

# Formation and Characterization of Neutral and Cationic Amino(thio)carbene Complexes of Gold(I) from Thiazolyl Precursors†

Helgard G. Raubenheimer,\* Fred Scott, Gert J. Kruger, James G. Toerien, Ronald Otte, Werner van Zyl, Itha Taljaard, Pierre Olivier and Lorna Linford

Department of Chemistry, Rand Afrikaans University, Auckland Park, Johannesburg 2006, South Africa

Benzothiazole-2-yl-, 4-methylthiazolyl- and thiazolyl-lithium reacted with  $[\text{AuCl}(\text{tht})]$  (tht = tetrahydrothiophene) to form bis(thiazolyl)aurate compounds which can be protonated or alkylated to give mono- and bis-(carbene) complexes of the type  $[\text{Au}(\text{C}=\text{NCX}^1=\text{CX}^2\text{S})(\text{CNRCX}^1=\text{CX}^2\text{S})]$  and  $[\text{Au}(\text{CNRCX}^1=\text{CX}^2\text{S})_2]^+$  ( $\text{X}^1\text{X}^2 = \text{C}_6\text{H}_4$ ;  $\text{X}^1 = \text{Me}$ ,  $\text{X}^2 = \text{H}$ ;  $\text{X}^1 = \text{X}^2 = \text{H}$ ;  $\text{R} = \text{H}$  or  $\text{Me}$ ). The strongly ligated gold phosphine and perfluorophenyl complexes  $[\text{AuCl}(\text{PPh}_3)]$  and  $[\text{Au}(\text{C}_6\text{F}_5)(\text{tht})]$  as well as  $\text{AuCN}$  also reacted with the thiazolyl-lithiums to afford, upon protonation or alkylation, cationic and neutral carbene compounds. Complicating side-reactions, such as homoleptic rearrangement, protonation or alkylation on carbon rather than nitrogen and dissociative polymerization were observed. The crystal structure of the neutral mono(carbene) complex  $[\text{Au}(\text{C}=\text{NCMe}=\text{CHS})(\text{CNH}(\text{CMe}=\text{CHS}))]$  shows a gold-gold interaction with a distance of 3.075(1) Å.

The most useful route towards gold carbene complexes is the addition of alcohols or amines to isocyanide complexes.<sup>1-3</sup> Other synthetic methods make use of the cleavage of electron-rich olefins<sup>4</sup> or carbene transfer from tungsten pentacarbonyl complexes.<sup>5</sup> The well known Fischer route<sup>6</sup> which involves electrophilic addition to metal acyls, thioacyls or even imidoys is not generally available for gold since few of these precursor complexes are known. We imitated the latter method by utilizing the tendency of gold to form aurate complexes with thiazol-2-yl-lithium reagents, and then obtained carbene complexes by protonation or alkylation of one or both nitrogen atoms. The method was applied successfully and could also be extended to include gold moieties with strongly bound neutral or anionic ligands such as  $\text{PPh}_3$  or  $\text{C}_6\text{F}_5^-$  and  $\text{CN}^-$  respectively.

Stone and co-workers<sup>7,8</sup> prepared thiazolynylidene complexes of various metals from thiazolylum compounds. We have isolated similar complexes containing chromium(0)<sup>9</sup> and iron.<sup>10</sup> Our results are also related to the recent work of Burini and co-workers<sup>11</sup> who prepared gold derivatives of imidazoles and unexpectedly also obtained a carbene complex. Some of the results reported here formed part of a preliminary communication.<sup>12</sup>

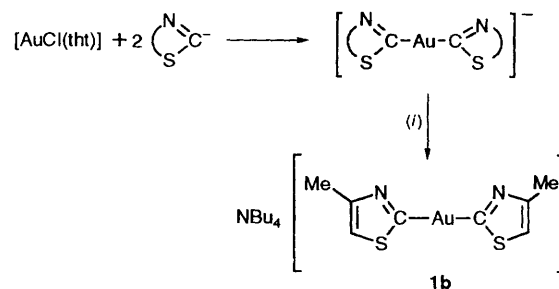
Various complicating reactions were observed in the preparation of the present compounds: (i) acidification or alkylation sometimes occurred on a metal-bonded carbon atom; (ii) in the attempted formation of monoalkylated compounds, dialkylated compounds tended to be the major products; (iii) certain gold thiazolyl complexes formed polymeric substances; (iv) certain products with mixed ligands spontaneously rearranged to form homoleptic gold compounds. Problem (i) could not be avoided. However, by working under mild conditions, C-protonated or alkylated ligands remained co-ordinated and were identified. Polymerization occurred relatively slowly and was contained by working at a low temperature. The polymerization also provided the reagents needed for an entry into the field of carbene(chloro) complexes which will form the central theme of a future paper.

Various crystalline-containing products were subjected to X-ray diffraction studies and the most characteristic feature of the new gold(I) compounds is the formation of dimers in the solid state due to gold-gold interactions.<sup>13,14</sup>

## Results and Discussion

Analytical and physical, as well as spectroscopic, data for all the new compounds described are collected in Tables 1 and 2 and are discussed where relevant. To simplify the drawings in the schemes the counter ion  $\text{CF}_3\text{SO}_3^-$  is not included when cationic complexes are formed.

**Preparation of Thiazolylaurates.**—Benzothiazole, 4-methylthiazole and thiazole are all easily lithiated at  $\text{C}^2$  by  $\text{LiBu}$  at  $-70^\circ\text{C}$ .<sup>15</sup> Addition of a solution of thiazol-2-yl-lithium in tetrahydrofuran (thf) to half a molar amount of  $[\text{AuCl}(\text{tht})]$  (tht = tetrahydrothiophene) produced the corresponding soluble aurate complexes **A** according to Scheme 1 (thiazolyls derived from benzothiazole are designated **a**, those from 4-methylthiazole **b** and from thiazole **c**). These formulations are in accordance with that found for the complex  $[\text{NBu}_4][\text{Au}(\text{C}=\text{NCMe}=\text{CHS})_2]$  **1b**. The salt has a sharp decomposition point, but the crystals were not suitable for an X-ray study. The most remarkable feature in its  $^{13}\text{C}$  NMR spectrum is the chemical shifts of the alkene carbons ( $\delta$  116.2 and 146.5 in  $\text{CDCl}_3$ ) which show little change compared to free 4-methylthiazole ( $\delta$  113.0 and 152.0 in  $\text{CDCl}_3$ ), while the co-ordinated



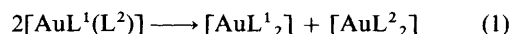
Scheme 1 (i) 'Thiazolyl' = 4-methylthiazolyl,  $\text{NBu}_4^+$

† Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii-xxviii.

carbon (C<sup>2</sup>) resonates at  $\delta$  205.5 ( $\delta$  153.8 for the free thiazole) despite the negative charge on the complex. This result could be interpreted as evidence for the carbenoid character of the C<sup>2</sup> carbons. Various resonance structures for the aurate complexes of type **A** are given in Scheme 2. The aurates were normally not isolated but prepared in thf at  $-70^\circ\text{C}$  and used immediately.

