Triorganophosphinegold(I) Complexes of Pyridine-2-thionate and Pyrimidine-2-thionate†

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Triorganophosphinegold(I) complexes of the anions derived from pyridine-2-thione (2-pySH) and 1*H*-pyrimidine-2-thione (2-pymSH), [Au(PR$_3$)(SR')] (R = Et, Ph or C_6H_{11}), have been prepared and characterized by spectroscopic (IR, ^{1}H and ^{13}C NMR and fast atom bombardment MS) methods and for the PPh$_3$ compounds by X-ray crystallographic techniques. The mononuclear compounds feature linear gold atom geometries defined by P and S atoms with important parameters for [Au(PPh$_3$)(2-pyS)]: Au–P 2.258(1), Au–S 2.297(2) Å and P–Au–S 177.9(1)° and for [Au(PPh$_3$)(2-pymS)]: Au–P 2.253(2), Au–S 2.310(3) Å and P–Au–S 174.7(1)°. The [Au(PPh$_3$)(2-pyS)] complex **2** crystallizes in the monoclinic space group $P2_1/c$ with unit-cell dimensions a = 12.235(1), b = 10.009(2), c = 17.292(2) Å, β = 104.08(1)° and Z = 4; [Au(PPh$_3$)(2-pymS)] **5** crystallizes in the triclinic space group $P\bar{1}$ with a = 11.006(2), b = 11.356(4), c = 8.873(1) Å, α = 109.85(2), β = 95.72(1), γ = 93.55(2)° and Z = 2. The structures were refined to final R = 0.025 for 2527 reflections with $I \geqslant 2.5\sigma(I)$ and R = 0.057 for 3416 reflections with $I \geqslant 2.5\sigma(I)$ for **2** and **5**, respectively.

Interest in the co-ordination chemistry of gold(I) complexes arises in part from the use and potential use of certain gold(I) complexes in medicine. Water-soluble, polymeric gold(I) thiolates such as gold sodium thiomalate (Myochrysin) and gold sodium thiosulfate (Sanochrysin) are used in the treatment of rheumatoid arthritis.[1,2] Also employed in this context is the monomeric, lipid-soluble triethylphosphinogold(I)–thioglucose derivative, Auranofin [(1-thio-β-D-glucopyranose 2,3,4,6-tetraacetato-*S*)(triethylphosphine)gold(I)].[3,4] Despite the effectiveness of gold(I) thiolates against rheumatoid arthritis a major drawback for this class of compound is their associated toxicity.[2] A more recent development concerns an examination of the anti-tumour activity of gold(I) phosphine complexes containing the P–Au–S chromophore and, in particular, the bis-chelated gold(I) complex of dppe [where dppe is 1,2-bis(diphenylphosphino)ethane], [Au(dppe)$_2$]$^+$.[5,6] Despite showing promising activity, problems concerning the toxicity of the latter compound have precluded its further development as a potential anti-tumour drug.[7] As a consequence of the above mentioned medicinal applications, the chemistry of gold(I) has attracted renewed attention generated by the necessity to prepare less toxic derivatives while retaining efficacy. This contribution reports the characterization of a series of complexes of the general formula [Au(PR$_3$)(SR')] [R = Et, Ph or C_6H_{11}; HSR' = pyridine-2-thione (2-pySH) or 1*H*-pyrimidine-2-thione (2-pymSH)] which were investigated as an extension of previous studies in the field. The preparation of the two PPh$_3$ complexes, [Au(PPh$_3$)(SR')], has been reported briefly as has a crystal-structure determination for [Au(2-pyS)$_2$]ClO$_4$.[8]

Experimental

Elemental analyses were performed by the Chemical and Analytical Services (Geelong, Victoria). Infrared spectra were measured on a Perkin Elmer 1720X FT spectrometer, in KBr discs, calibrated using the polystyrene absorption at 1601.4 cm^{-1}. NMR spectra were recorded in (CD$_3$)$_2$SO solutions on an ACP300 spectrometer (^{1}H at 300.13, ^{13}C at 75.47 MHz); the internal reference was SiMe$_4$ in all cases. Fast atom bombardment (FAB) mass spectra were obtained on a VG ZAB 2HF instrument equipped with a FAB source. Argon was used as the exciting gas with the source pressure typically 10^{-6} mbar (≈1 × 10^{-4} Pa), the FAB voltage was 7 kV and the current 1 mA. The ion accelerating potential was 8 kV and the matrix employed was 3-nitrobenzyl alcohol. The complexes were made up as *ca.* 0.5 mol dm^{-3} solutions in dichloromethane; a drop was added to a drop of the matrix and the mixture was applied to the FAB probe tip.

