Preparation and Characterization of the First Isothiazolyl and Isothiazolinylidene Complexes of Gold(I)†

Helgard G. Raubenheimer,* Mieke Desmet and Gert J. Kruger
Department of Chemistry and Biochemistry, Rand Afrikaans University, Auckland Park 2006, South Africa

Isothiazolyl complexes have been synthesized by the addition of isothiazol-5-yllithium to gold(I) chloride or tetrahydrothiophene(pentafluorophenyl)gold complexes. Protonation or alkylation of these isothiazolyl complexes yielded the corresponding isothiazolinylidene complexes. The mono(isothiazolyl)-aurate and mono(isothiazolinylidene) complexes undergo homoleptic rearrangement. The molecular structure of the mono(isothiazolyl) complex [Au(C=CHCH=NS)(PPh$_3$)] shows a gold–carbon bond length of 2.032(7) Å.

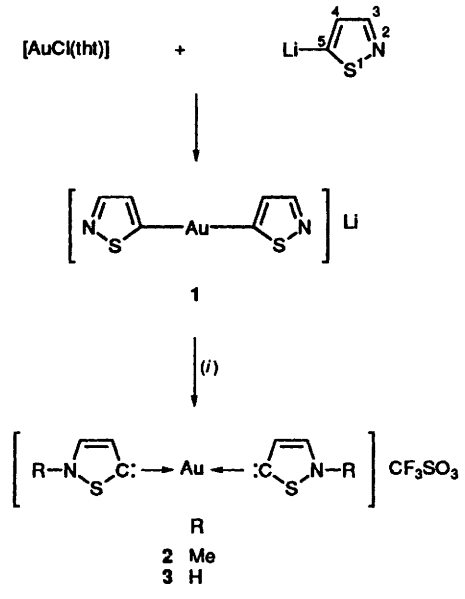
In previous papers we have described the synthesis of isothiazolinylidene complexes of iron[1] and tungsten[2] by the addition of isothiazolyllithiums to metal halides and subsequent alkylation or protonation of the products formed. These organo(thio)carbene complexes are unique in that they have been prepared from precursors in which the nucleophilic heteroatom is situated γ to the co-ordinated carbon atom. In contrast, when Fischer-type carbene complex synthesis involves a similar alkylation or protonation step, the nucleophilic heteroatom is located α to the co-ordinated carbon atom.[3,4] In this paper, the preparation and characterization of the related isothiazolinylidene complexes of gold(I) as well as the precursor isothiazolyl complexes are described. These complexes are isomers of thiazolyl and thiazolinylidene compounds of gold recently reported[5] and they are also related to imidazolyl and imidazolinylidene complexes prepared independently by Burini,[6] Arduengo[7] and Kuhn[8] and their co-workers.

The various gold compounds [AuCl(tht)] (tht = tetrahydrothiophene), [AuCl(PPh$_3$)] and [Au(C$_6$F$_5$)(tht)] were treated with isothiazol-5-yllithium to form precursor isothiazolyl gold compounds which where then alkylated or protonated with CF_3SO_3Me or CF_3SO_3H to form isothiazolinylidene complexes. We surprisingly found that the bis(isothiazolyl)aurate and bis(isothiazolinylidene) compounds show similar ^{13}C chemical shifts. Furthermore, the mono(isothiazolyl)aurate and mono(isothiazolinylidene) complexes spontaneously rearranged to form homoleptic compounds. The rearrangement process was followed by ^1H NMR spectroscopy. This type of rearrangement has been observed before[5] in the related thiazolinylidene gold compounds. The crystal and molecular structures of the mono(isothiazolyl) gold(I) complex [Au(C=CHCH=NS)(PPh$_3$)] have been determined by X-ray methods and are described.

Results and Discussion

Preparation of Bis(isothiazolyl)aurate and Bis(isothiazolinylidene) Complexes.—The reaction of 2 molar equivalents of isothiazol-5-yllithium with [AuCl(tht)] at −78 °C afforded the air-sensitive isothiazolylaurate complex **1** (Scheme 1). Large quantities of tetrahydrofuran (thf) were found to be present in the NMR spectra of this complex even though it was kept *in vacuo* for 24 h. The thf, which resonates in its usual position, probably solvates the small lithium counter ion.

† *Supplementary data available*: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.



Scheme 1 (*i*) CF_3SO_3Me or CF_3SO_3H

Direct alkylation or protonation of the aurate complex **1**, at −78 °C with 2 molar equivalents of CF_3SO_3Me or CF_3SO_3H respectively, produced yellow solutions of the cationic bis(carbene) complexes **2** and **3** (Scheme 1). Upon standing at −20 °C, long, yellow, needle-like crystals of the isothiazolinylidene complexes were obtained.