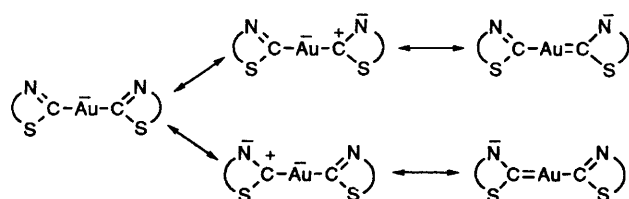
**Preparation of Amino(thio)carbene Complexes.**—Direct protonation (with  $\text{CF}_3\text{SO}_3\text{H}$ ) or alkylation (with  $\text{CF}_3\text{SO}_3\text{Me}$ ) of the aurate complexes produced the neutral monocarbene compounds **2** and **3**, which could be further protonated or methylated to give cationic bis(carbene) complexes of the type **4** and **6** (Scheme 3; once again thiazolinyldene compounds derived from benzothiazole are designated **a**, those from 4-methylthiazole **b**, and from thiazole **c**). We found that once compounds **3** were crystalline, they were too insoluble to be recrystallized and purified before recording the  $^{13}\text{C}$  NMR spectra. The spectra were, therefore, generally measured before the products were properly dried or recrystallized. Certain complexes which probably formed according to the reactions in Scheme 3 could not be isolated in a pure form or characterized satisfactorily. Compounds **2c** and **3c** are extremely insoluble, while attempts to prepare **3c** at low temperature afforded a mixture of **3c** and **6c** (see Tables 1 and 2 for full formulae). Furthermore, when the alkylation in the preparation of **3b** was carried out at room temperature  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy indicated a C-alkylation process leading to **7b**. Further alkylation of **7b** did not give **B**, which contains both a 4-methylthiazolinyldene and a neutral 4-methylthiazole ligand, but rather the bis(carbene) complex **6b** (ca. 20% yield) by homoleptic rearrangement [see

equation (1), in which charges are omitted]. Complexes **6b** and

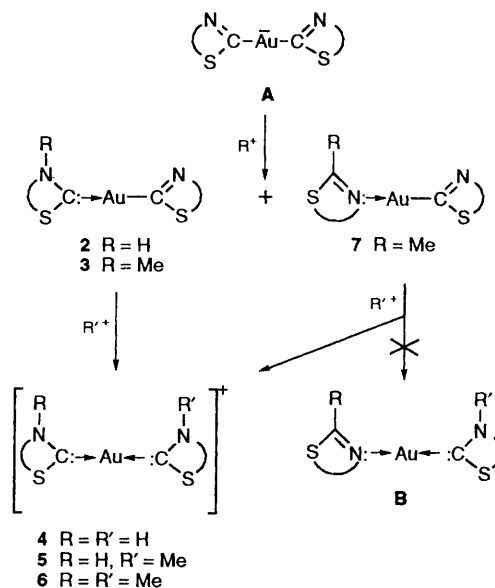


**6c** were the only products obtained when the aurates **A** (thiazolyl =  $\text{C}=\text{NCMe}=\text{CHS}$  or  $\text{C}=\text{NCH}=\text{CHS}$ ) were treated directly with 2 molar equivalents of  $\text{CF}_3\text{SO}_3\text{Me}$ . We have so far been unsuccessful in preparing the mixed bis(carbene) complexes **5**, which contain both secondary and tertiary amino groups. Similarly, the dialkylated complex **6a** could not be prepared according to the procedure given in Scheme 1 but only in an indirect way (see below).

All the new compounds in Table 1 have low solubilities in pentane, hexane and diethyl ether but are much more soluble in  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$  and acetone. They are thermodynamically stable in air at room temperature. The molecular structures of the carbene complexes **2b**, **4a**, **4b** (crystallized as the  $\text{ZnCl}_4^{2-}$



Scheme 2



Scheme 3

Table 1 Analytical and physical data for the new complexes

Complex	Method <sup>a</sup>	Yield (%)	M.p./°C	Colour	Analysis (%) <sup>b</sup>		
					C	H	N
<b>1b</b> $[\text{NBu}_4][\text{Au}(\text{C}=\text{NCMe}=\text{CHS})_2]$	—	76	$\geq 144$ (decomp.)	Colourless	45.0 (45.3)	6.9 (7.0)	6.5 (6.6)
<b>2a</b> $[\text{Au}(\text{C}=\text{NC}_6\text{H}_4\text{S}-o)(\text{CNHC}_6\text{H}_4\text{S}-o)]$	(a)	72	144–145	Yellow	36.1 (36.1)	2.0 (1.9)	6.0 (6.0)
<b>2b</b> $[\text{Au}(\text{C}=\text{NCMe}=\text{CHS})(\text{CNHCMe}=\text{CHS})]$	(a)	74	$\geq 295$ (decomp.)	Colourless	23.9 (24.3)	2.2 (2.3)	7.1 (7.1)
<b>3a</b> $[\text{Au}(\text{C}=\text{NC}_6\text{H}_4\text{S}-o)(\text{CNMeC}_6\text{H}_4\text{S}-o)]$	(a)	49	$\geq 138$ (decomp.)	Yellow	37.9 (37.5)	2.4 (2.3)	5.7 (5.8)
<b>3b</b> $[\text{Au}(\text{C}=\text{NCMe}=\text{CHS})(\text{CNMeCMe}=\text{CHS})]$	(a)	45	183 (decomp.)	Colourless	26.1 (26.5)	2.7 (2.7)	7.1 (6.9)
<b>4a</b> $[\text{Au}(\text{CNHC}_6\text{H}_4\text{S}-o)_2][\text{CF}_3\text{SO}_3]$	(b)	56	220–221 <sup>c</sup>	Yellow	28.9 (29.2)	1.6 (1.6)	4.6 (4.5)
<b>4b</b> $[\text{Au}(\text{CNHCMe}=\text{CHS})_2][\text{CF}_3\text{SO}_3]$	(b)	72	143–146	Colourless	22.0 (21.8)	2.1 (2.0)	5.9 (5.6)
<b>6a</b> $[\text{Au}(\text{CNMeC}_6\text{H}_4\text{S}-o)_2][\text{CF}_3\text{SO}_3]$	(d)	22	174 (decomp.)	Yellow	31.6 (31.7)	2.0 (2.2)	4.4 (4.3)
<b>6b</b> $[\text{Au}(\text{CNMeCMe}=\text{CHS})_2][\text{CF}_3\text{SO}_3]$	(b)	78	212–213	Colourless	22.9 (23.1)	2.5 (2.5)	5.0 (4.9)
<b>6c</b> $[\text{Au}(\text{CNMeCH}=\text{CHS})_2][\text{CF}_3\text{SO}_3]$	(b)	81	163–164	Yellow	19.9 (19.8)	1.9 (1.8)	5.0 (5.1)
<b>8a</b> $[\text{Au}(\text{C}=\text{NC}_6\text{H}_4\text{S}-o)(\text{PPh}_3)]$	(c)	80	155–156	Yellow	50.2 (50.6)	3.2 (3.2)	2.3 (2.4)
<b>9b</b> $[\text{Au}(\text{C}=\text{NCMe}=\text{CHS})]$	(d)	82	—	Colourless	16.4 (16.3)	1.3 (1.4)	4.6 (4.7)
<b>10b</b> $[\text{AuCl}(\text{CNHCMe}=\text{CHS})]$	(e)	72	183–184	Colourless	14.3 (14.5)	1.3 (1.5)	4.3 (4.2)
<b>11b</b> $[\text{Au}(\text{CNHCMe}=\text{CHS})(\text{PPh}_3)][\text{CF}_3\text{SO}_3]$	(f)	74	159–161	Colourless	47.1 (47.3)	3.6 (3.6)	2.5 (2.5)
<b>12a</b> $[\text{Au}(\text{C}_6\text{F}_5)(\text{CNHC}_6\text{H}_4\text{S}-o)]$	(g)	54	$\geq 220$ (decomp.)	Light yellow	26.5 (26.2)	0.7 (0.8)	2.2 (2.4)
<b>14b</b> $[\text{Au}(\text{C}_6\text{F}_5)(\text{CNMeCMe}=\text{CHS})]$	(g)	70	187–188	Colourless	27.5 (27.7)	1.5 (1.5)	2.8 (2.9)
<b>15a</b> $[\text{Au}(\text{CN})(\text{CNMeC}_6\text{H}_4\text{S}-o)]$	(h)	41	194 (decomp.)	Yellow	29.3 (29.0)	1.8 (1.9)	7.6 (7.5)

<sup>a</sup> See Experimental section. <sup>b</sup> Required values are given in parentheses. <sup>c</sup> Colour changes to bright orange at  $106^\circ\text{C}$ .