The [Au(PR$_3$)Cl] compounds were prepared according to the literature procedure.[9] The 2-pySH and 2-pymSH thioligands were purchased from Sigma. Analytical grade solvents were used without further purification.

Preparation of [Au(PEt$_3$)(2-pyS)].—To an ethanolic solution (20 cm^3) of [Au(PR$_3$)Cl] (200 mg, 0.572 mmol) was added 1 mol equivalent of 2-pySH and KOH (ethanol solution, *ca.* 0.2 mol dm^{-3}, added dropwise over 5 min). The mixture was stirred for 2 h at room temperature and left to stand overnight. The product that precipitated from this solution was filtered off and recrystallized from acetone; the remaining complexes were prepared in a similar manner. Physical data are listed in Table 1.

Crystallography.—Intensity data for colourless crystals of [Au(PPh$_3$)(2-pyS)] **2** and [Au(PPh$_3$)(2-pymS)] **5** were measured at room temperature on an Enraf-Nonius CAD4*F* diffractometer equipped with Mo-Kα radiation (graphite monochromator), λ = 0.7107 Å using the ω–2θ scan technique. Neither crystal exhibited significant decay during X-ray exposure. The data sets were corrected for Lorentz and polarization effects and for absorption employing an analytical procedure;[10] crystal data are compiled in Table 2.

The structures were each solved by the Patterson method and refined by a full-matrix least-squares procedure based on *F*.[10] Non-hydrogen atoms were refined with anisotropic thermal parameters and H atoms were included in each model at their calculated positions (C–H 0.97 Å) and assigned a common isotropic thermal parameter. A weighting scheme of the form

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Table 1 Analytical, physical and infrared (cm^{-1}) data for the [Au(PR_3)(SR′)] complexes[a]

Compound	Yield (%)	Physical state	M.p./°C	Analysis (%)[b] C	Analysis (%)[b] H	Selected infrared vibrations[c]
1 [Au(PEt_3)(2-pyS)]	88	Pale yellow solid	77–78	31.30 (31.05)	4.65 (4.50)	1572s, 1547m, 1447m
2 [Au(PPh_3)(2-pyS)]	96	Yellow solid	193–194	49.55 (48.50)	3.50 (3.35)	1574s, 1547m, 1449m, 1408s
3 [Au{P(C_6H_{11})$_3$}(2-pyS)]	70	Pale green solid	162–163	44.80 (44.90)	6.25 (6.15)	1571s, 1547m, 1408s
4 [Au(PEt_3)(2-pymS)]	60	Pale green solid	41–42	28.25 (28.20)	4.45 (4.25)	1266s, 1203m, 1177m
5 [Au(PPh_3)(2-pymS)]	86	Pale yellow solid	196–197	46.70 (46.35)	3.25 (3.20)	1239m, 1200m, 1180m, 1170s, 1161 (sh)
6 [Au{P(C_6H_{11})$_3$}(2-pymS)]	69	Pale yellow solid	174–175	44.80 (44.90)	6.25 (6.15)	1236m, 1195m, 1169s

[a] Measured in KBr discs. [b] Calculated values in parentheses. [c] Selected bands for 2-pySH, 1573s, 1494m, 1478 (sh) and 1438m; for 2-pymSH, 1212s, 1187s and 1169 (sh).

Table 2 Crystal data for [Au(PPh_3)(2-pyS)] and [Au(PPh_3)(2-pymS)]

Compound	[Au(PPh_3)(2-pyS)]	[Au(PPh_3)(2-pymS)]
Formula	$C_{23}H_{19}AuNPS$	$C_{22}H_{18}AuN_2PS$
M	569.4	570.4
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
a/Å	12.235(1)	11.006(2)
b/Å	10.009(2)	11.356(4)
c/Å	17.292(2)	8.873(1)
α/°	90	109.85(2)
β/°	104.08(1)	95.72(1)
γ/°	90	93.55(2)
U/Å^3	2054.0	1032.5
Z	4	2
D_c/g cm^{-3}	1.841	1.835
Crystal size (mm)	0.06 × 0.56 × 0.16	0.25 × 0.06 × 0.41
μ/cm^{-1}	72.98	72.61
Maximum, minimum transmission factors	0.657, 0.298	0.574, 0.112
F(000)	1096	548
No. data measured	4414	5502
θ_{max}/°	25.0	27.5
No. unique data	3617	4749
No. observed data, $I \geqslant 2.5\sigma(I)$	2527	3416
R	0.025	0.057
k	1.0	0.78
g	0.0011	0.0064
R'	0.027	0.058