Complexes **1** and **2** are soluble in acetone and thf. Complex **3** in its microcrystalline form is much less soluble than its alkylated counterpart, yet the crystals when formed, are extremely hygroscopic and no elemental analysis was undertaken.

A few interesting features arise when the ^{13}C NMR data of free isothiazole and the complexes **1**, **2** and **3** are compared (see Experimental section). (*i*) The alkene carbons (δ 155.9 and 127.6) of complex **1** show little change compared to free isothiazole (δ 158.1 and 124.4) while the co-ordinated carbon resonates at δ 195.0 compared to δ 149.1 for the free ligand. (*ii*) There is little change in the chemical shifts of the carbons in the precursor aurate complex **1** (δ 127.6, 155.9 and 195.0) and the corresponding isothiazolinylidene complexes (for **2** δ 128.9, 156.1 and 197.3; for **3** δ 128.8, 152.7 and 197.0).

The chemical shifts of the carbon atoms (with the exception of the co-ordinated carbon atoms) in both the aurate and the

carbene complexes still lie in the aromatic region. The π electrons in the complexes are delocalized to a large extent and their structures may be represented by many resonance forms. This is not surprising, since the free heterocyclic reactants are aromatic in nature and the co-ordinated carbon atom in both complexes is sp^2 hybridized.

Preparation of a Mono(isothiazolinylidene) Complex of Pentafluorophenylgold.—The neutral mono(carbene) complex **5** (Scheme 2) was prepared by treating $[Au(C_6F_5)(tht)]$ with isothiazol-5-yllithium in thf at −78 °C followed by direct alkylation of the aurate complex **4** with CF_3SO_3Me at −65 °C. The solvent was removed under vacuum and complex **5** extracted with methylene chloride before filtration through silica gel. Crystallization from methylene chloride–diethyl ether, however, afforded a mixture of the cation in the bis(carbene) complex **2** (Scheme 1) and the neutral carbene complex **5**. After repeated recrystallizations, colourless prisms of complex **5** were obtained. The crystals are thermally stable in air, but the complex slowly undergoes homoleptic rearrangement [see equation (1), in which charges are omitted] in

$$AuL^1L^2 \longrightarrow AuL^1{}_2 + AuL^2{}_2 \qquad (1)$$

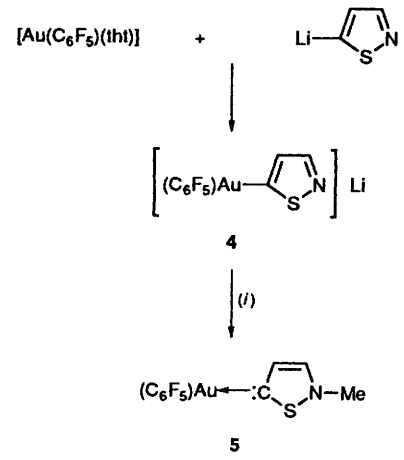
solution. Similar rearrangement reactions have been reported for a variety of anionic gold(I) compounds,[9–11] whereas only a few have been observed for neutral complexes.[12,13]

Attempts to isolate the precursor mono(isothiazolyl)aurate complex **4** by crystallization yielded only the bis(isothiazolyl)-aurate complex **1**. Complex **4** is labile at room temperature and the anionic $C_6F_5^-$ ligand is displaced by the isothiazolyl ligand. It is for this reason that the precursor complex **4** was prepared *in situ* at low temperature and directly alkylated to form the carbene complex **5**.

There are two possible pathways that account for the formation of the cation in the bis(carbene) complex **2** in the alkylation process. These are: (*i*) a certain amount of the bis(isothiazolyl)aurate complex **1** forms during the formation of the precursor complex **4**, and is subsequently alkylated with CF_3SO_3Me to form the bis(carbene) complex **2**; (*ii*) the mono(carbene) complex **5** undergoes homoleptic rearrangement to form the cation in complex **2** now with $[Au(C_6F_5)_2]^-$ as counter ion.

The homoleptic rearrangement of the pentafluorophenyl(carbene) complex **5** occurs slowly and was followed by a ^1H NMR study. Crystals of the complex were dissolved in $[^2H_6]$acetone in an NMR tube and a ^1H NMR spectrum was measured; four days later the same sample was measured and subsequent spectra were collected every seven days for four weeks. Fig. 1 shows the first three ^1H NMR spectra obtained. The spectra indicate that an equilibrium is established after 18 days after which no further conversion of complex **5** into complex **2** {and, not observable $[Au(C_6F_5)_2]^-$} occurs. An equilibrium is reached when an approximate concentration ratio of 4.1 : 1 : 1 {**5**:**2**: $[Au(C_6F_5)_2]^-$} exists in solution.