**Table 2** NMR<sup>a</sup> and mass spectroscopic data

Complex		
<b>1b</b>	$\delta_{\text{H}}$	6.96 (s, 1 H, CH), 3.18 (m, 8 H, NCH <sub>2</sub> ), 2.40 (s, 3 H, Me), 1.48 (m, 8 H, NCH <sub>2</sub> CH <sub>2</sub> ), 1.26 (m, 8 H, CH <sub>2</sub> CH <sub>3</sub> ), 0.79 (t, 12 H, CH <sub>2</sub> CH <sub>3</sub> )
<b>2a</b>	$\delta_{\text{C}}$	205.5 (AuC), 146.5 (CMe), 116.2 (CH), 58.8, 24.0, 19.3, 13.6 (Bu), 13.8 (C=CMe)
	$\delta_{\text{H}}$	14.04 (br, 1 H, NH), 7.92 [d, 2 H, $J(\text{H}^4\text{H}^5)$ 8, 2 H <sup>4</sup> ], 7.62 [d, 2 H, $J(\text{H}^6\text{H}^7)$ 6, 2 H <sup>7</sup> ], 7.4–7.2 (m, 4 H, 2 N <sup>5</sup> , 2 H <sup>6</sup> )
<b>2b</b>	$\delta_{\text{C}}$	212.2 (AuC), 146.1, 133.8, 126.8, 125.0, 121.9, 117.4 (C <sub>5</sub> H <sub>4</sub> )
	$m/z$	466, $M^+$ ; 268, $[\text{o-SC}_6\text{H}_4\text{N}=\text{C}]_2^+$
<b>3a</b>	$\delta_{\text{H}}$	13.40 (br, 1 H, NH), 7.08 (s, 2 H, 2CH), 2.43 (s, 6 H, s, 2 Me)
	$\delta_{\text{C}}$	205.6 (AuC), 144.6 (CMe), 117.3 (CH), 13.0 (Me)
<b>3b</b>	$m/z$	394, $M^+$ ; 296, $[\text{Au}(\text{CNHCMe}=\text{CHS})]^+$ ; 196, $[\text{SCH}=\text{CMeN}=\text{C}]_2^+$
	$\delta_{\text{H}}$	7.99 [d, 2 H, $J(\text{H}^4\text{H}^5)$ 8, 2 H <sup>4</sup> ], 7.84 [d, 2 H, $J(\text{H}^6\text{H}^7)$ 7, 2 H <sup>7</sup> ], 7.6–7.4 (m, 4 H, 2 H <sup>5</sup> , 2 H <sup>6</sup> ), 4.40 (s, 3 H, NMe)
<b>3c</b>	$\delta_{\text{C}}$	214.0 (AuC), 142.8, 133.3, 128.1, 126.5, 122.7, 114.8 (C <sub>6</sub> H <sub>4</sub> ), 42.4 (NMe)
	$m/z$	450, $M^+$ ; 346, $[\text{Au}(\text{CNMeC}_6\text{H}_4\text{S-}o)]^+$ ; 298, 283, 268, $[\text{o-SC}_6\text{H}_4\text{NMeC}=\text{CNMeC}_6\text{H}_4\text{S-}o - n\text{Me}]^+$ where $n = 0, 1, 2$
<b>4a</b>	$\delta_{\text{H}}$	7.04 (s, 1 H, CH), 6.84 (s, 1 H, CH), 3.94 (s, 3 H, NMe), 2.36 (s, 3 H, CMe), 2.26 (s, 3 H, CMe)
	$\delta_{\text{C}}$	199.5 (AuC), 146.1 (CMe), 145.5 (CMe), 120.5 (CH), 119.3 (CH), 42.4 (NMe), 16.6 (CMe), 14.2 (CMe)
<b>4b</b>	$m/z$	408, $M^+$ ; 310, $[\text{Au}(\text{CNMeCMe}=\text{CHS})]^+$ ; 196, $[\text{SCH}=\text{CMeN}=\text{C}]_2^+$
	$\delta_{\text{H}}$	8.23 [d, 2 H, $J(\text{H}^4\text{H}^5)$ 4, 2 NCH], 7.72 [d, 2 H, $J(\text{H}^4\text{H}^5)$ 4, 2 SCH], 4.20 (s, 3 H, NMe)
<b>4c</b>	$\delta_{\text{C}}$	206.2 (AuC), 138.6 (NC), 124.8 (SCH), 44.6 (NMe)
	$\delta_{\text{H}}$	14.10 (br, 2 H, 2 NH), 8.02 [d, 2 H, $J(\text{H}^4\text{H}^5)$ 8, 2 H <sup>4</sup> ], 7.6–7.3 (m, 6 H, 2 H <sup>5-7</sup> )
<b>5a</b>	$\delta_{\text{C}}$	210.9 (AuC), 145.1, 133.4, 127.0, 125.2, 121.8, 117.4 (C <sub>6</sub> H <sub>4</sub> )
	$m/z$	466, $[\text{Au}(\text{CNHC}_6\text{H}_4\text{S-}o)]^+$ ; 332, $[\text{Au}(\text{CNHC}_6\text{H}_4\text{S-}o)]^+$ ; 268, $[\text{o-SC}_6\text{H}_4\text{N}=\text{C}]_2^+$
<b>5b</b>	$\delta_{\text{H}}$	12.42 (br, 2 H, 2 NH), 7.02 (s, 2 H, 2 CH), 2.43 (s, 6 H, 2 Me)
	$\delta_{\text{C}}$	205.7 (AuC), 144.9 (CMe), 117.1 (CH), 13.2 (Me)
<b>5c</b>	$m/z$	395, $[\text{Au}(\text{CNHCMe}=\text{CHS})_2]^+$ ; 296, $[\text{Au}(\text{CNHCMe}=\text{CHS})]^+$ ; 196, $[\text{SCH}=\text{CMeN}=\text{C}]_2^+$
	$\delta_{\text{H}}$	7.99 [d, 2 H, $J(\text{H}^4\text{H}^5)$ 8, 2 H <sup>4</sup> ], 7.8–7.6 (m, 6 H, 2 H <sup>5-7</sup> ), 4.46 (s, 6 H, 2 NMe)
<b>6a</b>	$\delta_{\text{C}}$	204.9 (AuC), 142.9, 133.1, 129.0, 127.3, 122.8, 115.9 (C <sub>6</sub> H <sub>4</sub> ), 43.4 (NMe)
	$m/z$	298, 283, 268, $[\text{o-SC}_6\text{H}_4\text{NMeC}=\text{CNMeC}_6\text{H}_4\text{S-}o - n\text{Me}]^+$ where $n = 0, 1, 2$