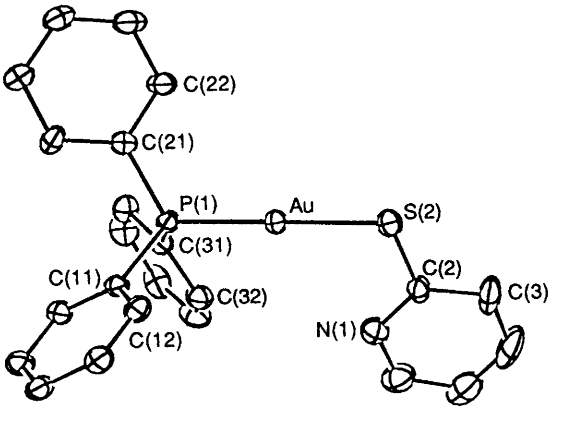

Fig. 1 Molecular structure and crystallographic numbering scheme for [Au(PPh_3)(2-pyS)]

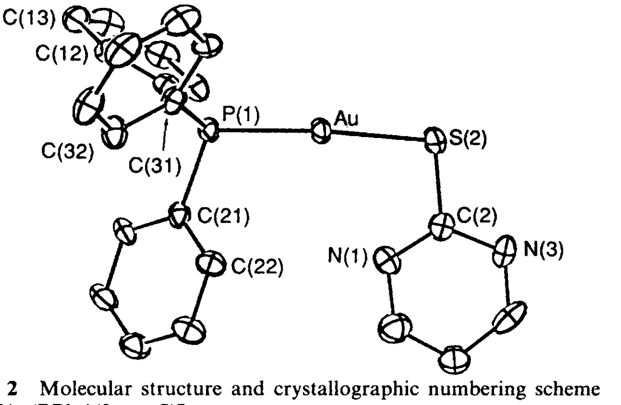

Fig. 2 Molecular structure and crystallographic numbering scheme for [Au(PPh_3)(2-pymS)]

$w = k/[\sigma^2(F) + |g|F^2]$ was introduced for both refinements which were continued until convergence; final refinement details are given in Table 2. The analysis of variance showed no special features indicating that an appropriate weighting scheme had been applied for both models. The maximum residual electron density peak in the final difference map for each structure, *i.e.* 1.24 and 2.91 e Å^{-3}, respectively, was located in the vicinity of the Au atom. Fractional atomic coordinates are listed in Tables 3 and 4 and the numbering schemes employed are shown in Figs. 1 and 2 which were drawn with ORTEP[11] with

Table 3 Fractional atomic coordinates ($\times 10^5$ for Au, $\times 10^4$ for remaining atoms) for [Au(PPh_3)(2-pyS)] **2**

Atom	*x*	*y*	*z*
Au	20 733(2)	7 793(2)	10 372(1)
P(1)	1 630(1)	−1 377(1)	1 196(1)
S(2)	2 534(1)	2 954(2)	832(1)
N(1)	3 752(4)	1 561(5)	15(3)
C(2)	3 358(4)	2 766(5)	141(3)
C(3)	3 599(6)	3 884(6)	−264(5)
C(4)	4 253(7)	3 723(9)	−799(5)
C(5)	4 638(6)	2 505(8)	−943(5)
C(6)	4 356(6)	1 474(8)	−521(5)
C(11)	2 757(4)	−2 282(5)	1 881(3)
C(12)	3 517(5)	−1 567(6)	2 460(3)
C(13)	4 386(5)	−2 205(6)	2 978(3)
C(14)	4 511(5)	−3 576(6)	2 932(4)
C(15)	3 757(5)	−4 291(6)	2 358(4)
C(16)	2 887(4)	−3 636(5)	1 838(3)
C(21)	359(4)	−1 631(5)	1 537(3)
C(22)	−494(5)	− 673(6)	1 349(4)
C(23)	−1 459(5)	− 823(6)	1 609(4)
C(24)	−1 605(5)	−1 926(6)	2 049(4)
C(25)	−797(5)	−2 893(6)	2 221(4)
C(26)	190(5)	−2 744(6)	1 969(4)
C(31)	1 448(4)	−2 274(5)	257(3)
C(32)	2 276(5)	−2 081(6)	−156(4)
C(33)	2 194(6)	−2 761(7)	−865(4)
C(34)	1 314(6)	−3 604(7)	−1 158(4)
C(35)	497(6)	−3 752(7)	−761(4)
C(36)	556(5)	−3 086(6)	−50(4)

