# Synthesis and Characterization of Mono(carbene) Complexes of Copper and Crystal Structure of a Linear Thiazolinylidene Compound†

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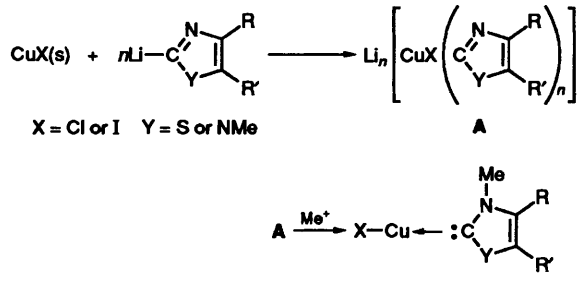
A series of neutral copper(I) mono(carbene) complexes was synthesized by the alkylation of thiazolyl- or imidazolyl-cuprates. The cuprates were prepared from CuCl or CuI and 4-methylthiazolyl-, benzothiazol-2-yl-, 1-methylimidazolyl- or 1-methylbenzoimidazol-2-yl-lithium. The crystal structure of [CuCl{CN(Me)C(Me)=CHS}] has been determined and shows a linear, monomeric thiazolinylidene copper chloride complex with a copper–carbene carbon bond length of 1.868(6) Å.

The existence of copper carbene complexes has been universally accepted.[1] Their formation as intermediates has been proposed during copper-catalysed additions of diazoalkanes to olefins[2,3] as well as in insertion reactions, ylide generation and rearrangement reactions with diazo compounds.[3] Carbene intermediates have also been proposed for the copper-catalysed formation of formamidines from isocyanides in alcohols[4] and the thermolysis of alkylcopper compounds.[5] Nevertheless, such complexes have only recently been isolated. We communicated the isolation of thiazolinylidene complexes[6] as well as the crystal-structure determination of a mono(carbene) copper complex, [CuCl{CN(Me)C(Me)=C(Me)S}],[7] whereas Arduengo *et al.*[8] reported the addition compound [Cu{CN($C_9H_{11}$)(CH=CH)N($C_9H_{11}$)}$_2$] albeit without a structure determination. An on-going investigation into the related chemistry of gold(I) involving heterocyclic precursors yielded stable mono- and bis-(carbene) complexes of the heavier congener. These complexes were prepared for example by protonation or alkylation of aurates generated from [AuCl(tht)] (tht = tetrahydrothiophene) and two molar amounts of a lithiated thiazole.[9]

Although the treatment of cuprates prepared from CuCl and lithiated thiazoles or imidazoles in thf (tetrahydrofuran) yielded copper carbene complexes upon alkylation with $CF_3SO_3Me$, a chloride ion was unexpectedly retained in all the products. The crystal structure of [CuCl{CN(Me)C(Me)=C(Me)S}] has been reported in a preliminary communication[7] and the structure of [CuCl{CN(Me)C(Me)=CHS}] is described in this paper. Acidification of the cuprates with $CF_3SO_3H$ did not afford carbene complexes but complexes of the type [{Cu(μ-Cl)(thiazole)$_2$}$_2$] were crystallized from the reaction mixture,[10] whereas the $C^2$-coupled dimer (*o*-$SC_6H_4N$=C–C=$NC_6H_4S$-*o*) or the thiazolyl copper compound [Cu{C=NC(Me)=CHS}] formed upon acidification with HCl.

## Results and Discussion

*Preparation and Structural Characterization of the Carbene Complexes.*—The reaction of CuCl or CuI with lithiated thiazoles or imidazoles followed by treatment with $CF_3SO_3Me$ (Scheme 1) yielded clear orange-brown solutions after filtration through anhydrous $MgSO_4$. The analytically pure, crystalline




| | X | Y | R, R′ |
|---|---|---|---|
| 1 | Cl | S | Me, H |
| 2 | Cl | S | Me, Me |
| 3 | Cl | S | CH=CHCH=CH |
| 4 | I | S | Me, H |
| 5 | I | S | Me, Me |
| 6 | I | S | CH=CHCH=CH |
| 7 | Cl | NMe | H, H |
| 8 | Cl | NMe | CH=CHCH=CH |

Scheme 1

copper carbene compounds **1**–**8** (the preparation and characterization data for **2** have been reported[7]) varying from colourless through yellow to light brown, crystallized from the filtrate at −20 °C. They are stable in air for only a limited period, and can be stored under an argon atmosphere at low temperature for several weeks. The light brown crystals of the imidazolinylidene **7** turned green or blue upon exposure to the atmosphere.

