $[Au_2(1,3\text{-}S_2C_6H_4)(PPh_3)_2]$, $[Au_3(3,4\text{-}S_2C_6H_3CH_3)(PPh_3)_3]ClO_4$, and $[Au(PPh_2Me)_2][Au(3,4\text{-}S_2C_6H_3CH_3)_2]$

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The reaction of $[AuCl(AsPh_3)]$ with potassium 1,2-benzenedithiolate or 3,4-toluenedithiolate (2:1 ratio) leads to $[Au_2(S\text{-}S)(AsPh_3)]_n$ [S-S = $1,2\text{-}S_2C_6H_4$ (**1**), $3,4\text{-}S_2C_6H_3CH_3$ (**2**)] but with 1,3-benzenedithiolate the homoleptic $[Au_2(1,3\text{-}S_2C_6H_4)]_n$ (**3**) is obtained. Other dinuclear complexes have been prepared by reacting **1–3** with phosphines, namely $[Au_2(S\text{-}S)(PR_3)_2]$ [S-S = $1,2\text{-}S_2C_6H_4$ (**4, 5**), $3,4\text{-}S_2C_6H_3CH_3$ (**6, 7**), $1,3\text{-}S_2C_6H_4$ (**8, 9**); PR_3 = PPh_3, PPh_2Me]. The reaction of $[Au_2(S\text{-}S)(PPh_3)_2]$ (**4** and **6**) with equimolecular amounts of $[Au(PPh_3)(acetone)]ClO_4$ affords the trinuclear complexes $[Au_3(S\text{-}S)(PPh_3)_3]ClO_4$ [S-S = $1,2\text{-}S_2C_6H_4$ (**10**) and $3,4\text{-}S_2C_6H_3CH_3$ (**11**)]. Gold(I)/gold(III) complexes $[Au(PR_3)_2][Au(3,4\text{-}S_2C_6H_3CH_3)_2]$ [PR_3 = PPh_3 (**12**), PPh_2Me (**13**)] have been obtained as byproducts in the preparation of **6** and **7**. X ray structure determinations were performed for complexes **6, 8, 11** and **13**. Complex **6** crystallizes in the space group $P2_1$, monoclinic, with a = 10.771(4) Å, b = 10.726(3) Å, c = 16.752(6) Å, β = 101.02(3)°, and Z = 2. Compound **8** crystallizes in space group $Fdd2$, orthorhombic, with a = 31.182(8) Å, b = 46.537(12) Å, c = 8.782(3) Å, and Z = 16. Complex **11** crystallizes in space group $C2/c$, monoclinic, with a = 39.583(8) Å, b = 11.347(3) Å, c = 31.703(7) Å, β = 120.66(2)°, and Z = 8. Compound **13** crystallizes in space group $C2/c$, monoclinic, with a = 17.890(7) Å, b = 11.038(6) Å, c = 20.817(11) Å, β = 110.96(3)°, and Z = 4. Short Au···Au contacts (ca. 3 Å) are observed in **6** and **11** (intramolecular) and **8** (intermolecular). Complexes **6** and **11** also display intramolecular Au–S contacts of ca. 2.6–2.7 Å, leading to an increase of coordination number (to 3) at Au(1) in **6** and Au(2) in **11**.

Introduction

The widespread applications of mono- and dithiolate complexes of gold, e.g. as antiarthritic drugs and antitumor agents,[1–4] as electrical conductors and semiconductors,[5–9] or as "liquid gold"[10–12] in ceramics, have led to an increase of research activity in this area.

Although gold(III) complexes with dithiolate ligands have attracted the main attention,[13–18] complexes with the metal ion in other oxidation states[19–22] have recently been reported. Furthermore a formally gold(IV)[23] compound has been described that could be gold(III) with partially oxidized ligands, as in other dithiolate gold complexes.[16]

Here we report our results, mostly with gold(I), using dianionic sulfur ligands: 1,2-benzenedithiolate ($1,2\text{-}S_2C_6H_4$), its 3,4-dimercaptotoluene analogue ($3,4\text{-}S_2C_6H_3CH_3$), and 1,3-benzenedithiolate ($1,3\text{-}S_2C_6H_4$). The structures of $[Au_2(3,4\text{-}S_2C_6H_3CH_3)(PPh_3)_2]$, $[Au_2(1,3\text{-}S_2C_6H_4)(PPh_3)_2]$, $[Au_3(3,4\text{-}S_2C_6H_3CH_3)(PPh_3)_3]ClO_4$, and $[Au(PPh_2Me)_2][Au(3,4\text{-}S_2C_6H_3CH_3)_2]$ have been established by single-crystal X-ray analysis.

Results and Discussion

The reactions between chloro(triphenylarsine)gold(I) and 1,2 benzenedithiolate, 1,3-benzenedithiolate or 3,4-toluenedithiolate (2:1 ratio) (prepared in situ from the reaction of dithiols with KOH in methanol), lead, despite the similarity of the ligands, to different types of product. With 1,2-benzenedithiolate and its toluene analogue, complexes **1** or **2**, with an $AsPh_3$:Au ratio of only 1:2 were obtained (eq 1) whereas with 1,3 benzenedithiolate (eq 2) a polymeric derivative containing no arsine was formed.

Complexes **1–3** are air- and moisture-stable white (**1, 2**) or pale yellow (**3**) solids. Because of their insolubility in common organic solvents, no NMR data can be measured. It is plausible

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Table 1. Analytical and Spectroscopic Data for Complexes

complex		anal. (%)[a]			
no.	formula	C	H	Λ_M[b]	$\delta(^{31}P\{^1H\})$[c]
1	$[Au_2(1,2\text{-}S_2C_6H_4)(AsPh_3)]_n$	34.3 (34.3)	3.35 (3.35)		
2	$[Au_2(3,4\text{-}S_2C_6H_3CH_3)(AsPh_3)]_n$	34.8 (35.15)	2.4 (2.45)		
3	$[Au_2(1,3\text{-}S_2C_6H_4)]_n$	13.5 (13.5)	0.55 (0.75)		
4	$[Au_2(1,2\text{-}S_2C_6H_4)(PPh_3)_2]$	47.9 (47.75)	3.15 (3.25)	5.6	35.6 (s)
5	$[Au_2(1,2\text{-}S_2C_6H_4)(PPh_2Me)_2]$	41.35 (41.1)	3.4 (3.25)	3.4	20.2 (s)
6	$[Au_2(3,4\text{-}S_2C_6H_3CH_3)(PPh_3)_2]$	47.85 (48.1)	3.85 (3.35)	4.0	36.3 (s)
7	$[Au_2(3,4\text{-}S_2C_6H_3CH_3)(PPh_2Me)_2]$	41.75 (41.7)	3.45 (3.35)	2.7	20.0 (s)
8	$[Au_2(1,3\text{-}S_2C_6H_4)(PPh_3)_2]$	47.15 (47.55)	3.15 (3.25)	6.6	39.3 (s)
9	$[Au_2(1,3\text{-}S_2C_6H_4)(PPh_2Me)_2]$	41.7 (41.1)	3.4 (3.25)		23.8 (s)
10	$[Au_3(1,2\text{-}S_2C_6H_4)(PPh_3)_3]ClO_4$	44.5 (44.25)	2.9 (3.05)	120.9	38.0 (br)[d]
11	$[Au_3(3,4\text{-}S_2C_6H_3CH_3)(PPh_3)_3]ClO_4$	44.85 (44.9)	2.95 (3.15)	115.8	35.6 (br)[e]
12	$[Au(PPh_3)_2][Au(3,4\text{-}S_2C_6H_3CH_3)_2]$	48.7 (48.9)	3.25 (3.3)	78.0	30.5 (s)
13	$[Au(PPh_2Me)_2][Au(3,4\text{-}S_2C_6H_3CH_3)_2]$	43.3 (43.55)	3.25 (3.45)	80.3	16.7 (s)

