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Synthesis and characterisation of N-coordinated pentafluorophenyl gold(I) thiazole-derived complexes and an unusual self-assembly to form a tetrameric gold(I) complex †

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Treatment of $[Au(C_6F_5)(SC_4H_8)]$ (**1**) (SC_4H_8 = tetrahydrothiophene or tht) with $HC{=}NC(CH_3){=}C(H)S$, $CH_3SC{=}NC(CH_3){=}C(H)S$, (**I**) or piperidine yields the neutral mononuclear imine complexes $[Au(C_6F_5)\{N{=}C(H)SC(H){=}CCH_3\}]$ (**2**) and $[Au(C_6F_5)\{N{=}C(SCH_3)SC(H){=}CCH_3\}]$ (**3**), or the amine complex $[Au(C_6F_5)\{N(H)CH_2(CH_2)_3CH_2\}]$ (**4**). The reaction of **1** with $S{=}CN(H)C(CH_3){=}C(H)S$, (**II**) affords the thione complex $[Au(C_6F_5)\{S{=}CN(H)C(CH_3){=}C(H)S\}]$ (**5**), which, in CH_2Cl_2 *via* spontaneous intermolecular deprotonation of the thione ligand, self-assembles to an unique tetramer of Au(I), $[Au\{S{=}CNC(CH_3){=}C(H)S\}]_4$ (**6**) containing a folded rectangle of Au-atoms with aurophlilic interactions [av. Au ··· Au distance, 3.02(4) Å and av. Au–Au–Au angle, 87(2)°]. N-coordination of the imine complexes has been confirmed by ^{15}N NMR and the crystal structure determination of **2** which exhibits the expected linear N-coordination and intermolecular Au ··· Au [3.345(1) Å] contacts. The crystal structure of **5** shows thione S-coordination of **II** to the central Au atom.

Introduction

Medical interest in gold compounds that are used to treat rheumatoid arthritis and display anticancer, antiviral and antimicrobial activity, can be sustained with improved understanding of the molecular and biochemical mechanism of their pharmacological action.[1,2] The coordination of gold(I) to ligands from biological systems (purines, pyrimidines, vitamins, coenzymes and anitbiotics) or even ligands analogous to those found in biological systems, can provide important information in this regard. Of biological interest are nitrogen donor ligands (*e.g.* amines and five-membered heterocycles), thioethers, thiolates, thiols and thiones.[2]

Although many gold complexes containing five-membered heterocycles like imidazole,[3–6] pyrazole,[6–8] oxazole[8,9] and thiazole[8] have been described, only a few containing neutral imidazole,[10,11] oxazole,[11] triazole[12] and azaphosphole[13] ligands have been reported. This investigation of the coordination of a group of ligands derived from the vitamin B1 analogue,[14] 4-methylthiazole, now reveals that the soft metal centre Au(I) prefers imine coordination when provided with a choice between the borderline (hard/soft) imine and soft endo- and exocyclic thioether ligands. This result supports the structures $[Au\{N{=}C(C{=}CHCH{=}CHS)OCH_2C(CH_3)_2\}_2]^+$ and $C_6F_5Au[N{=}C(C{=}CHCH{=}CHS)OCH_2C(CH_3)_2]$ proposed in previous work.[9] The generalization sometimes made that gold(I) prefers S-donor to N-donor ligands[15–17] should thus be treated with caution as demonstrated by the many Au(I) imine[17–25] and amine[16,17,26–29] complexes, prepared mostly from Au(I) thioether complexes,[16–18,20–22,24–27] isolated and characterised in recent years. The crystal structures of gold(I) amine and imine complexes show extensive aurophilic and coulombic interactions as well as interhalogen contacts and hydrogen bonding which also stabilise these compounds.[17–20]

Neutral thione-coordinated gold(I) complexes have previously been prepared by coordination of the ligand to AuCl[30,31] and AuCN[32] or by the substitution of tht in AuX(tht) (X = Cl or C_6F_5).[33] Cationic thione-coordinated gold(I) complexes, obtained by the substitution of tht in $[Au(PPh_3)(tht)]^+$,[33] reduction of $HAuCl_4$ with excess thione ligand[12,34,35] or treatment of $Au(PPh_3)Cl$ with thione (1 : 1) (helped along by $AgPF_6$[36] or by refluxing in methanol[37]) are also known.

Instances in which simple syntheses of linear two-coordinate gold(I) compounds were attempted have surprisingly resulted in the isolation of dimers, tetramers, oligomers and polymers of gold compounds.[38–41] This phenomenon, promoted by gold(I) atoms with a closed-shell electronic configuration, and showing a strong tendency to form aggregates through aurophilic interaction, has projected gold compounds into the realm of supramolecular chemistry. The slow deprotonation of $[Au(SCNHCH_2CH_2NH)_2Cl]$ has produced a tetrameric gold complex with N and S donor atoms.[38] Two neutral tetrameric complexes $\{(^iPr_3P)_2Au_4[S_2C_6H_4]_2\}$ and $\{(^iPr_3P)_2Au_4[S_2C_6H_3Me]_2\}$ were prepared by treating the corresponding phenyl-1,2-dithiol with $[(^iPr_3PAu)_3O]BF_4$.[41] The crystal structures of these compounds show a rhombus formed by four Au atoms with Au ··· Au contacts of *ca.* 3.11 Å.

By using 4-methylthiazole, its derivatives $CH_3SC{=}NC(CH_3){=}C(H)S$ (**I**) and $S{=}CN(H)C(CH_3){=}C(H)S$ (**II**), and an amine, we prepared the linear N- and S-coordinated gold(I) complexes, $[Au(C_6F_5)\{N{=}C(H)SC(H){=}CCH_3\}]$ (**2**), $[Au(C_6F_5)\{N{=}C(SCH_3)SC(H){=}CCH_3\}$ (**3**), $[Au(C_6F_5)\{N(H)CH_2(CH_2)_3CH_2\}]$ (**4**) and $[Au(C_6F_5)$-

† Electronic supplementary information (ESI) available: Characterisation data for **1**. See http://www.rsc.org/suppdata/dt/b3/b303625a/

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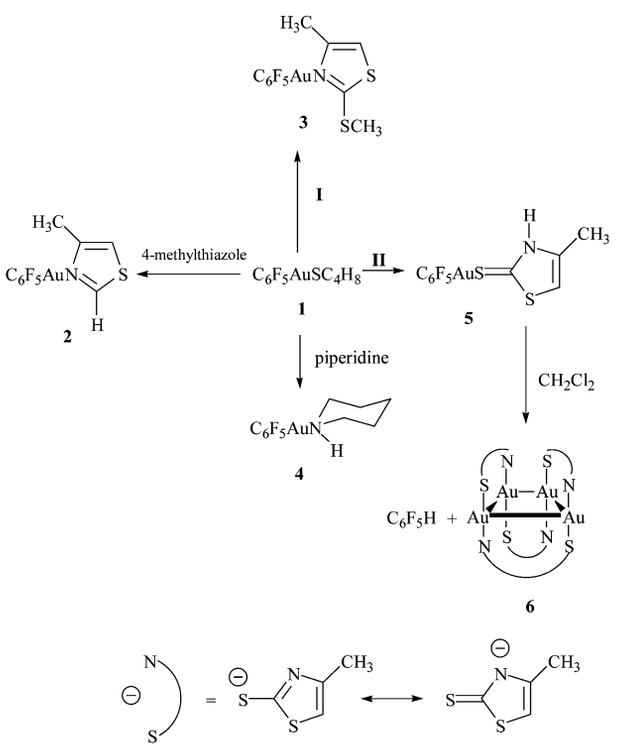
{S=CN(H)C(CH_3)=C(H)S}] (**5**) as well as an unusual tetrameric gold compound, [Au{S=CNC(CH_3)=C(H)S}]$_4$ (**6**).

