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Synthesis and crystallographic characterization of thiazole-2-dithiocarboxylate methyl ester complexes of chromium, tungsten and iron carbonyls†

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Co-ordination of 4-methylthiazole-2-dithiocarboxylate methyl ester, **I**, or benzothiazole-2-dithiocarboxylate methyl ester, **II**, to $[Cr(CO)_5(THF)]$, $[W(CO)_5(THF)]$ or $[Fe(CO)_4(THF)]$ afforded the new complexes $[M(CO)_4\{S{=}C(SCH_3)C{=}NC(CH_3){=}CHS\}]$ (M = Cr **1** or W **2**), $[Cr(CO)_4\{S{=}C(SCH_3)C{=}NC_6H_4S\text{-}o\}]$ **3**, $[Fe(CO)_3\{S{=}C(SCH_3)C{=}NC(CH_3){=}CHS\}]$ **4** and $[Fe(CO)_3\{S{=}C(SCH_3)C{=}NC_6H_4S\text{-}o\}]$ **5**. Single crystal X-ray structure determinations of **1** and **5** revealed co-ordination of the bidentate ligands through the exocyclic thione sulfur and endocyclic imine nitrogen atoms by five-membered chelate ring formation. Compound **5** has a unique trigonal bipyramidal configuration.

Introduction

Pseudoaromatic azolyl compounds are important both from a biological[1,2] and an industrial[3] viewpoint and their co-ordination chemistry merits further investigation. The rich organic chemistry of azoles[4] provides a myriad of ligands for complexation to transition metals. Our investigation involves the co-ordination of thiazolyldithiocarboxyl esters, derived from the same type of heterocycle that occurs in vitamin B_1, to Group 6 transition metal and iron carbonyl complexes. The presence of a N atom in the pseudoaromatic ring provides an alternative co-ordination possibility to the usual η^1-*S* or η^2-*S*,*S* co-ordination of the dithiocarboxyl ester ligand.

Ligands containing exocyclic S- and endocyclic N- and S-donor atoms and their co-ordination possibilities have been explored for different metals and in different media.[5,6] Although iron(II) and iron(III) complexes containing 2-quinolinedithiocarboxylate ligands are known,[7] X-ray crystallographic data for these complexes, or any other iron(0) or Group 6 transition metal complexes containing ligands with an imine group and a dithiocarboxylate group or dithiocarboxyl ester, have not been reported.

Despite the similarity between Group 6 transition metal and iron complexes containing deprotonated 1,1-dithioacid ligands and metalloenzymes as well as their ability to form complexes with high co-ordination numbers and different oxidation states,[8,9] few examples of complexes of Group 6 transition metals and iron with dithiocarboxyl ester derivatives are known.

The η^1-*S*, η^2-*S*,*C* and unusual η^3-*S*,*C*,*S* co-ordination modes of $S{=}C(R)SCH_3$ ($R = CH_3$ or C_6H_5) and other S–P ligands to Group 6 metal and iron carbonyl fragments have been described.[10,11] Reaction of the thio-Schiff base $R(R^1)C{=}NNHC(S)SCH_3$ [$R = C_6H_5$, C_4H_3O or *o*-$C_4H_4(OH)$ and $R^1 = H$ or CH_3] with $M(CO)_6$ (M = Cr or Mo) yields tetracarbonyl complexes co-ordinated through the C=S group and the azomethine nitrogen.[12]

We report here the synthesis of thiazolyldithiocarboxyl esters and the co-ordination of these esters to iron, chromium and tungsten carbonyls as well as the first crystal and molecular structures of bidentate thiazolyldithiocarboxyl ester iron and chromium carbonyl complexes.

Results and discussion

Preparation and characterization of the ligands

Thiazole derived esters $S{=}C(SCH_3)C{=}NC(CH_3){=}CHS$ I and $S{=}C(SCH_3)C{=}NC_6H_4S\text{-}o$ II. We achieved C–C bond formation readily by treating thiazol-2-yllithium with CS_2 followed by conversion of the dithiocarboxylate into the ester with $CF_3SO_3CH_3$ (Scheme 1). Purification by column chromatography and crystallization produced red, air stable $S{=}C(SCH_3)C{=}NC(CH_3){=}CHS$ **I** or $S{=}C(SCH_3)C{=}NC_6H_4S\text{-}o$ **II**, soluble in the polar organic solvents, diethyl ether and CH_2Cl_2. The ligands were characterized by elemental analysis (Table 1), mass spectra (that showed all molecular ions) and ^1H and ^{13}C NMR spectra (see Experimental section).