Table 4 Fractional atomic coordinates ($\times 10^5$ for Au, $\times 10^4$ for remaining atoms) for [Au(PPh_3)(2-pymS)] **5**

Atom	*x*	*y*	*z*
Au	3 569(3)	33 168(4)	11 852(4)
P(1)	2 143(2)	4 040(2)	612(3)
S(2)	−1 366(3)	2 499(3)	1 925(4)
N(1)	362(8)	974(8)	1 928(9)
N(3)	−1 537(8)	503(8)	2 784(9)
C(2)	−776(8)	1 196(8)	2 243(9)
C(4)	−1 068(11)	−471(8)	3 065(10)
C(5)	112(10)	−790(9)	2 784(11)
C(6)	759(11)	−48(10)	2 180(12)
C(11)	2 600(8)	5 705(8)	1 646(9)
C(12)	3 195(9)	6 434(8)	944(10)
C(13)	3 571(10)	7 668(9)	1 778(11)
C(14)	3 323(11)	8 216(10)	3 369(12)
C(15)	2 725(10)	7 504(10)	4 086(11)
C(16)	2 339(9)	6 239(9)	3 236(10)
C(21)	3 362(7)	3 232(8)	1 246(9)
C(22)	4 481(8)	3 863(9)	2 134(10)
C(23)	5 380(9)	3 178(10)	2 567(11)
C(24)	5 173(10)	1 905(10)	2 112(11)
C(25)	4 083(10)	1 287(10)	1 240(11)
C(26)	3 160(9)	1 957(9)	816(10)
C(31)	2 226(8)	3 742(8)	−1 510(9)
C(32)	3 281(9)	3 389(9)	−2 210(10)
C(33)	3 273(11)	3 158(10)	−3 851(10)
C(34)	2 221(11)	3 276(10)	−4 767(10)
C(35)	1 200(11)	3 601(10)	−4 115(10)
C(36)	1 184(9)	3 850(8)	−2 461(9)

15% probability ellipsoids. Scattering factors for neutral Au (corrected for *f′* and *f″*) were from ref. 12 while those for the remaining atoms were those incorporated in SHELX 76.[10] Refinements were performed on a SUN4/280 workstation.

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

Results and Discussion

The equimolar reaction between [Au(PR_3)Cl], base and 2-pySH or 2-pymSH in ethanol solution yielded solid complexes of the general formula [Au(PR_3)(SR′)], Table 1. The important features of the infrared spectra recorded in KBr discs for the free ligands and the complexes **1**–**6** are listed in Table 1. Although not particularly informative the spectra do confirm the presence of both the phosphine and thioligands. Noteworthy in the spectra of the complexes **1**–**3** is the absence of ν(NH) [and ν(SH)] suggesting deprotonation of the ligand. Confirmation of the presence of the thiolate anion, [2-pyS]$^-$, is found in the set of bands in the region 1400–1600 cm^{-1} which are attributable to ring vibration,[13] after allowance has been made for the absorptions due to the phosphine ligands which occur in the overlapping region 1400–1500 cm^{-1}. For the 2-pymS complexes **4**–**6** the bands due to ν(NH) in the free ligand (3076m and 3054m cm^{-1}) are absent, again suggesting deprotonation of the ligand. The spectra of **4**–**6** contain bands in the region 1270–1150 cm^{-1} which have been assigned to a mixture of ν(CN), ν(NCS) and ν(CS) modes[14] and are often labelled the 'thioamide III' region.[15]

The FAB MS of the R = Et or Ph compounds were relatively featureless and contrasted with those of the R = C_6H_{11} complexes. The spectra of **2**, **5** and **6** were virtually identical with only two ions being observed, *i.e.* [Au(PR_3)]$^+$, the most abundant ion, and the molecular ion, [*M*]$^+$. For **1** two ions were again observed, *i.e.* [*M*]$^+$ with relative abundance 92% with the other being [Au(PEt_3)$_2$]$^+$. The spectra of the two cyclohexyl compounds featured many more ions with the most abundant being [Au{P(C_6H_{11})$_3$}]$^+$ and [*M*]$^+$ for **3** and **6**, respectively (both being present in each spectrum). The other major ions common to both complexes were [Au{P(C_6H_{11})$_3$}$_2$]$^+$, [S{Au[P(C_6H_{11})$_3$]}$_2$]$^+$, [AuS{Au[P(C_6H_{11})$_3$]}$_2$]$^+$ and [S{Au[P(C_6H_{11})$_3$]}$_3$]$^+$.