Results and discussion

Synthetic aspects

The thioether, **I**, was previously prepared by the addition of MeI to the corresponding thione[42] in a basic medium followed by distillation to purify the product. The new preparation *via* deprotonation of 4-methylthiazole followed by reaction with MeSSMe produces the thioether in very high yield (70%) after a simple filtration to purify it. The product is a colourless liquid in contrast to the crystalline thioethers $CH_3SC{=}NC_6H_4S$-*o*[43] and $CH_3SC{=}NC(H){=}C(C_6H_4OH)S$.[44] A convenient simplification of a cyclization reaction (reaction of bromoacetone with dithiocarbamate followed by a dehydration[45]) achieved by reacting 4-methylthiazolyl-2-lithium with S_8 and quenching with H_2O, yielded 43% of the thione **II** after crystallisation. Both ligands are soluble in polar and nonpolar organic solvents.

The treatment of equimolar amounts of the starting material, **1**, with 4-methylthiazole, **I**, piperidine or **II** (Scheme 1) readily effects substitution of the tht (SC_4H_8, tetrahydrothiophene) ligand to produce colourless N-coordinated **2**, **3**, **4** and light yellow thione-coordinated **5** in very high yields. The reaction mixtures were filtered through $MgSO_4$ to remove solids and evaporated to complete dryness. The products are soluble in CH_2Cl_2, acetone and THF.



Scheme 1

Complex **4** is stable at room temperature under inert atmosphere but is more air- and moisture-sensitive than the imine complexes **2** and **3**. These compounds are isolable and characterisable eventhough their "instability" was predicted on many occasions.[16,18] The formation of **6** is described below.

Characterisation

No unexpected features were observed in the mass, IR, ^{1}H and ^{13}C NMR spectra of **I**. The ^{1}H NMR of **II** in d_6-acetone shows a signal at 11.75 ppm for the N–H proton and only the CH_3-signal in the region where S–H protons (2–4 ppm)[46,47] are expected indicating that the thione tautomer predominates in solution. The ^{13}C NMR chemical shifts of the NCS and SC*C*(CH_3)N carbons at 191.2 and 139.3 ppm are similar to values observed for the thiazole rings of carbene compounds.[48] A weak S–H vibration at (2500 cm^{-1})[42,46] was observed in the infrared spectrum recorded (KBr pellet) along with the N–H vibration (3000 cm^{-1}). This is not quite unexpected as strong hydrogen bonding between the S and N–H of adjacent molecules of the thiones was observed in the crystal structures of 1,3-thiazoline-2-thione, 4-(3-nitrophenyl)thiazole-2(3*H*)-thione and benzothiazole-2-thione.[49]

The ^{1}H and ^{13}C NMR spectra of **2**, **3** and **5** provide no clues as to the identity of the coordinated heteroatom. The signals in the ^{1}H NMR spectra are shifted not more than 0.7 ppm downfield from their positions in the spectra of the free ligand. In the ^{13}C NMR most signals are also shifted downfield, but not more than 4.5 ppm from those in the free ligand. The exception is the signal for the NCS-carbon which is shifted downfield in the thiazole compound, **2** (11.1 ppm), and in the thioether compound, **3** (6.5 ppm), but upfield in the the thione, **5** (4.5 ppm).

The signals in the ^{1}H NMR spectrum of the amine complex, **4**, are shifted not more than 0.5 ppm from the signals of the free ligand and equatorial and axial protons can be distinguished for the β- and γ-CH_2 groups. The ^{13}C NMR signals are shifted upfield and downfield (4 ppm) from those in the free ligand.

The N–H signal for the piperidine is observed at 2.08 ppm for the free ligand but appears at 5.17 ppm when the ligand is coordinated. While the N–H signal of **II** appeared at 11.75 ppm as mentioned before, it was observed at 8.94 and 5.27 ppm in **5** for different concentrations.[47] The ^{19}F NMR spectra display the normal pattern observed for C_6F_5-groups in gold(I) complexes.[18,50]

The endocyclic thioether S is unlikely to be the site of coordination as ^{14}N NMR data suggests that the lone pair of the sulfur is delocalized into the conjugated ring.[51] For **2** this only leaves imine coordination to gold, which was confirmed by a crystal structure determination, and for **5** thione or amine coordination.

To determine the site of coordination in **3** we resorted to ^{15}N NMR spectra as no suitable crystals for a crystal structure determination could be grown and at least two coordination sites, the imine N-atom and exocyclic thioether S-atom were available. The low natural abundance and severe sensitivity of the ^{15}N nucleus makes direct NMR measurement difficult but very useful.[52] The use of labelled ligands though successful,[53] has been limited to C^{15}N$^-$ ligands. ^{15}N chemical shifts have been reported for 2,3-dihydro-1*H*-imidazol-2-ylidene-gold complexes.[54]

An upfield shift of 59.2 ppm was observed for the ^{15}N-atoms in the thiazole gold complex **2** compared to the signal for the free thiazole upon coordination. A similar result was obtained for the thioether gold complex **3** (upfield shift 57.7 ppm) thus confirming imine coordination above endocyclic and exocyclic thioether coordination. The signal for the ^{15}N-atoms in the thione gold complex **5** showed a small downfield shift ($\Delta\delta$ = 6.7 ppm) when compared to the ^{15}N-atoms of the amine N-atom in the free thione ligand. However, the amine complex, **4**, (also characterised by other means) exhibits a small downfield ($\Delta\delta$ = 4.5 ppm) shift compared to the free ligand in contrast to the changes in the imine complexes. This could be because π-back bonding possibilities in **4** are non-existent. π-Back bonding in **5** is possible and thus a conclusive result as to the coordination site of the thione could only be achieved by determining the crystal structure of the compound.

Efforts to crystallise the thione gold complex were complicated by unexpected proton transfer from the amine group on the thione to the C_6F_5-ligand yielding C_6F_5H and **6** (15 mg,

CD_2Cl_2, 20 days). The formation of insoluble **6** was slow enough to give crystals suitable for a structure determination. Crystals of **5** were finally obtained within 7 days by dissolving some microcrystalline material in a minimum of CH_2Cl_2 and layering with pentane. The X-ray crystal structure determination confirmed thione coordination.