Preparation and structural characterization of Group 6 transition metal compounds

Disubstituted carbonyl complexes $[M(CO)_4\{S{=}C(SCH_3)C{=}NC(CH_3){=}CHS\}]$ (M = Cr 1 or W 2) and $[Cr(CO)_4\{S{=}C(SCH_3)C{=}NC_6H_4S\text{-}o\}]$ 3. Addition of compound **I** or **II** to $[M(CO)_5(THF)]$ (M = Cr or W) in THF not only substitutes THF but also a CO group to yield the tetracarbonyl complexes $[M(CO)_4\{S{=}C(SCH_3)C{=}NC(CH_3){=}CHS\}]$ (M = Cr **1** or W **2**) and $[Cr(CO)_4\{S{=}C(SCH_3)C{=}NC_6H_4S\text{-}o\}]$ **3** (Scheme 1), which were purified by column chromatography at −20 °C and recrystallization. Crystals of **1**, **2** and **3** are stable in the absence

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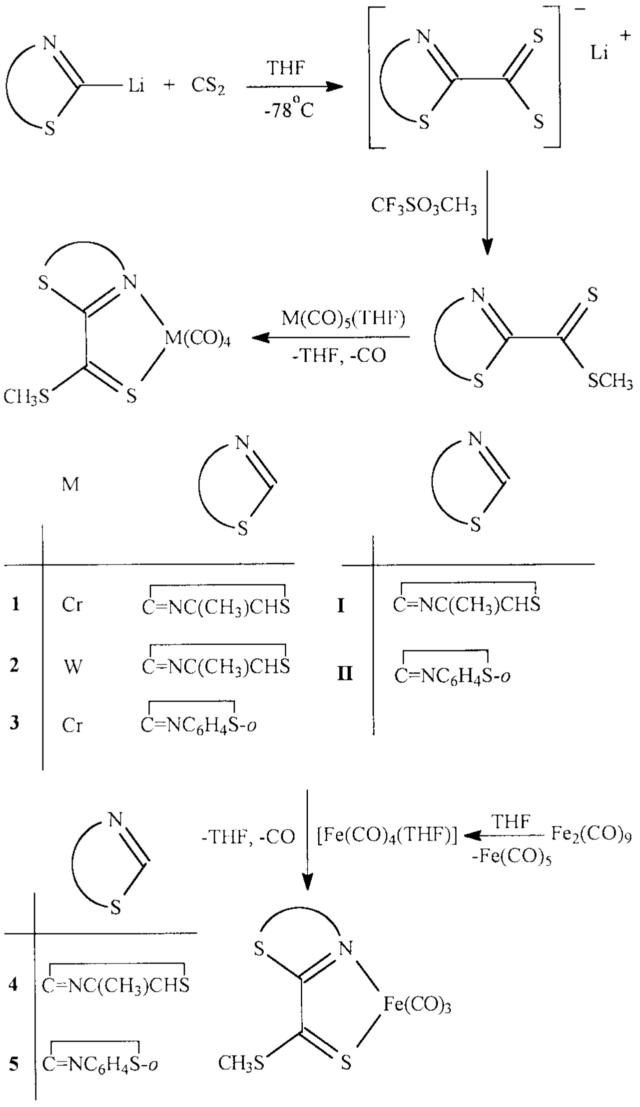
† Dedicated to Professor Herbert Schumann of the Technical University of Berlin on the occasion of his 65th birthday.

Table 1 Analytical, physical and infrared data for compounds **I**, **II** and **1**–**5**

Compound	mp/°C	Colour	Yield (%)	$\tilde{\nu}$(CO)/cm^{-1}			Analysis[a] (%) C	H	N
I S=C(SCH$_3$)C=NC(CH$_3$)=CHS	93–94	Red	72[b]				38.3 (38.1)	3.7 (3.7)	7.2 (7.4)
II S=C(SCH$_3$)C=NC$_6$H$_4$S-*o*	175–176	Red	67[b]				48.3 (48.0)	3.3 (3.1)	6.0 (6.2)
1 [Cr(CO)$_4${S=C(SCH$_3$)C=NC(CH$_3$)=CHS}]	94[c]	Blue-green	31[d]	$A_1^{(1)}$ 2014m	$B_1 + A_1^{(2)}$ 1949s (br)	B_2 1899m[e]	34.4 (34.0)	2.2 (2.0)	4.0 (4.0)
2 [W(CO)$_4${S=C(SCH$_3$)C=NC(CH$_3$)=CHS}]	126[c]	Dark blue	27[d]	$A_1^{(1)}$ 2020m	$B_1 + A_1^{(2)}$ 1939s (br)	B_2 1899m[e]	24.9 (24.8)	1.6 (1.5)	2.8 (2.9)
3 [Cr(CO)$_4${S=C(SCH$_3$)C=NC$_6$H$_4$S-*o*}]	95[c]	Dark green	29[d]	$A_1^{(1)}$ 2015m	$B_1 + A_1^{(2)}$ 1944s (br)	B_2 1877m[f]	39.7 (40.1)	1.9 (1.8)	3.5 (3.6)
4 [Fe(CO)$_3${S=C(SCH$_3$)C=NC(CH$_3$)=CHS}]	82[c]	Blue-purple	26[d]	2A′ 2039s	A″ 1972 (br)[e]		32.9 (32.8)	2.3 (2.1)	4.5 (4.3)
5 [Fe(CO)$_3${S=C(SCH$_3$)C=NC$_6$H$_4$S-*o*}]	87[c]	Blue	27[d]	2A′ 2045s	A″ 1982 (br)[e]		39.7 (39.5)	2.0 (1.9)	3.6 (3.8)