The ^1H and ^{13}C NMR data recorded in $(CD_3)_2SO$ solution for the ligands and complexes are listed in Table 5; similar results were obtained in $(CD_3)_2CO$ solution. The integration and multiplicities for the ^1H NMR spectra are consistent with the formulations of the compounds as [Au(PR_3)(SR′)]. As expected the resonances due to NH in the free ligands are absent in the spectra of the complexes confirming deprotonation of the ligands. Noteworthy in the spectra of **4**–**6** is the equivalence of the H(4) and H(6) protons which suggests free rotation about the S–C bond in solution in contrast to that found in the solid-state structure of **5** (see below). The ^{13}C NMR spectra show systematic trends upon co-ordination of the thioligands. For the [Au(PR_3)(2-pyS)] complexes the C^2, C^3 and C^4 resonances are shifted upfield whereas C^5 and C^6 are shifted downfield compared with the free ligand. The changes in the positions of the ^{13}C resonances are less pronounced for the [Au(PR_3)(2-pymS)] complexes. There has been a small upfield shift for the C^2 resonance and similarly the C^4 and C^5 resonances have been shifted upfield. The C^6 resonance has been shifted downfield so that it is now coincident with the resonance assigned to the C^4 atom consistent with the ^1H spectra.

The molecular structures of [Au(PPh_3)(2-pyS)] **2** and [Au(PPh_3)(2-pymS)] **5** have been determined and are illustrated in Figs. 1 and 2, respectively; selected interatomic parameters are listed in Table 6. The Au atom in **2** exists in the expected linear geometry defined by the P atom of the PPh_3 ligand [Au–P 2.258(1) Å] and the S atom of the 2-pyS anion [Au–S 2.297(2) Å] such that the P–Au–S angle is 177.9(1)°. The C(2)–S(2) bond distance of 1.750(6) Å is substantially longer than 1.692(2) Å, the C=S bond distance found in the crystal structure of the free ligand, 2-pySH, which exists as a thione in the solid state.[16] This observation suggests that the 2-pyS anion is functioning as a thiolate ligand in the structure of **2**. The 2-pyS ligand (including the S atom) is planar to ±0.01(1) Å and the Au atom lies 0.5391(2) Å out of this plane as manifested in the torsion angle of −14.4° for Au–S(2)–C(2)–N(1). As can be seen

Table 5 Proton and $^{13}C-\{^1H\}$ NMR data (δ) for the $[Au(PR_3)(SR')]$ complexes in $(CD_3)_2SO$ solution[a]

^1H NMR Compound	H^1	H^3	H^4	H^5	H^6	H_α	H_β	H_γ	H_δ
2-pySH	13.51 (s)	7.32 (m)	7.43 (m)	6.77 (m)	7.68 (m)				
1	—	7.31 (m)	7.33 (m)	6.83 (m)	8.03 (m)	1.91 (dq) (7.78)[b] (9.51)[c]	1.13 (dt) (7.65)[b] (18.69)[c]		
2	—	7.36 (m)	7.43 (m)	6.94 (m)	8.22 (m)	*d*			
3	—	7.32 (br)	7.61 (br)	6.61 (br)	7.98 (br)	2.16 (m)	1.97 (m)	1.77 (m)	1.65 (m)
2-pymS	13.40 (s)	—	8.29 (br)	6.85 (m) (5.40)[b]	7.38 (m) (4.80)[b]				
4	—	—	8.33 (d) (4.77)[b]	6.95 (t) (4.80)[b]	8.33 (d) (4.77)[b]	1.93 (dq) (7.74)[b] (10.01)[c]	1.16 (dt) (7.62)[b] (18.73)[c]		
5	—	—	8.41 (d) (4.26)[b]	7.01 (t) (4.92)[b]	8.41 (d) (4.26)[b]	*e*			
6	—	—	8.28 (d) (4.71)[b]	6.84 (t) (4.74)[b]	8.28 (d) (4.71)[b]	2.16 (m)	1.98 (m)	1.79 (m)	1.69 (m)