No homoleptic rearrangement to yield AuL_2^+ and $(C_6F_5)_2Au^-$ occurred in **2**, **3**, **4** and **5** as only one set of peaks is observed in the NMR spectra of each compound. Homoleptic rearrangements have previously been observed for $C_6F_5Au[\overline{CNHCH{=}CHN}(CH_3)]$ (accompanied by proton migration) and $C_6F_5Au[\overline{CCHCHN(CH_3)S}]$[55] but not for $C_6F_5Au(NC_5H_4CH_3\text{-}3)$[18] and $C_6F_5Au[\overline{CN(CH_3)C(CH_3){=}CHS}]$.[9] Pseudopotential *ab initio* calculations on the molecular and ionic dimers of the type $[(H_3P)AuCl]_2$ and $\{[(H_3P)_2Au]^+[AuCl_2]^-\}$ have shown that the compounds are closely comparable in energy.[56] The same is probably true for C_6F_5AuL compounds and ClAuL compounds of which many species *viz*. $[AuL_2]^+[LAuCl][AuCl_2]^-$,[16] $[AuL_2]^+[AuCl_2]^-$,[24,18,20,25] and $[L_2Au]^+Cl^-$[16] have been crystallised. Most examples were prepared with a huge excess of ligand although the rearrangement was also observed when equimolar amounts were used.[57] The occurrance of homoleptic rearrangements are unpredictable.

The molecular ions of all the new products were observed in the mass spectra (electron impact is the preferred method as FAB samples are dissolved creating an opportunity for homoleptic rearrangement[18]) indicating that these compounds were all neutral monomers.

Molecular structure

The molecular structures of **2**, **5** and **6** are shown in Figs. 1–3 and selected bond lengths and angles in Table 1. The approximately linear two-coordinate Au atoms in **2** and **5** are bonded to a C_6F_5-group and to the imine N-atom of a thiazole ligand in **2** [N(1)–Au–C(5) 174.0(4)°] or the thione S-atom of a thiazole-thione ligand in **5** [S(1)–Au–C(5) 178.7(4)°].

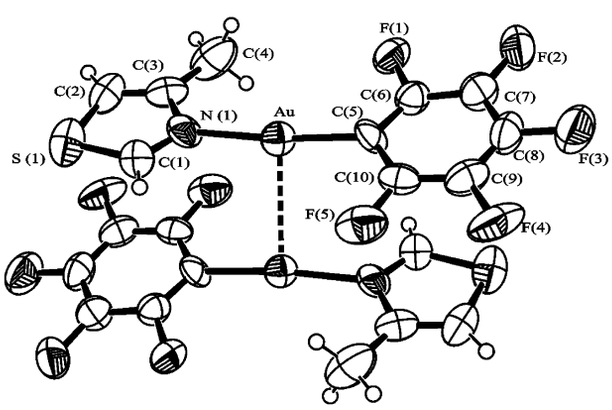


Fig. 1 Molecular structure of **2** showing the numbering scheme and intermolecular interaction with a neighbouring molecule. Ellipsoids are shown at the 50% probability level.

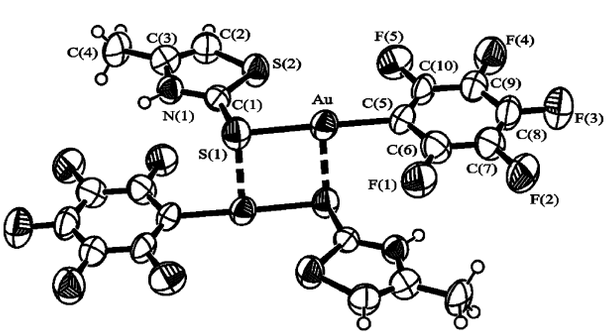


Fig. 2 Molecular structure of **5** showing the numbering scheme and intermolecular interaction with a neighbouring molecule. Ellipsoids are shown at the 50% probability level.

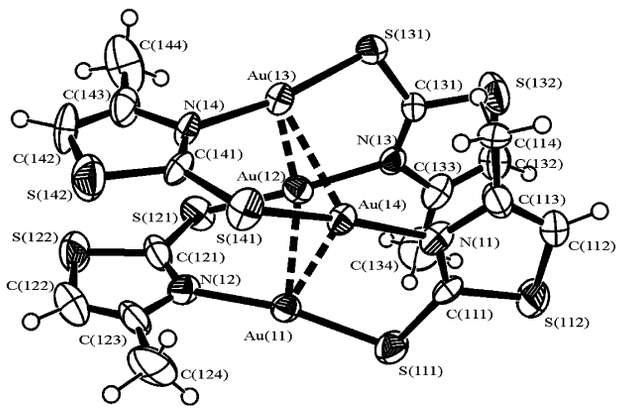


Fig. 3 Molecular structure of **6** showing only one of the two molecules per asymmetric unit and the numbering scheme. Ellipsoids are shown at the 50% probability level.

The ligands in these compounds are almost co-planar [angle between the plane of the thiazole ring and the plane of the C_6F_5 ring = 10.0(2)° for **2** and 5.5(4)° for **5**].

In **6** the ligands are coordinated to two different Au atoms, one through the thione S-atom and the other through the amide N-atom. Although the N(1)–Au–S(1) angle [169(3)°] in **6** is slightly smaller than similar angles in **2** and **5**, as a result of the distortion due to the aurophilic interactions [3.02(4) Å] of the four Au-atoms in the 16-membered ring of **6**, the coordination of the Au-atoms is still approximately linear. The same distortion of the linear geometry of the Au-atoms was observed for the tetramer $[Au\overline{SCNHCH_2CH_2N}]_4$ in which the ligands, contrary to the situation in **6**, are arranged homoleptically around each Au-atom.[38]

The ligands in **6**, forming loops connecting the Au atoms together, with two ligands above the four-membered Au ring and two below it, remain planar (maximum deviations from planarity for each ligand: 0.019(12), 0.032(13) 0.027(7), 0.012(10), 0.030(7), 0.024(7), 0.009(7), 0.010(10)Å). The four-membered ring is folded (deviations from planarity in the four-membered Au rings: 0.3731(3) Au11, −0.3625(3) Au12, 0.3599(3) Au13, −0.3705(3) Au14, −0.3210 (3) Au21, 0.3293(4) Au22, −0.3310(4) Au23, 0.3227(3) Au24). This contrasts with most previously published complexes containing similar four-membered Au rings where the gold atoms form a planar rhombus, although smaller distortions do occur in some examples.[26,41,58] The rings are no longer co-planar with each other as they were in **2** and **5**, although the thiazole rings lying opposite each other are almost parallel [angles between the planes of the two thiazole ligands above the four-membered Au ring in the two molecules = 8.1(7), 4.9(7)°; angles between the planes of the two thiazole rings lying below the four-membered Au ring = 2.3(1)°, 4.4(1)]. The planes of the thiazole rings of adjoining ligands, *i.e.* where the ligands are coordinated to a common Au atom, are perpendicular to each other [angles between 87.1(4) and 90.0(4)°]. Furthermore, the plane of each ligand is twisted by about 20° with respect to the bond between the two Au atoms it is coordinated to (Au–Au–N–S torsion angles = −17.8(3), 19.6(3), −19.3(3), 18.6(3), −17.2(3), 18.5(3), −14.6(3), 17.1(3)°). In literature examples containing comparable tetrameric complexes the bidentate ligands twist out of the plane much less, with equivalent torsion angles no greater than 8.8°.[58,38,59,60] Closer investigation shows that the reason for the twisting is the formation of weak face-to-face arene–arene interactions between the thiazole rings of opposing ligands (distances between centroids of pairs of thiazole rings: 3.654, 3.569, 3.572, 3.618 Å).