<b>6b</b>	$\delta_{\text{H}}$	7.73 (s, 2 H, 2 CH), 4.33 (s, 6 H, 2 NMe), 2.61 (s, 6 H, 2 CMe)
	$\delta_{\text{C}}$	207.0 (AuC), 148.7 (CMe), 121.4 (CH), 43.8 (NMe), 14.2 (CMe)
<b>6c</b>	$m/z$	423, $[\text{Au}(\text{CNMeCMe}=\text{CHS})_2]^+$ ; 310, $[\text{Au}(\text{CNMeCMe}=\text{CHS})]^+$ ; 196, $[\text{SCH}=\text{CMeNMeC}=\text{CNMeCMe}=\text{CHS} - 2\text{Me}]^+$
	$\delta_{\text{H}}$	8.54 [d, 2 H, $J(\text{H}^4\text{H}^5)$ 4, 2 NCH], 8.15 [d, 2 H, $J(\text{H}^5\text{H}^4)$ 4, 2 SCH], 4.42 (s, 3 H, NMe)
<b>6d</b>	$\delta_{\text{C}}$	206.9 (AuC), 140.2 (NC), 125.9 (SCH), 44.9 (NMe)
	$m/z$	296, $[\text{Au}(\text{CNMeCH}=\text{CHS})]^+$ ; 268, $[\text{Au}(\text{CNMeCH}=\text{CHS}) - \text{C}_2\text{H}_4]^+$ ; 198, 168, $[\text{SCH}=\text{CHNMeC}=\text{CNMeCH}=\text{CHS} - n\text{Me}]^+$ where $n = 0, 2$
<b>7b</b>	$\delta_{\text{H}}$	7.25 (s, 1 H, CH), 7.05 (s, 1 H, CH), 2.58 (s, 3 H, N=CMe), 2.46 (s, 6 H, 2 $\times$ Me)
	$\delta_{\text{C}}$	205.9 (AuC), 153.6 (NCS), 146.0 (CMe), 130.7 (CMe), 118.9 (CH), 118.0 (CH), 14.0 (N=CMe), 12.9 (Me)
<b>8a</b>	$m/z$	408, $M^+$ ; 393, $[\text{M} - \text{Me}]^+$ ; 196, $[\text{SCH}=\text{CMeN}=\text{C}]_2^+$
	$\delta_{\text{H}}$	8.54 [d, 1 H, $J(\text{H}^4\text{H}^5)$ 15, H <sup>4</sup> ], 8.46 [d, 1 H, $J(\text{H}^6\text{H}^7)$ 14, H <sup>7</sup> ], 8.1–7.9 (m, 2 H, H <sup>5</sup> and H <sup>6</sup> ), 7.6–7.4 (m, 15 H, Ph)
<b>10b</b>	$\delta_{\text{C}}$	206.0 [d, $J(\text{PC})$ 92, AuC], 145.1, 135.1, 124.6, 123.5, 122.1, 121.2 (C <sub>6</sub> H <sub>4</sub> ), 134.6–128.3 (Ph)
	$\delta_{\text{H}}$	13.30 (br, 1 H, NH), 7.64 (s, 1 H, CH), 2.58 (s, 3 H, Me)
<b>11b</b>	$\delta_{\text{C}}$	192.5 (AuC), 145.1 (CMe), 117.7 (CH), 13.1 (Me)
	$m/z$	196, $[\text{SCH}=\text{CMeN}=\text{C}]_2^+$
<b>12a</b>	$\delta_{\text{H}}$	13.96 (br, 1 H, NH), 7.6–7.5 (m, 15 H, 3 Ph), 7.28 (s, 1 H, CH), 2.57 (s, 3 H, Me)
	$\delta_{\text{C}}$	209.8 [d, $J(\text{PC})$ 126, AuC], 146.6 (CMe), 134.8–129.7 (Ph), 117.6 (CH), 13.4 (Me)
<b>13a</b>	$\delta_{\text{H}}$	14.12 (br, 1 H, NH), 8.11–7.51 (m, 4 H, C <sub>6</sub> H <sub>4</sub> )
	$\delta_{\text{C}}$	148.5, 141.6, 135.9 (C <sub>6</sub> F <sub>5</sub> ), 143.9, 133.1, 128.7, 126.6, 123.8, 116.6 (C <sub>6</sub> H <sub>4</sub> )
<b>14b</b>	$m/z$	499, $M^+$ ; 364, $[\text{Au}(\text{C}_6\text{F}_5)]^+$ ; 332, $[\text{Au}(\text{CNHC}_6\text{H}_4\text{S-}o)]^+$ ; 168, $\text{C}_6\text{F}_5\text{H}^+$
	$\delta_{\text{H}}$	7.14 (s, 1 H, CH), 4.17 (s, 3 H, NMe), 2.46 (s, 3 H, CMe)
<b>15a</b>	$\delta_{\text{C}}$	145.6 (CMe), 119.1 (CH), 42.6 (NMe), 12.5 (CMe)
	$m/z$	477, $M^+$ ; 364, $[\text{Au}(\text{C}_6\text{F}_5)]^+$ ; 310, $[\text{Au}(\text{CNHCMe}=\text{CHS})]^+$ ; 196, $[\text{SCH}=\text{CMeN}=\text{C}]_2^+$ ; 168, $\text{C}_6\text{F}_5\text{H}^+$
<b>15b</b>	$\delta_{\text{H}}$	8.27 [d, 1 H, $J(\text{H}^4\text{H}^5)$ 7, H <sup>4</sup> ], 8.15 [d, 1 H, $J(\text{H}^6\text{H}^7)$ 8, H <sup>7</sup> ], 7.78–7.70 (m, 2 H, H <sup>5</sup> and H <sup>6</sup> ), 4.36 (s, 3 H, NMe)
	$\delta_{\text{C}}$	210.5 (AuC), 149.9 (N=C), 143.4, 132.8, 128.1, 126.6, 123.4, 116.2 (C <sub>6</sub> H <sub>4</sub> ), 42.7 (NMe)
<b>15c</b>	$m/z$	372, $M^+$ ; 346, $[\text{Au}(\text{CNMeC}_6\text{H}_4\text{S-}o)]^+$ ; 298, 283, 268, $[\text{o-SC}_6\text{H}_4\text{NMeC}=\text{CNMeC}_6\text{H}_4\text{S-}o - n\text{Me}]^+$ where $n = 0, 1, 2$