^{13}C NMR Compound	C^2	C^3	C^4	C^5	C^6	C_α	C_β	C_γ	C_δ
2-pySH	177.7	133.0	137.4	112.7	137.8				
1	168.8	127.3	135.8	117.2	146.7	17.1 (d) (34.04)[f]	9.02		
2	167.5	126.6	136.5	118.1	147.4	129.1 (d) (57.63)[f]	134.0 (d) (13.89)[f]	129.7 (d) (11.55)[f]	132.2
3	168.9	128.4	137.3	117.2	144.8	32.4 (d) (29.4)[f]	26.3 (d) (11.77)[f]	30.3	25.6
2-pymSH	181.4	—	158.6	119.1	154.0				
4	180.4	—	156.4	115.3	156.4	17.2 (d) (33.96)[f]	8.96		
5	180.0	—	156.8	115.8	156.8	129.2 (d) (58.87)[f]	133.9 (d) (14.40)[f]	129.6 (d) (11.04)[f]	132.1 (2.57)[f]
6	180.2	—	156.3	114.7	156.3	32.4 (d) (28.38)[f]	26.4 (d) (12.07)[f]	30.2	25.6

[a] The numbering schemes for SR′ are as shown in the figures and Greek letters are used for the phosphine ligands, coupling constants in Hz are given in parentheses. [b] *J*(H–H). [c] *J*(P–H). [d] Multiplet in the range δ 7.64–7.60. [e] Multiplet in the range 7.63–7.55. [f] *J*(P–C).

Table 6 Selected bond distances (Å) and angles (°) for $[Au(PPh_3)(2\text{-pyS})]$ and $[Au(PPh_3)(2\text{-pymS})]$

$[Au(PPh_3)(2\text{-pyS})]$		$[Au(PPh_3)(2\text{-pymS})]$	
Au–P(1)	2.258(1)	Au–P(1)	2.253(2)
Au–S(2)	2.297(2)	Au–S(2)	2.310(3)
P(1)–C(11)	1.826(5)	P(1)–C(11)	1.811(9)
P(1)–C(21)	1.810(5)	P(1)–C(21)	1.819(8)
P(1)–C(31)	1.821(5)	P(1)–C(31)	1.810(7)
S(2)–C(2)	1.750(6)	S(2)–C(2)	1.748(9)
N(1)–C(2)	1.336(7)	N(1)–C(2)	1.33(1)
N(1)–C(6)	1.322(8)	N(1)–C(6)	1.34(1)
C(2)–C(3)	1.389(8)	N(3)–C(2)	1.34(1)
C(3)–C(4)	1.37(1)	N(3)–C(4)	1.34(1)
C(4)–C(5)	1.35(1)	C(4)–C(5)	1.39(2)
C(5)–C(6)	1.36(1)	C(5)–C(6)	1.35(2)
P(1)–Au–S(2)	177.9(1)	P(1)–Au–S(2)	174.7(1)
Au–P(1)–C(11)	112.8(2)	Au–P(1)–C(11)	115.2(3)
Au–P(1)–C(21)	115.1(2)	Au–P(1)–C(21)	108.3(3)
Au–P(1)–C(31)	110.1(2)	Au–P(1)–C(31)	115.2(3)
C(11)–P(1)–C(21)	107.0(2)	C(11)–P(1)–C(21)	105.8(4)
C(11)–P(1)–C(31)	104.1(2)	C(11)–P(1)–C(31)	106.3(4)
C(21)–P(1)–C(31)	107.0(2)	C(21)–P(1)–C(31)	105.3(4)
Au–S(2)–C(2)	102.0(2)	Au–S(2)–C(2)	98.9(3)
S(2)–C(2)–N(1)	119.9(4)	S(2)–C(2)–N(1)	118.2(7)
S(2)–C(2)–C(3)	119.1(5)	S(2)–C(2)–N(3)	115.7(7)
C(2)–N(1)–C(6)	117.3(6)	C(2)–N(1)–C(6)	115.4(9)
C(2)–C(3)–C(4)	118.4(7)	C(2)–N(3)–C(4)	115.4(9)

from Fig. 1, the thiolate ligand is orientated so as to place the N(1) atom in close proximity of the Au atom with the Au ··· N(1) separation of 3.118(4) Å being less than 3.25 Å, the sum of the van der Waals radii for these atoms.[17] The presence of this weak intramolecular interaction may be responsible for the slight deviation from the ideal linear geometry about the Au atom. The relatively close Au ··· N(1) interaction notwithstanding, the 2-pyS ligand in **2** must be considered as co-ordinating essentially in the monodentate mode. There are no significant intermolecular contacts in the lattice of **2** and the closest Au ··· Au′ contact (symmetry operation: $-x, -y, -z$) is 5.673(1) Å.