[a] Calculated values are given in parentheses. [b] In acetone, values in Ω^{-1} cm^2 mol^{-1} [c] In $CDCl_3$, values in ppm, at room temperature. [d] At -55 °C, δ = 44.7 (s) and 32.7 (s). [e] At -55 °C, δ = 44.9 (s) and 34.0 (s).

$$2[AuCl(AsPh_3)] + K_2(S\text{-}S) \rightarrow (1/n)[Au_2(S\text{-}S)(AsPh_3)]_n + AsPh_3 + 2KCl \quad (1)$$

1, 2

$$S\text{-}S^{2-} = 1,2\text{-}S_2C_6H_4\ (\mathbf{1});\ 3,4\text{-}S_2C_6H_3CH_3\ (\mathbf{2})$$

$$2[AuCl(AsPh_3)] + K_2(1,3\text{-}S_2C_6H_4) \rightarrow (1/n)[Au_2(1,3\text{-}S_2C_6H_4)]_n + 2AsPh_3 + 2KCl \quad (2)$$

3

that complexes **1** and **2** have similar structures to the recently reported $[Au_4(S\text{-}S)_2(PEt_3)_2]$ [S-S = $1,2\text{-}S_2C_6H_4$,[22] $3,4\text{-}S_2C_6H_3CH_3$[20]]. Complex **3** is an interesting example of a stable gold thiolate derivative with an exceedingly high gold content (73.7% by weight).

Complexes **1–3** are good starting materials for the synthesis of gold(I) dinuclear complexes; on reaction with PPh_3 or PPh_2Me, derivatives **4–9** can be prepared (eq 3)

$$(1/n)[Au_2(S\text{-}S)AsPh_3]_n \text{ (or } (1/n)[Au_2(S\text{-}S)]_n) + 2PR_3 \rightarrow [Au_2(S\text{-}S)(PR_3)_2] + AsPh_3 \quad (3)$$

4–9

$$S\text{-}S^{2-} = 1,2\text{-}S_2C_6H_4;\ PR_3 = PPh_3\ (\mathbf{4}),\ PPh_2Me\ (\mathbf{5})$$

$$S\text{-}S^{2-} = 3,4\text{-}S_2C_6H_3CH_3;\ PR_3 = PPh_3\ (\mathbf{6}),\ PPh_2Me\ (\mathbf{7})$$

$$S\text{-}S^{2-} = 1,3\text{-}S_2C_6H_4;\ PR_3 = PPh_3\ (\mathbf{8}),\ PPh_2Me\ (\mathbf{9})$$

Complexes **4–9** are air- and moisture-stable white solids, nonconducting in acetone solutions. The spectroscopic data for complexes **4** and **8** are the same as previously reported by Fackler[20] and Schmidbaur,[18] which were obtained starting from AuCl(PPh_3). The $^{31}P\{^1H\}$ NMR spectra of **4–9** show a singlet, for **6** and **7** even at low temperatures (–70 °C) (See Table 1). The ^1H NMR spectra of the phenyl ring of the dithiolate ligand are, as expected, more complicated (see Experimental Section). Complex **7** shows a singlet for the toluene methyl group, and a doublet for the resonance of the phosphine–methyl groups is observed in complexes **5**, **7**, and **9**.

The mass spectra (FAB(+) technique, NBA as matrix) show the $[M]^+$ peak at m/z 1058 (12%) (**4**), 934 (38%) (**5**), 1072 (21%) (**6**), 948 (10%) (**7**), 1058 (32%) (**8**), and 934 (28%) (**9**); the presence of peaks with higher m/z values that are even more intense than the parent ion, corresponding to $[M + AuPPh_3]^+$, it is noteworthy: m/z 1517 (48%) (**4**), 1330 (57%) (**5**), 1531 (34%) (**6**), and 1345 (22%) (**7**). These peaks are absent for complexes with $1,3\text{-}S_2C_6H_4$ (**8** and **9**).

The structures of complexes **6** and **8** have been established by X-ray diffraction. The molecular structure of $[Au_2(3,4\text{-}S_2C_6H_3CH_3)(PPh_3)_2]$ **6** is shown in Figure 1. Atomic positional and thermal parameters are given in Table 2, with selected bond lengths and angles in Table 3. The two gold atoms are bridged by the 1,2-dithiolate ligand. The coordination at the gold atoms is different: for Au(2) it is slightly distorted from linear [P(2)–Au(2)–S(2) 172.98(10)°], while Au(1) possesses a very irregular trigonal planar geometry, P(1)–Au(1)–S(1) = 160.84(9)°, P(1)–Au(1)–S(2) = 113.56(9), and S(1)–Au(1)–S(2) = 85.15(9)°, the reason being the weaker interaction between S(2) and Au(1) of 2.714(3) Å (0.4 Å longer than normal Au–S bonds). There is a intramolecular Au(1)–Au(2) contact of 3.096(2) Å, which is typical of this type of complex and has been attributed to relativistic effects in the valence orbitals of gold.[24] The Au–P distances, Au(1)–P(1) = 2.252(3) and Au–P(2) = 2.258(3) Å,

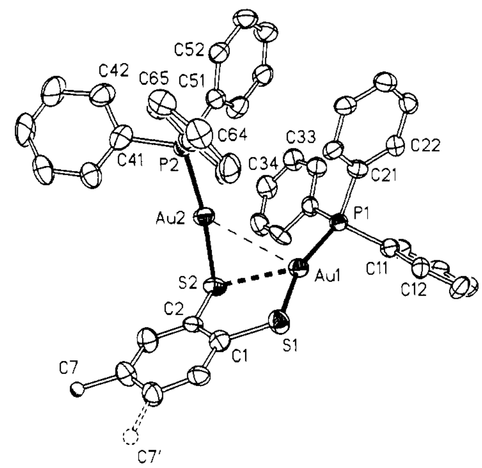

Figure 1. Molecule of complex **6** in the crystal (50% ellipsoids). H atoms are omitted. Both positions of the disordered methyl group (C(7), C(7′) are shown as circles of arbitrary radius.

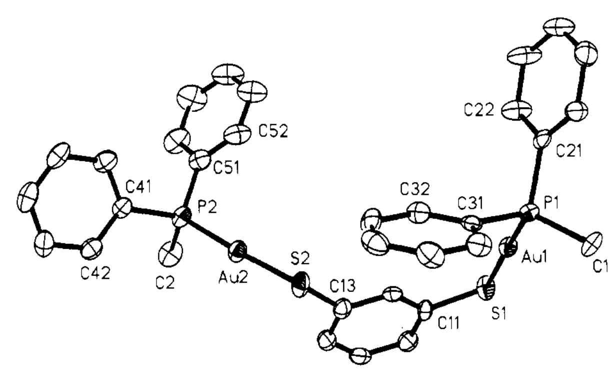

Figure 2. Molecule of complex **8** in the crystal (50% ellipsoids). H atoms are omitted.

