Synthesis and Electrochemistry of Heterobridged Gold(I) and Gold(II) Complexes of Pyridine-2-thiolate. Crystal Structures of $[Au_2\{\mu\text{-}(CH_2)_2PPh_2\}(\mu\text{-}C_5H_4NS)]$ and $[Au_2\{\mu\text{-}(CH_2)_2PPh_2\}(\mu\text{-}C_5H_4NS)Br_2]$†

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The reaction of $[Au_2\{\mu\text{-}(CH_2)_2PPh_2\}_2]$ or $[Au_2(\mu\text{-}L\text{–}L)_2][ClO_4]_2$ [L–L = dppm ($Ph_2PCH_2PPh_2$) or dppe ($Ph_2PCH_2CH_2PPh_2$)] with $[Au_n(\mu\text{-}C_5H_4NS)_n]$ led to the heterobridged dinuclear complexes $[Au_2\{\mu\text{-}(CH_2)_2PPh_2\}(\mu\text{-}C_5H_4NS)]$ or $[Au_2(\mu\text{-}C_5H_4NS)(\mu\text{-}L\text{–}L)]ClO_4$. The structure of $[Au_2\{\mu\text{-}(CH_2)_2PPh_2\}(\mu\text{-}C_5H_4NS)]$ has been established by X-ray crystallography and exhibits a short intramolecular gold–gold distance of 2.8623(7) Å, whereas the shortest intermolecular distance is 3.984 Å. The complex crystallized in the monoclinic space group $P2_1/n$ with a = 9.430(2), b = 8.819(2), c = 22.786(5) Å, β = 99.08(3)°, Z = 4. Cyclic voltammograms showed that this complex is irreversibly oxidised at a platinum electrode; chemical oxidation with the ferrocenium ion in the presence of halide or pseudohalide ions gave the gold(II) complexes $[Au_2\{\mu\text{-}(CH_2)_2PPh_2\}(\mu\text{-}C_5H_4NS)X_2]$ (X = Cl, Br, I or SCN). The same derivatives can be obtained by oxidative addition of halogen and/or by subsequent substitution with other halogens or pseudohalogens. The complex $[Au_2\{\mu\text{-}(CH_2)_2PPh_2\}(\mu\text{-}C_5H_4NS)Br_2]$ crystallized in the triclinic space group $P\bar{1}$ with a = 14.810(10), b = 14.908(10), c = 17.041(12) Å, α = 70.20(5), β = 69.77(5), γ = 89.19(5)°, Z = 6 (at −100 °C). The Au–Au bond lengths in the three independent molecules are 2.564(4), 2.548(4) and 2.547(4) Å.

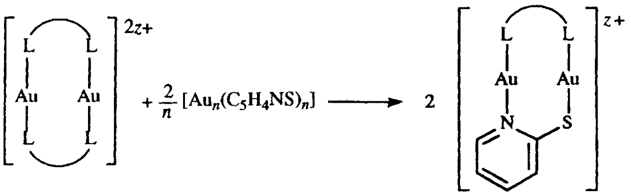
Pyridine-2-thiol (C_5H_5NS) and pyridine-2-thiolate ($C_5H_4NS^-$) complexes have been extensively synthesized because of their versatile co-ordination behaviour; they can act as monodentate (S- or N-donor)[1,2] or bidentate ligands, in the latter as a chelate,[3] or as a bridge between two,[4] three[5] or even four[6] metal centres. In contrast, only a few gold(I) and gold(III) derivatives[7–10] have been obtained, most of them with the ligand acting as an S-donor, and no gold(II) complexes have been reported so far. Some thiolate–gold(I) derivatives have been shown to be effective against rheumatoid arthritis.[11,12]

In this paper we report the preparation of heterobridged dinuclear gold(I) complexes containing pyridine-2-thiolate and a (bis)ylide or a diphosphine, *via* bidentate ligand transfer between homoleptic gold(I) compounds. Cyclic voltammograms show that $[Au_2\{\mu\text{-}(CH_2)_2PPh_2\}(\mu\text{-}C_5H_4NS)]$ is easily oxidised, and the ferrocenium ion, a mild oxidant, in the presence of the appropriate halide or pseudohalide gives the gold(II) complexes $[Au_2\{\mu\text{-}(CH_2)_2PPh_2\}(\mu\text{-}C_5H_4NS)X_2]$ (X = Cl, Br, I or SCN). These species can also be obtained by oxidative addition of halogen and/or by later substitution with other halogens or pseudohalogens. The molecular structures of $[Au_2\{\mu\text{-}(CH_2)_2PPh_2\}(\mu\text{-}C_5H_4NS)]$ and $[Au_2\{\mu\text{-}(CH_2)_2PPh_2\}(\mu\text{-}C_5H_4NS)Br_2]$ have been solved by X-ray analysis.

Results and Discussion

We have recently described series of di- and tri-nuclear gold(I) complexes synthesized by bidentate ligand-transfer reactions.[13–15] Following a similar pattern, we have carried out reactions in dichloromethane between $[Au_2\{\mu\text{-}(CH_2)_2PPh_2\}_2]$ or $[Au_2(\mu\text{-}L\text{–}L)_2][ClO_4]_2$ [L–L = dppm ($Ph_2PCH_2PPh_2$) or dppe ($Ph_2PCH_2CH_2PPh_2$)] and the poorly soluble complex $[Au_n(\mu\text{-}C_5H_4NS)_n]$, leading to heterobridged complexes **1**–**3** (Scheme 1). Ligand redistributions are not really predictable, but, in our experience,[14,15] the formation of heterobridged combinations in dinuclear gold(I) derivatives are favoured over the homobridged derivatives.