Preparation of Isothiazolyl and Mono(isothiazolinylidene) Complexes of (Triphenylphosphine)gold.—Reaction of isothiazol-5-yllithium with $[AuCl(PPh_3)]$ at −78 °C afforded, after crystallization, the neutral isothiazolyl complex **6** (Scheme 3). The off-white prisms obtained were suitable for a single crystal X-ray crystallographic investigation. Complex **6** is thermally stable in air at room temperature and is soluble in methylene chloride, benzene and most polar organic solvents. The greater solubility of this complex compared to the isothiazolylaurate complex **1**, and the bis(carbene) complexes **2** and **3**, is probably due to the presence of the neutral PPh_3 group. The ^{13}C resonance of the co-ordinated carbon appears at δ 190.6. This agrees with the results obtained for the bis(isothiazolyl)aurate complex **1**, in which the co-ordinated carbon also resonates at a lower field than expected.



Scheme 2 (*i*) CF_3SO_3Me

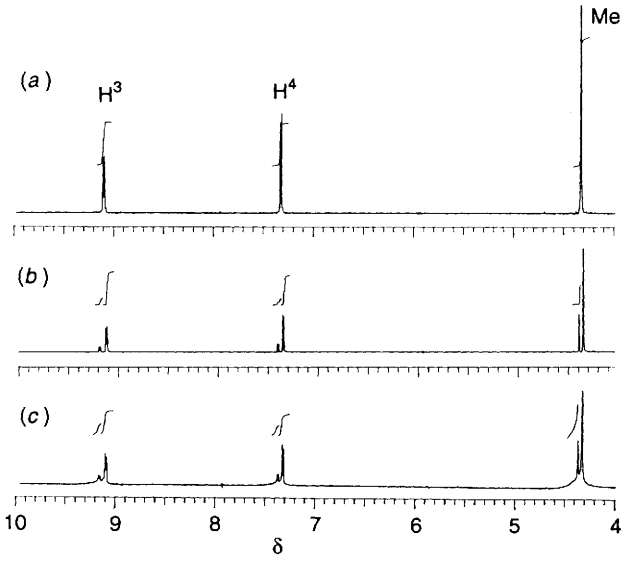
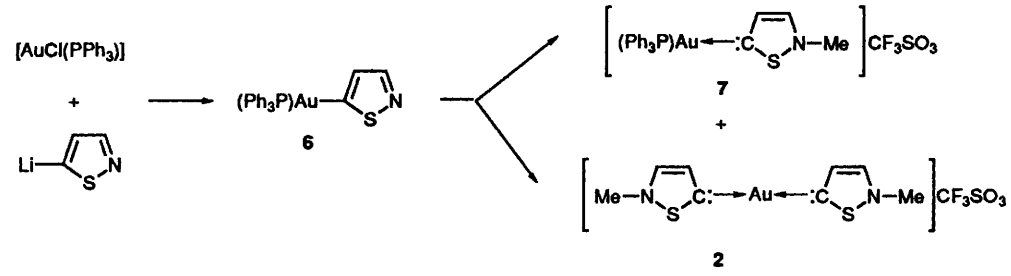


Fig 1 Proton NMR spectra of complex **5** showing homoleptic rearrangement into complex **2** (*a*) day 1, (*b*) day 5, (*c*) day 12

Depending on the work-up conditions, alkylation of the neutral complex **6** with CF_3SO_3Me in thf at −78 °C yielded either the cationic mono(carbene) complex **7** (Scheme 3) or the cationic bis(carbene) complex **2**. Complex **7** was obtained after methylene chloride extraction followed by immediate precipitation on addition of diethyl ether, whereas crystals of complex **2** were obtained by allowing the solvent to evaporate slowly. The precursor complex **6** was either prepared *in situ* and directly alkylated, or first isolated and then alkylated. It was only possible to isolate complex **7** once. The preparation could not be repeated and thereafter, only crystals of complex **2** were obtained. Furthermore, complex **7** could not be isolated in a pure form or analysed satisfactorily. Since the isothiazolyl complex **6** is very stable in solution at room temperature and does not decompose into complex **1**, homoleptic rearrangement of **7** is probably the major cause for the formation of complex **2**. Since complex **7** could not be readily crystallized, it is likely that the rearrangement occurs faster than in the case of complex **5** discussed previously.