The crystal structure determination of the closely related complex $[Au(2\text{-pyS})_2]ClO_4$ was reported recently.[8] The Au atoms (there are four independent Au atoms in the lattice) are linearly co-ordinated by S atoms [range of S–Au–S 174.3(1)–180(–)°] derived from monodentate 2-pyS ligands; the range of Au–S bond distances is 2.278(2)–2.291(3) Å.[8]

The Au atom geometry in **5** is virtually identical to that found for **2**: Au–P 2.253(2), Au–S 2.310(3) Å and P–Au–S 174.7(1)°. The 2-pymS ligand is planar to ±0.02(1) Å and the Au atom lies 0.1544(3) Å out of this plane leading to a torsion angle Au–S(2)–C(2)–N(1) of −3.5°, *cf.* the equivalent angle of −14.4° in **2**. The C(2)–S(2) separation of 1.748(9) Å is equivalent to that found in **2** (the crystal structure of the free ligand, 2-pymSH is not available for comparison) and is consistent with the presence of a monodentate thiolate ligand in **5**. As for **2**, the structure of **5** also features a close intramolecular contact between the Au and N(1) atoms, with the separation of 2.951(8) Å being less than that in **2** and is presumably responsible for the larger deviation in the P–Au–S angle. There are no significant intermolecular contacts in the lattice

Table 7 Selected bond distances (Å) and angles (°) for related $[Au(PR_3)(SR')]$ compounds[a]

Compound	Au–P	Au–S	P–Au–S	Ref.
$[Au(PEt_3)L^1]$	2.248(2)	2.310(2)	176.9(1)	20
$[Au(PEt_3)L^2]$[b]	2.249(5)	2.328(4)	175.0(2)	22
	2.255(5)	2.314(5)	176.9(2)	
$[Au(PPh_3)L^1]$[b]	2.248(2)	2.296(2)	175.4(2)	21
	2.248(2)	2.300(2)	177.0(2)	
$[Au(PPh_3)(2\text{-pymS})]$	2.253(2)	2.310(3)	174.7(1)	This work
$[Au(PPh_3)L^3]$	2.256(2)	2.308(2)	178.6(2)	23
$[Au(PPh_3)(2\text{-pyS})]$	2.258(1)	2.297(2)	177.9(1)	This work
$[Au(PPh_3)L^4]$	2.258(2)	2.299(2)	176.43(8)	24
$[Au\{P(C_6H_{11})_3\}L^5]$	2.271(1)	2.313(1)	176.8(1)	25
$[Au\{P(C_6H_{11})_3\}L^6]$	2.292(3)	2.330(3)	172.0(1)	26

[a] Abbreviations: HL^1 = 2-thiouracil, HL^2 = 6-propyl-2-thiouracil, HL^3 = 8-mercaptotheophylline, HL^4 = 2-mercaptobenzoxazole, HL^5 = 2-mercaptobenzoic acid and HL^6 = 2-mercaptoimidazole. [b] Two independent molecules in the crystallographic asymmetric unit.

of **5**, the shortest Au ··· Au′ separation (symmetry operation: $-x, 1-y, -z$) is 5.016(1) Å.

The deprotonated anions $[2\text{-pyS}]^-$ and $[2\text{-pymS}]^-$ may co-ordinate metal centres in a variety of modes.[13] The most commonly observed co-ordination modes are bidentate employing the N- and S-donor atoms, *i.e.* chelating a metal centre or bridging two metal atoms, or the monodentate mode *via* the S-donor atom; a monodentate mode involving the N-donor atom is also possible but thus far has not been structurally characterized. The anions in **2** and **5** are examples of monodentate thiolate co-ordination *via* the S atom; examples of monodentate sulfur co-ordination have been observed previously for both the $[2\text{-pyS}]^-$ [18] and $[2\text{-pymS}]^-$ [19] anions.

Selected interatomic parameters for a range of related triorganophosphinegold(I) thiolates[20–26] are listed in Table 7 from which it can be seen that the Au atom parameters in **2** and **5** lie in the expected ranges. Although comparisons between structures in which the nature of the phosphine or thiolate ligand varies is difficult and the number of structures available is relatively small, some general conclusions may be made. The Au–P and Au–S bond distances for the PEt_3 and PPh_3 compounds are similar to each other and lie in narrow ranges 2.248(2)–2.258(2) Å and 2.296(2)–2.328(4) Å, respectively. Furthermore the Au–P bond distances in the two $P(C_6H_{11})_3$ compounds[25,26] are longer than the Au–P distances in the PEt_3 and PPh_3 compounds,[20–24] a result which may suggest that the sums of the electronic and steric profiles of the latter phosphines are similar.