[a] Required values are given in parentheses. [b] Based on thiazole. [c] With decomposition. [d] Based on metal carbonyl. [e] In hexane. [f] In CH$_2$Cl$_2$.



Scheme 1

of air and moisture, soluble in polar solvents, *e.g.* diethyl ether and CH$_2$Cl$_2$, only slightly soluble in the less polar solvents hexane and pentane, and slowly decompose in solution.

Characterization data of complexes **1**, **2** and **3** are shown in Table 1. The mass and infrared spectra confirm the presence of four carbonyl ligands and bidentate co-ordination for the thiazolyldithiocarboxyl ester. Molecular ions were observed in their mass spectra. Peaks in the infrared spectra were assigned (Table 1) for *cis*-tetracarbonyl complexes with octahedral co-ordination.[13] The broad band at *ca.* 1945 cm^{-1} represents the B_1 and $A_1^{(2)}$ vibrations which overlap in certain solvents[14] or when the carbonyl ligands are bent away from the sterically demanding bidentate ligand [C(1)–Cr–S(1) 177.02(1), C(2)–Cr–N 169.96(13), C(3)–Cr–C(4) 171.21(14)°].[15]

A small but significant downfield shift is observed in the ^{1}H NMR spectra of complexes **1**–**3** for all the protons in the ligands as can be expected with negative charge donation to the metal centre upon co-ordination of the ligand. Although it is generally accepted that ^{13}C NMR spectra give a better indication of electron density redistribution,[16] it has, nevertheless, been shown that ^{13}C chemical shifts do not always represent electron charge densities[17] and that the paramagnetic component of the ^{13}C chemical shift cannot always be ignored as for ^{1}H chemical shifts when correlating chemical shifts and charge densities. Keeping these facts in mind it seems that the ^{13}C chemical shift changes from the "free" to the co-ordinated ligand, $\Delta\delta$ −2.5 to 5 ppm for thiazole ring carbons and 15.4 to 17.2 for the CS$_2$ carbon, can be interpreted as the result of two opposing effects, *viz.* a downfield shift caused by donation of electron density to the metal opposed by an upfield shift caused by π-back donation into the d orbitals of the S atoms of the CS$_2$ carbon and thus a π-electron redistribution along the S=CCSC backbone of the bidentate ligand.

The single signal observed for the CO ligands in complex **2** and no signals for **1** and **3** in the ^{13}C NMR spectra at room temperature (in CDCl$_3$) indicate that the molecules are fluxional[18,19] and involved in intramolecular carbonyl scrambling at room temperature. Spectra recorded in d_8-THF at −90, −45 and 45 °C confirmed this impression. At −90 °C the configurations in **2** become distinguishable. Three signals, *viz.* two at δ 216.1 and 211.1 for the two *trans*-carbonyl ligands and one at δ 194.8 for the two *cis*-carbonyl ligands, are assigned. At −45 °C these disappear and collapse into one signal, a broad based singlet at δ 204.2 (204.6 is the weighted average of the CO signals at −90 °C),[20] at room temperature and 45 °C.

Similar results were obtained for the CO ligands of complex **1** (δ 234.9, 229.5 for CO$_{trans}$ and 210.4 for CO$_{cis}$) and **3** (δ 237.6, 229.3 for CO$_{trans}$ and 211.4 for CO$_{cis}$). Efforts to locate the single collapsed signal at higher temperatures (expected at δ 221 for **1** and 222 for **3**) were unsuccessful because the complexes decompose at 45 °C. Diimine chelates of Group 6 transition metals previously yielded analogous results.[15] The distorted angle (<180°) between the *cis*-carbonyl groups, identified in the infrared spectra of **1**, **2** and **3** and the molecular structure of **1** (see below), implies that the distorted octahedral co-ordination has a tendency towards a trigonal prismatic arrangement of