Complexes **1**–**3** are white solids, air- and moisture-stable at room temperature, which behave as non-conducting (**1**) or 1 : 1 electrolytes (**2** and **3**) in acetone solutions. The IR spectra show bands in the region 1400–1600 cm⁻¹ assignable to ring vibration of the thiolate anion,[3,9] at 573m cm⁻¹ from ν(Au–C$_{ylide}$)[16] for **1**, and at 1100s (br) and 623m cm⁻¹ from the perchlorate anion[17] for **2** and **3**. The $^{31}P\text{-}\{^1H\}$ NMR spectra at room temperature show a singlet (Table 1) even for complexes **2** and **3**



Scheme 1 z = 0, L–L = $(CH_2)_2PPh_2$ **1**; z = 1, L–L = dppm **2** or dppe **3**

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† *Supplementary data available:* Complete crystallographic details have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für Wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany. Any request for this material should quote a full literature citation and the reference numbers CSD 401797 and 401798.

Table 1 Analytical and spectroscopic data for complexes **1**–**7**

	Analysis[a] (%)			^{31}P-{^{1}H}[b]		^{1}H[c]
Complex	C	H	N	δ_{ylide}	δ_P	δ(Au–CH$_2$)
1 $[Au_2\{\mu\text{-}(CH_2)_2PPh_2\}(\mu\text{-}C_5H_4NS)]$	31.75	2.55	1.85	37.4 (s)	—	2.01 (d) (12.4), 1.79 (d) (12.4)
	(31.8)	(2.55)	(1.95)			
2 $[Au_2(\mu\text{-}C_5H_4NS)(\mu\text{-dppm})]ClO_4$	36.0	2.45	1.45	—	28.1 (s)	—
	(36.45)	(2.65)	(1.4)		27.9,[d] 25.6[d]	
3 $[Au_2(\mu\text{-}C_5H_4NS)(\mu\text{-dppe})]ClO_4$	37.55	2.95	1.6	—	32.2 (s)	—
	(37.15)	(2.8)	(1.4)		35.9 (s),[e] 29.5 (s)[e]	
4 $[Au_2\{\mu\text{-}(CH_2)_2PPh_2\}(\mu\text{-}C_5H_4NS)Cl_2]$	29.0	2.3	1.65	45.0 (s)	—	2.81 (d) (8.7), 2.37 (d) (8.4)
	(28.95)	(2.3)	(1.8)			
5 $[Au_2\{\mu\text{-}(CH_2)_2PPh_2\}(\mu\text{-}C_5H_4NS)Br_2]$	26.05	1.9	1.7	48.6 (s)	—	2.93 (d) (8.9), 2.44 (d) (8.0)
	(26.0)	(2.05)	(1.6)			
6 $[Au_2\{\mu\text{-}(CH_2)_2PPh_2\}(\mu\text{-}C_5H_4NS)I_2]$	23.35	1.8	1.15	55.3 (s)	—	2.97 (d) (8.8), 2.42 (d) (8.6)
	(23.5)	(1.85)	(1.45)			
7 $[Au_2\{\mu\text{-}(CH_2)_2PPh_2\}(\mu\text{-}C_5H_4NS)(SCN)_2]$	30.35	2.2	4.75	44.1 (s)	—	2.62 (d) (9.3), 2.19 (d) (9.0)
	(30.25)	(2.2)	(5.05)			

[a] Calculated values are given in parentheses. [b] Recorded in CDCl$_3$, referenced to external H$_3$PO$_4$, values in ppm; s = singlet. [c] In CDCl$_3$ at 300 MHz referenced to external SiMe$_4$, values in ppm. Coupling constants in Hz are given in parentheses; d = doublet. [d] Measured at −60 °C, AB pattern with ^2J(PP) = 46.8 Hz. [e] Measured at −60 °C.

Table 2 Atomic coordinates (× 10^4) for compound **1**

Atom	*x*	*y*	*z*
Au(1)	7 887.4(4)	353.1(4)	4 838.5(2)
Au(2)	5 711.2(3)	2 591.9(4)	4 506.0(2)
P	6 888(2)	2 239(3)	5 851.3(11)
S	8 221(3)	330(3)	3 859.3(14)
N	6 143(9)	2 529(9)	3 648(4)
C(1)	7 505(12)	413(11)	5 709(5)
C(2)	5 264(11)	2 666(13)	5 333(5)
C(3)	7 117(9)	1 619(10)	3 432(4)
C(4)	7 281(12)	1 736(14)	2 834(5)
C(5)	6 478(13)	2 722(14)	2 454(5)
C(6)	5 495(11)	3 621(15)	2 667(5)
C(7)	5 350(11)	3 492(14)	3 250(5)
C(11)	6 565(9)	2 372(10)	6 613(5)
C(12)	5 460(11)	1 501(14)	6 787(5)
C(13)	5 227(14)	1 506(15)	7 361(6)
C(14)	6 023(13)	2 388(13)	7 766(6)
C(15)	7 103(12)	3 258(16)	7 615(5)
C(16)	7 357(10)	3 239(13)	7 038(4)
C(21)	8 231(8)	3 619(10)	5 781(4)
C(22)	9 670(9)	3 221(12)	5 898(4)
C(23)	10 724(11)	4 306(15)	5 865(6)
C(24)	10 384(12)	5 735(13)	5 722(5)
C(25)	8 969(13)	6 159(13)	5 605(5)
C(26)	7 888(11)	5 111(11)	5 642(5)