Table 1 Selected bond lengths (Å) and angles (°) for **2**, **5** and **6**

Bond distances	**2**		**5**		**6**[a]	Bond angles	**2**		**5**		**6**[a]
Au ··· Au	3.345(1)			Au ··· Au	3.02(4)					Au–Au–Au	87(2)
Au–N(1)	2.081(8)			Au–N(1)	2.06(2)	N(1)–Au–C(5)	174.0(4)	S(1)–Au–C(5)	178.7(4)	N(1)–Au–S(1)	169(3)
		Au–S(1)	2.304(4)	Au–S(1)	2.259(4)	Au–N(1)–C(1)	122.6(8)			Au–N(1)–C(1)	124(1)
Au–C(5)	2.00(1)	Au–C(5)	2.057(14)			Au–C(5)–C(6)	121.8(8)	Au–C(5)–C(6)	121.4(12)		
		S(1)–C(1)	1.686(15)	S(1)–C(1)	1.719(17)			Au–S(1)–C(1)	102.5(5)	Au–S(1)–C(1)	108(1)
N(1)–C(1)	1.27(1)	N(1)–C(1)	1.36(2)	N(1)–C(1)	1.33(2)	S(1)–C(1)–N(1)	113.1(9)	S(2)–C(1)–N(1)	107.8(10)	S(2)–C(1)–N(1)	112(1)
S(1)–C(1)	1.70(1)	S(2)–C(1)	1.704(13)	S(2)–C(1)	1.72(2)	C(1)–S(2)–C(2)	89.7(6)	C(1)–S(2)–C(2)	91.1(8)	C(1)–S(2)–C(2)	90.2(7)
S(1)–C(2)	1.71(1)	S(2)–C(2)	1.734(17)	S(2)–C(2)	1.70(3)	S(1)–C(2)–C(3)	112.0(9)	S(2)–C(2)–C(3)	111.8(12)	S(2)–C(2)–C(3)	114(6)
C(2)–C(3)	1.32(2)	C(2)–C(3)	1.29(2)	C(2)–C(3)	1.35(2)	C(2)–C(3)–N(1)	112(1)	C(2)–C(3)–N(1)	112.8(14)	C(2)–C(3)–N(1)	112(2)
C(3)–C(4)	1.46(2)	C(3)–C(4)	1.47(2)	C(3)–C(4)	1.49(4)	C(3)–N(1)–C(1)	113.5(9)	C(3)–N(1)–C(1)	116.3(12)	C(3)–N(1)–C(1)	113.0(17)
C(3)–N(1)	1.42(1)	C(3)–N(1)	1.349(19)	C(3)–N(1)	1.40(2)			S(1)–C(1)–N(1)	126.3(10)	S(1)–C(1)–N(1)	129.1(14)
C–F[b]	1.36	C–F[b]	1.34								
C–C[b]	1.37	C–C[b]	1.37								

[a] Average of 8 units. [b] Average of bonds in C_6F_5 unit.

The Au–C(5) distances in **2** and **5** are similar and correspond to the separations in [Au(C_6F_5){$\overline{CN(CH_3)C(CH_3)=CHS}$}] [1.993(10) Å][61] and [$\overline{Au(C_6F_5)(Ph_2C=NN=CPPh_2)}$] [1.992(6) Å].[62] The observed Au–N(1) distances in **2** and **6** are comparable to Au–N distances in gold(I) amine {[Au-{$\overline{NH(CH_2)_4CH_2}$}Cl], Au–N 2.068(18) Å[26]}, imine {[Au($NC_5H_4CH_3$-3)(C_6F_5)], Au–N 2.066(5) Å,[18] [Au(mmb)-(PPh_3)], mmb = 1-methyl-2-(methylthiomethyl)-1*H*-benzimidazole, Au–N 2.080(6) Å[19] and [Au{$\overline{C=C[C=CN(CH_3)_2CH_2O]SCH=CH}$}]$_2$, Au–N 2.065(8) Å[9]} and amide {[Au(L)(PPh_3)], HL = pyrazole, Au–N 2.024(7) Å, HL = imidazole, Au–N 2.027(4) Å[63]} complexes. The Au–S(1) distances in **5** and **6** are the same as the Au–S distances in gold(I) thione {[AuCl(S=$\overline{CSCH_2CH_2S}$)], Au–S 2.258(4) Å,[31] [Au(HL)$_2$]ClO_4, HL = C_5H_5NS, Au–S 2.388(3) and 2.282(3) Å[33]} and thiolate {[Au(2-Spym-4-NH_2)(PEt_3)], Au–S 2.291(3) Å, [Au(2-Spym-4-NH_2)(PPh_3)], Au–S 2.308(1) Å, 2-Spym-4-NH_2 = 4-amino-2-pyrimidinethiol[64]}compounds. The S(1)–C(1) distances in **5** and **6** are also similar to C=S distances in similar complexes {[AuCl(S=$\overline{CSCH_2CH_2S}$)], C(1)–S(1) 1.687(12) Å,[31] [Au(HL)$_2$]ClO_4, HL = C_5H_5NS, C(1)–S(1) 1.719(11) and 1.727(11) Å[33]}. The Au–S(1)–C(1) angle in **6** [av. 108.3(1)°] is slightly enlarged [102.5(5)° in **5**] as a result of the rectangular aurophilic interactions. A reduction in the same angle [92.3(4) and 92.6(4)°] is observed in [Au$\overline{SCNHCH_2CH_2N}$]$_4$[38] as a result of rhombic Au ··· Au contacts. The bond lengths and angles in the C_6F_5-group and thiazole units do not differ significantly from those reported for [Au(C_6F_5)$\overline{CN(CH_3)C(CH_3)=CHS}$],[61] [CuCl{$\overline{CN(CH_3)C(CH_3)=CHS}$}][65] and [Fe($\eta^5$-$C_5H_5$)(CO)$_2$-{$\overline{CNHC(CH_3)=CHS}$}]$CF_3SO_3$·0.5$H_2O$.[66]

