Syntheses of Dinuclear Gold(I) Ring Complexes containing Two Different Bridging Ligands. Crystal Structure of $[Au_2\{\mu\text{-}(CH_2)_2PPh_2\}(\mu\text{-}S_2CNEt_2)]$†

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The reaction of $[Au_2\{\mu\text{-}(CH_2)_2PPh_2\}_2]$ with $[Au_2(\mu\text{-}L\text{–}L)_2]^{n+}$ [$n = 0$, L–L = S_2CNMe_2, S_2CNEt_2 or $S_2CN(CH_2Ph)_2$; $n = 2$, L–L = $Ph_2PCH_2PPh_2$ (dppm), $Ph_2P(CH_2)_2PPh_2$ or $Ph_2PNHPPh_2$] led to heterobridged dinuclear complexes $[Au_2\{\mu\text{-}(CH_2)_2PPh_2\}(\mu\text{-}L\text{–}L)]^{n+}$ (n = 0 or 1). The same complexes can also be obtained by reaction of $[N(PPh_3)_2][(AuCl)_2\{\mu\text{-}(CH_2)_2PPh_2\}]$ with the silver compounds $[Ag(S_2CNMe_2)]_6$ or $[Ag_2(OClO_3)_2(dppm)_3]$ or by reaction of $[(AuPPh_3)_2\{\mu\text{-}(CH_2)_2PPh_2\}][ClO_4]$ with $[\{Au(C_6F_5)\}_2(\mu\text{-}L\text{–}L)]$ (L–L = diphosphines or o-$Ph_2PC_5H_4N$). The structure of $[Au_2\{\mu\text{-}(CH_2)_2PPh_2\}(\mu\text{-}S_2CNEt_2)]$ has been established by X-ray crystallography. Two molecules are bonded through an intermolecular gold–gold interaction, thus forming a linear chain of four gold atoms with Au–Au (intramolecular) 2.867, 2.868, (intermolecular) 2.984 Å.

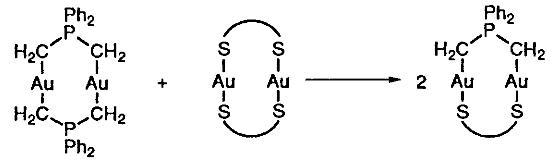
The synthesis of dinuclear gold(I) complexes has attracted considerable attention in recent years [1-3] and provides a handle for the study of the weak metal–metal interactions that have been attributed to relativistic effects.[4,5] Many of these dinuclear complexes are homobridged diauracycles, with the same bridging ligand on each side,[6-8] but a few examples of heterobridged derivatives have been reported.[9-11]

In the present paper we describe the preparation of several heterobridged dinuclear gold(I) complexes containing dithiocarbamate, diphosphine or bis(ylide) as ligands. The molecular structure of $[Au_2\{\mu\text{-}(CH_2)_2PPh_2\}(\mu\text{-}S_2CNEt_2)]$ has been established by X-ray studies and shows the presence of inter- and intra-molecular gold–gold interactions.

Results and Discussion

We have studied three different types of reactions.

(*a*) *Ligand Exchange Reactions.*—The reaction of the homobridged dinuclear $[Au_2\{\mu\text{-}(CH_2)_2PPh_2\}_2]$ with $[Au_2(\mu\text{-}S_2CNR_2)_2]$ (R = Me, Et or CH_2Ph) leads to heterobridged complexes (Scheme 1) in a ligand-exchange reaction similar to the ylide-transfer processes previously observed by us[12] with mononuclear gold(I) derivatives. Complexes **1**–**3** are air- and moisture-stable green solids and their acetone solutions are non-conducting (Table 1). The positive-ion fast atom bombardment (FAB) mass spectra show in all cases the molecular cation peak (M) at m/z = 727 (25, **1**), 755 (80, **2**) and 879 (25%, **3**). Other peaks appear at m/z = 530 (20, $[M - Au]^+$) for **1**, 558 (50, $[M - Au]^+$), 903 {30, $[M + (S_2CNEt_2)]^+$} and 1362 (25, $[2M]^+$) for **2** and 682 (80, $[M - Au]^+$) and 1151 {80%, $[M + S_2CN(CH_2Ph)_2]^+$} for **3**. The IR spectra show bands at *ca.* 570m cm^{-1} due to $\nu(Au\text{–}C_{ylide})$[13] and at *ca.* 1495s cm^{-1} due to $\nu(C{=}N)$.[14] The $^{31}P\text{-}\{^1H\}$ NMR spectra show a singlet at *ca.* δ 35.1 for the phosphorus atom (see Table 1) and the ^1H NMR spectra a doublet at *ca.* δ 1.9 (see Experimental section) for the ylide methylene protons.



Scheme 1 S–S = S_2CNMe_2 **1**, S_2CNEt_2 **2** or $S_2CN(CH_2Ph)_2$ **3**

The cyclic voltammograms of complexes **1**–**3** (in CH_2Cl_2, scan rate 200 mV s^{-1}) show irreversible oxidation waves with peak potentials at 0.30, 0.37 and 0.42 V respectively. These waves are ill defined due to electrode coating during voltammetry. Nevertheless, a qualitative comparison shows complexes **1**–**3** to be oxidised at potentials between those of $[Au_2\{\mu\text{-}S_2CN(CH_2Ph)_2\}_2]$ (irreversible peak potential 1.15 V) and that reported[15] for the first wave of $[Au_2\{\mu\text{-}(CH_2)_2PPh_2\}_2]$ (0.11 V *vs.* Ag–AgCl).