The ^{13}C-{^1H} NMR spectrum of complex **7** showed poor resolution and as a result the signals are broad and are not split into doublets. The assignment of the carbene carbon resonance at δ 195.9 is somewhat uncertain since it was only observed in one spectrum.



Scheme 3

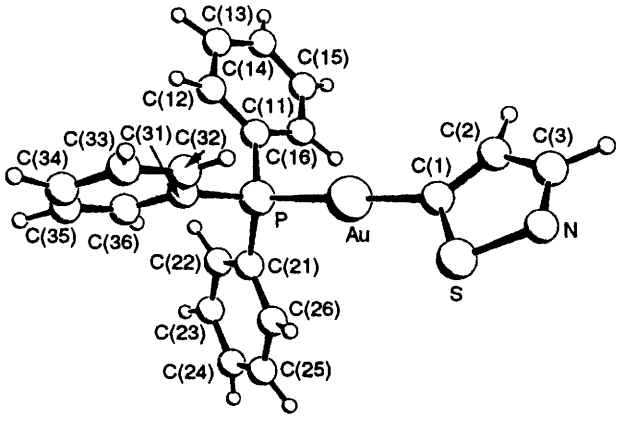


Fig 2 View of the molecular structure of [Au(C=CHCH=NS)(PPh$_3$)] **6** (SCHAKAL), with the atomic numbering scheme

Structure of [Au(C=CHCH=NS)(PPh$_3$)] **6**.—The molecular structure of complex **6** is shown in Fig. 2. Final atomic coordinates are given in Table 1 and selected bond lengths and angles in Table 2. The gold atom is linearly co-ordinated to a phosphorus atom of PPh_3 and to a carbon atom of the isothiazolyl ligand. The P–Au–C angle is 177.1(2)°. The Au–P bond length of 2.290(2) Å is similar to the distances found in other linear, two-co-ordinate gold(I) compounds, *e.g.* 2.284(1) Å in [Au{$C_6H_3(OMe)_2$-2,6}(PPh_3)],[14] 2.286(3) Å in [Au(PPh_3)$_2$]$^+$ [15] and 2.291 Å in [Au{$CH_2C(O)Ph$}(PPh_3)].[16] The Au–C(sp^2) bond length of 2.032(7) Å is similar to most other reported Au–C(sp^2) bond lengths, for example, 2.050(4) Å in [Au{$C_6H_3(OMe)_2$-2,6}(PPh_3)],[14] 2.063 Å in [Au(C_6F_5)(PPh_3)][17] and 2.056(1) Å in [Au(PPh_3){C(OMe)=NC_6H_4-Me-*p*}].[18] Interestingly, it is also comparable to the formal Au–C(sp^2) double bond distances found in gold(I) carbene complexes such as [Au{C=NC(Me)=CHS}{CNHC(Me)=CHS}] [average of 2.03(1) Å],[5] [Au{$CN(CH_2Ph)CH$=CHNH}$_2$]Cl [average of 2.027(7) Å][19] and [Au{C(Ph)NMe_2}Cl] [2.03(3) Å].[20]

The aromatic character of the ligand is clearly shown by the relatively short bond lengths therein. The rather large values of U_{eq} of the heterocycle atoms (0.051–0.091 Å^2) does not affect the bond lengths significantly as these values are caused by large anisotropic thermal displacement parameters normal to the plane of the ring only.

Experimental

Materials.—The gold compounds [AuCl(tht)], [Au-Cl(PPh_3)] and [Au(C_6F_5)(tht)],[21] as well as the free isothiazole[22] were prepared according to literature methods; CF_3SO_3Me and CF_3SO_3H were purchased from Aldrich and *n*-butyllithium from Merck. Tetrahydrofuran and diethyl ether were distilled under nitrogen from sodium diphenylketyl and CH_2Cl_2 from CaH_2.