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Table 2. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for Complex **6**[a]

	x	*y*	*z*	*U*(eq)
Au(1)	6848.6(3)	5000.0(3)	8061.4(2)	33.6(2)
Au(2)	4525.0(3)	4178.3(3)	6781.1(2)	36.4(2)
P(1)	6264(2)	6919(2)	8391(2)	30.7(11)
P(2)	2561(2)	3683(2)	6964(2)	34.3(12)
S(1)	7769(3)	3031(2)	8176(2)	40.0(15)
S(2)	6465(2)	4587(2)	6434(2)	35.5(12)
C(1)	7628(8)	2433(7)	7178(5)	34(5)
C(2)	7048(8)	3035(7)	6464(6)	32(4)
C(3)	6943(10)	2410(8)	5727(6)	42(6)
C(4)	7448(10)	1231(8)	5675(6)	43(6)
C(5)	8081(9)	657(8)	6383(6)	42(5)
C(6)	8130(9)	1251(8)	7122(5)	36(5)
C(7)	7301(22)	615(22)	4875(13)	56(6)
C(7′)	8715(21)	−561(19)	6323(16)	59(6)
C(11)	7557(9)	7819(8)	8973(6)	33(2)
C(12)	8310(9)	7264(9)	9648(6)	38(3)
C(13)	9296(10)	7889(9)	10123(7)	43(4)
C(14)	9563(9)	9121(10)	9919(7)	43(4)
C(15)	8862(9)	9662(9)	9256(7)	40(4)
C(16)	7847(9)	9050(9)	8784(6)	38(3)
C(21)	5072(9)	6919(8)	9025(6)	32(2)
C(22)	4931(10)	7917(9)	9549(6)	35(3)
C(23)	3984(10)	7887(9)	9998(6)	38(4)
C(24)	3184(10)	6886(10)	9967(7)	41(4)
C(25)	3321(9)	5890(10)	9438(6)	38(3)
C(26)	4286(8)	5908(9)	8995(6)	35(3)
C(31)	5616(9)	7901(9)	7536(6)	37(4)
C(32)	4678(10)	8791(8)	7567(7)	41(4)
C(33)	4221(11)	9479(10)	6866(7)	47(5)
C(34)	4674(11)	9355(11)	6168(7)	50(5)
C(35)	5602(11)	8491(11)	6138(7)	48(4)
C(36)	6064(11)	7764(10)	6798(6)	41(4)
C(41)	1652(10)	3090(9)	6015(6)	41(3)
C(42)	378(11)	3427(13)	5707(7)	53(3)
C(43)	−250(13)	2892(15)	4971(8)	71(4)
C(44)	407(14)	2031(15)	4585(8)	72(4)
C(45)	1608(13)	1725(12)	4896(7)	57(4)
C(46)	2257(12)	2236(9)	5590(7)	44(3)
C(51)	1722(9)	5008(10)	7300(6)	38(3)
C(52)	657(9)	4825(10)	7674(6)	41(3)
C(53)	91(10)	5854(10)	7961(7)	44(4)
C(54)	578(10)	7034(10)	7862(8)	47(4)
C(55)	1605(10)	7215(9)	7512(7)	43(3)
C(56)	2156(10)	6186(9)	7225(7)	43(4)
C(61)	2511(9)	2407(9)	7653(7)	37(3)
C(62)	3567(11)	2149(10)	8266(7)	44(3)
C(63)	3540(12)	1142(10)	8790(7)	48(4)
C(64)	2479(11)	417(10)	8707(7)	47(4)
C(65)	1420(10)	650(9)	8099(7)	42(4)
C(66)	1444(10)	1635(8)	7581(7)	39(3)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

and Au–S bond lengths, Au(1)–S(1) = 2.325(3) and Au(2)–S(2) = 2.316(3) Å are similar to those found in other gold(I) complexes. Au(1) is only 0.11 Å out of the plane formed by S(1)–C(1)–C(2)–S(2); in contrast, Au(2) is located almost perpendicular to the plane. The methyl group is disordered over two positions of the phenyl ring. The crystal structure of $[Au_2(1,2\text{-}S_2C_6H_4)(PPh_3)_2]$ has been recently reported by Schmidbaur[17] and Fackler[20] and the overall bond lengths and angles resemble well those in our complex; the phenyl and tolyl analogues are essentially isostructural.

The molecular structure of $[Au_2(1,3\text{-}S_2C_6H_4)(PPh_2Me)_2]$ (**8**) is shown in Figure 2. Atomic coordinates are given in Table 4 and selected bond lengths and angles in Table 5. As in **6**, the ligand coordinates to both gold atoms, but because of the 1,3-pattern of the sulfur donor atoms there can be no intramolecular gold–gold interaction. However, there are short intermolecular gold–gold contacts, Au(1)–Au(2i) = 3.0834(8) Å, that link the molecules along the short *z* axis. The coordination around the gold atoms is approximately linear, P(1)–Au(1)–S(1) = 172.50(8) and P(2)–Au(2)–S(2) = 177.02(9)°, and the Au–P and the Au–S bond lengths are very similar to those found in complex **6**: Au(1)–P(1) = 2.260(2), Au(2)–P(2) = 2.252(2), Au(1)–S(1) = 2.311(2), and Au(2)–S(2) = 2.302(2) Å. Complex **8** crystallizes as a dichloromethane hemisolvate; the solvent molecule displays crystallographic 2-fold symmetry.

The structure of complexes **6** and **8** and the mass spectrometry data indicate that a further $AuPPh_3^+$ fragment could be incorporated into complexes with 1,2-dithiolate ligands. Thus the reaction of complexes **4** and **6** with $AuPPh_3^+$ (generated in

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Complex **6**

Au(1)–P(1)	2.252(3)	Au(1)–S(1)	2.325(3)
Au(1)–S(2)	2.714(3)	Au(1)–Au(2)	3.096(2)
Au(2)–P(2)	2.258(3)	Au(2)–S(2)	2.316(3)
P(1)–C(31)	1.808(10)	P(1)–C(21)	1.816(10)
P(1)–C(11)	1.817(9)	P(2)–C(61)	1.798(11)
P(2)–C(41)	1.815(11)	P(2)–C(51)	1.829(10)
S(1)–C(1)	1.770(9)	S(2)–C(2)	1.777(8)
P(1)–Au(1)–S(1)	160.84(9)	P(1)–Au(1)–S(2)	113.56(9)
S(1)–Au(1)–S(2)	85.15(9)	P(1)–Au(1)–Au(2)	101.73(7)
S(1)–Au(1)–Au(2)	94.24(7)	S(2)–Au(1)–Au(2)	46.40(6)
P(2)–Au(2)–S(2)	172.98(10)	P(2)–Au(2)–Au(1)	128.83(8)
S(2)–Au(2)–Au(1)	58.07(7)	C(31)–P(1)–C(21)	104.7(5)
C(31)–P(1)–C(11)	104.8(4)	C(21)–P(1)–C(11)	104.0(5)
C(31)–P(1)–Au(1)	114.9(3)	C(21)–P(1)–Au(1)	114.0(3)
C(11)–P(1)–Au(1)	113.3(3)	C(61)–P(2)–C(41)	102.6(5)
C(61)–P(2)–C(51)	108.5(5)	C(41)–P(2)–C(51)	109.0(5)
C(61)–P(2)–Au(2)	114.2(3)	C(41)–P(2)–Au(2)	109.0(4)
C(51)–P(2)–Au(2)	112.9(3)	C(1)–S(1)–Au(1)	107.0(3)
C(2)–S(2)–Au(2)	98.4(3)	C(2)–S(2)–Au(1)	98.0(3)
Au(2)–S(2)–Au(1)	75.54(8)		