Table 3 Selected bond lengths (Å) and angles (°) for compound **1**

Au(1)–C(1)	2.072(11)	Au(1)–S	2.302(3)
Au(1) · · · Au(2)	2.8623(7)	Au(2)–C(2)	1.996(11)
Au(2)–N	2.060(10)	P–C(1)	1.760(10)
P–C(21)	1.782(9)	P–C(11)	1.814(10)
P–C(2)	1.819(11)	S–C(3)	1.733(10)
N–C(3)	1.369(13)	N–C(7)	1.375(14)
C(3)–C(4)	1.40(2)	C(4)–C(5)	1.37(2)
C(5)–C(6)	1.36(2)	C(6)–C(7)	1.36(2)
C(1)–Au(1)–S	177.7(3)	C(1)–Au(1) · · · Au(2)	90.6(3)
S–Au(1) · · · Au(2)	87.22(7)	C(2)–Au(2)–N	179.2(3)
C(2)–Au(2) · · · Au(1)	91.3(3)	N–Au(2) · · · Au(1)	89.5(2)
C(1)–P–C(21)	110.4(4)	C(1)–P–C(11)	110.3(5)
C(21)–P–C(11)	105.7(4)	C(1)–P–C(2)	109.8(5)
C(21)–P–C(2)	109.7(5)	C(11)–P–C(2)	110.9(5)
C(3)–S–Au(1)	112.2(4)	C(3)–N–C(7)	116.8(10)
C(3)–N–Au(2)	127.0(7)	C(7)–N–Au(2)	116.2(7)
P–C(1)–Au(1)	108.2(5)	P–C(2)–Au(2)	108.9(5)
N–C(3)–C(4)	119.4(9)	N–C(3)–S	124.1(8)
C(4)–C(3)–S	116.6(8)	C(5)–C(4)–C(3)	121.9(11)
C(6)–C(5)–C(4)	119.0(11)	C(7)–C(6)–C(5)	118.4(11)
C(6)–C(7)–N	124.6(11)		

in which two chemically non-equivalent phosphorus nuclei are expected for the proposed S,N-co-ordination mode. At −60 °C the ^{31}P-{^{1}H} NMR spectrum of **2** shows an AB pattern for the two dppm phosphorus atoms whereas the spectrum of **3** consists of two resonances for the two dppe phosphorus atoms (Table 1), implying that the pyridine-2-thiolate is acting as a bidentate ligand. Fluxional processes involving this ligand (through intermediates in which the ligand acts as an S-donor bridge) have already been proposed for dirhodium complexes[18] and could also be involved here. In the ^{1}H NMR spectrum of **1**, the ylide methylene proton resonances appear as two doublets (Table 1), which again implies bidentate co-ordination for the pyridine-2-thiolate rather than monodentate sulfur co-ordination. Complexes **1**–**3** were characterised by positive-ion fast atom bombardment (FAB) mass spectrometry. In the spectra of **2** and **3** the parent ion $[M - ClO_4]^+$ is the base peak at m/z = 888 and 902 respectively, whilst for **1** the parent ion $[M]^+$ appears at m/z = 718 (49%); peaks due to higher nuclearity species occur at 1324 ($[2M - C_5H_4NS]^+$, 32%) and 1632 ($[2M + Au]^+$, 21%).

The structure of complex **1** was confirmed by an X-ray diffraction analysis; the molecule is shown in Fig. 1. Atomic coordinates are collected in Table 2 and selected bond lengths and angles in Table 3. The structure shows the typical framework of a dinuclear gold(I) compound: an eight-membered ring with a short transannular gold–gold contact of 2.8623(7) Å. This distance is very similar to those found in other heterobridged gold(I) complexes such as $[Au_2\{\mu\text{-}(CH_2)_2PPh_2\}(\mu\text{-}S_2CNEt_2)]$ [2.868(1) and 2.867(1) Å, two independent molecules][14] or $[Au_2\{\mu\text{-}(CH_2)_2PPh_2\}(\mu\text{-}S_2COPr^i)]$ [2.8809(9) Å].[15] However, intermolecular gold–gold interactions can vary over a wide range, from 2.984(1) Å for the dithiocarbamate complex, 3.984 Å for compound **1** [Au(1)–Au(1^{I}) I = $-x + 2, -y, -z + 1$] to 4.571 Å for the xanthate derivative. Seven atoms of the ring are coplanar; the phosphorus atom lies 0.84 Å out of the plane. The Au–C bond lengths are different, 2.072(11) and 1.996(11) Å, which may be attributable to the greater *trans* influence of sulfur compared to nitrogen. The Au–S distance of 2.302(3) Å is longer than in mononuclear gold(I) complexes containing the pyridine-2-thiolate ligand, such as $[Au(C_5H_5NS)_2]ClO_4$ [2.288(3)–2.291(3) Å],[7] $[Au(C_5H_5NS)Cl]$ [2.261(5) Å][8] or $[Au(C_5H_4NS)(PPh_3)]$ [2.297(2) Å][9] but similar to other Au–S distances in heterobridged dinuclear gold(I) compounds. The Au–N bond length of 2.060(10) Å cannot readily be compared with those in other complexes containing this ligand, because X-ray structure determinations have not been carried out on complexes displaying N-co-ordination to the gold atom. However, the value is similar to others found in pyrazolate–gold(I) complexes.[19,20] The two gold atoms have the expected, essentially linear geometry, with C(1)–Au(1)–S 177.7(3) and C(2)–Au(2)–N 179.2(3)°.

The electrochemical behaviour of these complexes has been studied by cyclic voltammetry at a platinum electrode in CH_2Cl_2. The cyclic voltammograms of **2** and **3**, at a scan rate of 200 mV s^{-1}, show irreversible oxidation waves with peak potentials at 1.42 and 1.46 V respectively. In contrast, complex **1** shows an irreversible, extended, wave at a much less positive potential, *viz.* 0.53 V; no reduction waves were observed to −1.8 V.

A qualitative comparison shows that complex **1** is more difficult to oxidise than the starting material $[Au_2\{\mu\text{-}(CH_2)_2PPh_2\}_2]$ (0.11 V *vs.* Ag–AgCl)[21] or than similar heterobridged complexes such as $[Au_2\{\mu\text{-}(CH_2)_2PPh_2\}(\mu\text{-}S_2CNR_2)]$ (0.30–0.47 V).[14] After addition of chloride ion to the electrochemical cell, the oxidation peak current of **1** increased and the peak potentials shifted slightly, to 0.50 V. More striking, however, was an irreversible product reduction peak that appeared at −0.39 V. On adding $[Fe(C_5H_5)_2]PF_6$ to the cell a red solution formed, which showed only an irreversible reduction peak, at −0.43 V.