<sup>a</sup> Measured in CDCl<sub>3</sub> unless otherwise stated,  $J$  in Hz. <sup>b</sup> Measured in (CD<sub>3</sub>)<sub>2</sub>CO. <sup>c</sup> Measured in CD<sub>2</sub>Cl<sub>2</sub>. <sup>d</sup> Measured in (CD<sub>3</sub>)<sub>2</sub>SO.

salt) and **6a** were determined by X-ray diffraction, but only the results for the neutral **2b** are discussed here in detail.

**Spectroscopic Results.**—Molecular ions were observed in the mass spectra of the neutral compounds **2a**, **2b**, **3a**, **3b** and **7b**, and the cationic complexes **4a**, **4b** and **6b**. The benzothiazolyl fragments of **2a** combined in the mass spectrometer to form (C=NC<sub>6</sub>H<sub>4</sub>-S)<sub>*n*</sub><sup>+</sup> ions ( $n = 2-4$ ). In the spectrum of **2b** di- and tri-meric methylthiazolyl ions were identified. Other typical fragments observed are listed in Table 2.

The very small (< 2 Hz) allylic coupling between the CH<sub>3</sub> group and the  $\beta$ -proton, which is apparent only in very well resolved spectra, is ignored in the assignments made for the 4-methylthiazole derivatives in Table 2. Proton chemical shifts were used to differentiate between C- ( $\delta$  ca. 2.2) and N-methylation ( $\delta$  ca. 4.3) in compounds **3a** and **3b** or **7b**. The carbene carbons in the new complexes resonate between  $\delta$  195.8 and 214.0 while the signals for the 4-methylthiazole derivatives appear consistently upfield from those of their benzothiazole counterparts. The two cyclic ligands could be distinguished on

the basis of the NMR data only in compound **3b**, which contains both thiazolyl and thiazolinyldene ligands.

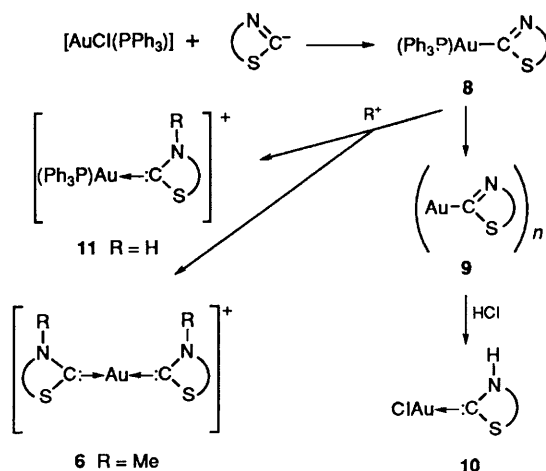
**Preparation of Monocarbene Complexes containing Triphenylphosphine.**—Scheme 4 depicts the preparation of various mono(carbene) complexes formed from the consecutive reactions of  $[\text{AuCl}(\text{PPh}_3)]$  with lithiated benzo- or 4-methylthiazole and  $\text{H}^+$  or  $\text{Me}^+$ . The substitution products **8** decomposed in solution to form the polymeric compounds **9**. Apart from the elemental analysis of **9b**, which indicated its composition, no further attempts were made to characterize these insoluble compounds. Based on the results of Bonati *et al.*<sup>11</sup> it is likely that compounds **9** exist as cyclic trimers ( $n = 3$ ).

We mention here that acidification of the polymers with HCl in diethyl ether gave the carbene(chloro) compounds **10** (only **10b** is described here), which served as starting materials in the syntheses of mixed-carbene complexes (to be described in a future paper). Despite the fact that the polymerization occurred more slowly for the benzothiazolyl derivative **8a** than for the 4-methylthiazolyl derivative **8b** (allowing the isolation and purification of **8a**), only the latter could be protonated successfully to give the 4-methylthiazolinyldene complex **10b** in pure form.

Acidification of complex **8b** with  $\text{CF}_3\text{SO}_3\text{H}$  at  $-40^\circ\text{C}$  yielded compound **11b** as its trifluoromethanesulfonate salt, the structure of which was determined by X-ray crystallography and will be described fully elsewhere. A strong gold–gold interaction occurs between two approximately linear gold complex units  $[\text{Au} \cdots \text{Au} \ 3.060(1) \text{ \AA}]$  which are arranged in an antiparallel fashion. Alkylation under similar conditions afforded, by homoleptic rearrangement, the bis(carbene) complex **6b** in a satisfactory yield. The polymeric compound **9b** could not be alkylated under similar conditions indicating that **8b** rather than **9b** is the precursor for **6b**.

No useful mass spectroscopic data were obtained for the new compounds **8a**, **10b** and **11b**. Only a small difference (3 ppm) was found in the chemical shifts of the respective co-ordinated carbons in the  $^{13}\text{C}$  NMR spectra of the precursor **8a** and carbene product **11b** (Table 2). The  $^{13}\text{C}$  NMR signals of the phosphine ligand of **11b** were well resolved, showing phosphorus coupling to all four chemically non-equivalent carbon atoms by the appearance of four doublets with coupling constants of between 2 and 58 Hz. The phosphorus–carbon coupling involving the carbene carbon atom has a large coupling constant of 126 Hz whereas the coupling constant for the phosphorus-co-ordinated carbon in **8a** is 92 Hz.

**Preparation of Mono(carbene) Complexes containing  $\text{C}_6\text{F}_5^-$  and  $\text{CN}^-$  as Ligands.**—The complex  $[\text{Au}(\text{C}_6\text{F}_5)(\text{tht})]$  reacts with lithium thiazol-2-yls probably to form aurates of type C which can be directly protonated or alkylated to afford the

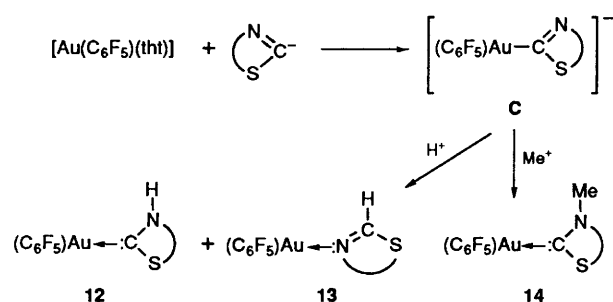


Scheme 4

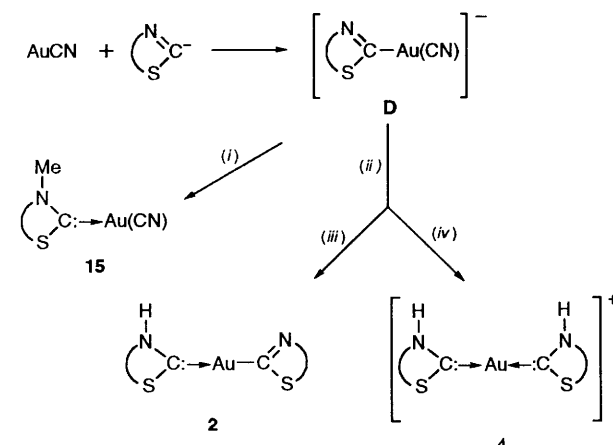
carbene complexes **12** and **14** respectively (Scheme 5). With the exception of the acidification of the aurate C (thiazolyl =  $\text{C}=\text{NCHMe}=\text{CHS}$ ) which did not afford **12b**, but rather the unstable complex **13b** which contains *N*-co-ordinated 4-methylthiazole, the reactions of  $[\text{Au}(\text{C}_6\text{F}_5)(\text{tht})]$  in Scheme 5 were straightforward. Owing to the instability of **13b** and the insolubility of the microcrystalline **14a**, we have only been able to isolate **12a** and **14b** in analytically pure form. These compounds are highly insoluble and their carbene–carbon resonances could not be detected in the  $^{13}\text{C}$  NMR spectra. However, the structures assigned to **12a** and **14b** are in agreement with that found in the X-ray diffraction studies performed on these complexes in our laboratories. No gold–gold interactions occur in either complex although the crystals of **14b** consist of gold chains with non-bonded gold–gold distances of 3.95 Å.<sup>12</sup> The structure assigned to **13b** is based on its  $^1\text{H}$  NMR spectrum in  $\text{CDCl}_3$  which shows the acidic proton at  $\delta$  8.92, the vinylic proton at  $\delta$  6.97 and the methyl group at  $\delta$  2.51, and its mass spectrum which confirmed its molecular constitution. Molecular ions were also observed in the mass spectra of the neutral compounds **12a** and **14b**; other fragments are indicated in Table 2.