Table 4. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for Complex **8**[a]

	x	*y*	*z*	*U*(eq)
Au(1)	7968.1(1)	4470.8(1)	1134.8(3)	24.3(1)
P(1)	7269.5(7)	4578.4(4)	757(2)	21.4(10)
S(1)	8686.8(7)	4415.2(5)	1708(3)	32.7(11)
C(1)	7194(3)	4893(2)	−436(10)	31(5)
C(11)	8732(2)	4432.3(14)	3718(9)	25(4)
C(12)	8373(3)	4409.0(13)	4665(8)	23(4)
C(13)	8418(3)	4397.6(13)	6247(10)	28(4)
C(14)	8825(3)	4418(2)	6886(10)	31(5)
C(15)	9177(3)	4449.3(15)	5946(10)	32(4)
C(16)	9134(3)	4456(2)	4367(10)	32(4)
C(21)	6939(3)	4299.5(14)	−105(9)	23(4)
C(22)	7066(3)	4016(2)	113(12)	39(5)
C(23)	6825(3)	3795(2)	−507(13)	47(5)
C(24)	6476(3)	3851(2)	−1383(13)	43(5)
C(25)	6343(3)	4134(2)	−1575(11)	35(4)
C(26)	6573(3)	4354.7(15)	−920(10)	28(4)
C(31)	7013(3)	4656.3(14)	2567(9)	23(4)
C(32)	7090(2)	4475.2(15)	3799(10)	29(4)
C(33)	6911(3)	4530(2)	5202(10)	33(5)
C(34)	6646(3)	4771(2)	5397(11)	38(5)
C(35)	6577(3)	4949(2)	4180(10)	36(5)
C(36)	6755(3)	4895(2)	2780(10)	32(5)
Au(2)	8095.9(1)	3973.7(1)	8858.2(4)	30.0(2)
P(2)	8228.9(8)	3577.8(4)	10256(3)	28.1(11)
S(2)	7942.5(8)	4363.2(4)	7338(3)	32.8(14)
C(2)	8778(3)	3566(2)	10954(13)	43(5)
C(41)	7896(3)	3560.7(14)	11936(10)	27(4)
C(42)	7987(3)	3742(2)	13150(10)	34(5)
C(43)	7714(3)	3750(2)	14409(10)	40(6)
C(44)	7357(3)	3583(2)	14456(11)	43(5)
C(45)	7265(3)	3402(2)	13279(11)	44(5)
C(46)	7537(3)	3385(2)	12030(11)	38(5)
C(51)	8139(3)	3249(2)	9230(10)	35(5)
C(52)	7917(3)	3249(2)	7888(12)	43(6)
C(53)	7853(4)	2997(2)	7058(14)	54(6)
C(54)	7995(3)	2740(2)	7614(14)	52(6)
C(55)	8206(4)	2732(2)	8953(15)	57(7)
C(56)	8284(4)	2987(2)	9791(13)	49(7)
Cl	9563.2(15)	4906.5(11)	657(7)	129(3)
C(3)	10000	5000	−425(38)	146(12)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for Complex **8**[a]

Au(1)-P(1)	2.260(2)	Au(1)-S(1)	2.311(2)
Au(1)-Au(2i)	3.0834(8)	P(1)-C(1)	1.815(8)
P(1)-C(31)	1.816(8)	P(1)-C(21)	1.823(8)
S(1)-C(11)	1.773(9)	C(13)-S(2)	1.773(9)
Au(2)-P(2)	2.252(2)	Au(2)-S(2)	2.302(2)
P(2)-C(51)	1.798(9)	P(2)-C(41)	1.806(9)
P(2)-C(2)	1.819(10)		
P(1)-Au(1)-S(1)	172.50(8)	P(1)-Au(1)-Au(2i)	101.28(5)
S(1)-Au(1)-Au(2i)	86.10(6)	C(1)-P(1)-C(31)	106.7(4)
C(1)-P(1)-C(21)	105.2(4)	C(31)-P(1)-C(21)	104.9(4)
C(1)-P(1)-Au(1)	112.8(3)	C(31)-P(1)-Au(1)	109.9(3)
C(21)-P(1)-Au(1)	116.7(3)	C(11)-S(1)-Au(1)	106.8(3)
P(2)-Au(2)-S(2)	177.02(9)	P(2)-Au(2)-Au(1ii)	106.51(6)
S(2)-Au(2)-Au(1ii)	76.01(6)	C(51)-P(2)-C(41)	106.4(4)
C(51)-P(2)-C(2)	106.8(4)	C(41)-P(2)-C(2)	105.3(5)
C(51)-P(2)-Au(2)	113.2(3)	C(41)-P(2)-Au(2)	112.0(3)
C(2)-P(2)-Au(2)	112.5(3)	C(13)-S(2)-Au(2)	102.2(3)

[a] Symmetry transformations used to generate equivalent atoms: (i) $x, y, z - 1$; (ii) $x, y, z + 1$.

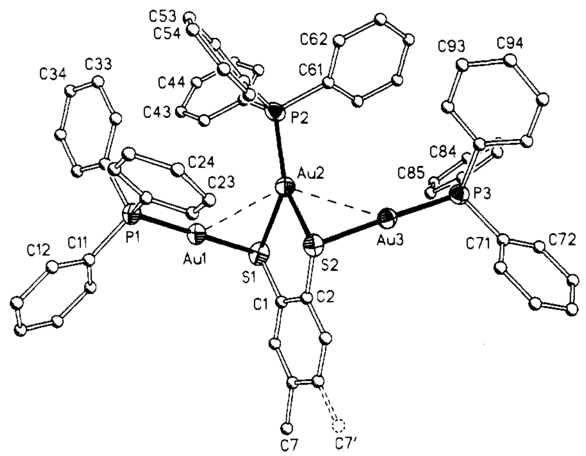

Figure 3. Cation of complex **11** in the crystal (50% ellipsoids for the heavy atoms, arbitrary radii for C atoms). H atoms are omitted. Both positions of the disordered methyl group (C(7), C(7')) are shown.

situ from the reaction of $AuCl(PPh_3)$ and $AgClO_4$ in acetone) leads to complexes **10** and **11** (eq 4).

$$[Au_2(S\text{-}S)(PPh_3)_2] + [Au(PPh_3)(acetone)]ClO_4 \rightarrow [Au_3(S\text{-}S)(PPh_3)_3]ClO_4 \quad (4)$$

10, 11

$$S\text{-}S^{2-} = 1,2\text{-}S_2C_6H_4\ (\mathbf{10}),\ 3,4\text{-}S_2C_6H_3CH_3\ (\mathbf{11})$$

Complexes **10** and **11** are air- and moisture-stable white solids. Their acetone solutions are conducting (1:1 electrolyte)[25] and their IR spectra show bands at 1100 (s, br) and 620 (m) cm^{-1} from ionic ClO_4^- (Td).[26] The mass spectra (FAB+) show the parent peak at m/z 1517 (61%) for **10** and 1531 (56%) for **11**. Their $^{31}P\{^1H\}$ NMR spectra at room temperature show a broad singlet at δ 38.0 (**10**) and δ 35.6 (**11**) which at low temperature (−55 °C) splits to two singlets in a 2:1 intensity ratio (Table 1), implying a different coordination mode for one $AuPPh_3$ fragment.

The molecular structure of $[Au_3(3,4\text{-}S_2C_6H_3CH_3)(PPh_3)_3]ClO_4$ (**11**) was confirmed by X-ray diffraction analysis, and the structure of the cation is shown in Figure 3. Atomic positional and thermal parameters are given in Table 6 and selected bond lengths and angles are listed in Table 7. The cation of **11** consists of a toluenedithiolate ligand unit bridged by three $AuPPh_3^+$ fragments. Two of the gold atoms are linearly coordinated, P(1)–

(25) Geary, W. *J. Coord. Chem. Rev.* **1971**, *7*, 81.
(26) Gowda, M. N.; Naikar, S. B.; Reddy, G. K. N. *Adv. Inorg. Chem Radiochem.* **1984**, *28*, 255.