Compounds **1**–**7** are soluble in thf, acetone and dichloromethane, whereas **8** is only moderately soluble in these solvents. The formulations of the carbene complexes in Scheme 1 are supported by elemental analyses, mass spectra and $^1H$ and $^{13}C$-{$^1H$} NMR spectra.

All the complexes **1**–**8** showed molecular ions in their mass spectra as well as a similar fragmentation pattern which involves the initial loss of Cl or I followed by Cu and then Me from the NMe unit. The benzothiazolyl fragments of **3** and **6** combined in the mass spectrometer to form [(C=$NC_6H_4S$-*o*)$_2$]$^+$ and [{CN(Me)$C_6H_4S$-*o*}$_2$]$^+$ ions whereas the mass spectrum of compound **9** showed the fragmentation of a trimeric structure

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

[{Cu[C=NC(Me)=CHS]}$_3$]. The presence of a higher oligomer cannot however be ruled out. Similar results were previously obtained for various gold(I) carbene complexes.[11,12]

The absence of the N–CH–Y proton (Y = NMe or S) and the appearance of an NMe peak at δ 4.00–4.50 indicate copper carbene formation. All the other $^1$H NMR signals of the complexed ligands are shifted downfield from those of the free ligands but never more than 0.5 ppm. In the $^{13}$C NMR spectra the carbene carbons of the thiazolinylidenes resonate at δ 216.3 and 214.3 for the two benzothiazolinylidenes **3** and **6** and at δ 203.5 for the methylthiazolinylidene **1**, while the same signal for the 4-imidazolinylidene complex **7** appears at δ 177.0 which is very similar to the δ 178.2 value reported for the homoleptic bis(carbene) complex [Cu(CNRCH=CHNR)$_2$][SO$_3$CF$_3$] (R = mesityl).[8] These chemical shifts are also comparable to those observed for analogous and linear gold(I) carbene complexes.[9,12] The NMe resonances appear at δ *ca.* 43.0 in the $^{13}$C NMR of the thiazolinylidenes and at δ 38.0 for the imidazolinylidene (8.0 ppm downfield from the NMe peak in the free ligand).

Whilst no attempt was made to correlate small differences in $^{13}$C chemical shifts with changing electronic distributions, it was noted that a definite pattern emerged when the free thiazoles are compared to copper (or gold[9]) thiazolinylidenes; the resonances of the carbon atoms α and β to nitrogen (excluding the carbene carbon) are moved upfield by 2–10 ppm whereas the carbon atoms α and β to sulphur appear 0–6 ppm downfield. By carefully studying the $^{13}$C NMR spectra of 4-methylthiazole, 3,4-dimethylthiazolium trifluoromethanesulfonate, lithium bis(4-methylthiazolyl)aurate(I) and bis(4-methylthiazolinylidene)gold(I) trifluoromethanesulfonate {$\delta_C$(50 MHz, CD$_3$COCD$_3$): 4-methylthiazole 16.8 (s, NC*C*H$_3$), 114.0 (s, SCH), 153.1 (s, N*C*Me), 154.2 (s, SCHN); 3,4-dimethylthiazolium trifluoromethanesulfonate 13.1 (s, NC*C*H$_3$), 40.5 (s, NMe), 121.5 (s, SCH), 147.9 (s, N*C*Me), 159.4 (s, SCHN); Li[Au{CNC(Me)=CHS}$_2$] 16.7 (s, NC*C*H$_3$), 112.8 (s, SCH), 152.6 (s, N*C*Me), 209.1 (s, AuC); [Au{CN(Me)C(Me)=CHS}$_2$][CF$_3$SO$_3$] 14.0 (s, NC*C*H$_3$), 43.5 (s, NMe), 121.1 (s, SCH), 148.4 (s, N*C*Me), 207.1 (s, AuC)} it is concluded that (*i*) sequential treatment of thiazoles with LiBu and [AuCl(tht)] (tht = tetrahydrothiophene) mainly changes the chemical shift of the C$^2$ carbon and (*ii*) alkylation of either a free thiazole or a thiazolyl gold compound (leading to a carbene) is responsible for changes in the chemical shifts of the other carbons α and β to either nitrogen or sulfur as explained above.