The structure of complex **2** was confirmed by X-ray diffraction analysis (Fig. 1). The asymmetric unit consists of two independent molecules, which show short intra- and intermolecular gold–gold contacts. This feature is characteristic of the related bis(dithiocarbamato)digold(I) derivatives,[15-18] which crystallise as discrete dimers in which the packing of the dimeric units produces linear chains of gold atoms. The intramolecular gold–gold distances in complex **2** are 2.868(1) and 2.867(1) Å, which are slightly longer than those found in $[Au_2(\mu\text{-}S_2CNR_2)_2]$[16-18] (2.76–2.8 Å), but shorter than in the bis(ylide)digold(I) complex $[Au_2\{\mu\text{-}(CH_2)_2PPh_2\}_2]$ (2.977(1) Å).[13] The gold–gold distance between dimers is 2.984(1) Å, which is of the same order as in the heterobridged $[Au_2(\mu$-

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† *Supplementary data available:* Further details of the structure determination (complete bond lengths and angles, H-atom coordinates, structure factors, thermal parameters) 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 number CSD 400672.

Table 1 Analytical and NMR data for the complexes

	Yield	Analysis[a] (%)				$^{31}P-\{^1H\}$ NMR[c]	
Complex	(%)	C	H	N	Λ_M[b]	δ_{ylide}	$\delta_{phosphine}$
1 $[Au_2\{\mu-(CH_2)_2PPh_2\}(\mu-S_2CNMe_2)]$	83	28.2 (28.05)	2.65 (2.75)	1.75 (1.95)	3	35.4 (s)	
2 $[Au_2\{\mu-(CH_2)_2PPh_2\}(\mu-S_2CNEt_2)]$	73	30.4 (30.2)	3.2 (3.2)	1.9 (1.85)	1	35.1 (s)	
3 $[Au_2\{\mu-(CH_2)_2PPh_2\}\{\mu-S_2CN(CH_2Ph)_2\}]$	84	39.8 (39.6)	3.1 (3.2)	1.45 (1.6)	16	35.1 (s)	
4 $[Au_2\{\mu-(CH_2)_2PPh_2\}(\mu\text{-dppm})][ClO_4]$	85	43.3 (42.95)	3.4 (3.35)	— —	133	34.7 (t) (12.6)	36.1 (d)
5 $[Au_2\{\mu-(CH_2)_2PPh_2\}(\mu\text{-dppe})][ClO_4]$	74	43.3 (43.5)	3.45 (3.45)	— —	126	35.3 (t) (11.5)	38.3 (d)
6 $[Au_2\{\mu-(CH_2)_2PPh_2\}(\mu\text{-dppa})][ClO_4]$	80	41.35 (41.8)	3.3 (3.25)	1.5 (1.3)	136	34.4 (t) (11.8)	80.3 (d)
7 $[Au_2\{\mu-(CH_2)_2PPh_2\}(\mu\text{-}o\text{-}Ph_2PC_5H_4N)][ClO_4]$	90	38.8 (38.4)	2.95 (2.9)	1.1 (1.45)	126	36.7 (d) (14.7)	42.5 (d)

[a] Calculated values in parentheses. [b] In acetone, ohm^{-1} cm^2 mol^{-1}. [c] Recorded in $CDCl_3$ at 121 MHz, referenced to external H_3PO_4. Coupling constants in Hz are given in parentheses; s = singlet, d = doublet and t = triplet.

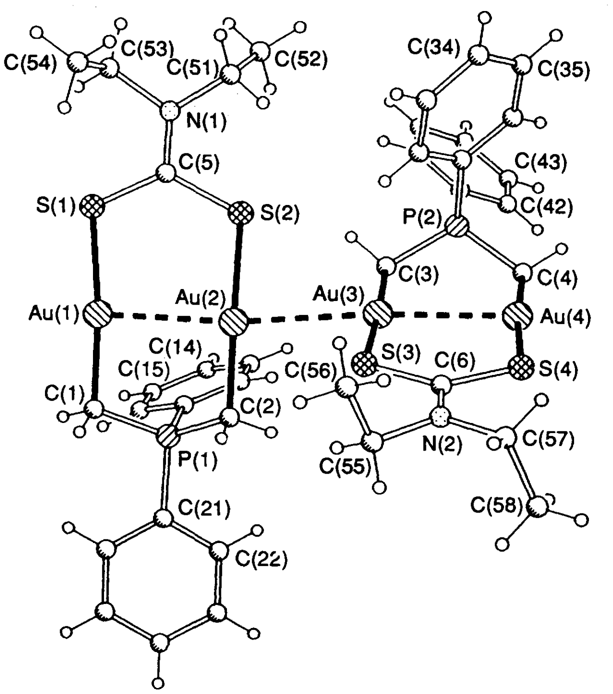


Fig. 1 The two independent molecules of complex **2** in the crystal. Radii are arbitrary

dppm)$\{(\mu-CH_2)_2S(O)NMe_2\}][BF_4]$[19] (dppm = $Ph_2PCH_2PPh_2$) where the cations pack pairwise with short intermolecular contacts (2.959 Å).