Table 6. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å² × 10³) for Complex **11**[a]

	x	*y*	*z*	*U*(eq)
Au(1)	1509.9(2)	2832.9(6)	6379.2(3)	31.0(2)
Au(2)	2346.0(2)	2970.6(7)	6657.9(3)	39.0(2)
Au(3)	3124.7(2)	3737.3(6)	7645.5(3)	33.0(2)
P(1)	1043.4(13)	4003(4)	5792(2)	29.5(11)
P(2)	2399.4(13)	2758(5)	5987(2)	37.0(12)
P(3)	3778.8(13)	3406(4)	7987(2)	34.1(12)
S(1)	1992.4(14)	1661(4)	6984(2)	38.6(12)
S(2)	2467.5(13)	4249(4)	7323(2)	32.8(11)
C(1)	2101(4)	2418(10)	7541(4)	43(5)
C(2)	2320(3)	3452(10)	7683(4)	36(5)
C(3)	2400(3)	4015(9)	8114(5)	56(6)
C(4)	2262(4)	3544(12)	8403(4)	62(6)
C(5)	2043(4)	2510(12)	8260(5)	66(7)
C(6)	1963(4)	1946(9)	7829(5)	60(6)
C(7)	1907(9)	2039(29)	8593(11)	69(9)
C(7')	2351(21)	4056(60)	8866(18)	69(9)
C(11)	611(2)	4013(9)	5841(4)	32(4)
C(12)	350(3)	4955(8)	5674(4)	34(4)
C(13)	8(3)	4901(8)	5695(4)	39(5)
C(14)	−73(3)	3904(10)	5883(4)	51(5)
C(15)	187(3)	2961(8)	6050(4)	50(5)
C(16)	529(3)	3016(8)	6029(4)	37(5)
C(21)	1232(3)	5471(7)	5833(4)	29(4)
C(22)	1572(3)	5773(8)	6267(3)	28(4)
C(23)	1743(3)	6872(9)	6315(3)	41(5)
C(24)	1574(3)	7670(7)	5928(4)	49(5)
C(25)	1234(3)	7368(8)	5494(3)	38(5)
C(26)	1063(3)	6269(9)	5447(3)	30(4)
C(31)	893(3)	3449(9)	5187(3)	29(4)
C(32)	1076(3)	3835(9)	4938(4)	41(5)
C(33)	977(3)	3337(11)	4489(4)	61(6)
C(34)	695(4)	2454(11)	4289(3)	57(6)
C(35)	512(3)	2068(9)	4539(4)	61(6)
C(36)	610(3)	2566(10)	4988(4)	36(5)
C(41)	2152(3)	1472(9)	5605(4)	34(4)
C(42)	1762(3)	1276(9)	5466(4)	44(5)
C(43)	1560(2)	328(10)	5164(4)	44(5)
C(44)	1747(3)	−423(9)	5002(4)	53(6)
C(45)	2137(3)	−227(10)	5141(5)	61(6)
C(46)	2340(3)	721(11)	5442(5)	58(6)
C(51)	2193(3)	4005(9)	5575(4)	33(4)
C(52)	2019(3)	3838(9)	5072(4)	45(5)
C(53)	1866(4)	4795(12)	4756(3)	59(6)
C(54)	1888(4)	5919(10)	4943(4)	61(6)
C(55)	2062(4)	6086(8)	5445(5)	64(6)
C(56)	2215(3)	5129(11)	5762(3)	53(6)
C(61)	2907(2)	2619(10)	6142(4)	27(4)
C(62)	3062(3)	3304(9)	5918(4)	43(5)
C(63)	3451(3)	3159(10)	6044(4)	56(6)
C(64)	3685(2)	2330(11)	6396(5)	53(5)
C(65)	3530(3)	1646(10)	6620(4)	60(6)
C(66)	3141(3)	1790(10)	6494(4)	51(5)
C(71)	4041(3)	3748(10)	8644(3)	37(4)
C(72)	4362(3)	3095(8)	8985(4)	41(5)
C(73)	4561(3)	3426(9)	9476(4)	45(5)
C(74)	4440(3)	4409(10)	9625(3)	41(5)
C(75)	4119(3)	5062(8)	9284(4)	48(5)
C(76)	3919(3)	4731(9)	8793(3)	25(4)
C(81)	3899(3)	1916(7)	7908(4)	28(4)
C(82)	4264(3)	1648(9)	7970(4)	53(6)
C(83)	4356(3)	490(11)	7925(4)	59(6)
C(84)	4083(4)	−400(8)	7818(4)	54(6)
C(85)	3718(3)	−132(9)	7757(4)	59(6)
C(86)	3626(2)	1026(10)	7802(4)	35(5)
C(91)	3994(4)	4343(11)	7731(4)	34(4)
C(92)	3798(3)	4486(11)	7225(4)	41(5)
C(93)	3954(4)	5218(12)	7015(4)	69(7)
C(94)	4306(4)	5806(12)	7310(6)	83(8)
C(95)	4502(3)	5662(13)	7816(6)	113(10)
C(96)	4346(4)	4931(13)	8026(4)	84(8)
Cl	5682(2)	3825(7)	3985(2)	108(3)
O(1)	5411(4)	3209(12)	3576(5)	75(5)
O(2)	5884(4)	4742(14)	3920(6)	92(5)
O(3)	5589(7)	4079(22)	4343(8)	201(12)
O(4)	5985(8)	2934(23)	4265(10)	278(18)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

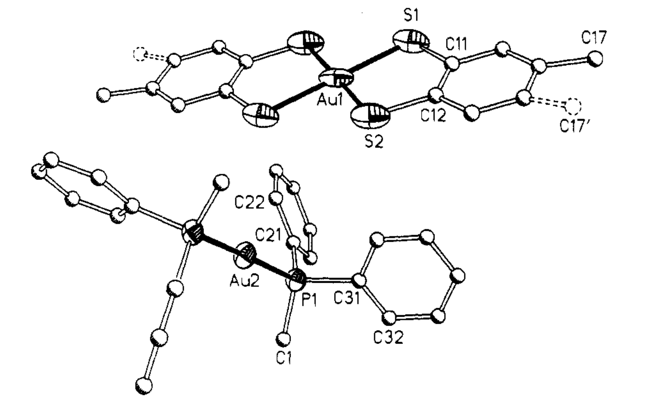

Figure 4. The formula unit of complex **13**, in the crystal (50% ellipsoids for the heavy atoms; arbitrary radii for C atoms). Only the asymmetric unit is numbered. H atoms are omitted. Both positions of the disordered methyl group (C(17), C(17')) are shown.