Elemental analysis of compounds **1**–**8** as well as the crystal-structure determinations of **1** and **2**[7] confirmed the presence of halide ions in the copper carbene complexes. Neither the exact mechanism for the formation of the carbene complexes nor the exact composition of the precursor cuprates are known.

Although the structures of some cuprates, [Li(12-crown-4)$_2$CuMe$_2$] (12-crown-4 = 1,4,7,10-tetraoxacyclododecane), [Li(12-crown-4)$_2$CuPh$_2$],[13] [Li$_2$Cu$_2$(C$_6$H$_4$CH$_2$NMe$_2$-2)$_4$],[14] [{Li(OEt$_2$)}CuPh$_2$]$_2$[15] and [Li$_2$Cu$_2$Ph$_4$(SMe$_2$)$_3$][16] have been reported, they were all prepared from halide-free organo-copper and -lithium compounds. Very little is known about the structures of the more reactive cuprates prepared from two equivalents of organolithium compound and copper(I) halide.[17] The mounting evidence that the halide ion forms part of the cuprate aggregate **A**[18] (Scheme 1) is now supported by the products **1**–**8** obtained by alkylation and by products of the type [Cu$_2$(μ-X)$_2$(thiazole)$_4$][10] resulting from the acidification of the thiazolyl- or imidazolyl-cuprate solutions in which the halides were retained. We have now embarked upon a study to prepare copper carbene complexes from halide-free copper reagents.

The activity of cuprates in cross coupling and conjugate addition is linked to the binding ability of the organic ligand.[17] The thiazolyl and imidazolyl ligands both have good binding ability as these cuprates do not engage either in coupling reactions (to form the C$^2$-coupled thiazole or imidazole dimers), in C$^2$ alkylation upon treatment with CF$_3$SO$_3$Me, in metal–trifluoromethanesulfonate exchange [a reaction similar to metal–halide exchange observed for organocopper compounds and organohalides (to form the methylcuprate)],[17] or in interaggregate exchange to form {R$_{2-n}$CuLi(O$_3$SCF$_3$)$_n$}$_m$.[18,19]

From the reaction of the cuprate with HCl(g) in diethyl ether only decomposition products like (C=NC$_6$H$_4$S-*o*)$_2$ and [Cu{C=NC(Me)=CHS}] **9** were isolated in crystalline form. The HCl is probably included in a loosely-bonded aggregate (the electron-rich halide anions could be associated with the co-ordinatively unsaturated Li ion[17,18]) which is stable at low temperature and then decomposes as the temperature of the reaction mixture rises to room temperature. Trifluoromethanesulfonic acid, as mentioned above, C$^2$ protonates the thiazolyl ligands and N-co-ordinated copper(I) halide compounds [Cu$_2$(μ-X)$_2$(thiazole)$_4$] were formed.[10]