The biological activity of these compounds will be reported elsewhere.

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References

1 R. V. Parish and S. M. Cottrill, *Gold Bull.*, 1987, **20**, 3.
2 D. R. Haynes and M. W. Whitehouse, in *New Developments in Antirheumatic Therapy*, eds. K. D. Rainsford and G. P. Velo, Kluwer, Dordrecht, 1989, ch. 8, p. 207.
3 B. M. Sutton, E. McGusty, D. T. Walz and M. J. DiMartino, *J. Med. Chem.*, 1972, **15**, 1095.
4 B. M. Sutton, *Gold Bull.*, 1986, **19**, 15.
5 C. K. Mirabelli, R. K. Johnson, C.-M. Sung, L. F. Faucette, K. Muirhead and S. T. Crooke, *Cancer Res.*, 1985, **45**, 32.
6 S. J. Berners-Price, C. K. Mirabelli, R. K. Johnson, M. R. Mattern, F. L. McCabe, L. F. Faucette, C.-M. Sung, S.-M. Mong, P. J. Sadler and S. T. Crooke, *Cancer Res.*, 1986, **46**, 5686.
7 G. F. Rush, D. W. Alberts, D. Meunier, K. Leffler and P. F. Smith, *Toxicologist*, 1987, **7**, 59.
8 R. Usón, A. Laguna, M. Laguna, J. Jiménez, M. P. Gómez, A. Sainz and P. G. Jones, *J. Chem. Soc., Dalton Trans.*, 1990, 3457.
9 A. K. Al-Saády, C. A. McAuliffe, R. V. Parish and J. A. Sandbank, *Inorg. Synth.*, 1985, **23**, 191.
10 G. M. Sheldrick, SHELX 76, Program for Crystal Structure Determination, University of Cambridge, 1976.
11 C. K. Johnson, ORTEP II, ORNL Report 5136, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.
12 J. A. Ibers and W. C. Hamilton, *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4, pp. 99, 149.
13 See, for example, R. Castro, M. L. Durán, J. A. García-Vázquez, J. Romero, A. Sousa, A. Castiñeiras, W. Hiller and J. Strähle, *J. Chem. Soc., Dalton Trans.*, 1990, 531.
14 R. Battistuzzi, T. Manfredini, L. P. Battaglia, A. B. Corradi and A. Marzotto, *J. Crystallogr. Spectrosc. Res.*, 1989, **19**, 513.
15 M. D. Gutiérrez, R. López, M. A. Romero and J. M. Salas, *Can. J. Chem.*, 1988, **66**, 249.
16 U. Ohms, H. Guth, A. Kutoglu and C. Scheringer, *Acta Crystallogr., Sect. B*, 1982, **38**, 831.
17 A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441.
18 See, for example, P. Mura, B. G. Olby and S. D. Robinson, *J. Chem. Soc., Dalton Trans.*, 1985, 2101; A. Castiñeiras, W. Hiller, J. Strähle, J. Bravo, J. S. Casas, M. Gayoso and J. Sordo, *J. Chem. Soc., Dalton Trans.*, 1986, 1945.
19 See, for example, C. Chieh, *Can. J. Chem.*, 1978, **56**, 560; J. Bravo, J. S. Casas, Y. P. Mascarenhas, A. Sánchez, C. de O. P. Santos and J. Cordo, *J. Chem. Soc., Chem. Commun.*, 1986, 1100.
20 C. S. W. Harker, E. R. T. Tiekink and M. W. Whitehouse, *Inorg. Chim. Acta*, 1991, **181**, 23.
21 B. F. Hoskins, L. Zhenrong and E. R. T. Tiekink, *Inorg. Chim. Acta*, 1989, **158**, 57.
22 P. D. Cookson and E. R. T. Tiekink, *J. Crystallogr. Spectrosc. Res.*, 1993, **23**, 273.
23 E. Colacio, A. Romerosa, J. Ruiz, P. Román, J. M. Gutiérrez-Zorrilla, A. Vegas and M. Martinez-Ripoll, *Inorg. Chem.*, 1991, **30**, 3743.
24 M. M. Muir, S. I. Cuadrado and J. A. Muir, *Acta Crystallogr., Sect. C*, 1989, **45**, 1420.
25 P. D. Cookson and E. R. T. Tiekink, *J. Coord. Chem.*, in the press.
26 F. Bonati, A. Burini, B. R. Pietroni, E. Giorgini and B. Bovio, *J. Organomet. Chem.*, 1988, **344**, 119.

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