Table 7. Selected Bond Lengths (Å) and Angles (deg) for Complex **11**

Au(1)–P(1)	2.265(4)	Au(1)–S(1)	2.315(5)
Au(1)–Au(2)	2.9624(12)	Au(2)–P(2)	2.255(5)
Au(2)–S(2)	2.397(5)	Au(2)–S(1)	2.591(5)
Au(2)–Au(3)	3.1966(14)	Au(3)–P(3)	2.271(5)
Au(3)–S(2)	2.332(4)	P(1)–C(11)	1.797(9)
P(1)–C(21)	1.803(8)	P(1)–C(31)	1.805(9)
P(1)–C(51)	1.813(10)	P(2)–C(61)	1.814(9)
P(2)–C(41)	1.829(10)	P(3)–C(91)	1.796(11)
P(3)–C(81)	1.809(10)	P(3)–C(71)	1.832(9)
S(1)–C(1)	1.806(10)	S(2)–C(2)	1.774(10)
P(1)–Au(1)–S(1)	179.2(2)	P(1)–Au(1)–Au(2)	122.19(12)
S(1)–Au(1)–Au(2)	57.25(12)	P(2)–Au(2)–S(2)	145.2(2)
P(2)–Au(2)–S(1)	130.2(2)	S(2)–Au(2)–S(1)	84.4(2)
P(2)–Au(2)–Au(1)	109.93(12)	S(2)–Au(2)–Au(1)	89.25(11)
S(1)–Au(2)–Au(1)	48.71(10)	P(2)–Au(2)–Au(3)	116.46(12)
S(2)–Au(2)–Au(3)	46.61(11)	S(1)–Au(2)–Au(3)	102.26(11)
Au(1)–Au(2)–Au(3)	132.77(3)	P(3)–Au(3)–S(2)	174.8(2)
P(3)–Au(3)–Au(2)	135.86(13)	S(2)–Au(3)–Au(2)	48.34(11)
C(11)–P(1)–C(21)	111.5(5)	C(11)–P(1)–C(31)	106.3(6)
C(21)–P(1)–C(31)	107.4(5)	C(11)–P(1)–Au(1)	110.2(4)
C(21)–P(1)–Au(1)	110.4(4)	C(31)–P(1)–Au(1)	111.0(4)
C(51)–P(2)–C(61)	107.1(6)	C(51)–P(2)–C(41)	104.7(6)
C(61)–P(2)–C(41)	104.7(6)	C(51)–P(2)–Au(2)	111.8(4)
C(61)–P(2)–Au(2)	112.1(4)	C(41)–P(2)–Au(2)	115.7(4)
C(91)–P(3)–C(81)	105.7(6)	C(91)–P(3)–C(71)	105.4(6)
C(81)–P(3)–C(71)	108.6(5)	C(91)–P(3)–Au(3)	112.0(5)
C(81)–P(3)–Au(3)	113.9(4)	C(71)–P(3)–Au(3)	110.7(4)
C(1)–S(1)–Au(1)	102.8(4)	C(1)–S(1)–Au(2)	102.1(4)
Au(1)–S(1)–Au(2)	74.04(13)	C(2)–S(2)–Au(3)	104.5(4)
C(2)–S(2)–Au(2)	105.9(4)	Au(3)–S(2)–Au(2)	85.1(2)
C(2)–C(1)–S(1)	121.2(8)	C(6)–C(1)–S(1)	118.8(8)
C(1)–C(2)–S(2)	125.2(8)	C(3)–C(2)–S(2)	114.4(8)
C(12)–C(11)–P(1)	121.8(6)	C(16)–C(11)–P(1)	118.1(6)

Au(1)–S(1) = 179.2(2) and P(3)–Au(3)–S(2) = 174.8(2)°, whereas Au(2) is in a distorted trigonal planar configuration. The distortion arises mainly from the restricted bite of the ligand, S(2)–Au(2)–S(1) = 84.4(2)°. This bite angle is similar to those found in the complexes $[Au_4(S\text{-}S)_2(PEt_3)_2]$ 84.4(1)° (S-S = 1,2-$S_2C_6H_4$)[22] and 84.1(4) and 83.5(4)° (S-S = 3,4-$S_2C_6H_3CH_3$),[20] where there are also gold atoms chelated by the dithiolate ligand.

The intramolecular gold–gold interactions are Au(1)–Au(2) = 2.9624(12) and Au(2)–Au(3) = 3.1966(14) Å. Au(1) and Au(3) are –2.21 and 2.15 Å out of the plane formed by S(1), S(2), Au(2), and P(2) (planar within 0.023 Å). There are also intermolecular Au–S contacts, the shortest being Au(3)–S(1i) = 3.627 Å (symmetry operator –0.5 – x, –0.5 + y, 0.5 – z). The bond distances Au(1)–S(1) = 2.315(5) and Au(3)–S(2) = 2.332(4) Å are very similar to those in complex **6** and **8**. However the Au–S bonds of the trigonal planar gold atom, Au(2)–S(1) = 2.591(5) and Au(2)–S(2) = 2.397(5) Å, are shorter than in the complex $[Au_4(3,4\text{-}S_2C_6H_3CH_3)(PEt_3)_2]$[20] for the three-coordinated gold atoms, although the difference may not be significant.

Table 8. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for Complex **13**[a]

	x	y	z	U(eq)
Au(1)	0	5000	5000	49.7(2)
S(1)	581.7(14)	4656(3)	6173.6(14)	63.8(12)
S(2)	–320(2)	2990(3)	4827(2)	65.6(14)
C(11)	486(6)	3083(10)	6240(4)	63(3)
C(12)	81(5)	2361(9)	5668(5)	62(3)
C(13)	–2(7)	1128(10)	5756(6)	78(3)
C(14)	309(8)	620(13)	6399(5)	85(4)
C(15)	713(8)	1310(11)	6965(7)	91(4)
C(16)	793(7)	2546(9)	6891(6)	73(3)
C(17)	1046(12)	575(19)	7581(10)	76(5)
C(17')	300(18)	–579(23)	6673(16)	76(5)
Au(2)	0	3593.5(5)	2500	41.5(2)
P(1)	1379.1(11)	3513(2)	2984.9(11)	36.2(9)
C(1)	1860(5)	3155(8)	2373(5)	45(2)
C(21)	1833(3)	4910(4)	3393(3)	33(2)
C(22)	1368(2)	5761(5)	3572(3)	42(2)
C(23)	1719(3)	6809(4)	3920(3)	53(2)
C(24)	2534(3)	7007(4)	4089(3)	45(2)
C(25)	2999(2)	6156(5)	3910(3)	46(2)
C(26)	2648(3)	5108(4)	3562(3)	36(2)
C(31)	1712(3)	2371(5)	3651(2)	35(2)
C(32)	2330(3)	1568(5)	3706(3)	48(2)
C(33)	2568(3)	726(5)	4237(3)	58(2)
C(34)	2188(4)	686(5)	4713(3)	56(2)
C(35)	1570(3)	1489(6)	4659(3)	50(2)
C(36)	1332(3)	2332(5)	4128(3)	50(2)

[a] U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 9. Selected Bond Lengths (Å) and Angles (deg) for Complex **13**[a]

Au(1)–S(2)	2.287(3)	Au(1)–S(1)	2.319(4)
S(1)–C(11)	1.755(12)	S(2)–C(12)	1.780(10)
Au(2)–P(1)	2.309(3)	P(1)–C(21)	1.807(4)
P(1)–C(31)	1.810(5)	P(1)–C(1)	1.817(9)
S(2)–Au(1)–S(1)	90.02(12)	S(2)–Au(1)–S(1i)	89.98(12)
C(11)–S(1)–Au(1)	103.0(3)	C(12)–S(2)–Au(1)	103.5(3)
P(1)–Au(2)–P(1ii)	175.60(12)	C(21)–P(1)–C(31)	105.4(3)
C(21)–P(1)–C(1)	105.6(4)	C(31)–P(1)–C(1)	106.1(4)
C(21)–P(1)–Au(2)	113.8(2)	C(31)–P(1)–Au(2)	111.6(2)
C(1)–P(1)–Au(2)	113.7(3)		

[a] Symmetry transformations used to generate equivalent atoms: (i) –x, 1 – y, 1 – z; (ii) –x, y, 0.5 – z.

The Au–P distances 2.255(5)–2.265(4) Å compare well with those in complexes **6** and **8**.

Whereas the solutions corresponding to eq 3 with 1,2-$S_2C_6H_4$ and 1,3-$S_2C_6H_4$ are colorless, a green color develops with 3,4-$S_2C_6H_3CH_3$, and it is possible to separate two green derivatives from the mother liquor by crystallization. Complexes **12** and **13** are air- and moisture-stable solids and their acetone solutions show conductivities of 1:1 electrolytes. Their mass spectra (FAB+) show peaks at m/z 721 (100%) (**12**) and 587 (100%) (**13**) corresponding to the $[Au(PR_3)_2]^+$ fragment and, in the FAB(–) spectra both complexes show the $[Au(S_2C_6H_3CH_3)_2]^-$ ion as the base peak at m/z 505, in accordance with the formulation as $[Au(PR_3)_2][Au(3,4S_2C_6H_3CH_3)_2]$, ($PR_3$ = PPh_3 (**12**), PPh_2Me (**13**)).