Table 2 Selected bond lengths (Å) and angles (°) of complex **1**

Cr–S(1)	2.3474(11)	Cr–N	2.137(3)
S(1)–C(9)	1.652(4)	N–C(5)	1.333(4)
C(5)–C(9)	1.421(5)		
Cr–C(1)	1.845(4)	Cr–C(2)	1.830(4)
Cr–C(3)	1.895(5)	Cr–C(4)	1.902(4)
S(3)–C(9)	1.725(3)	S(3)–C(10)	1.770(5)
N–C(7)	1.377(4)	C(7)–C(8)	1.487(5)
C(6)–C(7)	1.353(5)		
S(2)–C(6)	1.694(4)	S(2)–C(5)	1.716(3)
C(2)–Cr–S(1)	89.95(11)	C(1)–Cr–N	102.19(13)
N–Cr–S(1)	80.45(8)	C(1)–Cr–S(1)	177.02(11)
C(2)–Cr–N	169.96(13)	C(3)–Cr–C(4)	171.21(14)
C(5)–N–Cr	117.5(2)	C(9)–S(1)–Cr	102.85(13)
N–C(5)–C(9)	122.3(3)	C(5)–C(9)–S(1)	116.9(2)
C(5)–N–C(7)	110.8(3)	C(6)–S(2)–C(5)	89.44(17)
N–C(5)–S(2)	113.9(3)	C(6)–C(7)–N	113.9(3)
C(7)–C(6)–S(2)	112.0(3)	C(6)–C(7)–C(8)	124.59(4)
S(1)–C(9)–S(3)	127.0(2)	C(9)–S(3)–C(10)	103.5(2)

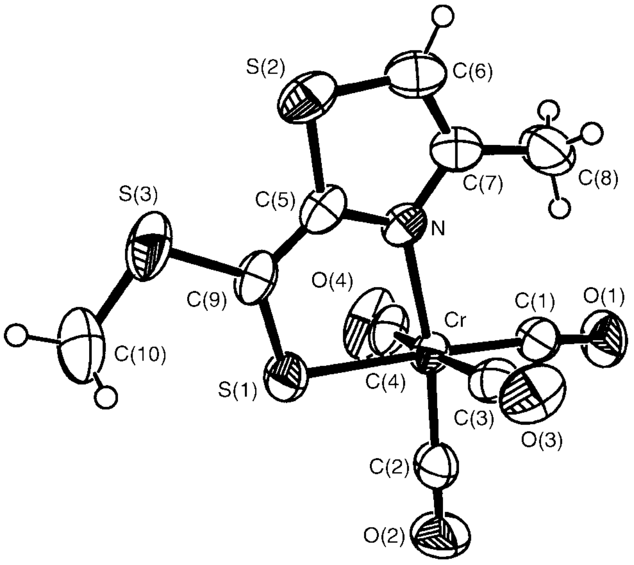


Fig. 1 An ORTEP[21] drawing of $[Cr(CO)_4\{S{=}C(SCH_3)C{=}NC(CH_3){=}CHS\}]$ **1** at 50% probability level.

the ligands, which would facilitate a *turnstile* or *umbrella*-like Berry pseudorotation of the four carbonyl ligands, although a Bailar twist favoured by a small bidentate ligand bite angle should also remain an option. A second mechanism described for racemization of octahedral complexes, the Rây-Dutt twist, could, however, also be considered.[19]

Structure of $[Cr(CO)_4\{S{=}C(SCH_3)C{=}NC(CH_3){=}CHS\}]$ 1. The crystal structure of **1** is shown in Fig. 1, and selected bond lengths and bond angles are in Table 2. The chromium atom is octahedrally surrounded by four carbonyl ligands and a bidentate 4-methylthiazole-2-dithiocarboxylate methyl ester. The N- and S-donor atoms of the bidentate ligand are co-ordinated to the metal *cis* to each other. Deviations from the idealized 90 and 180° angles around the Cr atom [C(2)–Cr–S(1) 89.95(11), N–Cr–S(1) 80.45(8), C(3)–Cr–C(4) 171.21(14) and C(1)–Cr–N 102.19(13)°] accommodate the five membered ring formed by the bidentate ligand and the Cr atom. Similar deviations have been observed in the structures of $[Cr(CO)_4\{NH{=}C(OCH_2CH_3)C(OCH_2CH_3){=}CS(CH_2)_3S\}]$[22] **A** and $[Cr(CO)_4\{N(CH_3){=}C(OCH_2CH_3)C(OCH_2CH_3){=}CHCHS(CH_2)_3S\}]$[23] **B**. With the exception of C(10) which is displaced 0.187(7) Å from the plane, the thiazoledithiocarboxyl ester ligand is planar and coplanar with the *trans*-CO ligands within 0.085(3) Å.