Table 1 Fractional atomic coordinates with estimated standard deviations (e.s.d.s) in parenthesis for complex **6**

Atom	*X/a*	*Y/b*	*Z/c*
Au	0.375 03(2)	0.225 75(2)	1.003 57(2)
P	0.396 5(1)	0.224 8(1)	0.818 5(1)
S	0.176 8(2)	0.238 5(2)	1.190 9(2)
N	0.243 7(7)	0.257 9(7)	1.341 2(5)
C(1)	0.354 0(7)	0.236 6(6)	1.169 5(5)
C(2)	0.466 8(8)	0.249 9(8)	1.282 8(5)
C(3)	0.399 2(9)	0.259 8(9)	1.373 4(6)
C(11)	0.603 6(5)	0.245 5(5)	0.825 3(4)
C(12)	0.669 6(6)	0.362 1(5)	0.812 0(5)
C(13)	0.829 9(7)	0.377 4(7)	0.829 4(6)
C(14)	0.921 0(7)	0.276 2(7)	0.857 5(6)
C(15)	0.853 7(7)	0.159 1(7)	0.869 0(6)
C(16)	0.693 9(6)	0.143 0(6)	0.853 1(5)
C(21)	0.297 6(5)	0.066 8(5)	0.689 1(4)
C(22)	0.342 6(6)	0.022 5(6)	0.584 9(5)
C(23)	0.257 3(7)	−0.092 1(6)	0.484 2(5)
C(24)	0.127 2(7)	−0.162 7(6)	0.486 9(6)
C(25)	0.080 5(6)	−0.118 8(6)	0.589 1(6)
C(26)	0.165 4(6)	−0.005 1(6)	0.689 2(5)
C(31)	0.308 2(5)	0.366 5(5)	0.771 7(4)
C(32)	0.279 5(6)	0.476 0(6)	0.861 2(5)
C(33)	0.207 5(8)	0.580 7(6)	0.827 7(6)
C(34)	0.162 2(7)	0.579 1(7)	0.706 3(7)
C(35)	0.192 2(7)	0.473 0(7)	0.616 5(5)
C(36)	0.264 2(6)	0.367 3(6)	0.649 7(5)
H(2)	0.595(6)	0.203(5)	1.302(5)
H(3)	0.470(6)	0.275(6)	1.464(5)
H(12)	0.590(6)	0.444(5)	0.759(5)
H(13)	0.882(6)	0.471(6)	0.827(5)
H(14)	1.031(6)	0.284(6)	0.875(5)
H(15)	0.929(6)	0.097(6)	0.907(5)
H(16)	0.661(6)	0.052(6)	0.870(5)
H(22)	0.444(6)	0.066(5)	0.582(5)
H(23)	0.280(6)	−0.135(6)	0.403(5)
H(24)	0.073(6)	−0.236(6)	0.428(5)
H(25)	−0.005(6)	−0.179(6)	0.592(5)
H(26)	0.152(6)	0.029(5)	0.772(5)
H(32)	0.301(6)	0.468(6)	0.944(5)
H(33)	0.197(7)	0.639(6)	0.888(5)
H(34)	0.107(7)	0.632(6)	0.681(6)
H(35)	0.171(6)	0.475(6)	0.529(5)
H(36)	0.279(6)	0.296(6)	0.592(5)

Physical Methods.—All reactions involving organometallic reagents were performed under an atmosphere of nitrogen using standard vacuum-line and Schlenk techniques. Melting points were determined on a standardized Buchi 535 apparatus. Mass spectra (electron impact) were recorded on a Finnigan Mat 8200 instrument at *ca.* 70 eV ($\approx 1.12 \times 10^{-17}$ J) and NMR spectra on a Varian 200 FT spectrometer. Elemental analyses were carried out by the Division of Energy Technology, Council for Scientific and Industrial Research, Pretoria, South Africa.

Preparations.—Li[Au(C=CHCH=NS)$_2$] **1**. Isothiazol-5-yllithium[23] was prepared from isothiazole (0.29 cm^3, 4.0 mmol)

Table 2 Selected bond lengths (Å) and angles (°) with e.s.d.s in parentheses for complex **6**

Au–P	2.290(2)	C(1)–C(2)	1.370(8)
Au–C(1)	2.032(7)	C(2)–C(3)	1.389(12)
S–N	1.652(6)	P–C(11)	1.839(5)
S–C(1)	1.693(7)	P–C(21)	1.817(4)
N–C(3)	1.320(10)	P–C(31)	1.814(5)
P–Au–C(1)	177.1(2)	S–C(1)–Au	122.5(3)
Au–P–C(11)	113.2(2)	C(2)–C(1)–Au	131.1(5)
Au–P–C(21)	113.7(2)	C(1)–C(2)–C(3)	111.7(6)
Au–P–C(31)	111.2(2)	N–C(3)–C(2)	118.2(6)
N–S–C(1)	97.8(3)		