The two dimers are located almost perpendicular to each other [the angle between the planes $Au_2(S_2C)(PP)$ is 70°] in such a manner as to form a chain of four gold atoms, with Au–Au–Au angles close to linearity (maximum deviation 6.5°). In the crystal the two dimeric units are paired across symmetry centres (Fig. 2) with the shortest Au(3) ··· Au(4i) contacts of 3.696(2) Å. Ignoring the Au ··· Au contacts, the co-ordination around the gold atoms is almost linear: the C–Au–S angles lie in the range 174.7(5)–178.3(6)°. The conformation of the eight-membered rings is an 'envelope' form, with the ylide P atom lying out of the plane of the other seven atoms.

The Au–C distances, which fall in the range 2.052(20)–2.086(23) Å, are similar to those found in $[Au_2\{\mu-(CH_2)_2PPh_2\}_2]$ [2.091(7) and 2.085(7) Å],[13] and the Au–S bond lengths 2.293(6)–2.323(6) Å are of the same order as those in bis(dithiocarbamato)digold(I) complexes.[16–18]

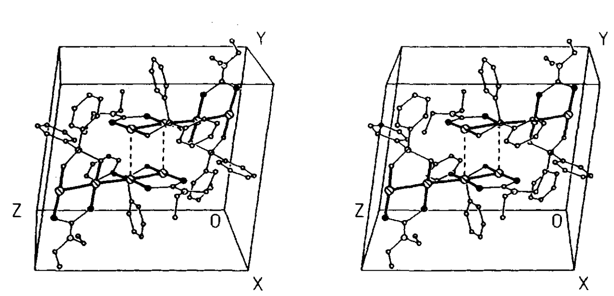
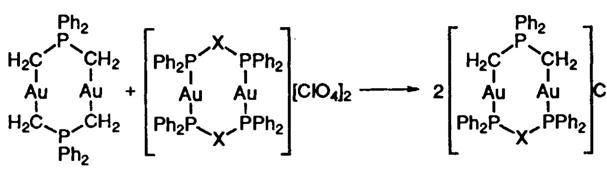


Fig. 2 Stereographic packing diagram for complex **2** with H atoms omitted for clarity. Short non-bonded contacts are indicated by dashed lines

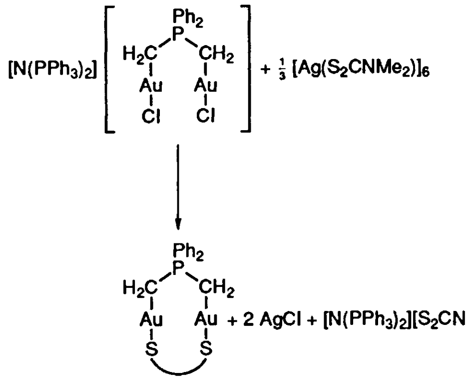
In a similar way, treating the same bis(ylide) dinuclear gold(I) complex with $[Au_2(\mu\text{-diphosphine})_2][ClO_4]_2$ [diphosphine = dppm, $Ph_2PCH_2CH_2PPh_2$ (dppe) or $Ph_2PNHPPh_2$ (dppa)] in 1 : 1 molar ratio gives the cationic heterobridged $[Au_2\{\mu-(CH_2)_2PPh_2\}(\mu\text{-diphosphine})][ClO_4]$ (Scheme 2). Complexes **4**–**6** are air- and moisture-stable white (**4**, **5**) or yellow (**6**) solids. They behave as 1 : 1 electrolytes in acetone solutions and their IR spectra show bands at 1100s (br) and 620m cm^{-1}, which are characteristic of the $[ClO_4]^-$ anion; a band at *ca.* 570m cm^{-1} is due to $\nu(Au-C_{ylide})$.[13] Compounds **4** and **5** were characterised by positive-ion FAB mass spectrometry. The highest peaks at m/z = 991 (**4**) and 1005 (**5**) correspond to the cations $[M - ClO_4]^+$. Other peaks appear at m/z = 581 and 595 {**4**, 44; **5**, 5; $[M - ClO_4 - Au - (CH_2)_2PPh_2]^+$} and 411 (**4**, 90; **5**, 10%; $[Au\{(CH_2)_2PPh_2\}]^+$). The $^{31}P-\{^1H\}$ NMR spectra show a triplet at *ca.* δ 34.8 for the ylidic phosphorus and a doublet for the two phosphorus atoms of the diphosphine (Table 1). The ^1H NMR spectra show the resonances of the ylide methylene protons at δ 1.9 as a doublet of doublets (**5**) or as apparent doublet of triplets (**4**, **6**) (see Experimental section). The cyclic voltammogram of complex **6** shows an irreversible oxidation wave with a peak potential at 0.92 V.