The proposed adduct of type D formed between gold(I) cyanide and benzothiazolyl lithium (Scheme 6) was not isolated but alkylated directly to produce complex **15a**. Direct acidification gives either **2a** or **4a** depending on the work-up conditions. Neither of these low-yield products contained any cyanide and probably formed by way of a homoleptic rearrangement upon acidification of D. A simple homoleptic rearrangement of the aurate D before acidification is excluded by the isolation of **15a**. Our failure to isolate pure compounds derived from AuCN and 4-methylthiazolyl lithium is due mainly to the formation of too many by-products.

**Structure of  $[\text{Au}(\text{C}=\text{NCHMe}=\text{CHS})(\text{CNHCHMe}=\text{CHS})]$  **2b**.**—The molecular structure of the first thiocarbene complex of gold to be determined, **2b**, is shown in Fig. 1. Final atomic coordinates are given in Table 3 and selected bond lengths and



Scheme 5

Scheme 6 (i)  $\text{CF}_3\text{SO}_3\text{Me}$ ; (ii)  $\text{CF}_3\text{SO}_3\text{H}$ ; (iii)  $\text{SiO}_2$ ; (iv) crystallization



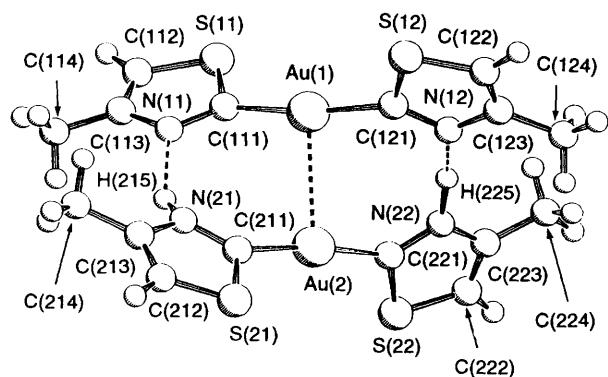


Fig. 1 Molecular structure of  $[\text{Au}(\text{C}=\text{NCMe}=\text{CHS})-(\text{CNHMe}=\text{CHS})] \mathbf{2b}$

angles in Table 4. The neutral compound crystallizes in dimeric units with a gold–gold separation of 3.075(1) Å indicating a strong interaction between the heavy  $d^{10}$  metal ions. There are two independent molecules in the asymmetric unit, but they have almost identical molecular parameters and conformations as shown by the data in Tables 3 and 4. Even the 4-methylthiazolyl and 4-methylthiazolylidene rings in each unit are structurally similar, allowing calculation of the mean ring parameters and the deviations from the means, from the four equivalent rings. These values are listed in Table 4. Coordination around the two central atoms is somewhat distorted from linearity [average C–Au–C angle 172(4)°] and the two ligand planes of each molecule are in staggered conformations with an average angle of 79.6(3)° between them. The Au–C(sp<sup>2</sup>) bonds with three distances of 2.02(1) Å and one of 2.05(1) Å are in agreement with those found in other acyclic neutral and cationic carbene complexes of gold.<sup>16,17</sup> They are also similar to the single-bond Au–C(sp<sup>2</sup>) distances in [methoxy(*p*-tolylimino)methyl](triphenylphosphine)gold(i) [2.056(1) Å],<sup>18</sup> in (2,6-dimethoxyphenyl)(triphenylphosphine)gold(i) [2.050(16) Å]<sup>19</sup> and to the gold–perfluorophenyl separation in (3,4-dimethylthiazol-5-yl)(perfluorophenyl)gold(i) [1.992(10) Å].<sup>12</sup> The NH hydrogens were placed in experimentally determined positions. They bridge the nitrogen atoms of each pair of molecules but, interestingly, both are situated nearer to the nitrogen atoms [N(21) and N(22)] of one of the units, which implies that compound **2b** consists of homoleptic  $[\text{Au}(\text{CNHMe}=\text{CHS})_2]^+$  cations and  $[\text{Au}(\text{C}=\text{NCMe}=\text{CHS})_2]^-$  anions as shown in Fig. 1. However, the positioning of H atoms is susceptible to large errors, and neither the Au–C nor the Au–N bonds in the two interacting complexes substantiate such an assumption. In line with previous results the co-ordinated carbon to nitrogen distances [average 1.33(1) Å] are somewhat shorter than the distances from the nitrogen to the other neighbouring sp<sup>2</sup> carbons [average 1.39(1) Å]. The two S–C(sp<sup>2</sup>) bonds which each sulfur forms are, however, of equal length [average 1.71(2) Å] implying no significant double-bond character between the carbene carbon and neighbouring sulfur. The structure determination shows that the two most important contributing resonance structures representing the carbene complex are E and F in Scheme 7. Stressing the relative importance of resonance form E which is usually ignored in discussions about metal–carbene bonding, we have represented the metal–carbene interaction in all other diagrams as a co-ordinate bond rather than as a double bond as has become the habit in transition-metal carbene chemistry.

## Experimental

**General.**—Reactions and manipulations were carried out under argon using standard Schlenk techniques. Solvents were dried and distilled under nitrogen before use.<sup>10</sup> The compounds

Table 3 Fractional coordinates for compound **2b**

Atom	X/a	Y/b	Z/c
Au(1)	0.901 97(4)	0.682 96(4)	0.825 60(4)
Au(2)	0.643 37(4)	0.788 93(4)	0.676 76(4)
S(11)	0.906 4(3)	0.882 9(3)	0.987 1(3)
S(12)	1.113 0(3)	0.404 4(3)	0.764 8(3)
S(21)	0.366 9(3)	0.627 4(3)	0.776 9(3)
S(22)	0.691 7(3)	1.028 9(3)	0.451 4(3)
N(11)	0.663 5(8)	0.797 8(8)	1.011 1(7)
N(12)	1.074 6(8)	0.605 4(8)	0.600 6(8)
N(21)	0.467 7(8)	0.705 3(8)	0.918 2(8)
N(22)	0.912 9(8)	0.844 6(8)	0.489 8(7)
C(111)	0.800(1)	0.792(1)	0.946(1)
C(112)	0.761(1)	0.932(1)	1.092(1)
C(113)	0.642(1)	0.877(1)	1.092(1)
C(114)	0.493(1)	0.893(1)	1.174(1)
C(121)	1.029(1)	0.568(1)	0.716(1)
C(122)	1.208(1)	0.390(1)	0.629(1)
C(123)	1.176(1)	0.505(1)	0.555(1)
C(124)	1.237(1)	0.537(1)	0.425(1)
C(211)	0.493(1)	0.702(1)	0.807(1)
C(212)	0.286(1)	0.595(1)	0.917(1)
C(213)	0.350(1)	0.643(1)	0.983(1)
C(214)	0.311(1)	0.643(1)	1.110(1)
C(221)	0.770(1)	0.882(1)	0.536(1)
C(222)	0.856(1)	1.038(1)	0.358(1)
C(223)	0.964(1)	0.930(1)	0.389(1)
C(224)	1.122(1)	0.900(1)	0.326(1)



Scheme 7

$[\text{AuCl}(\text{tht})]$ ,<sup>20</sup>  $[\text{AuCl}(\text{PPh}_3)]$ ,<sup>21</sup> and  $[\text{Au}(\text{C}_6\text{F}_5)(\text{tht})]$ <sup>22</sup> were prepared according to literature methods. Benzothiazole, 4-methylthiazole, methyl trifluoromethanesulfonate and trifluoromethanesulfonic acid were obtained from Aldrich, butyllithium from Merck. Only benzothiazole was distilled from P<sub>2</sub>O<sub>5</sub> before use and stored over molecular sieves.