The results of this electrochemical study suggested that it should be possible to oxidise complex **1** with a mild oxidant giving, in the presence of a halide ion, the corresponding gold(II) derivative. Accordingly, we treated **1** with the ferrocenium ion in the presence of halides (Cl, Br or I) or pseudohalides (SCN) in 1:2:2 molar ratio. These reactions result in oxidation of the gold centres and co-ordination of the halides or pseudohalides to give gold(II) derivatives **4**–**7**, the first gold(II) complexes containing pyridine-2-thiolate. The by-products, namely $Q[PF_6]$ (Q = halide-salt counter ion), can be completely separated only for **7** because of their different solubility in organic solvents; ferrocene was completely removed by washing the solids with hexane (Scheme 2). Similar processes between $[Au_2\{\mu\text{-}(CH_2)_2PPh_2\}(\mu\text{-}S_2CNR_2)]$, halides and the ferrocenium ion afford mixtures of products including the gold(II) complexes $[Au_2\{\mu\text{-}(CH_2)_2PPh_2\}_2X_2]$ and $[Au_2\{\mu\text{-}(CH_2)_2PPh_2\}(\mu\text{-}S_2CNR_2)X_2]$.

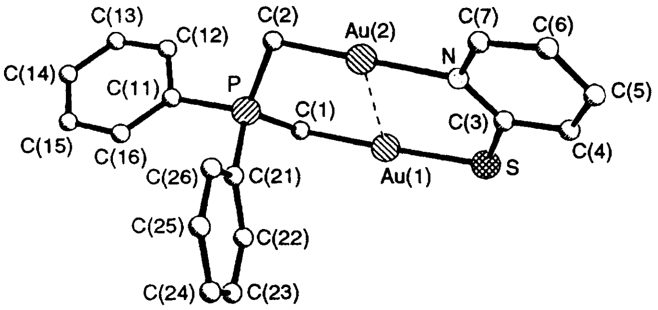
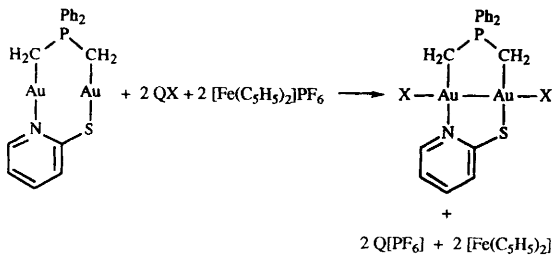


Fig. 1 The molecule of complex **1** in the crystal (H atoms omitted, radii arbitrary) showing the atom-numbering scheme

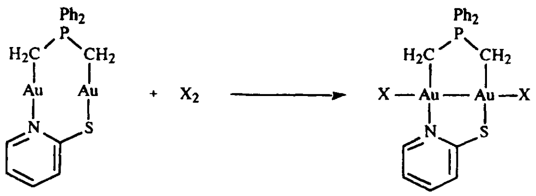


Scheme 2 Q = $NEt_3(CH_2Ph)$, X = Cl **4**; Q = NBu_4, X = Br **5**; Q = PPh_3Me, X = I **6**; Q = K, X = SCN **7**

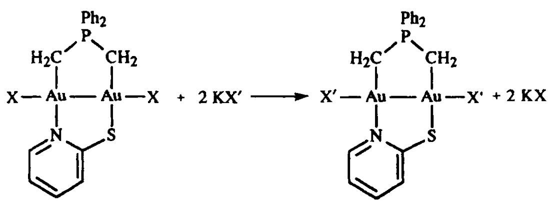
To characterise these compounds fully, they were also synthesized by a well established method of obtaining dinuclear gold(II) derivatives: oxidative addition of halogen. Thus the reaction of **1** with a halogen gives the corresponding gold(II) derivatives, according to Scheme 3. The reaction of the cationic derivatives **2** and **3** with an oxidant as strong as chlorine leads, after breaking the heterobridged diauracycle, to a mixture of complexes including $[(AuCl)_2(\mu\text{-}L\text{–}L)]$ (L–L = dppm or dppe).[22]

Complexes **4**–**6** undergo metathesis with halide or pseudohalide ions to afford new gold(II) derivatives *via* halide- or pseudohalide-exchange reactions (Scheme 4). Complexes **4**–**7** were isolated as red (**4** and **7**), orange (**5**) or garnet (**6**) solids, air- and moisture-stable at room temperature. Their acetone solutions are non-conducting and their IR spectra show absorptions at 1400–1600 cm^{-1} from ring vibrations of the pyridine-2-thiolate, medium intensity bands at *ca.* 575 cm^{-1} from $\nu(Au\text{–}C_{ylide})$, at 258m cm^{-1} assignable to $\nu(Au^{II}\text{–}Cl)$[23] for **4** and at 2111s cm^{-1} from ν(C–N)[24] for **7**. The $^{31}P\text{-}\{^1H\}$ NMR spectra show a singlet for the phosphorus atom of the ylide group (Table 1), shifted markedly to low-field compared with **1**, and display the order $\delta_I > \delta_{Br} > \delta_{Cl} > \delta_{SCN}$, as was found for $[Au_2\{\mu\text{-}(CH_2)_2PPh_2\}(\mu\text{-}S_2CNR_2)X_2]$ (X = Cl, Br or I)[25] and $[Au_2\{\mu\text{-}(CH_2)_2PPh_2\}_2X_2]$ (X = Cl, Br or I).[21] Their ^1H NMR spectra show two doublets for the ylide methylene protons, confirming the retention of the pyridine-2-thiolate as a bidentate ligand (Table 1). The positive-ion FAB mass spectra only show the molecular cation peak for **5** at m/z = 877 (8%), although in every spectrum the $[M - X]^+$ peak appears at m/z = 752 (25), 796 (60), 844 (37) and 775 (100%), respectively.