(*b*) *Reactions with Precipitation of* AgCl *or* [AgCl(dppm)].—The reaction of $[N(PPh_3)_2][(AuCl)_2\{\mu-(CH_2)_2PPh_2\}]$ with $[Ag(S_2CNMe_2)]_6$ in the molar ratio 3 : 1 in dichloromethane leads to the precipitation of AgCl. From the solution a mixture of complex **1** and $[N(PPh_3)_2][S_2CNMe_2]$ is obtained (Scheme 3) which cannot be separated because of their similar solubilities in organic solvents.

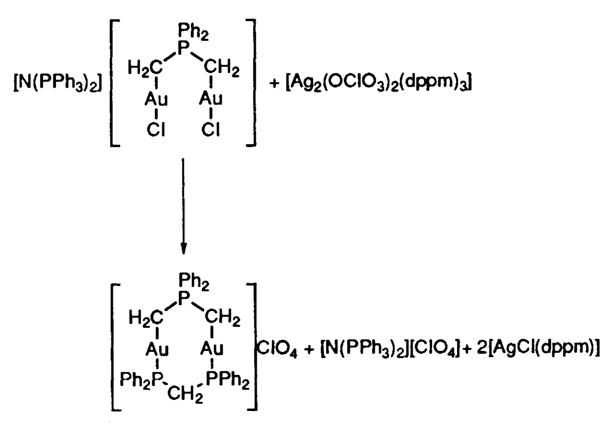
The complex $[N(PPh_3)_2][(AuCl)_2\{\mu-(CH_2)_2PPh_2\}]$ reacts with the silver derivative $[Ag_2(OClO_3)_2(dppm)_3]$ (1 : 1 molar ratio in dichloromethane) to give a white precipitate of



Scheme 2 X = CH_2 **4**, CH_2CH_2 **5** or NH **6**



Scheme 3 S–S = S_2CNMe_2 **1**



Scheme 4

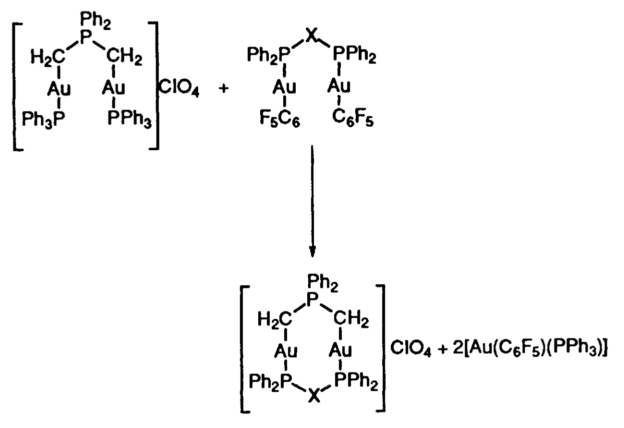
[AgCl(dppm)]. From the solution a mixture of complex **4** and $[N(PPh_3)_2][ClO_4]$ is obtained (Scheme 4), which can be separated because of their different solubilities in methanol.

(*c*) *Reactions with Formation of* $[Au(C_6F_5)(PPh_3)]$.—Complexes **4**–**6** can also be obtained by treating equimolar amounts of $[(AuPPh_3)_2\{\mu\text{-}(CH_2)_2PPh_2\}][ClO_4]$ and $[\{Au(C_6F_5)\}_2(\mu\text{-diphosphine})]$ according to Scheme 5. In a similar way, by treating the same cationic ylide with $[\{Au(C_6F_5)\}_2(\mu\text{-}o\text{-}Ph_2PC_5H_4N)]$ the new heterobridged complex **7** is obtained (Scheme 6). Complex **7** is an air- and moisture-stable yellow solid and behaves as a 1 : 1 electrolyte in acetone solution. The IR spectrum shows bands at 1100s, (br) and 620m cm^{-1} from ClO_4^- and at 565m cm^{-1}, from $\nu(Au\text{–}C_{ylide})$.

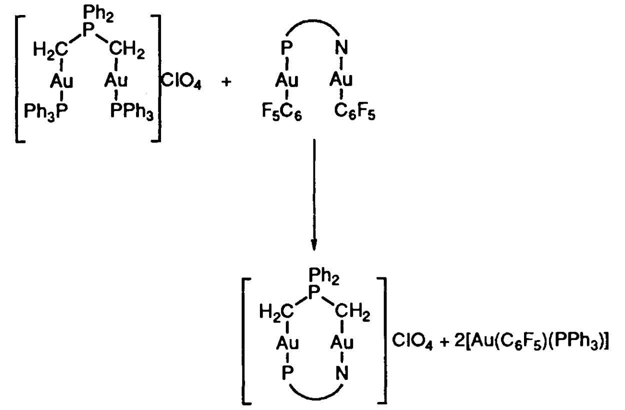
The $^{31}P\text{-}\{^1H\}$ NMR spectrum shows two doublets for the two different phosphorus atoms (Table 1) and the ^1H NMR spectrum two signals for the two different CH_2 groups at δ 2.15 [d, *J*(PH) 13.1] and 1.89 [dd, *J*(PH) 12.0 and 9.0 Hz].