In agreement with bond distances observed for the *trans*-CO ligands in **A** and **B**, the Cr–CO_{trans} bond lengths in complex **1** [Cr–C(1) 1.845(4) and Cr–C(2) 1.830(4) Å] are shorter than the Cr–CO_{cis} bond lengths [Cr–C(3) 1.895(5) and Cr–C(4) 1.902(4) Å] with the difference between the average Cr–CO_{cis} and Cr–CO_{trans} bond distances being 0.06 Å, similar to the value for **A** (0.06 Å). The C(3)–Cr–C(4) bond angle is 171.21(14)° with the two *cis*-CO ligands bent away from the bidentate ligand. The same effect was observed in **A** [176.9(3)°] and **B** [169.2(10)°].

As expected the N–Cr–S(1) angle is smaller for the five-membered chelate ring in complex **1** [80.45(8)°] than for the six membered chelate ring in **A** [84.9(1)°] and the seven membered chelate ring in **B** [91.7(4)°]. The Cr–S(1) bond distance of 2.3474(11) Å is shorter than the corresponding bonds in **A** [2.392(2) Å] and **B** [2.433(5) Å]. The Cr–N bond length [2.137(3) Å] is similar to the corresponding bond in **B** [2.133(15) Å] but longer than that in **A** [2.095(5) Å].

The single and double CS bonds are normal. Bond lengths and angles in the thiazole unit of the ligand in complex **1** are essentially the same as those of the thiazole unit in the pentacarbonyl complex $[Cr(CO)_5\{N{=}C(SCH_3)SC(H){=}C(CH_3)\}]$[24] and agree with average values obtained from microwave spectra.[25]

Preparation and structural characterization of the iron compounds

$[Fe(CO)_3\{S{=}C(SCH_3)C{=}NC(CH_3){=}CHS\}]$ 4 and $[Fe(CO)_3\{S{=}C(SCH_3)C{=}NC_6H_4S\text{-}o\}]$ 5. These were prepared by the addition of a solution of compound **I** or **II** in THF to a red solution of $[Fe_2(CO)_9]$ in THF (the dissociation of $[Fe_2(CO)_9]$ in THF yields $Fe(CO)_5$ and $[Fe(CO)_4(THF)]$ which is responsible for the red colour of the solution[26]). The THF and a CO ligand in $[Fe(CO)_4(THF)]$ are substituted by the bidentate thiazole-2-dithiocarboxylate methyl esters to generate the tricarbonyl iron complexes **4** and **5** (Scheme 1). The compounds were purified by column chromatography at −20 °C and crystallization at −25 °C.

Table 1 contains the physical and infrared data for complexes **4** and **5**. Further evidence for the formation of iron tricarbonyl complexes was obtained from the infrared spectra. Two carbonyl vibrations at ≈2041 (two A′ vibrational modes) and ≈1979 cm^{-1} (the A″ vibrational mode) were observed as expected for $[Fe(CO)_3(L–L)]$ compounds with a local C_s symmetry.[13] Overlap of the two A′ bands and the broadening of the A″ band can be ascribed to a deviation from C_s symmetry as verified in the solid state by the crystal structure determination of **5** showing essentialy trigonal bipyramidal configuration instead of the usual square pyramidal configuration observed for other $[Fe(CO)_3(L–L)]$ compounds.[27–29]

The downfield shift of the signals in the ^1H NMR spectra of complexes **1**–**3** when compared to the signals for **I** or **II** is also observed in the signals for **4** and **5** but to a lesser extent, indicating less negative charge transfer from the ligand to the metal centre in the case of the iron tricarbonyl complexes than for the Group 6 tetracarbonyl complexes. Like the results for **1**, **2** and **3**, an upfield shift of the ^{13}C NMR signals upon co-ordination is observed for **4** and **5** but the values for the CS_2 carbon $\Delta\delta$ >50 ppm and the NCS carbon $\Delta\delta$ ≈19 ppm are much larger than for the Group 6 complexes.

Comparing ^{13}C NMR spectra[30] and the molecular structures[31] of $[Fe(CO)_3(X{=}CHCH{=}Y)]$ compounds (X = NR, CHR or O and Y = NR or CHR) Leibfritz and Dieck[30] postulated that an upfield shift of 50 ppm in the ^{13}C signals of the CH carbons with respect to the "free" ligand serves as an indication for π-type donor interaction whereas a small upfield shift of 20 ppm indicates such interaction to be of the σ-type utilizing the heteroatoms. In the ^{13}C NMR data of both **4** and **5** the signal for the carbon connected to the S-donor atom is shifted upfield by 53.9 ppm and the one bonded to the N-donor atom by only ≈19 ppm. This would then suggest a σ-type interaction for N=C in the N=CC=S chelate ring and a π-type interaction for the C=S donor section.

It followed from the structure determination of complex **5** (see below) that co-ordination occurs only through the heteroatoms. The upfield shift of 53.9 ppm of the carbon connected to the S-donor is best explained by somewhat better π-back donation into the available d orbitals of S whereas the N-donor atom with no available d orbitals has little or no possibility for π acceptance and thus the carbon connected to the N atom is only shifted upfield by ≈19 ppm. S-donor systems have not been included in previous studies.