The structure of complex **5** was established by an X-ray diffraction analysis, the precision of which is however only moderate because of poor crystal quality and high absorption. The asymmetric unit contains three independent molecules, one of which is shown in Fig. 2. Positional parameters are collected in Table 4 and selected bond lengths and angles in Table 5. All three molecules display the general features of dinuclear gold(II) complexes: an eight-membered ring with a twisted conformation (the angles between the gold co-ordination planes are 26–30°) and a transannular metal–metal bond. The gold–gold distances 2.547(4), 2.548(4) and 2.564(4) Å are amongst the shortest found in gold(II) complexes {*cf.* 2.550(1) Å in $[NBu_4]_2[Au_2\{\mu\text{-}S_2C_2(CN)_2\}_2Cl_2]$},[26] despite the fact that gold–gold bonds are usually shorter in chloro than in bromo derivatives. However the high estimated standard deviations of the bond lengths do



Scheme 3 X = Cl **4**, Br **5** or I **6**



Scheme 4 X = Cl, X′ = Br **5**; X = Br, X′ = I **6**; X = Cl, X′ = SCN **7**

Table 4 Atomic coordinates (× 10^4) for compound **5**

Atom	*x*	*y*	*z*
Au(1)	1837.3(10)	1896.3(10)	594.9(9)
Au(2)	476.1(11)	2460.7(10)	1671.1(9)
Br(1)	3150(3)	1198(3)	−328(3)
Br(2)	−747(3)	3147(3)	2702(3)
P(1)	807(7)	267(6)	2412(6)
S(1)	797(7)	3953(6)	535(5)
N(1)	1693(20)	2994(20)	−543(19)
C(11)	1270(23)	3797(24)	−466(23)
C(12)	1190(23)	4467(25)	−1243(23)
C(13)	1537(22)	4388(23)	−2077(22)
C(14)	1939(23)	3564(25)	−2088(25)
C(15)	2020(23)	2929(25)	−1370(23)
C(1)	2018(26)	896(25)	1687(23)
C(2)	102(34)	1171(31)	2683(29)
C(31)	887(20)	−697(15)	3380(14)
C(32)	587(20)	−1648(17)	3559(16)
C(33)	638(21)	−2366(13)	4312(17)
C(34)	990(23)	−2133(17)	4885(15)
C(35)	1291(22)	−1182(20)	4705(17)
C(36)	1239(21)	−464(14)	3953(17)
C(41)	344(18)	−257(19)	1806(17)
C(42)	970(14)	−678(20)	1249(18)
C(43)	633(18)	−1081(20)	762(17)
C(44)	−330(19)	−1063(21)	831(18)
C(45)	−956(15)	−642(21)	1388(19)
C(46)	−619(17)	−240(20)	1876(17)
Au(3)	1316.7(10)	4703.1(10)	2666.8(9)
Au(4)	2550.0(11)	4043.0(10)	1596.7(10)
Br(3)	−18(3)	5324(3)	3657(3)
Br(4)	3683(3)	3317(2)	568(2)
P(2)	2358(7)	6264(7)	847(6)
S(2)	2126(8)	2566(6)	2787(6)
N(2)	1626(17)	3711(18)	3759(16)
C(16)	1885(21)	2830(23)	3766(22)
C(17)	2047(23)	2184(26)	4443(23)
C(18)	1927(22)	2444(25)	5211(23)
C(19)	1652(22)	3304(24)	5234(23)
C(20)	1466(23)	3958(27)	4528(24)
C(3)	1152(25)	5707(24)	1584(22)
C(4)	2920(25)	5330(22)	503(21)
C(51)	2385(20)	7279(15)	−138(14)
C(52)	2006(20)	7107(15)	−721(17)
C(53)	2097(21)	7835(19)	−1522(16)
C(54)	2567(22)	8734(17)	−1740(15)
C(55)	2947(21)	8906(14)	−1157(18)
C(56)	2856(20)	8179(18)	−356(16)
C(61)	2928(17)	6742(19)	1417(16)
C(62)	2361(13)	6993(19)	2136(17)
C(63)	2796(18)	7325(20)	2605(15)
C(64)	3798(18)	7406(21)	2356(17)
C(65)	4366(14)	7156(21)	1637(18)
C(66)	3931(16)	6825(20)	1168(15)
Au(5)	5200.7(11)	−1215.9(10)	3850.8(9)
Au(6)	3834.4(11)	−675.0(10)	4925.3(9)
Br(5)	6610(3)	−1758(3)	2894(3)
Br(6)	2562(3)	−36(3)	5944(2)
P(3)	4384(7)	−2771(6)	5719(6)
S(3)	4102(9)	775(7)	3754(6)
N(3)	4856(19)	−307(20)	2743(19)
C(21)	4491(22)	520(23)	2775(22)
C(22)	4314(22)	1136(24)	2036(22)
C(23)	4496(24)	921(27)	1323(25)
C(24)	4895(26)	65(29)	1262(28)
C(25)	5083(22)	−503(24)	2014(21)
C(5)	5484(23)	−2051(22)	4885(20)
C(6)	3560(26)	−1936(24)	6010(23)
C(71)	3968(17)	−3442(17)	5178(16)
C(72)	4641(13)	−3787(19)	4582(17)
C(73)	4331(17)	−4303(20)	4160(17)
C(74)	3348(18)	−4473(19)	4334(17)
C(75)	2675(13)	−4127(19)	4931(18)
C(76)	2985(15)	−3612(18)	5353(16)
C(81)	4539(19)	−3599(17)	6700(15)
C(82)	5385(17)	−3537(19)	6869(17)
C(83)	5462(18)	−4164(22)	7654(20)
C(84)	4693(23)	−4854(20)	8270(16)
C(85)	3847(19)	−4917(19)	8101(17)
C(86)	3770(16)	−4289(20)	7316(18)