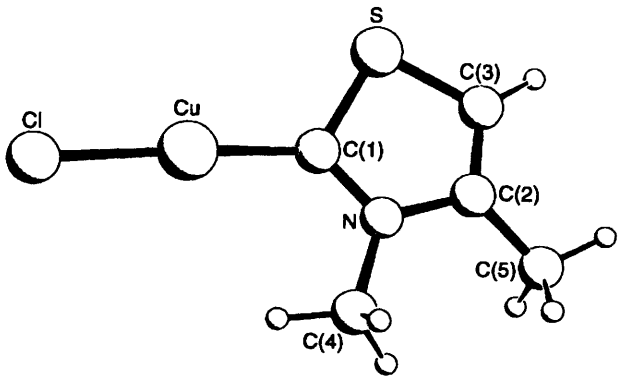



**Fig. 1** View of the molecular structure of **1** (SCHAKAL), with the atomic numbering scheme

**Table 1** Fractional coordinates (× 10$^4$) for **1**

| Atom | *x/a* | *y/b* | *z/c* |
|---|---|---|---|
| Cu | 2010(1) | 3447(1) | 827 |
| S | 3166(1) | 1641(2) | 858(23) |
| Cl | 973(1) | 4043(2) | 763(18) |
| N | 3540(2) | 3518(4) | 859(48) |
| C(1) | 2938(3) | 2940(6) | 929(77) |
| C(2) | 4172(3) | 2937(5) | 869(54) |
| C(3) | 4050(3) | 1904(6) | 816(52) |
| C(4) | 3539(3) | 4695(5) | 945(69) |
| C(5) | 4863(3) | 3504(6) | 1162(39) |

*Structure of* [CuCl{CN(Me)C(Me)=CHS}] **1**.—The molecular structure of complex **1** is shown in Fig. 1. Final atomic coordinates are given in Table 1 and selected bond lengths and angles of **1** and **2**[7] in Table 2. The two-co-ordinate copper atom in **1** is bonded to the carbene carbon of the thiazolinylidene and to a chloride ligand. The Cu–C(1) bond length of 1.868(6) Å is identical to the Cu–C(1) bond length in **2** [1.888(6) Å],[7] which is shorter than known Cu–C bonds (for example 1.906(2) Å in [CuCl{C(PPh$_3$)$_2$}][20]). Although the Cu–Cl bond length of 2.099(2) Å is comparable to the Cu–Cl bond length in **2** [2.122(2) Å] and also in [CuCl{C(PPh$_3$)$_2$}] [2.113(1) Å],[21] the weaker Cu · · · Cl interaction (2.905 Å) observed in **2** is not present in **1** (Cu · · · Cl 3.967 Å). The Cu · · · Cu separation in **1** (3.884 Å) is also longer than in **2** (3.390 Å).

The absence of chloride 'bridging' is probably responsible for the fact that the Cl–Cu–C(1) backbone in **1** is more linear [178.6(13)°] than in **2** [Cl–Cl–C(1) 166.9(2)°]. The other bond angles and bond lengths in the thiazole rings [S–C(1)–N, Cu–C(1)–N, Cu–C(1)–S, N–C(1) and S–C(1)] are similar to those in **2**.

**Table 2** Selected bond lengths (Å) and angles (°) for complexes **1** and **2**[7] with estimated standard deviations in parentheses

| | 1 | 2 | | 1 | 2 |
|---|---|---|---|---|---|
| Cu–Cl | 2.099(2) | 2.122(2) | Cu–C(1) | 1.868(6) | 1.888(6) |
| N–C(1) | 1.350(7) | 1.350(6) | S–C(1) | 1.681(7) | 1.665(6) |
| Cu···Cu | 3.884 | 3.390 | Cu···Cl | 3.967 | 2.905 |
| Cl–Cu–C(1) | 178.6(13) | 166.9(2) | S–C(1)–N | 107.3(5) | 107.9(4) |
| Cu–C(1)–N | 127.7(6) | 128.0(5) | Cu–C(1)–S | 124.6(4) | 124.0(3) |

The monomeric complexes **1** are as flat as the 'dimeric' units in **2**. The non-hydrogen atoms in **1** do not deviate more than 0.13 Å from the best plane through them.

## Experimental

*Materials.*—Benzothiazole was purchased from Fluka, distilled and stored over molecular sieves (4 Å). The other thiazoles, 4-methylthiazole and 4,5-dimethylthiazole as well as $CF_3SO_3Me$ were purchased from Aldrich and used without further purification. Butyllithium was purchased from Merck, CuI from Riedel-De Haën and CuCl was prepared from $CuCl_2$.[22] Benzoimidazole (BDH) was used to prepare 1-methylbenzoimidazole.[23] Tetrahydrofuran (thf) and diethyl ether were distilled under nitrogen from sodium diphenylketyl, $CH_2Cl_2$ from $CaH_2$ and pentane from sodium.