The remaining singlets at δ 213.3 for **4** and 212.7 for **5** in the ^{13}C NMR spectra were assigned to the three CO ligands. It is difficult to reconcile three identical CO ligands when the non-C_{2v}-symmetric thiazoledithiocarboxyl ester ligands in **4** and **5** are considered. The ^{13}C NMR spectra recorded at −90 °C do not differ from those recorded at room temperature and we conclude that a rapid Berry pseudorotation or turnstile rotation, as proposed for Fe(α-diimine)(CO)$_3$ complexes[19,32] and for complexes of the formula [Fe(CO)$_3$(X=CHCH=Y)] (X = NR, CHR or O; Y = NR or CHR),[30] is responsible for the chemical equivalence of the CO ligands.

Structure of [Fe(CO)$_3${S=C(SCH$_3$)C=NC$_6$H$_4$S-*o*}] 5. The molecular structure of complex **5** shown in Fig. 2 reveals a five-co-ordinate iron atom. Viewed as a trigonal bipyramid, the S(1) atom of the bidentate benzothiazole-2-dithiocarboxylate methyl ester ligand and the carbonyl ligands, C(1)–O(1) and C(3)–O(3) are in the equatorial positions and the N atom and carbonyl ligand C(2)–O(2) axially positioned. This unique configuration for iron tricarbonyl compounds with bidentate ligands, which usually have a square pyramidal configuration, *e.g.* in [Fe(CO)$_3${N(2,6-^{i}Pr$_2$C$_6$H$_3$)CHCHN(2,6-^{i}Pr$_2$C$_6$H$_3$)}][28] and [Fe(CO)$_3${N(CH$_3$)=NN=N(CH$_3$)}],[29] is probably a consequence of the rigid and sterically demanding phenyl ring contained in the benzothiazoledithiocarboxyl ester ligand.

The Fe–S(1)–C(1)–C(3) plane [Fe has a maximum deviation from the plane of 0.028(1) Å], with an approximate C_s symmetry about the Fe–S(1) bond, has a distorted trigonal planar geometry with C(1)–Fe–S(1) 130.7(7), C(3)–Fe–S(1) 128.5(8) and C(3)–Fe–C(1) 100.8(3)° (Table 3) but the angles in the plane add up to 360° confirming planarity. Accommodation of the bidentate ligand in the structure necessitates a significant distortion of the C(2)–Fe–N bond angle [167.1(9)°] from linearity. Only the C(12) atom of the SCH$_3$ group in the bidentate ligand is displaced more than 0.080(4) Å from the plane formed by the benzothiazole-2-dithiocarboxylate methyl ester ligand and this plane is arranged at an angle of 89.1(1)° with the trigonal Fe–S(1)–C(1)–C(3) plane. The N–Fe–S(1) bond angle in the five membered chelate ring is 84.2(1)° similar to the N–Fe–N bond angle [80.1(10)°] in the disubstituted carbonyl complex [Fe(CO)$_3$N(2,6-^{i}Pr$_2$C$_6$H$_3$)CHCHN(2,6-^{i}Pr$_2$C$_6$H$_3$)}].[28] Although the Fe–N bond length 1.958(4) Å (Table 3) is slightly longer than that of 1.928 Å in the latter compound and the Fe–S(1) bond distance [2.191(1) Å] is at the short end of the range of reported Fe–S bond distances (2.18–2.35 Å),[33] the Fe · · · C(11) [3.022(4) Å] and the Fe · · · C(4) separations [2.856(5) Å] dispel any possibility of major π-type interaction that typically leads to Fe–C distances of 2.03–2.07 Å, *e.g.* 2.06 ± 0.03 Å in [Fe(CO)$_3$(CH$_2$CHCHCH$_2$)] and 2.067(4) and 2.031(5) Å in [Fe(CO)$_3${C$_6$H$_5$CHCHC(O)H}],[31] at least in the solid state.