The Au-atoms in **2** are involved in aurophilic interactions [Au ··· Au 3.345(1) Å] across the inversion centre at the centre of the unit cell. The dihedral angle N–Au–Au–N is −180.0(4)° thus placing the C_6F_5-unit of one molecule across the thiazole unit of a neighbour. No aurophilic interactions are observed in the crystal structure of **5** but hydrogen bonding and arene–arene interactions seem to dominate lattice organisation. The molecules in the crystal are arranged in sheets with the C_6F_5-unit of one molecule across from the thiazole unit in the neighbouring molecule as a result of the N–H ··· F(1)′ [3.203(15) Å] and N–H ··· F(2)′ [3.310(17) Å] interactions. These interactions lead one to speculate that the formation of the H-bond in **5** may play a role in the deprotonation that results in the formation of **6**. In the above mentioned sheets the molecules are arranged to form "dimers" with the molecules in the neighbouring sheets. These "dimers" associate *via* intermolecular Au ··· S(1) contacts and are related by a crystallographic centre of inversion. The atoms Au, S(1), Au′ and S(1)′ form a parallelogram with the Au ··· S(1)′ edges 3.529(4) Å and an Au ··· Au′ diagonal of 4.177(1) Å. This general pattern also occurs in [2,6-(CH_3)$_2$$C_6H_3$NCAuSCN] [Au ··· S(1)′ 3.459(2) and Au ··· Au 3.983(1) Å] and [2,3,6-(CH_3)$_3$$C_6H_2$NCAuSCN] [Au ··· S(1)′ 3.938(2), 3.719(2) and Au ··· Au 3.397(1), 5.125(1) Å].[40]

Substitution reactions

Piperidine substituted the 4-methyl-2-methylsulfanylthiazole ligand in **3** and tht in **1** in diethyl ether solution at 32 °C. The addition of the imine, 4-methylthiazole, to a solution of **4** or a solution of **5** did not yield any substitution products. The addition of the thione to a solution of **2** in diethyl ether, however, yielded **5**.

As a result of these reactions and the preferred coordination sites observed for **5** and **2**, a new series in order of increasing preference for the coordination of ligands to the soft Au^+ centre

can be proposed: tht < 4-methylthiazole and 4-methyl-2-methylsulfanylthiazole < piperidine < 4-methyl-3*H*-thiazole-2-thione. According to SHAB principles the series should be: piperidine < 4-methylthiazole and 4-methyl-2-methylsulfanylthiazole < tht < 4-methyl-3*H*-thiazole-2-thione.[67]

Conclusions

The thiazolylthione, **II**, which contains three possible coordination centres *viz.* thione, amine and endocyclic thioether, substitutes tht in **1** to yield the thione coordinated compound **5**. Complex **5** converts very slowly in a CH_2Cl_2 solution by nucleophilic attack of C_6F_5 on the amine hydrogen to the unusual Au(I) tetramer **6**. The lablile tht ligand in **1** is easily substituted by 4-methylthiazole (two coordination sites, imine N-atom and thioether S-atom) to produce an imine complex **2**. Since the tht in **1** is substituted by 3-methylpyridine to form $Au(C_6F_5)$-(*N*-3-methylpyridine),[18] $H_2N(CH_2)_nNH_2$ to form $Au(C_6F_5)$-$NH_2(CH_2)_nNH_2$[27] (n = 2 or 3), $Ph_2C{=}N{-}N{=}CPh_2$ to form $\overline{Au(C_6F_5)(Ph_2C{=}NN{=}CPPh_2)}$[59] or piperidine to form the neutral monomeric complex **4** and the imine coordinated ligand, **I**, in **3** is also substituted by piperidine, the following substitution series in order of decreasing preference for ligands on the C_6F_5Au centre (Au^+ soft acid) can be proposed: >C=S **>** R_2NH (hard base) **>** >C=N– (borderline base) **>** RSR (soft base). This series contradicts the expected order, >C=S **>** RSR **>** >C=N– **>** R_2NH, according to the typical classification of hard and soft acids and bases.[67]

The successful preparation and characterisation of **2**, **3**, **4** and the many other reported examples of Au(I) imine[17–25,68] and amine[17,26–29] complexes as well as the observed substitution reactions add to the evidence that soft Au^+ centres do form stable imine and amine complexes.

Experimental

General

Reactions were carried out under argon using standard Schlenk and vacuum-line techniques. Tetrahydrofuran and diethyl ether were distilled under N_2 from sodium diphenylketyl, CH_2Cl_2 from CaH_2 and hexane from sodium. Butyllithium was purchased from Merck and CH_3SSCH_3, 4-methylthiazole and CF_3SO_3Me from Aldrich. Literature methods were used to prepare $[Au(C_6F_5)(SC_4H_8)]$ (**1**)[69] from $HAuCl_4$.[70] Melting points were determined on a Büchi 535 apparatus in unsealed capillary tubes. Mass spectra (electron impact) were recorded on a Finnigan Mat 8200 instrument, the infrared spectra, using KBr pellets or NaCl disks, on a Perkin-Elmer 841 spectrometer and NMR spectra on a Varian Gemini 2000, Varian 300 FT or INOVA 600MHz spectrometer (^{1}H NMR at 200/300/600 MHz and $^{13}C\{^1H\}$ NMR at 50/75/151 MHz, δ reported relative to the solvent resonance converted to TMS). ^{15}N NMR (60.8 MHz, CH_3NO_2 external reference) spectra (concentration 450 mg in 0.75 cm^3) were determined on an INOVA 600MHz spectrometer. Elemental analyses were carried out by the Department of Chemistry, University of Cape Town, South Africa. The full characterisation data of **1** is available electronically (ESI). †

Preparation of $CH_3S\overline{C{=}NC(CH_3){=}C(H)S}$ I. Methylthiazol-2-yllithium[71] was prepared by the addition of 4-methylthiazole (0.50 cm^3, 5.5 mmol) to 1.6 mol dm^{-3} *n*-butyllithium in hexane (3.10 cm^3, 5.0 mmol) in THF (20 cm^3) at −80 °C, and was stirred at −80 °C for 15 min before CH_3SSCH_3 (0.40 cm^3, 5.4 mmol) was added. Stirring was continued at this temperature for 1 h before warming to room temperature. The solvent was removed *in vacuo*. The residue was extracted with diethyl ether (2 × 60 cm^3) and the extract was filtered through *n*-alumina (15 g) and evaporated to dryness *in vacuo*. The clear oil was diluted with 10 ml of diethyl ether and the mixture was cooled to −80 °C. Colourless crystals isolated at −80 °C melted before reaching room temperature and the colourless oil obtained was used without further purification (0.56g, 70%) (Found: C, 41.40; H, 4.79; N, 9.59%; $C_5H_7NS_2$ requires C, 41.35; H, 4.86; N, 9.64%); ν_{max}/cm^{-1} 3107s, 2981m, 2954m, 2923s, 2858m, 1527s, 1492w, 1437s, 1410s, 1371s, 1310m, 1292s, 1060m, 1037s, 993w, 961s, 637w, 928w, 873w, 845w, 804w, 715m (Nujol); δ_H (CD_3COCD_3) 6.72 [1H, q, J_{HH} = 1.2Hz, $CH_3SC{=}NC(CH_3){=}C(H)$S], 2.66 [3H, s, $CH_3SC{=}NC(CH_3){=}C(H)S$], 2.32 [3H, d, J_{HH} = 1.2Hz, $CH_3SC{=}NC(CH_3){=}C(H)S$]; δ_C (CD_3COCD_3) 165.4 (s, NCS), 153.0 [s, C=N$C(CH_3)$], 112.6 [s, $NC(CH_3){=}CHS$], 17.0 (s, SMe), 16.8 [s, $NC(CH_3){=}CHS$]; δ_N (CD_3COCD_3) −63.8; *m*/*z* 145 (M^+), 112 (M − SH), 99 [HC=$NC(CH_3){=}C(H)S$], 86 [HC=$NC(CH_3){=}C(H)S$ − CH], 71($SCCCH_3$), 45 (HCS).