and 1.6 mol dm^{-3} *n*-butyllithium in hexane (2.5 cm^3, 4.0 mmol) in thf (35 cm^3) at −78 °C and stirred for 45 min before [AuCl(tht)] (0.64 g, 2.0 mmol) was added. The reaction mixture was stirred for 2 h at this temperature, before warming to room temperature. The solvent was removed *in vacuo*, the residue washed with CH_2Cl_2 (3 × 15 cm^3) and dried under vacuum for 24 h to give **1** as a light yellow powder (0.61 g, 81%); δ_H[200 MHz, $(CD_3)_2CO$] 7.08 [2 H, d, *J*(HH) 1.56, H^4] and 8.59 [2 H, d, *J*(HH) 1.62 Hz, H^3]; δ_C[50 MHz, $(CD_3)_2CO$] 127.6 (1 C, s, C^4), 155.9 (1 C, s, C^3) and 195.0 (1 C, s, C^5); *m/z* 365 {16%, $[Au(\overline{C{=}CHCH{=}NS})_2]^+$}, 281 {3, $[Au(\overline{C{=}CHCH{=}NS})]^+$}, 168 {4, $[(\overline{C{=}CHCH{=}NS})_2]^+$} and 85 {100, $[\overline{C{=}CHCH{=}NS}]^+$}.

$[Au\{\overline{CCH{=}CHN(Me)S}\}_2]CF_3SO_3$ **2**. Isothiazol-5-yllithium was prepared from isothiazole (0.15 cm^3, 2.1 mmol) and 1.6 mol dm^{-3} *n*-butyllithium in hexane (1.31 cm^3, 2.1 mmol) in thf (25 cm^3) at −78 °C and stirred for 45 min before [AuCl(tht)] (0.34 g, 1.05 mmol) was added. The reaction mixture was stirred for 2 h at this temperature, then for 1 h at −50 °C before the addition of CF_3SO_3Me (0.24 cm^3, 2.1 mmol) at −80 °C. The reaction mixture was stirred at −50 °C for 1 h before warming to room temperature. Filtration through anhydrous $MgSO_4$ and cooling to −20 °C afforded yellow needle-like crystals of **2** (0.37 g, 66%), m.p. 159 °C (decomp.) (Found: C, 19.90; H, 1.80; N, 5.25. $C_9H_{10}AuF_3N_2O_3S_3$ requires C, 19.85; H, 1.85; N, 5.15%); δ_H[200 MHz, $(CD_3)_2CO$] 4.38 (6 H, s, NMe), 7.40 [2 H, d, *J*(HH) 2.63, H^4] and 9.20 [2 H, d, *J*(HH) 2.07 Hz, H^3]; δ_C[50 MHz, $(CD_3)_2CO$] 40.4 (1 C, s, NMe), 128.9 (1 C, s, C^4), 156.1 (1 C, s, C^3) and 197.3 (1 C, s, C^5); *m/z* 168 {50%, $[(\overline{C{=}CHCH{=}NS})_2]^+$}, 85 {100, $[\overline{C{=}CHCH{=}NS}]^+$}, 57 {83, $[C_2SH]^+$} and 45 {23, $[HCS]^+$}.

$[Au\{\overline{CCH{=}CHN(H)S}\}_2]CF_3SO_3$ **3**. Complex **3** was prepared according to the same procedure as **2** from isothiazole (0.18 cm^3, 2.5 mmol), 1.6 mol dm^{-3} *n*-butyllithium in hexane (1.56 cm^3, 2.5 mmol), [AuCl(tht)] (0.40 g, 1.25 mmol) and CF_3SO_3H (0.22 cm^3, 2.5 mmol). The reaction mixture was filtered through a sinterglass filter, the solvent removed *in vacuo*, the residue washed with diethyl ether (3 × 15 cm^3) and acetone (1 × 10 cm^3) and dried under vacuum. The resulting red powder was crystallized from thf at −25 °C to give long yellow needle-like crystals of **3** (0.49 g, 75%); δ_H\{200 MHz, $[^2H_8]$thf\} 6.08 (2 H, br s, NH), 7.45 [2 H, d, *J*(HH) 1.97, H^4] and 9.15 [2 H, d, *J*(HH) 2.41 Hz, H^3]; δ_C\{50 MHz, $[^2H_8]$thf\} 128.8 (1 C, s, C^4), 152.7 (1 C, s, C^3) and 197.0 (1 C, s, C^5); *m/z* 364 {2%, $[Au\{\overline{CCH{=}CHN(H)S}\}_2]^+$}, 282 {7, $[Au\{\overline{CCH{=}CHN(H)S}\}]^+$}, 251 {7, $[Au\{CCH{=}CHN(H)\}]^+$} 168 {100, $[(\overline{C{=}CHCH{=}NS})_2]^+$}, 141 {20, $[(CCH{=}CHNS)(C{=}CHS)]^+$} and 85 {50, $[\overline{C{=}CHCH{=}NS}]^+$}.