Once again (compare **1** above) the S(1)–C(11) [1.678(5) Å] and S(3)–C(11) [1.738(4) Å] bond distances do not differ significantly from the reported average values for C=S (1.67 Å) and C–S (1.71 Å)[34] bond distances. Bond lengths and angles in the thiazole unit of the ligand in complex **5** are essentially the same as those of the thiazole unit in [Fe(η^5-C$_5$H$_5$)(CNHC$_6$H$_4$S-*o*)(C=NC$_6$H$_4$S-*o*)(dppe)].[35]

Table 3 Selected bond lengths (Å) and angles (°) of complex **5**

Fe–S(1)	2.191(1)	Fe–N	1.958(4)
S(1)–C(11)	1.678(5)	N–C(4)	1.337(5)
C(11)–C(4)	1.389(6)		
Fe–C(1)	1.820(2)	Fe–C(2)	1.759(8)
Fe–C(3)	1.750(2)		
S(3)–C(11)	1.738(4)	S(3)–C(12)	1.747(6)
N–C(6)	1.402(6)	C(5)–C(6)	1.390(6)
C(6)–C(7)	1.392(6)	C(7)–C(8)	1.366(5)
C(8)–C(9)	1.398(8)	C(9)–C(10)	1.378(7)
C(5)–C(10)	1.391(5)		
S(2)–C(5)	1.732(5)	S(2)–C(4)	1.726(5)
N–Fe–S(1)	84.2(1)	C(1)–Fe–S(1)	130.7(7)
C(3)–Fe–S(1)	128.5(8)	C(3)–Fe–C(1)	100.8(3)
C(2)–Fe–N	167.1(9)		
C(4)–N–Fe	119.0(3)	C(11)–S(1)–Fe	101.9(2)
N–C(4)–C(11)	119.9(4)	C(4)–C(11)–S(1)	114.9(3)
N–C(4)–S(2)	115.5(3)	C(4)–S(2)–C(5)	89.08(18)
C(4)–N–C(6)	110.7(3)	C(5)–C(6)–N	113.3(3)
C(6)–C(5)–S(2)	111.4(2)		
S(1)–C(11)–S(3)	124.9(2)	C(11)–S(3)–C(12)	102.5(3)

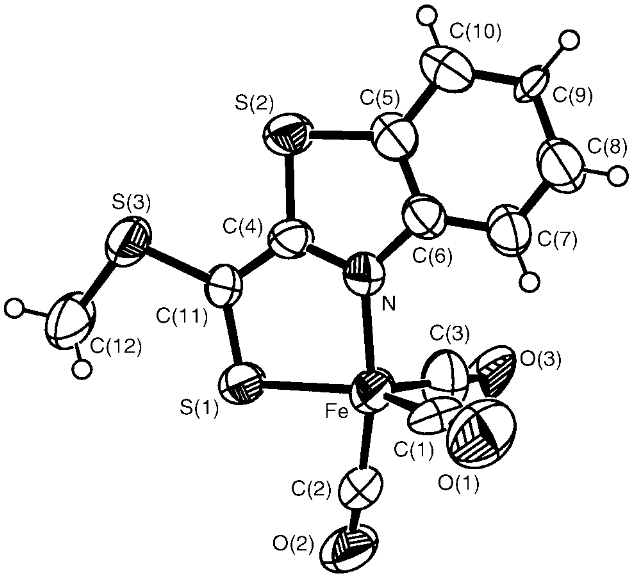


Fig. 2 An ORTEP[21] drawing of [Fe(CO)$_3${S=C(SCH$_3$)C=NC$_6$H$_4$S-*o*}] **5** at 50% probability level.

The average Fe–CO bond distance (1.776 Å) is in agreement with the corresponding bond lengths in the square pyramidal complexes [Fe(CO)$_3${N(2,6-^{i}Pr$_2$C$_6$H$_3$)CHCHN(2,6-^{i}Pr$_2$C$_6$H$_3$)}] (Fe–CO$_{\text{average}}$ 1.792 Å)[28] and [Fe(CO)$_3${N(CH$_3$)=NN=N(CH$_3$)}] (Fe–CO$_{\text{average}}$ 1.760 Å),[29] and the trigonal bipyramidal complexes *trans*-[Fe(CO)$_3$(PPh$_3$)$_2$] (1.770 Å)[36] and *trans*-[Fe(CO)$_3$(Ph$_2$Ppy)$_2$]·$\frac{1}{2}$C$_6$H$_6$ (1.783 Å).[37]

Experimental

General procedures

All reactions and manipulations were performed under a nitrogen atmosphere with the use of standard vacuum-line and Schlenk techniques. Melting points were determined on a Büchi 535 apparatus and are uncorrected. Mass spectra (electron impact at 70 eV) were recorded on a Finnigan Mat 8200 instrument, infrared on a Perkin-Elmer 841 spectrometer and NMR spectra (^{1}H at 300.1 MHz and ^{13}C at 75.5 MHz in d_8-THF, referenced to the internal standard TMS at 20 °C) on a Gemini 2000 spectrometer. Elemental analyses were carried out by the Division of Materials Science Technology, Council for Scientific and Industrial Research, Pretoria.

Materials

Benzothiazole, 4-methylthiazole, methyl trifluoromethanesulfonate, $[Cr(CO)_6]$, $[Fe_2(CO)_9]$ (Aldrich), CS_2, silica gel 60 and *n*-butyllithium (Merck) were used without further purification. Tetrahydrofuran and diethyl ether were distilled under N_2 from sodium diphenylketyl, pentane and hexane from sodium wire and CH_2Cl_2 from CaH_2.