Their ^1H NMR spectra show a different pattern from that of complexes **6**, **7**, and **11** and are similar to the spectrum previously reported for $NBu_4[Au(3,4\text{-}S_2C_6H_3CH_3)_2]$. Their $^{31}P\{^1H\}$ NMR spectra show singlets at δ 30.5 (**12**) and δ 16.7 ppm (**13**), at higher fields than reported for $[Au(PR_3)_2]ClO_4$ species.[27]

The structure of compound **13** has been confirmed by X-ray diffraction; the anion and cation are shown in Figure 4. Atom coordinates are given in Table 8 and selected bond lengths and angles in Table 9. The anion possesses crystallographic inversion symmetry. High displacement parameters (for a low-temperature

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Table 10. Details of Data Collection and Structure Refinement for the Complexes **6**, **8**, **11** and **13**

	6	8·$^1/_2$CH$_2$Cl$_2$	11	13
chem formula	$C_{43}H_{36}Au_2P_2S_2$	$C_{32.5}H_{31}Au_2ClP_2S_2$	$C_{61}H_{51}Au_3ClO_4P_3S_2$	$C_{40}H_{38}Au_2P_2S_4$
cryst habit	colorless prism	colorless tablet	colorless prism	green prism
cryst size/mm	0.50 × 0.45 × 0.40	0.50 × 0.33 × 0.17	0.35 × 0.15 × 0.10	0.60 × 0.35 × 0.20
space group	$P2_1$	$Fdd2$	$C2/c$	$C2/c$
a/Å	10.771(4)	31.182(8)	39.583(8)	17.890(7)
b/Å	10.726(3)	46.537(12)	11.347(3)	11.038(6)
c/Å	16.752(6)	8.782(3)	31.703(7)	20.817(11)
β/deg	101.02(3)		120.66(2)	110.96(3)
U/Å^3	1899.7(11)	12744(6)	12249(5)	3838.7(33)
Z	2	16	8	4
D_c/Mg m^{-3}	1.875	2.037	1.769	1.908
M	1072.71	977.02	1631.40	1102.82
F(000)	1028	7408	6240	2120
T/°C	−100	−130	−100	−130
$2\theta_{max}$/deg	50	55	45	50
μ(Mo Kα)/mm^{-1}	7.94	9.53	7.4	8.0
transm	0.37–0.96	0.42–0.97	0.28–0.58	0.45–0.95
no. of reflcns measd	7207	18050	12407	6775
no. of unique reflcns	6703	7343	7985	3391
R_{int}	0.036	0.063	0.081	0.051
R^a (F, $F > 4\sigma(F)$)	0.036	0.036	0.055	0.043
$R_w{}^b$ (F^2, all reflcns)	0.096	0.084	0.145	0.110
no. of params	442	356	227	101
no. of restraints	378	281	97	32
S^c	1.022	1.055	0.854	1.017
max. $\Delta\rho$/e Å^{-3}	1.19	1.26	1.88	1.46

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum\{w(F_o^2 - F_c^2)2\}/\sum\{w(F_o^2)^2\}]^{0.5}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = [F_o^2 + 2F_c^2]/3$ and a and b are constants adjusted by the program. ^{c} $S = [\sum\{w(F_o^2 - F_c^2)^2\}/(n - p)]^{0.5}$, where n is the number of data and p the number of parameters.

structure) may indicate some static disorder or libration. The gold atom display square-planar geometry, being surrounded by four sulfur atoms. The angles S(2)–Au(1)–S(1) = 90.02(12) and S(2)–Au(1)–S(1i) = 89.98(12)° are almost ideal. The Au–S distances Au(1)–S(2) = 2.287(3) and Au(1)–S(1) = 2.319(4) Å are close to those observed for other bis(dithiolato)gold(III) complexes: mean values are 2.288 Å in [PClPh$_3$][Au{S$_2$C$_2$(CF$_3$)$_2$}$_2$],[28] 2.309 Å in [Au(S$_2$CN^{n}Bu$_2$)$_2$][Au{S$_2$C$_2$(CN)$_2$}$_2$],[29] 2.310 Å in [NBu$_4$][Au(3,4-S$_2$C$_6$H$_3$CH$_3$)$_2$],[15] and 2.305 Å in [Au(PEt$_3$)$_2$][Au(1,2-S$_2$C$_6$H$_4$)$_2$].[18] The Au–S bond lengths in the complex [Au(1,2-S$_2$C$_6$H$_4$)$_2$] obtained by electrochemical oxidation of the gold(III) derivative[23] are very similar to those observed in our complex. The methyl groups of the anion are disordered over two sites. The cation possesses crystallographic 2-fold symmetry; the geometry around the gold atom is almost linear, P(1)–Au(2)–P(1ii) = 175.60(12)°, and the Au(2)–P(1) bond length of 2.309(3) Å is similar to those found in other [Au(PR$_3$)$_2$]$^+$ complexes, 2.316(4) in [Au(PPh$_2$Me)$_2$]PF$_6$,[30] 2.224(4) in [Au(PCy$_3$)$_2$]Cl,[31] and 2.31(1) Å in [Au(PPh$_3$)$_2$]TCNQ (TCNQ = 7,7′,8,8′-tetracyanoquinodimethane).[27]

Experimental Section

All the reactions were carried out under nitrogen. The starting materials [AuCl(PPh$_3$)] and [AuCl(AsPh$_3$)] were prepared as described previously[32] and all other reagents were commercially available.

The C, H analyses were carried out on a Perkin-Elmer 2400 microanalyzer. Conductivities were measured in approximately 5 × 10^{-4} mol dm^{-3} acetone solutions with a Philips PW 9501/01 conductimeter. The infrared spectra were recorded (4000–200 cm^{-1}) on a Perkin-Elmer 599 spectrophotometer using Nujol mulls between polyethylene sheets. The NMR spectra were recorded on Varian XL 200 and 300 spectrometers in CDCl$_3$. Chemical shifts are cited relative to SiMe$_4$ (^{1}H) and 85% H$_3$PO$_4$ (external ^{31}P). Mass spectra were recorded on a VG Autospec, FAB Technique using 3-nitrobenzylalcohol as matrix. The elemental analyses, conductivities, and ^{31}P{1H}NMR data of the new complexes are listed in Table 1.

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Safety Note. *Caution!* Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of material should be prepared and these should be handled with great caution.

Synthesis. [Au$_2$(S-S)(AsPh$_3$)]$_n$ [S-S = 1,2-S$_2$C$_6$H$_4$ (1), 3,4-S$_2$C$_6$H$_3$-CH$_3$ (2)], or [Au$_2$(1,3-S$_2$C$_6$H$_4$)]$_n$ (3). To an ethanolic solution (30 mL) of the corresponding dithiol (0.5 mmol) was added 5 mL of an ethanolic KOH solution (0.1 M). After 15 min [AuCl(AsPh$_3$)] (0.539 g, 1 mmol) was added. After this mixture was stirred for 24 h, a white (**1**, **2**) or pale yellow (**3**) precipitate was filtered off. Yield: 85% **1**, 78% **2**, 69% **3**.