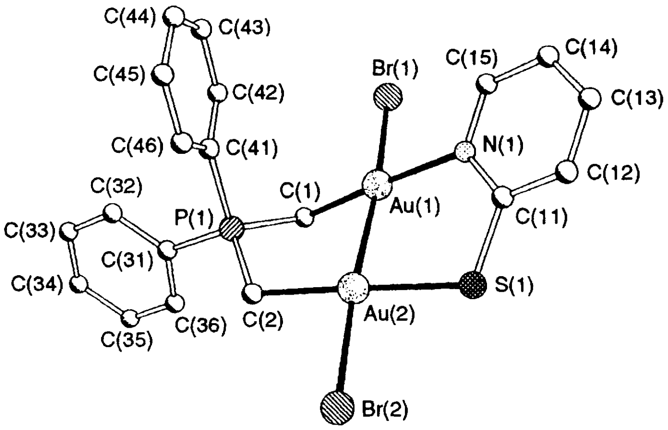
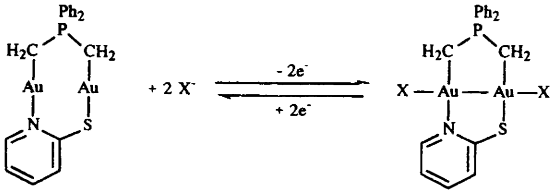


Fig. 2 One of the three independent molecules of complex **5** in the crystal (H atoms omitted, radii arbitrary) showing the atom-numbering scheme



Scheme 5 X = Cl, Br, I or SCN

not allow significant comparisons. There are also intermolecular gold–gold interactions: Au(2)···Au(4) 3.840(5), Au(1)···Au(4) 4.395(6), Au(2)···Au(3) 4.585(6), Au(6)···Au(6$^{\text{I}}$) (I = $-x + 1$, $-y$, $-z + 1$) 4.146(6) and Au(5)···Au(6$^{\text{I}}$) 4.527(6) Å and gold–bromine interactions Au(1)···Br(4) 3.461(6), Au(3)···Br(2) 3.835(6) and Au(5)···Br(6$^{\text{I}}$) 4.000(6) Å. The Au–S and Au–N ranges are 2.318(10)–2.343(9) and 2.137(26)–2.148(29) Å respectively, and are longer than in the gold(I) precursor, as was previously observed in gold(II) dithiocarbamate[25] or xanthate[15] complexes compared to their gold(I) precursors. The Au–Br bond lengths in each molecule are somewhat different, although the differences may not be highly significant; the range of values is 2.482(5)–2.526(5) Å. A similar difference was also found in the complex [$Au_2\{\mu\text{-}(CH_2)_2PPh_2\}\{\mu\text{-}S_2CN(CH_2Ph)_2\}Br_2$] [2.502(1) and 2.525(1) Å].[25] The co-ordination around the gold atoms is essentially square-planar with no deviations greater than 6° from ideal angles. The chains Br–Au–Au–Br are almost linear, with Br–Au–Au angles of 174.32(13)–176.57(12)°.

The cyclic voltammograms of complexes **4** and **5** (in CH_2Cl_2, scan rate 200 mV s^{-1}) show irreversible reduction waves at −0.44 (**4**) and −0.43 (**5**) V, associated in both cases with an irreversible oxidation peak at 0.55 V, suggesting that **1** is reformed after reduction. A similar observation [on dinuclear gold(I)–gold(II) derivatives] was previously made in cyclic voltammetric studies of [$Au_2\{\mu\text{-}(CH_2)_2PPh_2\}_2X_2$].[21] All these

Table 5 Selected bond lengths (Å) and angles (°) for compound **5**

Au(1)–C(1)	2.052(36)	Au(1)–N(1)	2.148(29)
Au(1)–Br(1)	2.505(5)	Au(1)–Au(2)	2.564(4)
Au(2)–C(2)	2.025(43)	Au(2)–S(1)	2.324(9)
Au(2)–Br(2)	2.526(5)	Au(3)–C(3)	2.034(34)
Au(3)–N(2)	2.137(26)	Au(3)–Br(3)	2.512(5)
Au(3)–Au(4)	2.548(4)	Au(4)–C(4)	2.087(32)
Au(4)–S(2)	2.343(9)	Au(4)–Br(4)	2.502(5)
Au(5)–C(5)	1.960(31)	Au(5)–N(3)	2.138(30)
Au(5)–Br(5)	2.482(5)	Au(5)–Au(6)	2.547(4)
Au(6)–C(6)	2.065(34)	Au(6)–S(3)	2.318(10)
Au(6)–Br(6)	2.506(5)		
C(1)–Au(1)–N(1)	177.2(12)	C(1)–Au(1)–Br(1)	86.2(10)
N(1)–Au(1)–Br(1)	94.2(8)	C(1)–Au(1)–Au(2)	88.4(10)
N(1)–Au(1)–Au(2)	91.2(8)	Br(1)–Au(1)–Au(2)	174.38(13)
C(2)–Au(2)–S(1)	176.2(13)	C(2)–Au(2)–Br(2)	88.4(13)
S(1)–Au(2)–Br(2)	88.9(3)	C(2)–Au(2)–Au(1)	95.0(13)
S(1)–Au(2)–Au(1)	87.9(2)	Br(2)–Au(2)–Au(1)	174.48(13)
C(3)–Au(3)–N(2)	174.6(11)	C(3)–Au(3)–Br(3)	88.8(10)
N(2)–Au(3)–Br(3)	93.7(7)	C(3)–Au(3)–Au(4)	88.1(10)
N(2)–Au(3)–Au(4)	89.7(7)	Br(3)–Au(3)–Au(4)	174.32(13)
C(4)–Au(4)–S(2)	177.6(9)	C(4)–Au(4)–Br(4)	86.9(9)
S(2)–Au(4)–Br(4)	91.4(3)	C(4)–Au(4)–Au(3)	95.0(9)
S(2)–Au(4)–Au(3)	86.5(3)	Br(4)–Au(4)–Au(3)	176.57(12)
C(5)–Au(5)–N(3)	178.6(12)	C(5)–Au(5)–Br(5)	87.6(9)
N(3)–Au(5)–Br(5)	93.7(8)	C(5)–Au(5)–Au(6)	88.2(9)
N(3)–Au(5)–Au(6)	90.6(8)	Br(5)–Au(5)–Au(6)	174.99(13)
C(6)–Au(6)–S(3)	177.3(10)	C(6)–Au(6)–Br(6)	87.0(10)
S(3)–Au(6)–Br(6)	90.4(3)	C(6)–Au(6)–Au(5)	95.8(10)
S(3)–Au(6)–Au(5)	86.8(3)	Br(6)–Au(6)–Au(5)	176.07(12)

data lead us to propose the reversible interconversion shown in Scheme 5.