Experimental

Infrared spectra were recorded on a Perkin-Elmer 559 or 883 spectrophotometer, over the range 4000–200 cm^{-1}, by using Nujol mulls between polyethylene sheets, ^1H and ^{31}P NMR spectra on a Varian UNITY 300 in $CDCl_3$ solutions; chemical shifts are quoted relative to $SiMe_4$ (^1H) and H_3PO_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. Mass spectra were recorded on a VG Autospec.



Scheme 5 X = CH_2 **4**, CH_2CH_2 **5** or NH **6**



Scheme 6 P–N = $o\text{-}Ph_2PC_5H_4N$ **7**

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 a platinum bead. 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_2Cl_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. Under these conditions the E° values for the couples $[Fe(\eta\text{-}C_5H_5)_2]^+\text{–}[Fe(\eta\text{-}C_5H_5)_2]$ and $[Fe(\eta\text{-}C_5Me_5)_2]^+\text{–}[Fe(\eta\text{-}C_5Me_5)_2]$ used as internal standards, are 0.47 and −0.09 V respectively.

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

Syntheses.—$[Au_2\{\mu\text{-}(CH_2)_2PPh_2\}(\mu\text{-}S_2CNR_2)]$ (R = Me **1**, Et **2** or CH_2Ph **3**). These complexes can be obtained in three different ways.

(*a*) To a solution of $[Au_2\{\mu\text{-}(CH_2)_2PPh_2\}_2]$[15] (0.082 g, 0.1 mmol) in dichloromethane (40 cm^3) was added $[Au_2(\mu\text{-}S_2CNR_2)_2]$ {obtained by reaction of $[Au(tht)_2][ClO_4]$[20] and a slight excess of NaS_2CNR_2} [0.1 mmol; R = Me (0.064 g), Et (0.069 g), or CH_2Ph (0.094 g)]. After stirring for 4 d (**1**), 1 d (**2**) or 2 h (**3**) the unreacted starting material was filtered off. The clear solution was evaporated to *ca*. 5 cm^3 and addition of diethyl ether led to precipitation of complexes **1**–**3**.

(*b*) To a solution of $[N(PPh_3)_2][(AuCl)_2\{\mu\text{-}(CH_2)_2PPh_2\}]$ (0.122 g, 0.1 mmol) in dichloromethane (20 cm^3) was added $[Ag(S_2CNMe_2)]_6$ (obtained by reaction of $AgClO_4$ and a slight excess of NaS_2CNMe_2) (0.046 g, 0.033 mmol) and the mixture was stirred for 90 min, protected from light. The AgCl precipitated was filtered off and the solution evaporated to *ca.* 5 cm^3. Addition of diethyl ether (15 cm^3) led to precipitation of a mixture of complex **1** and $[N(PPh_3)_2][S_2CNMe_2]$.

Table 2 Selected bond lengths (Å) and angles (°) for complex **2**

Au(1)–C(1)	2.083(19)	Au(1)–S(1)	2.305(6)
Au(1)–Au(2)	2.868(1)	Au(2)–C(2)	2.052(20)
Au(2)–S(2)	2.307(6)	Au(2)–Au(3)	2.984(1)
P(1)–C(1)	1.749(20)	P(1)–C(2)	1.777(20)
P(1)–C(11)	1.805(12)	P(1)–C(21)	1.819(12)
S(1)–C(5)	1.721(21)	S(2)–C(5)	1.737(22)
C(5)–N(1)	1.305(27)	Au(3)–C(3)	2.071(19)
Au(3)–S(3)	2.323(6)	Au(3)–Au(4)	2.867(1)
Au(3) ··· Au(4i)	3.696(2)	Au(4)–C(4)	2.086(23)
Au(4)–S(4)	2.293(6)	P(2)–C(4)	1.738(22)
P(2)–C(3)	1.766(19)	P(2)–C(31)	1.809(13)
P(2)–C(41)	1.843(10)	S(3)–C(6)	1.736(19)
S(4)–C(6)	1.719(20)	C(6)–N(2)	1.304(27)
C(1)–Au(1)–S(1)	174.7(5)	C(1)–Au(1)–Au(2)	90.8(5)
S(1)–Au(1)–Au(2)	94.12(14)	C(2)–Au(2)–S(2)	178.3(6)
C(2)–Au(2)–Au(1)	90.0(5)	S(2)–Au(2)–Au(1)	91.00(14)
C(2)–Au(2)–Au(3)	96.5(5)	S(2)–Au(2)–Au(3)	82.52(14)
Au(1)–Au(2)–Au(3)	173.4(1)	C(1)–P(1)–C(2)	110.7(10)
C(1)–P(1)–C(11)	108.8(8)	C(2)–P(1)–C(11)	111.5(8)
C(1)–P(1)–C(21)	109.0(8)	C(2)–P(1)–C(21)	111.4(8)
C(11)–P(1)–C(21)	105.2(7)	C(5)–S(1)–Au(1)	113.1(8)
C(5)–S(2)–Au(2)	115.4(8)	P(1)–C(1)–Au(1)	110.6(10)
P(1)–C(2)–Au(2)	110.4(10)	N(1)–C(5)–S(1)	119.5(17)
N(1)–C(5)–S(2)	114.7(16)	S(1)–C(5)–S(2)	125.8(14)
C(3)–Au(3)–S(3)	175.5(6)	C(3)–Au(3)–Au(4)	89.1(5)
S(3)–Au(3)–Au(4)	92.89(13)	C(3)–Au(3)–Au(2)	92.2(5)
S(3)–Au(3)–Au(2)	86.06(13)	Au(4)–Au(3)–Au(2)	175.7(1)
C(4)–Au(4)–S(4)	175.4(6)	C(4)–Au(4)–Au(3)	92.0(6)
S(4)–Au(4)–Au(3)	92.63(14)	C(4)–P(2)–C(3)	112.3(10)
C(4)–P(2)–C(31)	109.4(10)	C(3)–P(2)–C(31)	111.7(9)
C(4)–P(2)–C(41)	109.8(9)	C(3)–P(2)–C(41)	110.4(8)
C(31)–P(2)–C(41)	102.9(7)	C(6)–S(3)–Au(3)	113.0(7)
C(6)–S(4)–Au(4)	114.6(7)	P(2)–C(3)–Au(3)	112.0(10)
P(2)–C(4)–Au(4)	107.8(12)	N(2)–C(6)–S(4)	115.7(15)
N(2)–C(6)–S(3)	117.4(16)	S(4)–C(6)–S(3)	126.8(12)