The NMR spectra were recorded on a Varian VXR 200 FT instrument and mass spectra (electron impact) on a Finnigan Mat 8200 apparatus. Melting points were determined on a standardized Büchi 535 apparatus and are corrected. Analyses were carried out by the analytical laboratories of the CSIR Pretoria, and the Mikroanalytisches Labor of Pascher in Bonn.

**Preparation of the Various Thiazolylithium Solutions and Compound 1b.**—A solution of 4-methylthiazole (0.21 cm<sup>3</sup>, 1.5 g cm<sup>-3</sup>, 3.2 mmol), benzothiazole (0.35 cm<sup>3</sup>, 1.24 g cm<sup>-3</sup>, 3.2 mmol) or thiazole (0.23 cm<sup>3</sup>, 1.2 g cm<sup>-3</sup>, 3.2 mmol) in thf (20 cm<sup>3</sup>) was cooled to –75 °C and treated with butyllithium (2.3 cm<sup>3</sup>, 1.3 mol dm<sup>-3</sup>, 3.2 mmol). These yellow solutions were stirred at –75 °C for 20 min before use. When the synthesis involved aurate formation by double ligand substitution, the chosen thiazolylithium (6.4 mmol) was prepared in thf (30 cm<sup>3</sup>).

To prepare complex **1b**,  $[\text{AuCl}(\text{tht})]$  (1.0 g, 3.2 mmol) was added to a solution of 4-methylthiazol-2-ylithium (6.4 mmol) and the mixture stirred at –75 °C for 2 h before tetrabutylammonium bromide (1.0 g, 3.2 mmol) was added. It was allowed to reach room temperature and the solvent removed under vacuum. The residue was redissolved in CH<sub>2</sub>Cl<sub>2</sub> (15 cm<sup>3</sup>) and the solution filtered through Celite. Concentration of the solution to 8 cm<sup>3</sup>, addition of pentane (5 cm<sup>3</sup>), and cooling to –25 °C afforded colourless crystals (0.81 g, 80%) of **1b** (see Table 1).

**Table 4** Bond lengths (Å) and angles (°) with estimated standard deviations (e.s.d.s) in parentheses for compound **2b**

Individual and average ligand parameters							
	Ring 11	Ring 12	Ring 21	Ring 22	Average*		
Au–C(1)	2.02(1)	2.02(1)	2.05(1)	2.02(1)	2.03(1)		
S–C(1)	1.73(1)	1.71(1)	1.68(1)	1.70(1)	1.71(2)		
S–C(2)	1.72(1)	1.71(1)	1.69(1)	1.69(1)	1.70(2)		
N–C(1)	1.33(1)	1.35(1)	1.33(1)	1.32(1)	1.33(1)		
N–C(3)	1.40(2)	1.38(1)	1.39(1)	1.39(1)	1.39(1)		
C(2)–C(3)	1.35(2)	1.32(1)	1.33(1)	1.34(1)	1.34(1)		
C(3)–C(4)	1.52(1)	1.54(2)	1.50(1)	1.49(1)	1.51(2)		
Au–Au–C(1)	94.6(1)	93.1(1)	91.9(1)	95.6(1)	93.8(16)		
C(1)–S–C(2)	92.4(6)	92.4(5)	92.2(5)	93.2(5)	92.6(4)		
C(1)–N–C(3)	112.2(9)	113.1(8)	114.4(8)	115.8(8)	113.9(16)		
S–C(1)–N	111.0(8)	109.5(7)	110.3(7)	108.6(7)	109.9(10)		
S–C(2)–C(3)	108.5(10)	109.6(9)	111.5(8)	110.5(8)	110.0(13)		
N–C(3)–C(2)	115.8(9)	115.3(10)	111.6(9)	111.8(9)	113.6(22)		
N–C(3)–C(4)	119.2(11)	117.4(9)	118.6(8)	121.9(8)	119.3(19)		
C(2)–C(3)–C(4)	125.0(12)	127.3(11)	129.8(9)	126.3(9)	127.1(20)		
Interligand parameters							
Au(1) ... Au(2)	3.0750(6)	C(111)–Au(1)–C(121)		172.1(4)	C(211)–Au(2)–C(221)	172.5(4)	
Hydrogen bonding							
N(11) ... N(21)	2.76(1)	N(11) ... H(215)		1.82(1)	N(12) ... H(225)	1.49(1)	
N(12) ... N(22)	2.75(1)	N(21) ... H(215)		1.12(1)	N(22) ... H(225)	1.27(1)	
Interplanar angles							
Ring 11–ring 12	80.2(3)	Ring 21–ring 22	79.0(3)	Ring 11–ring 21	147.8(4)	Ring 12–ring 22	34.8(4)
Dihedral angles							
C(111)–Au(1)–Au(2)–C(211)	–64.8(4)		C(111)–Au(1)–Au(2)–C(221)		115.7(4)		

\* Sample standard deviations calculated for the average of the four equivalent values in each row.

**Synthesis of the Other Complexes.**—The complexes were prepared according to the methods (a)–(h) below. The general work-up procedure comprised filtering of the final reaction mixture through anhydrous  $\text{MgSO}_4$  or Celite, reducing the volume under vacuum to about  $10 \text{ cm}^3$  and slowly adding pentane (*ca.*  $8 \text{ cm}^3$ ). The solutions were then left at  $-25^\circ\text{C}$  to crystallize. After collecting the crystals by filtration or decanting the solvent, they were quickly washed with pentane ( $2 \times 10 \text{ cm}^3$ ) and dried under vacuum. Analytical and physical data are given in Tables 1 and 2.

**Method (a).** As in the preparation of complex **1b** [ $\text{AuCl}(\text{tht})$ ] ( $1.02 \text{ g}$ ,  $3.2 \text{ mmol}$ ) was added to 4-methylthiazol-2-yl-lithium, benzothiazolyl-lithium or thiazolyl-lithium ( $6.4 \text{ mmol}$ ) in thf at  $-75^\circ\text{C}$  and stirred for 2 h before raising the temperature to  $-10^\circ\text{C}$  over a period of 2 h. Dropwise addition of  $\text{CF}_3\text{SO}_3\text{H}$  ( $0.28 \text{ cm}^3$ ,  $1.70 \text{ g cm}^{-3}$ ,  $3.2 \text{ mmol}$ ) or  $\text{CF}_3\text{SO}_3\text{Me}$  ( $0.36 \text{ cm}^3$ ,  $1.45 \text{ g cm}^{-3}$ ,  $3.2 \text{ mmol}$ ) to the reaction mixture was accompanied by an immediate change from orange to light yellow. The solvent was removed under vacuum, the residue redissolved in  $\text{CH}_2\text{Cl}_2$  and worked up.

**Method (b).** The neutral gold carbene starting material **2** or **3** ( $2.4 \text{ mmol}$ ) was dissolved in thf ( $20 \text{ cm}^3$ ) and cooled to  $-10^\circ\text{C}$  before adding  $\text{CF}_3\text{SO}_3\text{H}$  ( $0.21 \text{ cm}^3$ ,  $1.70 \text{ g cm}^{-3}$ ,  $2.4 \text{ mmol}$ ) or  $\text{CF}_3\text{SO}_3\text{Me}$  ( $0.27 \text{ cm}^3$ ,  $1.45 \text{ g cm}^{-3}$ ,  $2.5 \text{ mmol}$ ) dropwise. The mixture was stirred for 2 h at room temperature and worked up. Better total overall yields (reported in Table 1) were obtained according to method (a) but required the use of double the amount of acid or alkylating agent.