$[Au(C_6F_5)\{\overline{CCH{=}CHN(Me)S}\}]$ **5**. Isothiazol-5-yllithium was prepared from isothiazole (0.15 cm^3, 2.0 mmol) and 1.6 mol dm^{-3} *n*-butyllithium in hexane (1.25 cm^3, 2.0 mmol) in thf (30 cm^3) at −78 °C and stirred for 45 min before $[Au(C_6F_5)(tht)]$ (0.90 g, 2.0 mmol) was added. The reaction mixture was stirred for 2 h at this temperature, then for 1 h at −60 °C, before the addition of CF_3SO_3Me (0.23 cm^3, 2.0 mmol) at −65 °C. The reaction mixture was stirred for 1 h before raising the temperature to −30 °C over a period of 1 h. The mixture was stirred for a further 30 min at room temperature and the solvent removed under vacuum. The residue was redissolved in CH_2Cl_2, filtered through silica (*ca.* 5 cm thick) and the filtrate concentrated *in vacuo*. Crystallization (vapour diffusion) from CH_2Cl_2–diethyl ether at 0 °C afforded crystals consisting of a mixture of complexes **2** and **5**. Repeated recrystallizations using the above technique yielded pure crystals of complex **5** (0.30 g, 33%), m.p. 178 °C (decomp.) (Found: C, 25.90; H, 1.05; N, 3.00. $C_{10}H_5AuF_5NS$ requires C, 25.95; H, 1.10; N, 3.00%); δ_H[200 MHz, $(CD_3)_2CO$] 4.35 (3 H, s, NMe), 7.34 [1 H, d, *J*(HH) 2.57, H^4] and 9.12 [1 H, d, *J* (HH) 2.47 Hz, H^3]; δ_C[50 MHz, $(CD_3)_2CO$] 40.1 (1 C, s, NMe), 136.6–152.4 (6 C, m, C_6F_5) 127.4 (1 C, s, C^4), 155.5 (1 C, s, C^3) and 200.8 (1 C, s, C^5); *m/z* 463 (100%, M^+), 365 {18, $M^+ - [\overline{CCH{=}CHN(Me)S}]$}, 296 (90, $M^+ - C_6F_5$), 198 {13, $[\{(\overline{CCH{=}CHN(Me)S}\}_2]^+$}, 168 {38, $[(\overline{C{=}CHCH{=}NS})_2]^+$} and 99 {32, $[\overline{CCH{=}CHN(Me)S}]^+$}.

$[Au(\overline{C{=}CHCH{=}NS})(PPh_3)]$ **6**. Isothiazol-5-yllithium was prepared from isothiazole (0.15 cm^3, 2.0 mmol) and 1.6 mol dm^{-3} *n*-butyllithium in hexane (1.25 cm^3, 2.0 mmol) in thf (30 cm^3) at −78 °C and stirred for 45 min before $[AuCl(PPh_3)]$ (0.99 g, 2.0 mmol) was added. The reaction mixture was stirred for 1 h before raising the temperature to −30 °C over a period of 2 h. The mixture was stirred for a further 30 min at room temperature and the solvent removed under vacuum. The residue was redissolved in CH_2Cl_2 and filtered through silica (*ca.* 5 cm thick). Solvent was removed *in vacuo* and the residue crystallized from benzene–pentane (vapour diffusion) to give off-white prisms of **6** (0.96 g, 83%), m.p. 157–158 °C (Found: C, 46.50; H, 3.20; N, 2.65. $C_{21}H_{17}AuNPS$ requires C, 46.40; H, 3.15; N, 2.60%); δ_H(200 MHz, CD_2Cl_2) 7.29 [1 H, d, *J*(HH) 1.46, H^4], 7.54 (15 H, m, Ph) and 8.77 [1 H, d, *J*(HH) 1.52 Hz, H^3]; δ_C(50 MHz, CD_2Cl_2) 127.9 (3 C, s, C_{ipso}) (the second peak of the doublet was obscured), 129.6 [6 C, d, ^3J(PC) 11.1, *m*-C], 130.3 [1 C, d, ^3J(PC) 53.8, C^4], 131.9 [3 C, d, ^4J(PC) 2.3, *p*-C], 134.6 [6 C, d, ^2J(PC) 13.7, *o*-C], 155.9 [1 C, d, ^4J(PC) 6.9, C^3] and 190.6 [1 C, d, ^2J(PC) 118.4 Hz, C^5]; δ_P(81 MHz, CD_2Cl_2) 45.59 (1 P, s); *m/z* 543 (2%, M^+), 459 {4, $M^+ - [\overline{C{=}CHCH{=}NS}]^+$}, 262 {100, $[PPh_3]^+$}, 185 {81, $[PPh_2]^+$} 168 {4, $[(\overline{C{=}CHCH{=}NS})_2]^+$}, 108 {45, $[PPh]^+$} and 77 {14, $[Ph]^+$}.