[Au$_2$(S-S)(PR$_3$)$_2$] [S-S = 1,2-S$_2$C$_6$H$_4$, PR$_3$ = PPh$_3$ (4), PPh$_2$Me (5); S-S = 3,4-S$_2$C$_6$H$_3$CH$_3$, PR$_3$ = PPh$_3$ (6), PPh$_2$Me (7); S-S = 1,3-S$_2$C$_6$H$_4$, PR$_3$ = PPh$_3$ (8), PPh$_2$Me (9)] and [Au(PR$_3$)$_2$][Au(3,4-S$_2$C$_6$H$_3$CH$_3$)$_2$] [PR$_3$ = PPh$_3$ (12), PPh$_2$Me (13)]. To a dichloromethane (30 mL) suspension (0.084 g, 0.1 mmol) of **1**, (0.085 g, 0.1 mmol) of **2**, or (0.053 g, 0.1 mmol) of **3** was added PPh$_3$ (0.054 g, 0.2 mmol) or PPh$_2$Me (0.037 mL, 0.2 mmol). After being stirred for 3 h, the solutions were filtered through a 1-cm layer of Celite. The solutions were concentrated to 5 mL. Addition of diethyl ether (20 mL) led to precipitation of **4**–**9** as white solids. Yield of **4**: 83%. ^{1}H NMR (in ppm): δ 7.93 (m, 2H, 3,6-S$_2$C$_6$H$_4$), 7.44–7.21 (m, 30H, PPh$_3$), 6.86 (m, 2H, 4,5-S$_2$C$_6$H$_4$). Yield of **5**: 37%. ^{1}H NMR: δ 7.92 (m, 2H, 3,6-S$_2$C$_6$H$_4$), 7.57–7.24 (m, 20H, PPh$_2$Me), 6.85 (m, 2H, 4,5-S$_2$C$_6$H$_4$), 1.83 (d, $^2J_{PH}$ = 9.3 Hz, 6H, PPh$_2$Me). Yield of **6**: 69%. ^{1}H NMR: δ 7.81 (d, $^3J_{H5H6}$ = 8.0 Hz, 1H, 5-S$_2$C$_6$H$_3$CH$_3$), 7.79 (d, $^4J_{H2H6}$ = 1.2 Hz, 1H, 2-S$_2$C$_6$H$_3$CH$_3$), 7.44–7.21 (m, 30H, PPh$_3$), 6.88 (dd, 1H, 6-S$_2$C$_6$H$_3$CH$_3$); 2.25 (s, 3H, S$_2$C$_6$H$_3$CH$_3$). Yield of **7**: 51%. ^{1}H NMR: δ 7.81 (d, $^3J_{H5H6}$ = 8.0 Hz, 1H, 5-S$_2$C$_6$H$_3$CH$_3$), 7.78 (d, $^4J_{H2H6}$ = 1.3 Hz, 1H, 2-S$_2$C$_6$H$_3$CH$_3$), 7.60–7.27 (m, 20H, PPh$_2$Me); 6.68 (dd, 1H, 2-S$_2$C$_6$H$_3$CH$_3$); 2.26 (s, 3H, S$_2$C$_6$H$_3$CH$_3$); 1.84 (d, $^2J_{PH}$ = 9.3 Hz, 6H, PPh$_2$Me). Yield of **8**: 80%. ^{1}H NMR: δ 8.01, 7.35, and 6.90 (m, 4H, 1,3-S$_2$C$_6$H$_4$); 7.58–7.23 (m, 30H, PPh$_3$). Yield of **9**, 90%. ^{1}H NMR: δ 7.94, 7.21, and 6.84 (m, 4H, 1,3-S$_2$C$_6$H$_4$), 7.68–7.23 (m, 20H, PPh$_2$Me), 2.07 (d, $^2J_{PH}$ = 9.6 Hz, 6H, PPh$_2$Me).

When the green mother liquor of complexes **6** and **7** is cooled to −30 °C a crop of green crystals appears, characterized as [Au(PPh$_3$)$_2$][Au(3,4-S$_2$C$_6$H$_3$CH$_3$)$_2$] (**12**) (3%) [^{1}H NMR: δ 7.36–7.18 (m, 30H, PPh$_3$), 6.80 (m, 2H, 5-S$_2$C$_6$H$_3$CH$_3$), 6.70 (s, 2H, 2-S$_2$C$_6$H$_3$CH$_3$), 6.45 (m, 2H, 6-S$_2$C$_6$H$_3$CH$_3$), 2.17 (s, 6H, S$_2$C$_6$H$_3$CH$_3$)] or [Au(PPh$_2$Me)$_2$][Au(3,4-S$_2$C$_6$H$_3$CH$_3$)$_2$] (**13**) (5%) [^{1}H NMR: δ 7.43–7.25 (m, 20H, PPh$_2$Me), 6.87 (d, $^3J_{H5H6}$ = 8.0 Hz, 2H, 5-S$_2$C$_6$H$_3$CH$_3$), 6.76 (br, 2H, 2-S$_2$C$_6$H$_3$-CH$_3$), 6.56 (dd, $^4J_{H2H6}$ = 1.1 Hz, 2H, 6-S$_2$C$_6$H$_3$CH$_3$); 2.15 (s, 6H, S$_2$C$_6$H$_3$-CH$_3$); 1.88 (d, $^2J_{PH}$ 2.7 Hz, 6H, PPh$_2$Me)].

[Au$_3$(S-S)(PPh$_3$)$_3$] [S-S = 1,2-S$_2$C$_6$H$_4$ (10), 3,4-S$_2$C$_6$H$_3$CH$_3$ (11)]. To a dichloromethane solution of [AuCl(PPh$_3$)] (0.114 g, 0.23 mmol) was added AgClO$_4$ (0.048 g, 0.23 mmol). After 1 h of stirring the suspension was filtered through a 1 cm layer of Celite. [Au$_2$(S-S)(PPh$_3$)$_2$] (0.212 g, 0.2 mmol, **4**, or (0.214, 0.2 mmol, **5**) was added to the resulting solution. After being stirred for 2 h, the solutions were concentrated to 2 cm^3. Addition of diethyl ether (15 mL) led to precipitation of white solids **10** (81%) or **11** (83%). ^{1}H NMR (**10**): δ 8.06 (m, 2H, 3,6-$S_2C_6H_4$), 7.53–7.16 (m, 45H, PPh_3), 7.17 (m, 2H, 4,5-$S_2C_6H_4$). ^{1}H NMR **11**: δ 7.94 (d, $^3J_{H5H6}$ 7.8 Hz, 1H, 5-$S_2C_6H_3CH_3$); 7.91 (s, 1H, 2-$S_2C_6H_3CH_3$); 7.43–7.25 (m, 45H, PPh_3); 7.00 (d, 1H, 6-$S_2C_6H_3CH_3$); 2.37 (s, 3H, $S_2C_6H_3CH_3$).

X-ray Structure Determinations

Crystals were mounted in inert oil (type RS3000, donated by Riedel de Haën) on glass fibers. Data were collected using monochromated Mo Kα radiation (λ = 0.710 73 Å). Diffractometer type: Siemens R3 (**6**, **11**), Stoe STADI-4 (**8**, **13**), both with Siemens LT-2 low temperature attachment. Scan type: ω (**6**, **11**), ω/θ (**8**, **13**). Cell constants were refined from setting angles (**6**, **11**) or ±ω angles (**8**, **13**) of ca. 50 reflections in the range 2θ = 20–23°. Absorption corrections were applied on the basis of ψ-scans (**6**, **8**, **13**) or, for **11**, using the program SHELXA (G. M. Sheldrick, unpublished).

Structures were solved by the heavy-atom method and refined on F^2 using the program SHELXL-93.[33] For **6** and **8** all non-H atoms were refined anisotropically, whereas for **11** and **13** idealized isotropic aromatic rings were employed. Hydrogen atoms were included using a riding model. For **6** and **8**, which crystallize in polar space groups, the absolute structure was determined by an *x* refinement[34] and the origin fixed by the method of Flack and Schwarzenbach.[35] For **6**, **11**, and **13**, the tolyl methyl group is disordered over two positions (refined isotropically with a total occupation factor of 1). Further details are given in Table 10.

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Supplementary Material Available: A description of the crystal structure determinations, including tables of crystal data, data collection and solution and refinement parameters, hydrogen atomic coordinates, bond distances and angles, and thermal parameters (18 pages). Ordering information is given on any current masthead page.

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