*Physical Methods.*—All reactions and manipulations were performed under an argon atmosphere with use of standard vacuum-line and Schlenk techniques. Melting points were determined on a Büchi 535 apparatus. Mass spectra (electron impact) were recorded on a Finnigan Mat 8200 instrument and NMR spectra on a VXR 200 FT spectrometer. Elemental analyses were carried out by the Mikroanalytisches Labor of Pascher in Bonn and the Division of Energy Technology, CSIR, Pretoria.

*Preparations.*—[CuCl{CN(Me)C(Me)=CHS}] **1**. 4-Methylthiazol-2-yllithium,[24] was prepared from 4-methylthiazole (0.40 $cm^3$, 4.4 mmol) and butyllithium (2.5 $cm^3$, 1.6 mol $dm^{-3}$, 4.0 mmol) in thf (20 $cm^3$) at −80 °C and stirred for 15 min before a suspension of CuCl (0.20 g, 2.0 mmol) in thf (20 $cm^3$) was added. The mixture was stirred for 2 h before the addition of $CF_3SO_3Me$ (0.22 $cm^3$, 2.0 mmol) at −80 °C. Stirring was continued at this temperature for 1 h, then for 1 h at −50 °C, for 1 h at −20 °C and at 0 °C for 1 h, before warming to room temperature. After filtration through anhydrous $MgSO_4$ (18 g) and concentration *in vacuo* to *ca.* 75 $cm^3$, light brown crystals (0.10 g, 23%) suitable for X-ray crystallography formed at −20 °C, m.p. 96 °C (decomp.) (Found: C, 28.0; H, 3.5; N, 6.8. $C_5H_7ClCuNS$ requires C, 28.3; H, 3.5; N, 6.6%). NMR: $\delta_H$(200 MHz, $CD_2Cl_2$) 2.46 [3 H, d, *J*(HH) 1 Hz, NCMe], 4.08 (3 H, s, NMe) and 7.14 (1 H, br s, SCH); $\delta_C$(50 MHz, $CD_2Cl_2$) 14.1 (s, NC*C*$H_3$), 42.8 (s, NMe), 119.2 (s, SCH), 145.6 (s, N*C*Me) and 203.5 (s, CuC). Mass spectrum: *m*/*z* 211 (100%, $M^+$), 176 (99, *M* − Cl), 113 (37, *M* − Cu − Cl), 99 {5, [HCNC(Me)=CHS]$^+$}.

[CuCl{CN(Me)$C_6H_4$S-*o*}] **3**. The analogous reaction using benzothiazole (0.50 $cm^3$, 4.6 mmol), butyllithium (3.0 $cm^3$, 1.6 mol $dm^{-3}$, 4.8 mmol), CuCl (0.22 g, 2.2 mmol) and $CF_3SO_3Me$ (0.25 $cm^3$, 2.3 mmol) afforded yellow crystals of **3** (0.29 g, 52%), m.p. 78 °C (decomp.) (Found: C, 38.8; H, 2.8; N, 5.6. $C_8H_7ClCuNS$ requires C, 38.7; H, 2.8; N, 5.6%). NMR: $\delta_H$(200 MHz, $CD_2Cl_2$) 4.39 (3 H, s, $NCH_3$), 7.53 [2 H, m, SCCH(C*H*)$_2$CHCN], 7.71 (1 H, m, SCCH) and 7.86 (1 H, m, NCCH); $\delta_C$(50 MHz, $CD_2Cl_2$) 41.8 (s, $NCH_3$), 114.1, 122.4, 125.0 and 126.9 [s, SC(*C*H)$_4$CN], 134.4 (s, SC), 143.9 (s, NC) and 216.3 (s, CuC). Mass spectrum: *m*/*z* 247 (9%, $M^+$), 212 (8, *M* − Cl), 149 (75, *M* − Cu − Cl), 135 {40, [HC=N$C_6H_4$S-*o*]$^+$}, 268 (8), 283 (100) and 298 (30) [*o*-S$C_6H_4$N(Me)C=CN(Me)$C_6H_4$S-*o* − *n*$CH_3$]$^+$ where *n* = 0, 1 or 2.