Preparation of $S{=}\overline{CN(H)C(CH_3){=}C(H)S}$ II. Methylthiazol-2-yllithium was prepared as described above from 4-methylthiazole (0.60 cm^3, 6.1 mmol) and 1.6 mol dm^{-3} *n*-butyllithium in hexane (3.80 cm^3, 6.1 mmol). The mixture was stirred for 15 min at −80 °C before a suspension of S_8 (0.192 g, 6.0 mmol) in 10 ml of THF was added. The mixture was stirred for 2 h at −70 °C prior to the addition of H_2O (0.11 cm^3, 6.1 mmol). Stirring was continued at this temperature for 1 h, before warming to room temperature. The solvent was removed *in vacuo*. The residue was extracted with diethyl ether (2 × 60 cm^3) and the extract was filtered through SiO_2 (10 g) and evaporated to dryness *in vacuo*. The formed microcrystalline off-white product (0.35 g, 43%) was washed with three portions (20 cm^3) of hexane to remove unreacted 4-methylthiazole and dried *in vacuo*. Alternatively the product can be purified by flash column chromatography[72] on SiO_2 (230–400 mesh) with diethyl ether–hexane (1 : 4) as eluent. The last fraction contained 0.26 g (33%) of the off-white product, mp 87 °C (decomp.) (Found: C, 36.57; H, 3.88; N, 10.70%, $C_4H_5NS_2$ requires C, 36.61; H, 3.84; N, 10.67%); ν_{max}/cm^{-1} 3200 (sh), 3106m, 3050w, 3019w, 2940m, 2920m, 2878m, 2712m, 1604s, 1466s, 1440sh, 1428s, 1384s, 1320s, 1247s, 1207m, 1146m, 1140m, 1123w, 1075s, 1044sh, 1063s, 988m, 944s, 919w, 838m, 781s, 741s, 679s (KBr); δ_H (CD_3COCD_3) 11.75 [1H, br s, S=CN(H)C(CH_3)=C(H)S], 6.41 [1H, q, J_{HH} = 1.2 Hz, S=CN(H)C(CH_3)=C(H)S], 2.21 [3H, d, J_{HH} = 1.2 Hz, S=CN(H)C(CH_3)=C(H)S]; δ_C (CD_3COCD_3) 191.2 (s, NCS), 139.3 [s, N$C(CH_3)$], 108.4 [s, $NC(CH_3){=}CHS$], 13.5 [s, $NC(CH_3)$]; δ_N (CD_3COCD_3) −185.3; *m*/*z* 131 (M^+), 99 (M − S), 86 (M − S − CH), 71 ($SCCCH_3$), 45 (HCS).

Preparation of $[Au(C_6F_5)\{\overline{N{=}C(H)SC(H){=}CCH_3}\}]$ 2. The addition of 4-methylthiazole (0.15 cm^3, 1.6 mmol) to a solution of **1** (0.452 g, 1.6 mmol) in diethyl ether (40 cm^3) and stirring for 1.5 h at room temperature produces a clear solution of **2**. The solution was reduced to dryness *in vacuo*, the residue extracted with diethyl ether (2 × 30 cm^3), the extract was filtered through anhydrous $MgSO_4$ (18 g) and the filtrate again reduced to dryness *in vacuo*. Colourless **2** (0.73g, 99%) was recrystallised by layering a diethyl ether solution of **2** with hexane. Needle-like crystals suitable for a crystal structure determination were obtained, mp 58 °C (decomp.) (Found: C, 25.89; H, 1.11; N, 3.00%, $C_{10}H_5AuF_5NS$ requires C, 25.93; H, 1.09; N, 3.02%); ν_{max}/cm^{-1} 3137m, 1640m, 1612m, 1541s, 1501s, 1460s, 1453s, 1438s, 1420s, 1380m, 1356m, 1311m, 1279w, 1252w, 1227m, 1144m, 1113w, 1070m, 1055s, 1001m, 985s, 948s, 884s, 818s, 799s, 742s, 717w, 704w, 667w (KBr); δ_H (CD_3COCD_3) 9.55 [1H, d, J_{HH} = 2.1 Hz, HC=NC(CH_3)=C(H)S)], 7.81 [1H, dq, J_{HH} = 1.2 Hz, J_{HH} = 2.1 Hz, HC=NC(CH_3)=C(H)S], 2.68 [3H, d, J_{HH} = 1.2 Hz, HC=NC(CH_3)=C(H)S]; δ_C (CD_3COCD_3) 160.8 (s, NCS), 153.2 [s,N$C(CH_3)$], 150.2 (ddm, J_{CF} = 231.4 Hz, J_{CF} = 23.5 Hz, AuCCFCFCFCFCF), 139.2 (dm, J_{CF} = 244.5 Hz, AuCCFCFCFCFCF), 137.4 (dm, J_{CF} = 249.3 Hz, AuC-CFCFCFCFCF), 118.7 (tm, J_{CF} = 52.7 Hz, AuC-

CFCFCFCFCF), 118.2 [s, NC(CH_3)=*C*HS], 17.3 [s, NC(*C*H_3)]; δ_F (CD_3COCD_3) −112.9 (2F, dd, J_{FF} = 9.3 Hz, J_{FF} = 19.99 Hz, AuCC*F*CFCFCFC*F*), −158.7 (1F, t, J_{FF} = 19.9 Hz, AuCCFCFC*F*CFCF), −161.7 (2F, dt, J_{FF} = 9.3, J_{FF} = 19.9 Hz, AuCCFC*F*CFC*F*CF); δ_N (CD_3COCD_3) −108.3; δ_N (4-methylthiazole) (CD_3COCD_3) −49.1; *m*/*z* 463 (M^+), 364 [M − HC=NC(CH_3)=C(H)S], 334 ($C_{12}F_{10}$), 296 (M − C_6F_5), 265 [F_5C_6C=NC(CH_3)=C(H)S], 99 [HC=NC(CH_3)=C(H)S], 71 (CH_3CCS), 45 (HCS).