Symmetry operator: (i) $1 - x$, $1 - y$, $1 - z$.

(*c*) To a solution of $[(AuPPh_3)_2\{\mu\text{-}(CH_2)_2PPh_2\}][ClO_4]$ (0.123 g, 0.1 mmol) in dichloromethane (20 cm^3) was added $[NBu_4][\{Au(C_6F_5)\}_2(\mu\text{-}S_2CNMe_2)]$ {obtained by reaction of $[Au(C_6F_5)(tht)]$[21] (tht = tetrahydrothiophene) and a slight excess of $[NBu_4][S_2CNMe_2]$} (0.109 g, 0.1 mmol) and the mixture stirred for 4 h. Concentration of the solution to *ca.* 3 cm^3 and addition of diethyl ether (15 cm^3) gave a mixture of complex **1**, $[Au(C_6F_5)(PPh_3)]$ and NBu_4ClO_4. The complex $[Au(C_6F_5)(PPh_3)]$ was removed by washing the solid with diethyl ether (4 × 5 cm^3) and NBu_4ClO_4 was removed by washing the resulting solid with MeOH–Et_2O (1 : 1 ratio, 4 × 5 cm^3). Complex **1** was recrystallised from dichloromethane–diethyl ether.

^{1}H NMR: **1**, δ 7.78–7.45 (m, Ph), 3.46 (s, Me) and 1.87 [d, *J*(PH) = 12.9, CH_2]; **2**, δ 7.78–7.46 (m, Ph), 3.88 [c, *J*(HH) = 7.0, CH_2N], 1.87 [d, *J*(PH) = 12.7, CH_2P] and 1.27 (t, CH_3); **3**, δ 7.78–7.28 (m, Ph), 5.14 (s, CH_2N) and 1.91 [d, *J*(PH) = 12.7 Hz, CH_2P].

$[Au_2\{\mu\text{-}(CH_2)_2PPh_2\}(\mu\text{-}L\text{–}L)][ClO_4]$ (L–L = dppm **4**, dppe **5**, dppa **6**, *or* *o*-$Ph_2PC_5H_4N$ **7**). These complexes can be obtained in three different ways.

(*a*) To a solution of $[Au_2\{\mu\text{-}(CH_2)_2PPh_2\}_2]$[15] (0.082 g, 0.1 mmol) in dichloromethane (30 cm^3) was added $[Au_2(\mu\text{-}L\text{–}L)_2][ClO_4]_2$[22] [0.1 mmol; L–L = dppm (0.136 g), dppe (0.139 g), or dppa (0.136 g)]. After stirring for the mixture for 2 h the solution was concentrated to *ca.* 5 cm^3. Addition of diethyl ether (20 cm^3) led to precipitation of complexes **4**–**6**.

(*b*) To a solution of $[N(PPh_3)_2][(AuCl)_2\{\mu\text{-}(CH_2)_2PPh_2\}]$ (0.122 g, 0.1 mmol) in dichloromethane (20 cm^3) was added $[Ag_2(OClO_3)_2(dppm)_3]$ (0.157 g, 0.1 mmol) and the mixture was stirred for 2 h, protected from light. The [AgCl(dppm)] precipitated was filtered off and the solution was evaporated to *ca.* 5 cm^3. A new crop of [AgCl(dppm)] was formed. Filtration and subsequent addition of diethyl ether (20 cm^3) led to the precipitation of a mixture containing complex **4**, $[N(PPh_3)_2][ClO_4]$ and a small amount of [AgCl(dppm)]. The salt $[N(PPh_3)_2][ClO_4]$ was removed by washing with methanol (2 × 2 cm^3). Complex **4** was recrystallised from dichloromethane–diethyl ether.