Experimental

Infrared spectra were recorded on a Perkin-Elmer 883 spectrophotometer, over the range 4000–200 cm^{-1}, by using Nujol mulls between polyethylene sheets. Proton and ^{31}P NMR spectra were recorded on a Varian UNITY 300 spectrometer in CDCl$_3$ solutions; chemical shifts are quoted relative to SiMe$_4$ (external, ^{1}H) and H$_3$PO$_4$ (external, ^{31}P). The C, H and N analyses were performed with a Perkin-Elmer 2400 microanalyser. Conductivities were measured in acetone solution with a Philips PW 9509 apparatus. Melting points were measured on a Büchi apparatus and are uncorrected. Mass spectra were recorded on a VG Autospec mass spectrometer using positive-ion fast atom bombardment (FAB) techniques.

Electrochemical studies were carried out using an EG and G model 273 potentiostat, in conjunction with a three-electrode cell. The auxiliary electrode was a platinum wire and the working electrode was a platinum disc. The reference was an aqueous saturated calomel electrode (SCE) separated from the test solution by a fine-porosity frit and an agar bridge saturated with KCl. The CH$_2$Cl$_2$ solutions were 5 × 10^{-4} mol dm^{-3} in complex and 0.1 mol dm^{-3} in [NBu$_4$]PF$_6$ as the supporting electrolyte. All potentials are standardised against either the [Fe(η-C$_5$H$_5$)$_2$]$^+$–[Fe(η-C$_5$H$_5$)$_2$] or the [Fe(η-C$_5$Me$_5$)$_2$]$^+$–[Fe(η-C$_5$Me$_5$)$_2$] couple as an internal standard ($E°$ = 0.47 and −0.09 V respectively).

The C, H and N analyses, ^{31}P-{^{1}H} and some ^{1}H NMR data are listed in Table 1. All reactions were carried out at room temperature.

Syntheses.—[Au$_2${μ-(CH$_2$)$_2$PPh$_2$}(μ-C$_5$H$_4$NS)] **1** and [Au$_2$(μ-C$_5$H$_4$NS)(μ-L–L)]ClO$_4$ (L–L = dppm **2** or dppe **3**). To a solution of [Au$_2${μ-(CH$_2$)$_2$PPh$_2$}$_2$][21] (0.082 g, 0.1 mmol) or [Au$_2$(μ-L–L)$_2$][ClO$_4$]$_2$[23,27] (0.1 mmol; L–L = dppm 0.136 g or dppe 0.139 g) in dichloromethane (40 cm^3) was added the stoichiometric amount of the poorly soluble complex [Au$_n$(μ-C$_5$H$_4$NS)$_n$][7] (C$_5$H$_4$NS = pyridine-2-thiolate, 0.061 g). After stirring for 1 d (**1**) or 2 h (**2** and **3**), the solution was filtered. Concentration of the filtrate to *ca.* 5 cm^3 and addition of diethyl ether (15 cm^3) led to the precipitation of **1**–**3**, which were washed with diethyl ether (2 × 5 cm^3). Yield of **1** 84%, m.p. 174 °C (decomp.); Λ_M = 1 ohm^{-1} cm^2 mol^{-1}; ^{1}H NMR (not included in Table 1): δ 8.10–6.80 (m, Ph and C$_5$H$_4$NS). Yield of **2** 71%, m.p. 190 °C (decomp.); Λ_M = 120 ohm^{-1} cm^2 mol^{-1}; ^{1}H NMR: δ 8.10–7.17 (m, Ph and C$_5$H$_4$NS) and 4.32 [t, J(HP) = 12.7 Hz, PCH$_2$P]. Yield of **3** 78%, m.p. 152 °C; Λ_M = 134 ohm^{-1} cm^2 mol^{-1}; ^{1}H NMR: δ 8.25–7.24 (m, Ph and C$_5$H$_4$NS) and 3.05 [d, J(HP) = 12.0 Hz, P(CH$_2$)$_2$P].

[Au$_2${μ-(CH$_2$)$_2$PPh$_2$}(μ-C$_5$H$_4$NS)X$_2$] (X = Cl **4**, Br **5**, I **6** *or* SCN **7**). These complexes can be obtained in three different ways.

(*a*) To an anhydrous dichloromethane solution (30 cm^3) of [Au$_2${μ-(CH$_2$)$_2$PPh$_2$}(μ-C$_5$H$_4$NS)] (0.072 g, 0.1 mmol) were added QX [0.2 mmol; Q = NEt$_3$(CH$_2$Ph), X = Cl, 0.046 g; Q = NBu$_4$, X = Br, 0.064 g; Q = PPh$_3$Me, X = I, 0.081 g; Q = K, X = SCN, 0.020 g] in anhydrous acetone (10 cm^3) and [Fe(C$_5$H$_5$)$_2$]PF$_6$ (0.066 g, 0.2 mmol). The mixture was stirred for 45 min, and then filtered through diatomaceous earth. The clear solution was evaporated to *ca.* 2 cm^3 and toluene was added (15 cm^3). After filtration, the solution was concentrated to *ca.* 5 cm^3. Addition of hexane (15 cm^3) led to precipitation of a mixture containing complexes **4**–**7** and Q[PF$_6$] (except for **7**, due to the insolubility of K[PF$_6$] in toluene); [Fe(C$_5$H$_5$)$_2$] was completely removed by washing with hexane (4 × 5 cm^3). Yield of **7** 61%.

(*b*) To a solution of [Au$_2${μ-(CH$_2$)$_2$PPh$_2$}(μ-C$_5$H$_4$NS)] (0.072 g, 0.1 mmol) in dichloromethane (20 cm^3) was added the stoichiometric amount of halogen X$_2$ (0.1 mmol; X$_2$ = Cl$_2$ or Br$_2$ in CCl$_4$ solution; X$_2$ = I$_2$, 0.025 g). After stirring for about 30 min, the solution was concentrated to *ca.* 5 cm^3. Addition of diethyl ether (20 cm^3) afforded complexes **4**–**6**. The solids were washed with diethyl ether (2 × 5 cm^3). Yields 81 (**4**), 78 (**5**) and 87 (**6**)%.