**Method (c).** To a yellow solution of 4-methylthiazol-2-yl- or benzothiazolyl-lithium ( $3.2 \text{ mmol}$ ) at  $-75^\circ\text{C}$  was added [ $\text{AuCl}(\text{PPh}_3)$ ] ( $1.58 \text{ g}$ ,  $3.2 \text{ mmol}$ ), after which the temperature of the now colourless solution was allowed to rise to  $-10^\circ\text{C}$  over 2 h. The mixture was stirred for 30 min and the solvent removed under vacuum. The residue was redissolved in  $\text{CH}_2\text{Cl}_2$  and worked up.

**Method (d).** The colourless solution prepared at  $-75^\circ\text{C}$  according to method (c) was stirred at this temperature for 2 h

before the temperature was increased to  $22^\circ\text{C}$  over 2 h. At  $-5^\circ\text{C}$  a white substance started to precipitate. After filtering and washing with  $\text{CH}_2\text{Cl}_2$  ( $4 \times 30 \text{ cm}^3$ ) the product was dried under vacuum.

**Method (e).** A suspension of the white powder [obtained according to method (d)] in  $\text{CH}_2\text{Cl}_2$  ( $30 \text{ cm}^3$ ) was treated with a small excess of HCl in diethyl ether ( $1.9 \text{ mol dm}^{-3}$ ,  $2.1 \text{ cm}^3$ ,  $4.0 \text{ mmol}$ ). Work-up afforded colourless needle-like crystals.

**Method (f).** A solution of complex **8** (*ca.*  $3.2 \text{ mmol}$ ) was prepared according to method (c) and before work-up either  $\text{CF}_3\text{SO}_3\text{H}$  ( $0.28 \text{ cm}^3$ ,  $1.7 \text{ g cm}^{-3}$ ,  $3.2 \text{ mmol}$ ) or  $\text{CF}_3\text{SO}_3\text{Me}$  ( $0.36 \text{ cm}^3$ ,  $1.45 \text{ g cm}^{-3}$ ,  $3.2 \text{ mmol}$ ) was added at  $-75^\circ\text{C}$ . The mixture was stirred for 20 min and then allowed to warm to room temperature over 45 min before work-up.

**Method (g).** A solution of [ $\text{Au}(\text{C}_6\text{F}_5)(\text{tht})$ ] ( $1.4 \text{ g}$ ,  $3.2 \text{ mmol}$ ) in thf ( $20 \text{ cm}^3$ ) was added at  $-75^\circ\text{C}$  to a thf solution of benzothiazolyl- or 4-methylthiazol-2-yl-lithium (*ca.*  $3.2 \text{ mmol}$ ) and the mixture stirred for 1 h. The temperature was allowed to rise to  $-10^\circ\text{C}$  over 3 h before  $\text{CF}_3\text{SO}_3\text{H}$  ( $0.28 \text{ cm}^3$ ,  $3.2 \text{ mmol}$ ) or  $\text{CF}_3\text{SO}_3\text{Me}$  ( $0.36 \text{ cm}^3$ ,  $3.2 \text{ mmol}$ ) was added dropwise. The mixture was stirred at  $-10^\circ\text{C}$  for 1 h before allowing it to warm to room temperature. After filtration through Celite, the solvent was removed under vacuum and the residue chromatographed on  $\text{SiO}_2$  using  $\text{CH}_2\text{Cl}_2$ –hexane (1:1) as eluent to separate the main light yellow product from two less-polar by-products. The solvent was removed and the product recrystallized from  $\text{CH}_2\text{Cl}_2$  and pentane as in the standard work-up procedure.

**Method (h).** Gold(I) cyanide ( $0.71 \text{ g}$ ,  $3.2 \text{ mmol}$ ) was added slowly to a solution of benzothiazolyl- or 4-methylthiazol-2-yl-lithium (*ca.*  $3.2 \text{ mmol}$ ) in thf ( $20 \text{ cm}^3$ ) at  $-75^\circ\text{C}$ . The yellow mixture was stirred for 2 h at this temperature and then allowed to reach room temperature over 4 h. After cooling the solution to  $-40^\circ\text{C}$ ,  $\text{CF}_3\text{SO}_3\text{H}$  ( $0.28 \text{ cm}^3$ ,  $3.2 \text{ mmol}$ ) or  $\text{CF}_3\text{SO}_3\text{Me}$  ( $0.36 \text{ cm}^3$ ,  $3.2 \text{ mmol}$ ) was added and the solution stirred for 2 h at this temperature. The mixture was allowed to reach room temperature before work-up. If the  $\text{CH}_2\text{Cl}_2$  solution was filtered through  $\text{SiO}_2$ , before final concentration and crystallization,

**Table 5** Crystal data, collection and refinement details for complex **2b**

Formula	C <sub>8</sub> H <sub>9</sub> AuN <sub>2</sub> S <sub>2</sub>
<i>M</i>	394.27
Crystal size/mm	0.12 × 0.10 × 0.06
Colour and shape	Yellow skew six-sided plates
Crystal system	Triclinic
Space group	<i>P</i> $\bar{1}$
<i>a</i> /Å	9.150(1)
<i>b</i> /Å	10.529(1)
<i>c</i> /Å	12.045(1)
$\alpha$ /°	75.227(8)
$\beta$ /°	78.409(8)
$\gamma$ /°	75.901(8)
<i>Z</i>	4
<i>U</i> /Å <sup>3</sup>	1076.2(2)
<i>D<sub>c</sub></i> /g cm <sup>-3</sup>	2.433
Radiation (λ/Å)	Mo-Kα (0.710 69)
μ/cm <sup>-1</sup>	144.08
<i>T</i> /°C	25
<i>F</i> (000)	728
Diffractometer	Enraf-Nonius CAD 4
Scan type	ω-2θ
Scan range, θ/°	2.5–25.0
Scan angle, ω/°	0.45 + 0.35 tan θ
<i>hkl</i> ranges	–10 to 10, –12 to 12, 0–14
Maximum scan rate/° min <sup>-1</sup>	16.48
Maximum scan time per reflection/s	120
Aperture size/mm	1.3
Reflections measured	3984
Observed reflections	3655 ( <i>I</i> > σ <sub><i>i</i></sub> )
Decay (%)	8.7
Absorption correction	Empirical (0.997–0.720)
Parameters refined	235
Maximum shift/e.s.d.	0.048
Residual electron density/e Å <sup>-3</sup>	1.9 (close to Au)
<i>R</i> , <i>R'</i>	0.050, 0.033

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

compound **2a** was obtained after the protonation step. Crystallization in the normal manner, however, afforded crystals of **4a** only.

**Structure Determination of [Au(C≡NCMe=CHS)-(CNHCMe=CHS)] 2b.**—The crystal data and data collection parameters are given in Table 5. The structure was determined by the heavy-atom method, followed by a Fourier difference map and full-matrix least-squares refinement. All non-H atoms were refined anisotropically and the H atoms were placed in calculated positions but not refined. The H atoms bonded to the N atoms and which are involved in hydrogen bonding were placed in positions observed in a difference map. Atomic positions and bond parameters are listed in Tables 3 and 4. The

computer program XTAL 3.2<sup>23</sup> was used for the structure determination and refinement, and SCHAKAL<sup>24</sup> for the preparation of the crystal-structure illustrations.

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

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Received 18th March 1994; Paper 4/01618A