$[Au\{\overline{CCH{=}CHN(Me)S}\}(PPh_3)]CF_3SO_3$ **7**. Methyl trifluoromethanesulfonate (0.17, 1.5 mmol) was added at −75 °C to a solution of complex **6** (0.82, 1.5 mmol) in thf. The reaction mixture was stirred for 30 min before raising the temperature to −10 °C over a period of 2 h. The mixture was stirred for a further 30 min at room temperature and the solvent removed under vacuum. The residue was redissolved in CH_2Cl_2 and filtered through anhydrous $MgSO_4$ and Celite (1:1). Concentration of the solution to −10 °C, addition of diethyl ether (8 cm^3) and cooling to −20 °C (4 h) afforded a white precipitate. The solvent was decanted, the precipitate washed with diethyl ether and dried under vacuum to give **7** as an off-white powder (0.79 g, 75%). δ_H (200 MHz, $CDCl_3$) 4.33 (3 H, s, NMe), 7.36 [1 H, d, *J*(HH) 2.55, H^4], 7.53 (15 H, m, Ph) and 9.27 [1 H, d, *J*(HH) 3.19 Hz, H^3]; δ_C(50 MHz, $CDCl_3$) 40.2 (1 C, s, NMe), 128.5 (1 C, s, C^4), 127.6 (3 C, s, C_{ipso}) 129.6 [6 C, br s, *m*-C], 132.2 [3 C, br s, *p*-C], 134.1 [6 C, br s, *o*-C], 155.4 (1 C, s, C^3) and 195.9 (1 C, s, C^5); δ_P(81 MHz, $CDCl_3$) 41.50 (1 P, s); *m/z* 503 {2%, $[PPh_3Au(C{=}S)]^+$}, 459 {4, $[PPh_3Au]^+$}, 296 {27, $[Au\{\overline{CCH{=}CHN(Me)S}\}]^+$}, 262 {90, $[PPh_3]^+$} 198 {15, $[\{\overline{CCH{=}CHN(Me)S}\}_2]^+$}, 108 {45, $[PPh]^+$} and 77 {32, $[Ph]^+$}.

Crystallography.—The crystal data and data collection parameters are given in Table 3. The position of the gold atom

Table 3 Crystal data, collection and refinement details for complex **6**

Formula	$C_{21}H_{17}AuNPS$
M	543.38
Crystal size/mm	0.13 × 0.12 × 0.07
Colour and shape	Off-white prisms
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	8.9856(6)
b/Å	10.1871(11)
c/Å	12.0069(6)
α/°	107.588(7)
β/°	109.034(6)
γ/°	91.633(7)
Z	2
U/Å^3	980.5(1)
D_c/gcm^{-3}	1.847
Radiation (γ/Å)	Mo-Kα (0.710 73 Å)
μ/cm^{-1}	79.16
T/°C	23
F(000)	520
Diffractometer	Enraf-Nonius CAD 4
Scan type	ω–2θ
Scan range, θ/°	3–30
Scan angle, ω/°	0.58
hkl Ranges	0.12, −14 to 14, −16 to 16
Maximum scan rate/° min^{-1}	5.5
Maximum scan time per reflection/s	1200
Reflections measured	5714
Unique reflections used to refine	5145, $F_o > 3\sigma(F_o)$
Decay (%) (corrected)	3.4
Absorption correction (empirical)	0.7826–0.9273
Parameters refined	277
Maximum shift/esd	0.03 Average, 0.44 maximum on H(2)
Difference map peaks/e Å^{-3}	0.88 Maximum
R,R' *	0.035, 0.028
Goodness of fit, S	1.772

* $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$, $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$, $w = 1/\sigma^2$.

was determined from a Patterson synthesis and subsequent difference maps revealed the rest of the structure. All the non-hydrogen atoms were refined anisotropically. The hydrogen atom positions were found from difference maps and refined with a constant isotropic thermal parameter of 0.08. The computer program XTAL 3.2[24] was used for the structure determination and refinement, and SCHAKAL[25] for the molecular structure illustration.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

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