[CuI{CN(Me)C(Me)=CHS}] **4**. Complex **4** was prepared similarly from 4-methylthiazole (0.90 $cm^3$, 9.9 mmol), butyllithium (6.2 $cm^3$, 1.6 mol $dm^{-3}$, 9.9 mmol), CuI (0.94 g, 4.9 mmol) and $CF_3SO_3Me$ (0.60 $cm^3$, 5.5 mmol) (the reaction mixture was stirred for 2 h at −80 °C before alkylation) as yellow crystals (0.34 g, 23%), m.p. 101 °C (decomp.) (Found: C, 19.6; H, 2.4; N, 4.7. $C_5H_7CuINS$ requires C, 19.8; H, 2.3; N, 4.6%). NMR: $\delta_H$(200 MHz, $CD_2Cl_2$) 2.52 [3 H, d, *J*(HH) 1 Hz, NCMe], 4.19 (3 H, s, NMe) and 7.29 (1 H, br s, SCH); $\delta_C$(50 MHz, $CD_2Cl_2$), 14.2 (s, NC*C*$H_3$), 44.1 (s, NMe), 120.8 (s, SCH), 146.9 (s, N*C*Me) and 202.5 (s, CuC). Mass spectrum: *m*/*z* 303 (37%, $M^+$), 176 (100, *M* − I), 113 (32, *M* − Cu − I), 98 {27, [CNC(Me)=CHS]$^+$}.

[CuI{CN(Me)C(Me)=C(Me)S}] **5**. The analogous method using 4,5-dimethylthiazole (0.70 $cm^3$, 6.6 mmol), butyllithium (4.0 $cm^3$, 1.6 mol $dm^{-3}$, 6.4 mmol), CuI (0.60 g, 3.2 mmol) and $CF_3SO_3Me$ (0.30 $cm^3$, 2.7 mmol) afforded yellow crystals of **5** (0.14 g, 14%), m.p. 119 °C (decomp.) (Found: C, 22.8; H, 2.6; N, 4.1. $C_6H_9CuINS$ requires C, 22.7; H, 2.6; N, 4.4%). NMR: $\delta_H$(200 MHz, $CD_2Cl_2$) 2.28 (6 H, s, CMe) and 4.07 (3 H, s, NMe); $\delta_C$(50 MHz, $CD_2Cl_2$) 12.4 (s, SC*C*$H_3$), 12.5 (s, NC*C*$H_3$), 43.6 (s, NMe), 130.8 (s, SC), 140.8 (s, NC) and 205.0 (s, CuC). Mass spectrum: *m*/*z* 317 (81%, $M^+$), 190 (100, *M* − I and *M* − $C_6H_9NS$), 127 (11, *M* − CuI), 113 {27, [NC(Me)=C(Me)SCH]$^+$}.

[CuI{CN(Me)$C_6H_4$S-*o*}] **6**. Complex **6** was prepared similarly from benzothiazole (0.8 $cm^3$, 7.4 mmol), butyllithium (4.7 $cm^3$, 1.6 mol $dm^{-3}$, 7.5 mmol), CuI (0.72 g, 3.8 mmol) and $CF_3SO_3Me$ (0.43 $cm^3$, 3.8 mmol) as yellow crystals (0.27 g, 21%), m.p. 94 °C (decomp.) (Found: C, 28.4; H, 2.5; N, 4.0. $C_8H_7CuINS$ requires C, 28.3; H, 2.1; N, 4.1%). NMR: $\delta_H$(200 MHz, $CD_2Cl_2$), 4.21 (3 H, s, NMe) and 7.51 [4 H, m, SC(CH)$_4$CN]; $\delta_C$(50 MHz, $CD_2Cl_2$), 42.2 (s, NMe), 114.6, 122.6, 125.7 and 127.5 [s, SC(*C*H)$_4$CN], 134.4 (s, SC), 144.2 (s, NC) and 214.3 (s, CuC). Mass spectrum: *m*/*z* 339 (8%, $M^+$), 212 (19, *M* − I), 149 (25, *M* − Cu − I), 135 {56, [HC=N$C_6H_4$S-*o*]$^+$}, 268 (65), 283 (100), 298 (29) [*o*-S$C_6H_4$N(Me)C=CN(Me)$C_6H_4$S-*o* − *n*Me]$^+$ where *n* = 0, 1 or 2.