Preparation of [Au(C_6F_5){N=C(SCH$_3$)SC(H)=CCH$_3$}] 3. This product was prepared in the same way as **2** from 4-methyl-2-methylsulfanylthiazole **I** (0.314 g, 2.2 mmol) and **1** (0.979 g, 2.2 mol). Colourless **3** (1.00 g, 91%) was obtained, mp 68 °C (Found: C, 25.90; H, 1.42; N, 2.76%, $C_{11}H_7AuF_5NS$ requires C, 25.94; H, 1.39; N, 2.75%); ν_{max}/cm^{-1} 3128m, 2917m, 1635m, 1609m, 1558s, 1540s, 1501s, 1458s, 1439s, 1394m, 1378m, 1356m, 1299m, 1253m, 1146vw, 1110s, 1056s, 1014w, 949s, 799s, 725m (KBr); δ_H (CD_3COCD_3) 7.44 [1H, q, J_{HH} = 1.2 Hz, CH_3SC=NC(CH_3)=C(*H*)S], 2.83 [3H, s, C*H*$_3$SC=NC(CH_3)=C(H)S], 2.55 [3H, d, J_{HH} = 1.2 Hz, CH_3SC=NC(C*H*$_3$)=C(H)S]; δ_C (CD_3COCD_3) 176.9 (s, NCS), 153.2 [s,NC(*C*H$_3$)], 151.6 (ddm, J_{CF} = 226.3 Hz, J_{CF} = 23.5 Hz, AuC*C*FCFCFCFC*F*F), 139.2 (dm, J_{CF} = 244.1 Hz, AuCCFCF*C*FCFCF), 137.5 (dm, J_{CF} = 249.3 Hz, AuCCF*C*FCF*C*FCF), 119.7 (tm, J_{CF} = 53.1 Hz, Au*C*CFCFCFCFCF), 116.1 [s, NC(CH_3)=*C*HS], 17.8 (S*CH*$_3$), 17.5 [s, NC(*C*H$_3$)]; δ_F (CD_3COCD_3) −112.9 (2F, dd, J_{FF} = 9.3 Hz, J_{FF} = 19.99 Hz, AuCC*F*CFCFCFC*F*), −158.8 (1F, t, J_{FF} = 19.9 Hz, AuCCFCFC*F*CFCF), −161.7 (2F, m, AuCCFC*F*CFC*F*CF); δ_N (CD_3COCD_3) −121.6; *m*/*z* 509 (M^+), 364 [M − CH_3SC=NC(CH_3)=C(H)S], 334 ($C_{12}F_{10}$), 296 [AuN=C(H)SC(H)=CCH$_3$], 265 [F_5C_6C=NC(CH_3)=C(H)S], 145 [CH_3SC=NC(CH_3)=C(H)S], 112 [CH_3C=NC(CH_3)=C(H)S], 99 [HC=NC(CH_3)=C(H)S], 86 [NC(CH_3)CHS], 71 (CH_3CCS), 45 (HCS).

Preparation of [Au(C_6F_5){N(H)CH$_2$(CH$_2$)$_3$CH$_2$}] 4. Compound **4** was prepared in the same way as **2** from piperidine (0.25 cm^3, 2.5 mmol) and **1** (1.152 g, 2.5 mmol). Colourless **4** was recrystallised from CH_2Cl_2 layered with hexane (1.06 g, 92%), mp 115 °C (decomp.) (Found: C, 29.38; H, 2.51; N, 3.09%, $C_{11}H_{11}AuF_5N$ requires C, 29.41; H, 2.47; N, 3.12%); ν_{max}/cm^{-1} 3216m, 2946s, 2937m, 2928m, 2884m, 1631s, 1603m, 1548w, 1497s, 1451s, 1438s, 1417m, 1368m, 1355m, 1340w, 1310m, 1304w, 1285m, 1252s, 1181s, 1158w, 1105s, 1095m, 1053s, 1035m, 1021vw, 1008w, 950s, 867s, 871m, 802s, 745vw, 715w, 632w, 604w, 667w, 494m (KBr); δ_H (CD_3COCD_3) 5.17 [1H, brs, N*H*], 3.21 [4H, m, α-CH_2], 1.96 [2H, m, β-CH_eH$_a$], 1.72 [1H, m, γ-CH_eH$_a$], 1.68 [2H, m, β-CH_eH$_a$], 1.45 [1H, m, γ-CH_eH$_a$]; δ_C (CD_3COCD_3) 149.9 (ddm, J_{CF} = 227.7 Hz, J_{CF} = 23.7 Hz, AuC*C*FCFCFCFC*F*), 138.9 (dm, J_{CF} = 230.8 Hz, AuCCFCF*C*FCFCF), 137.3 (dm, J_{CF} = 225.1 Hz, AuCCF*C*FCF*C*FCF), 120.0 (tm, J_{CF} = 55.0 Hz, Au*C*CFCFCFCFCF), 52.3 [s, α-CH_2], 27.0 [s, β-CH_2], 24.2 [s, γ-CH_2]; δ_F (CD_3COCD_3) −116.1 (2F, m, AuCC*F*CFCFCFC*F*), −161.8 (1F, t, J_{FF} = 19.9 Hz, AuCCFCFC*F*CFCF), −164.2 (2F, m, AuCCFC*F*CFC*F*CF); δ_N (CD_3COCD_3) −338.3; δ_N (piperidine) (CD_3COCD_3) −342.5; *m*/*z* 449 (M^+), 364 [M − HNCH$_2$(CH$_2$)$_3$CH$_2$], 334 ($C_{12}F_{10}$), 296 ($C_{10}H_5F_9$), 265 ($C_9H_5F_8$), 168 (C_6F_5), 99 ($C_3H_5F_3$), 85 [HNCH$_2$(CH$_2$)$_3$CH$_2$], 84 [NCH$_2$(CH$_2$)$_3$CH$_2$], 56 [(CH$_2$)$_4$], 28 (C_2H_6).