(*c*) To a dichloromethane solution (15 cm^3) of [Au$_2${μ-(CH$_2$)$_2$PPh$_2$}(μ-C$_5$H$_4$NS)X$_2$] (0.05 mmol; X = Cl 0.039 or Br 0.044 g) was added an aqueous solution (5 cm^3) containing an excess of KX′ (0.3 mmol; X′ = Br 0.036, I 0.050 or SCN 0.031 g). After stirring for 2 h, the organic phase was separated, dried over anhydrous MgSO$_4$ and concentrated to *ca.* 5 cm^3. Addition of diethyl ether (20 cm^3) afforded complexes **5**–**7**, which were washed with diethyl ether (2 × 5 cm^3). **4**, m.p. 184 °C; Λ_M = 11 ohm^{-1} cm^2 mol^{-1}; ^{1}H NMR (not included in Table 1): δ 8.88–6.87 (m, Ph and C$_5$H$_4$NS). Yield of **5** 75%, m.p. 170 °C; Λ_M = 8 ohm^{-1} cm^2 mol^{-1}; ^{1}H NMR: δ 8.97–6.86 (m, Ph and C$_5$H$_4$NS). Yield of **6** 80%, m.p. 136 °C; Λ_M = 11 ohm^{-1} cm^2 mol^{-1}; ^{1}H NMR: δ 9.06–6.88 (m, Ph and C$_5$H$_4$NS). Yield of **7** 79%, m.p. 132 °C; Λ_M = 10 ohm^{-1} cm^2 mol^{-1}; ^{1}H NMR: δ 8.29–7.01 (m, Ph and C$_5$H$_4$NS).

Structure Determination of Compound **1**.—*Crystal data.* C$_{19}$H$_{18}$Au$_2$NPS, M = 717.31, monoclinic, space group $P2_1/n$, a = 9.430(2), b = 8.819(2), c = 22.786(5) Å, β = 99.08(3)°, U = 1871.2(7) Å^3, Z = 4, D_c = 2.546 Mg m^{-3}, F(000) = 1312, λ(Mo-Kα) = 0.710 73 Å, μ = 15.86 mm^{-1}, T = 20 °C.

Data collection and reduction. Single crystals of compound **1** in the form of colourless plates were obtained by slow diffusion of diethyl ether into a dichloromethane solution. A crystal of size 0.70 × 0.30 × 0.02 mm was mounted on a Siemens R4 diffractometer, and used to collect 4377 intensities to 2θ_{max} 50° (monochromated Mo-Kα radiation). An absorption correction based on ψ scans was applied, with transmission factors 0.144–0.778. Merging equivalents gave 3264 independent reflections (R_{int} 0.099). Cell constants were refined from setting angles of 40 reflections in the 2θ range 10–25°.

Structure solution and refinement. The structure was solved by the heavy-atom method and subjected to full-matrix least-squares refinement on F^2 (program system SHELXL 93).[28] All non-hydrogen atoms were refined anisotropically; hydrogen atoms were included using a riding model. Refinement proceeded to $wR(F^2) = 0.111$ for 217 parameters and 163 restraints; conventional $R(F) = 0.045$, S 1.01, maximum $\Delta\rho$ 1.8 e Å^{-3} (near the gold atoms); $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR(F)^2 = [\Sigma\{w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o)^2\}^2]^{\frac{1}{2}}$, $w^{-1} = \sigma^2(F_o)^2 + (aP)^2 + bP$, where $P = (F_o{}^2 + 2F_c{}^2)/3$ and a and b are constants adjusted by the program.

Structure Determination of Compound **5**.—*Crystal data.* $C_{19}H_{18}Au_2Br_2NPS$, $M = 877.13$, triclinic, space group $P\bar{1}$, $a = 14.810(10)$, $b = 14.908(10)$, $c = 17.041(12)$ Å, $\alpha = 70.20(5)$, $\beta = 69.77(5)$, $\gamma = 89.19(5)°$, $U = 3299(4)$ Å^3, $Z = 6$, $D_c = 2.649$ Mg m^{-3}, $F(000) = 2388$, λ(Mo-Kα) = 0.710 73 Å, $\mu = 17.13$ mm^{-1}, $T = -130$ °C.

Data collection and reduction. A red prism of 0.50 × 0.40 × 0.30 mm was mounted on a glass fibre in inert oil and transferred to the cold gas stream of the diffractometer (Stoe STADI-4), and used to collect 13 348 intensities to $2\theta_{max}$ 50° (monochromated Mo-Kα radiation), of which 11468 were independent (R_{int} 0.063). An empirical absorption correction was applied with the program SHELXA,[29] with transmission factors 0.1–0.31. Merging equivalents gave 11468 independent reflections (R_{int} 0.063). Cell constants were refined from ± ω-angles of 52 reflections in the 2θ range 20–22°. The reorientation matrix -1 -1 0/-1 1 0/0 0 1 forms a C-centred cell that is metrically monoclinic, but with triclinic Laue symmetry (R_{int} 0.76).

Structure solution and refinement. The structure was solved by direct methods and refined as above, except that only the Au, Br, S and P atoms were refined anisotropically. Refinement proceeded to $wR(F^2) = 0.273$ for 11433 reflections, 331 parameters and 63 restraints, conventional $R(F) = 0.089$, S 1.045, maximum $\Delta\rho$ 4.9 e Å^{-3} (near the gold atoms).

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Acknowledgements

We thank the Dirección General de Investigación Científica y Técnica (no. PB91-0122) and the Fonds der Chemischen Industrie for financial support and the Ministerio de Educación y Ciencia for a grant (to M. B.).

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Received 24*th January* 1995; *Paper* 5/00401B