(*c*) To a solution of $[(AuPPh_3)_2\{\mu\text{-}(CH_2)_2PPh_2\}][ClO_4]$ (0.123 g, 0.1 mmol) in dichloromethane (20 cm^3) was added $[\{Au(C_6F_5)\}_2(\mu\text{-}L\text{–}L)]$[22,23] [0.1 mmol; L–L = dppm (0.111 g),

Table 3 Atomic coordinates (× 10^4) for complex **2**

Atom	*x*	*y*	*z*
Au(1)	1 982.8(7)	6 340.8(7)	729.2(5)
Au(2)	3 144.9(7)	6 293.3(7)	2 494.9(5)
P(1)	1 744(4)	4 015(5)	1 356(4)
S(1)	2 910(5)	8 158(5)	665(4)
S(2)	4 259(5)	8 068(5)	2 495(4)
C(1)	1 030(17)	4 714(16)	701(13)
C(2)	2 141(18)	4 727(17)	2 534(14)
C(5)	3 886(18)	8 747(19)	1 611(15)
N(1)	4 448(16)	9 783(16)	1 679(13)
C(11)	2 954(10)	3 852(12)	731(9)
C(12)	4 009(11)	4 074(12)	1 202(7)
C(13)	4 900(9)	3 859(14)	710(10)
C(14)	4 736(11)	3 422(14)	−253(10)
C(15)	3 681(13)	3 200(13)	−725(7)
C(16)	2 790(10)	3 416(13)	−233(9)
C(21)	847(11)	2 625(9)	1 367(10)
C(22)	1 163(10)	1 993(12)	1 988(9)
C(23)	513(13)	919(11)	2 003(10)
C(24)	−454(13)	477(9)	1 396(11)
C(25)	−770(10)	1 109(12)	774(10)
C(26)	−120(12)	2 183(11)	760(9)
C(51)	5 307(22)	10 397(24)	2 442(18)
C(52)	6 479(30)	10 364(31)	2 169(25)
C(53)	4 213(22)	10 494(22)	986(17)
C(54)	3 322(29)	10 983(29)	1 278(23)
Au(3)	4 538.2(6)	6 487.0(7)	4 295.8(5)
Au(4)	5 793.9(7)	6 500.3(8)	6 029.3(5)
P(2)	7 220(4)	7 201(5)	4 332(4)
S(3)	2 911(5)	6 494(5)	5 078(4)
S(4)	4 280(5)	6 492(5)	6 933(4)
C(3)	5 990(16)	6 600(17)	3 570(13)
C(4)	7 248(19)	6 516(20)	5 309(15)
C(6)	3 069(17)	6 463(17)	6 296(14)
N(2)	2 199(16)	6 466(16)	6 796(13)
C(31)	7 381(12)	8 638(10)	4 747(10)
C(32)	6 492(10)	9 088(12)	4 639(10)
C(33)	6 602(12)	10 169(12)	5 034(11)
C(34)	7 599(14)	10 800(10)	5 538(11)
C(35)	8 487(11)	10 350(12)	5 646(11)
C(36)	8 378(11)	9 269(13)	5 251(11)
C(41)	8 487(9)	7 242(11)	3 664(8)
C(42)	9 261(11)	6 726(11)	3 957(8)
C(43)	10 212(10)	6 743(12)	3 449(10)
C(44)	10 388(10)	7 276(13)	2 648(9)
C(45)	9 614(12)	7 791(12)	2 355(8)
C(46)	8 663(10)	7 774(11)	2 863(9)
C(55)	1 049(20)	6 370(20)	6 339(16)
C(56)	937(26)	7 496(25)	6 360(21)
C(57)	2 204(19)	6 490(18)	7 839(14)
C(58)	2 030(20)	5 323(20)	8 125(16)

dppe (0.113 g), dppa, (0.111 g) or o-$Ph_2PC_5H_4N$ (0.099 g)] and the mixture stirred for 1 h. Concentration of the solution to *ca.* 3 cm^3 and addition of diethyl ether (15 cm^3) gave a mixture of complexes **4**–**7** and $[Au(C_6F_5)(PPh_3)]$. The latter was removed by washing the solid with diethyl ether (4 × 5 cm^3). Complexes **4**–**7** were recrystallised from dichloromethane–diethyl ether.

^1H NMR: **4**, δ 7.78–7.35 (m, Ph), 3.68 [t, J(PH) = 11.4, PCH_2P] and 1.97 ['dt', J(PH) = 13.4, N = 8.2, CH_2P]; **5**, δ 7.75–7.35 (m, Ph), 2.79 [d, J(PH) = 11.9, $(CH_2)_2$] and 1.92 [dd, J(PH) = 13.1 and 8.1, CH_2P]; **6**, δ 7.78–7.35 (m, Ph), 6.7 (br s, NH) and 1.87 ['dt', J(PH) = 13.1, N = 8.2 Hz, CH_2P]; **7**, δ 7.74–7.35 (m, Ph and C_5H_4), 2.15 [d, J(PH) = 13.1, CH_2] and 1.89 [dd, J(PH) = 12.0 and 9.0 Hz, CH_2].

Structure Determination of Compound **2**.—*Crystal data.* $C_{19}H_{24}Au_2NPS_2$, M = 755.42, triclinic, space group $P\bar{1}$, a = 12.377(2), b = 12.806(3), c = 14.146(3) Å, α = 97.67(3), β = 91.40(3), γ = 106.18(3)°, U = 2129.6(8) $Å^3$, Z = 4, D_c = 2.356 Mg m^{-3}, λ(Mo-Kα) = 0.710 73 Å, μ = 14.04 mm^{-1}, T = −40 °C, F(000) = 1400.