[CuCl{CN(Me)CH=CHN(Me)}] **7**. Complex **7** was prepared from 1-methylimidazole (0.7 $cm^3$, 8.8 mmol), butyllithium (4.8 $cm^3$, 1.6 mol $dm^{-3}$, 7.7 mmol), CuCl (0.38 g, 3.8 mmol) and $CF_3SO_3Me$ (0.45 $cm^3$, 4.0 mmol). The mixture was stirred for 1.5 h at −80 °C, for 1 h at −40 °C and then alkylated at −40 °C with $CF_3SO_3Me$. Stirring was continued for 1 h at this temperature and then for 1 h at −20 °C before the mixture was allowed to reach room temperature. Crystallization yielded light brown crystals (0.36 g, 48%), m.p. 135 °C (decomp.) (Found: C, 31.0; H, 4.4; N, 14.6. $C_5H_8ClCuN_2$ requires C, 30.8; H, 4.1; N, 14.4%). NMR: $\delta_H$(200 MHz, $CD_2Cl_2$), 3.97 (6 H, s, NMe) and 7.33 [2 H, s, N(CH)$_2$N]; $\delta_C$(50 MHz, $CD_2Cl_2$) 38.0 (s, NMe), 123.3 [s, N(CH)$_2$N] and 177.0 (s, CuC). Mass spectrum:

*m/z* 255 {54, [Cu{CN(Me)CH=CHN(Me)}$_2$]$^+$} 194 (2%, $M^+$), 159 (100, $M$ − Cl), 96 (64, $M$ − Cl − Cu).

[CuCl{CN(Me)C$_6$H$_4$N(Me)-*o*}] **8**. Complex **8** was prepared according to the same procedure as **1** from 1-methylbenzoimidazole (0.98 g, 7.4 mmol), butyllithium (4.5 cm$^3$, 1.6 mol dm$^{-3}$, 7.2 mmol), CuCl (0.35 g, 3.5 mmol) and $CF_3SO_3Me$ (0.40 cm$^3$, 3.5 mmol). Work-up yielded white microcrystalline material (0.33 g, 38%), m.p. 133 °C (decomp.) (Found: C, 44.3; H, 4.4; N, 11.6. $C_9H_{10}ClCuN_2$ requires C, 44.1; H, 4.1; N, 11.4%). NMR: $\delta_H$(200 MHz, $CD_2Cl_2$) 3.82 (6 H, s, $NCH_3$) and 7.39 (4 H, m, $C_6H_4$); too insoluble for $^{13}$C NMR. Mass spectrum: *m/z* 244 (15%, $M^+$), 209 (10, $M$ − Cl), 160 {100, [MeCN(Me)C$_6$H$_4$N(Me)-*o*]$^+$}, 146 (74, $M$ − Cu − Cl), 131 (14, $M$ − Cu − Cl − Me).

(*o*-SC$_6$H$_4$N=C-C=NC$_6$H$_4$S-*o*). A suspension of CuCl (0.40 g, 4.1 mmol) in thf (20 cm$^3$) was added to benzothiazol-2-yllithium[24] obtained from benzothiazole (0.90 cm$^3$, 8.3 mmol) and butyllithium (5.1 cm$^3$, 1.6 mol dm$^{-3}$, 8.2 mmol) in thf (20 cm$^3$) at −80 °C. The dark red mixture was stirred for 1 h before HCl (g) in diethyl ether (1.2 cm$^3$, 3.4 mol dm$^{-3}$, 4.1 mmol) was added at −20 °C. Stirring was continued at −20 °C for 1 h before warming to room temperature. After filtration through anhydrous $MgSO_4$ and concentration to *ca.* 30 cm$^3$ white crystals (0.06 g, 5%) of (*o*-SC$_6$H$_4$N=C-C=NC$_6$H$_4$S-*o*) formed at −20 °C, m.p. > 280 °C (Found: C, 62.5; H, 3.2; N, 10.5. $C_{14}H_8N_2S_2$ requires C, 62.7; H, 3.0; N, 10.4%). NMR: $\delta_H$(200 MHz, $C_4D_8O$) 7.53 (4 H, m, NCCH and SCCH), 8.10 [4 H, m, NCCH(C*H*)$_2$CHS]; too insoluble for $^{13}$C NMR. Mass spectrum: *m/z* 268 (100%, $M^+$), 134 (11, $M$ − C=NC$_6$H$_4$S-*o*).