Preparation of [Au(C_6F_5){S=CN(H)C(CH$_3$)=C(H)S}] 5. Compound **5** was prepared in the same way as **2** from 4-methyl-3*H*-thiazole-2-thione (0.259 g, 2.0 mmol) and **1** (0.867 g, 1.9 mmol). Light yellow **5** was recrystallised from CH_2Cl_2 layered with hexane (0.93 g, 97%), mp 90 °C (decomp.) (Found: C, 24.28; H, 1.05; N, 2.79%, $C_{10}H_5AuF_5NS_2$ requires C, 24.25; H, 1.02; N, 2.83); ν_{max}/cm^{-1} 3368s, (N–H) 3085m, 1640m, 1597s, 1559s, 1542w, 1508s, 1459s, 1455s, 1425s, 1391m, 1358m, 1325m, 1278w, 1260w, 1144m, 1114w, 1097m, 1068s, 1056s, 1003m, 951s, 829w, 794s (KBr); δ_H (CD_3COCD_3) 6.94 [1H, s, S=CN(H)C(CH_3)=C(*H*)S], 5.27 [1H, brs, S=CN(*H*)C(CH_3)=C(H)S] 2.39 [3H, s, S=CN(H)C(C*H*$_3$)=C(H)S]; δ_C (CD_3COCD_3) 186.4 (s, NCS), 143.2 [s,N*C*(CH_3)], 149.6 (ddm, J_{CF} = 203.7 Hz, J_{CF} = 24.6 Hz, AuC*C*FCFCFCFC*F*), 139.1 (dm, J_{CF} = 243.8 Hz, AuCCFCF*C*FCFCF), 137.7 (dm, J_{CF} = 250.2 Hz, AuCCF*C*FCF*C*FCF), 128.6 (tm, J_{CF} = 57.1 Hz, Au*C*CFCFCFCFCF), 112.8 [s, NC(CH_3)=*C*HS], 13.7 [s, NC(*C*H$_3$)]; δ_F (CD_3COCD_3) −112.8 (2F, dd, J_{FF} = 9.3 Hz, J_{FF} = 19.99 Hz, AuCC*F*CFCFCFC*F*), −159.0 (1F, t, J_{FF} = 19.9 Hz, AuCCFCFC*F*CFCF), −161.4 (2F, m, AuCCFC*F*CFC*F*CF); δ_N (CD_3COCD_3) −178.6; *m*/*z* 495 (M^+), 364 [M − CH_3SC=NC(CH_3)=C(H)S], 328 [AuS=CN(H)C(CH_3)=C(H)S], 262 [{SCN(H)C(CH_3)=C(H)S}$_2$], 246 [{SCN(H)C(CH_3)=C(H)S}$_2$ − CH_3], 230 [S{CNC(CH_3)=C(H)S}$_2$], 215 [S{CNC(CH_3)=C(H)S}$_2$ − CH_3], 168 (C_6F_5H), 131 [S=CN(H)C(CH_3)=C(H)S], 99 [HC=NC(CH_3)=C(H)S], 71 (CH_3CCS), 45 (HCS).

Preparation of [Au{S=CNC(CH$_3$)=C(H)S}]$_4$ 6. ^{1}H NMR spectra of a solution of **5** (15 mg, 0.03 mmol) in 0.75 cm^3 of CD_2Cl_2 were recorded over 20 days. Insoluble yellow microcrystalline **6** precipitated (9 mg, 23%). Crystals suitable for a crystal structure determination were obtained from a solution of **5** in CH_2Cl_2 layered with hexane after several weeks at 4 °C, mp 128 °C (decomp.) (Found: C, 14.78; H, 1.05; N, 4.20%, $C_{16}H_{16}Au_4N_4S_8$ requires C, 14.68; H, 1.23; N, 4.28); ν_{max}/cm^{-1} 3102w, 3075m, 3012vw, 2986vw, 2968vw, 1548s, 1425m, 1376w, 1355s, 1285s, 1143m, 1078s, 931m, 848m, 754w, 727m, 713s (KBr).

Substitution reactions. All substitution reactions were performed in the same way.

(1) A solution of **3** (0.279 g, 0.55 mmol) in diethyl ether (40 cm^3) was treated with piperidine (0.054 cm^3, 0.55 mmol). The reaction mixture was stirred for 2 h at 32 °C, filtered to remove solids and evaporated to dryness *in vacuo*. The products and their yields (69.7% of **4**, 13.8% of **I** and 16.5% of **3**) were determined by ^{1}H NMR spectroscopy.

2) Reagents: **4** (0.408 g, 0.91 mmol) and 4-methylthiazole (0.08 cm^3, 0.91 mmol). Products: 1 : 1 **4** and 4-methylthiazole.

3) Reagents: **5** (0.322 g, 0.65 mmol) and 4-methylthiazole (0.06 cm^3, 0.65 mmol). Products: 1 : 1 **5** and 4-methylthiazole.

4) Reagents: **3** (0.276 g, 0.60 mmol) and **II** (0.078 g, 0.60 mmol). Products: 1 : 1 **5** and 4-methylthiazole.

X-Ray crystal structure determinations

Crystal structure determination of 2. $C_{10}H_5AuF_5NS$, M = 463.18, monoclinic, space group $P2_1/a$, a = 7.5140(15), b = 21.352(3), c = 8.1590(13) Å, β = 115.528(17)°, U = 1181.2(4) Å^3, T =293 K, Z = 4, μ(Mo-Kα) = 12.67 m^{-1}, 3443 reflections measured, 2521 unique (R_{int} = 0.055) which were used in all calculations. The final $wR(F^2)$ was 0.043 (all data). The diffraction data were collected on an Enraf-Nonius CAD-4F diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) using ω–2θ scans (Enraf-Nonius CAD-4 software[73]). Emperical absorption corrections were performed using psi scans.[74] The structure of **2** was solved by the heavy atom method. All non-H atoms were eventually refined with anisotropic displacement parameters. The positions of some of the H atoms could be found from difference maps. Their positions were therefore calculated in ideal positions. In the final cycles of refinement the H atoms were included with equal and constant isotropic displacement parameters and no positional parameters were refined. For structure solution and refinement the XTAL 3.4[74] computing system was used. Figures were generated utilizing Ortep3 for Windows;[75] displacement ellipsoids are at the 50% probability level.

Crystal structure determination of 5. $C_{10}H_5AuF_5NS_2$, M = 495.24, monoclinic, space group $P2_1/a$, a = 7.4858(5), b = 12.2944(9), c = 13.5153(10) Å, β = 92.933(2)°, U = 1242.23(15) Å^3, T = 293(2) K, Z = 4, μ(Mo-Kα) = 12.223 m^{-1}, 3901 reflections measured, 1846 unique (R_{int} = 0.0814) which were used in all calculations. The final $wR(F^2)$ was 0.1854 (all data). The diffraction data were collected on a Nonius Kappa CCD diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) using ϕ and ω scans to fill the Ewald sphere (Nonius COLLECT[76]). Data reduction was performed using DENZO.[77] Empirical absorption corrections were performed using SCALEPACK.[77] The initial structure solution was found using direct methods, while the rest of the atomic positions were found from difference Fourier maps. All non-hydrogen atoms were refined anisotropically by full-matrix least squares methods. The hydrogen atoms were fixed in calculated positions. All calculations were performed using SHELX-97[78] within the WINGX package.[79] Figures were generated utilizing Ortep3 for Windows;[75] displacement ellipsoids are at the 50% probability level.

Crystal structure determination of 6. $C_{32}H_{32}Au_8N_8S_{16}$, M = 1308.67, triclinic, space group $P\bar{1}$, a = 11.6203(2), b = 14.5242(2), c = 16.0147(2) Å, α = 88.2480(10), β = 89.3080(10), γ = 81.5490(10)°, U = 2672.21(7) Å^3, T = 173(2) K, Z = 2, μ(Mo-Kα) = 22.532 m^{-1}, 15382 reflections measured, 7405 unique (R_{int} = 0.0526) which were used in all calculations. The final $wR(F^2)$ was 0.1419 (all data). Other details are the same as for the structural determination of **5**. A small amount of disorder was observed, and could not be correctly modelled.

CCDC reference numbers 207317–207319.

See http://www.rsc.org/suppdata/dt/b3/b303625a/ for crystallographic data in CIF or other electronic format.

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