A yellow prism 0.36 × 0.17 × 0.13 mm was mounted on a glass fibre and used to collect 5867 intensities to $2\theta_{max}$ 45° (Siemens AED-2 diffractometer with monochromated Mo-Kα radiation). An absorption correction based on Ψ scans was applied, with transmission factors 0.24–0.62. Merging equivalents gave 5553 independent reflections (R_{int} 0.035) which were used for all calculations (program system SHELXL 93).[24] Cell constants were refined from setting angles of 72 reflections in the range 2θ 22.92–36.18°.

Structure solution and refinement. The structure was solved by the heavy-atom method and subjected to full matrix least-squares refinement on F^2 (Au, P and S atoms anisotropic, idealised phenyl groups and other H atoms using a riding model). The weighting scheme was $w^{-1} = \sigma^2(F^2) + (aP)^2 + bP$, where $3P = F_o^2 + 2F_c^2$, with a = 0.061 and b = 34.2014. Refinement proceeded to $wR(F^2)$ 0.156, conventional $R(F)$ 0.056 for 203 parameters, S = 1.054; maximum Δρ 1.4 e $Å^{-3}$. Selected bond lengths and angles are given in Table 2, final atomic coordinates in Table 3.

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

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References

1 H. Schmidbaur, *Organogold Compounds, Gmelin Handbuch der Anorganischen Chemie*, Springer, Berlin, 1980.
2 R. Usón and A. Laguna, *Coord. Chem. Rev.*, 1986, **70**, 1.
3 P. G. Jones, *Gold Bull.*, 1981, **14**, 102; 1981, **14**, 159; 1983, **16**, 114; 1986, **19**, 46.
4 P. Pyykko, *Chem. Rev.*, 1988, **88**, 563.
5 H. Schmidbaur, *Gold Bull.*, 1990, **23**, 11.
6 H. R. C. Jaw, M. M. Savas, R. D. Rogers and W. R. Mason, *Inorg. Chem.*, 1989, **28**, 1028.
7 Md. N. I. Khan, S. Wang and J. P. Fackler, jun., *Inorg. Chem.*, 1989, **28**, 3579.
8 Md. N. I. Khan, C. King, D. D. Heinrich, J. P. Fackler, jun. and L. C. Porter, *Inorg. Chem.*, 1989, **28**, 2150.
9 H. Schmidbaur and J. R. Mandl, *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 640.
10 R M. Davila, A. Elduque, T. Grant, R. J. Staples and J. P. Fackler, jun., *Inorg. Chem.*, 1993, **32**, 1749.
11 R. Narayanaswamy, M. A. Young, E. Parkhurst, M. Ouellette, M. E. Kerr, D. M. Ho, R. C. Elder, A. E. Bruce and M. R. M. Bruce, *Inorg. Chem.*, 1993, **32**, 2506.
12 R. Usón, A. Laguna, M. Laguna, A. Usón and M. C. Gimeno, *Organometallics*, 1987, **6**, 682.
13 H. Schmidbaur and R. Franke, *Inorg. Chim. Acta*, 1975, **13**, 85; *Angew. Chem.*, 1975, **108**, 1321.
14 H. J. A. Blaauw, R. J. F. Nivard and G. J. M. Van der Kerk, *J. Organomet. Chem.*, 1964, **2**, 236.
15 J. D. Basil, H. H. Murray, J. P. Fackler, jun., J. Tocher, A. M. Mazany, B. Trzcinska-Bancroft, H. Knachel, D. Dudis, T. J. Delord and D. O. Marler, *J. Am. Chem. Soc.*, 1985, **107**, 6908.
16 R. Hesse and P. Jennische, *Acta Chem. Scand.*, 1972, **26**, 3855.
17 P. Jennische, H. Anacker-Eickhoff and A. Wahlberg, *Acta Crystallogr., Sect A*, 1975, **31**, 5143.
18 D. D. Heinrich, J. C. Wang and J. P. Fackler, jun., *Acta Crystallogr. Sect. C*, 1990, **46**, 1444.
19 I. J. B. Lin, C. W. Liu, L. K. Lin and Y. S. Wen, *Organometallics*, 1992, **11**, 1447.
20 R. Usón, A. Laguna, M. Laguna, J. Jiménez, M. P. Gómez and A. Sainz, *J. Chem. Soc., Dalton Trans.*, 1990, 3457.
21 R. Usón, A. Laguna and M. Laguna, *Inorg. Synth.*, 1990, **26**, 85.
22 R. Usón, A. Laguna, M. Laguna, M. N. Fraile, P. G. Jones and G. M. Sheldrick, *J. Chem. Soc., Dalton Trans.*, 1986, 291.
23 R. Usón, A. Laguna, J. Vicente and J. García, *Rev. Acad. Cienc. Exactas, Fis. Quim. Nat. Zaragoza*, 1976, **31**, 77.
24 G. M. Sheldrick, SHELXL 93, A Program for Crystal Structure Refinement (pre-releasc version), University of Göttingen, 1992.

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