[Cu{C=NC(Me)=CHS}] **9**. Complex **9** was crystallized from a reaction mixture prepared in the same way as (*o*-SC$_6$H$_4$N=C-C=NC$_6$H$_4$S-*o*) from CuCl (0.59 g, 6.0 mmol), 4-methylthiazole (1.1 cm$^3$, 12.1 mmol), butyllithium (7.5 cm$^3$, 1.6 mol dm$^{-3}$, 12.0 mmol) and HCl (g) in diethyl ether (1.8 cm$^3$, 3.4 mol dm$^{-3}$, 6.1 mmol) and yielded white crystals (0.12 g, 12%), m.p. 110 °C (decomp.) (Found: C, 29.4; H, 2.4; N, 8.4; Cu, 39.7. $C_4H_4CuNS$ requires C, 29.7; H, 2.5; N, 8.7; Cu, 39.3%). NMR: $\delta_H$(200 MHz, $C_4D_8O$) 2.55 (3 H, s, NCMe), 7.14 (1 H, s, SCH); too insoluble for $^{13}$C NMR. Mass spectrum: *m/z* 485 (12%, $M_3^+$), 422 (22, $M_3$ − Cu), 324 (2, $M_2$), 259 (22, $M_2$ − Cu), 196 {18, [{C=NC(Me)=CHS}$_2$]$^+$}, 161 (6, $M^+$).

*Crystallography.—Crystal data for compound* [CuCl{CN(Me)C(Me)=CHS}] **1**. $C_5H_7ClCuNS$, $M$ = 212.1, orthorhombic, space group *Aba* 2, $a$ = 18.925(3), $b$ = 12.489(2), $c$ = 6.824(1) Å, α, β, γ = 90°, $U$ = 1612.9(4) Å$^3$ [based on the least-squares refinement of the diffractometer angles for 25 centred reflections with θ > 12° using Mo-Kα (λ = 0.7107 Å) radiation], $Z$ = 8, $D_c$ = 1.747 g cm$^{-3}$. Light brown rectangular plates, crystal dimensions 0.23 × 0.20 × 0.18 mm, μ(Mo-Kα) 32.9 cm$^{-1}$, $F$(000) = 848.

*Data collection and processing.* CAD4 diffractometer, graphite-monochromated Mo-Kα radiation, ω–2θ scan mode with ω = 0.75 + 0.35 tan θ, variable ω scan rate 1.37–5.49° s$^{-1}$, 866 unique reflections (*h* 0–26, *k* 0–17, *l* −7 to 7) with 2 ⩽ θ ⩽ 23° measured. A linear decay correction of 17.9% was applied as well as semi-empirical (Ψ-scan, $T_{min}$ = 0.778, $T_{max}$ = 0.999) absorption corrections yielding 645 reflections with $I$ > 3σ($I$) used for the analysis and refinement.

*Structure analysis and refinement.* The structure was solved by normal Patterson and Fourier methods using the programs SHELX 76 and SHELX 86.[25] Full matrix least-squares refinement with all non-hydrogen atoms anisotropic, all hydrogen atoms refined in experimentally calculated positions with a common isotropic thermal parameter that converged to $U_{iso}$ = 0.086(1) Å$^2$. The weighting scheme $w = 1/[\sigma^2(F) + 0.020F^2]$ was used and 95 parameters were refined. Final $R$,$R'$ are 0.0372 and 0.0373 [$R' = \Sigma(w^{\frac{1}{2}}|F_o| - |F_c|)/\Sigma(w^{\frac{1}{2}}|F_o|)$]. The computer program SCHAKAL[26] was used for the preparation of illustrations.

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

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