Preparations

$S{=}C(SCH_3)C{=}NC(CH_3){=}CHS$ I. Treatment of 4-methylthiazol-2-yllithium in THF (60 cm^3), prepared from 4-methylthiazole (0.46 cm^3, 5.0 mmol) and 1.6 mol dm^{-3} *n*-butyllithium in hexane (3.1 cm^3, 5.0 mmol) at −78 °C and stirring for 30 min,[38] with an excess of CS_2 (1.2 cm^3, 12.5 mmol) at −78 °C yielded a yellow reaction mixture. After gradually increasing the temperature to −50 °C the reaction mixture was stirred for 30 min at this temperature and a change from yellow to dark red was observed. The reaction mixture was alkylated with $CF_3SO_3CH_3$ (0.57 cm^3, 5.0 mmol) at −50 °C with stirring and allowed to reach room temperature after one hour. The mixture was reduced to dryness *in vacuo*. The residue was extracted with the minimum amount of CH_2Cl_2, the extract filtered through silica and reduced to dryness. The crude product was purified by column chromatography on silica with CH_2Cl_2–hexane (2:3) as eluent. Red microcrystalline **I** was obtained at −25 °C after layering of a saturated CH_2Cl_2 solution of **1** with hexane. Yield 0.68 g. MS: *m*/*z* 189 (M^+, 76%), 143 (M − CH_2S, 63), 142 (M − CH_3S, 100), 99 [$HC{=}NC(CH_3){=}CHS$, 4], 72 [$SCH{=}C(CH_3)$, 13], 71 ($S{=}CHC{=}CH_2$, 15) and 45 (HCS, 23). δ_H 7.44 (1H, s, SCH), 2.72 (3H, s, SCH_3) and 2.46 (3H, s, $NCCH_3$). δ_C 217.2 (s, CS_2CH_3), 171.5 (s, NCS), 156.7 (s, $NCCH_3$), 123.9 (s, SCH), 19.2 (s, SCH_3) and 17.2 (s, $NCCH_3$).

$S{=}C(SCH_3)C{=}NC_6H_4S$-*o* II. This compound was prepared in the same way as **I** from benzothiazole (0.55 cm^3, 5.0 mmol), 1.6 M *n*-butyllithium in hexane (3.1 cm^3, 5.0 mmol) (yellow after addition), CS_2 (1.2 cm^3, 12.5 mmol) (dark green after addition) and $CF_3SO_3CH_3$ (0.57 cm^3, 5.0 mmol) (red after addition). Yield 0.75 g. MS: *m*/*z* 225 (M^+, 69%), 179 (M − CH_2S, 86), 178 (M − CH_3S, 100), 135 ($HC{=}NC_6H_4S$-*o*, 13), 108 (C_6H_4S, 12), 91 (C_6H_4NH, 27) and 45 (HCS, 20). δ_H 8.15 [1H, m, $NCCH(CH)_3CS$], 8.02 [1H, m, $NC(CH)_3CHCS$], 7.53 [2H, m, $NCCH(CH)_2CHCS$] and 2.80 (3H, s, SCH_3). δ_C 218.5 (s, CS_2CH_3), 171.4 (s, NCS), 155.2 [s, $NC(CH)_4S$], 139.4 [s, $NC(CH)_4CS$], 128.2 [s, $NCCHCH(CH)_2CS$], 128.1 [s, $NC(CH)_2CHCHCS$], 126.5 [s, $NCCH(CH)_3CS$], 122.8 [s, $NC(CH)_3CHCS$] and 19.6 (s, SCH_3).

$[Cr(CO)_4\{S{=}C(SCH_3)C{=}NC(CH_3){=}CHS\}]$ 1. A solution of compound **I** (0.57 g, 3.0 mmol) in THF (25 cm^3) was added slowly to a solution of $[Cr(CO)_5(THF)]$, prepared from $[Cr(CO)_6]$ (0.66 g, 3.0 mmol) in THF (100 cm^3).[39] The dark green reaction mixture was stirred for 2 hours at room temperature and evaporated to dryness *in vacuo*. The residue was purified by column chromatography in silica at −20 °C and eluted with diethyl ether–hexane (1:3). The blue green fraction containing the product was evaporated to dryness *in vacuo*. Blue-green needle like crystals suitable for a crystal structure determination were obtained by layering a saturated solution of the residue in diethyl ether with hexane and cooling to −25 °C. Yield 0.33 g. MS: *m*/*z* 353 (M^+, 13%), 297 (M − 2CO, 6), 269 (M − 3CO, 35), 241 (M − 4CO, 100), 189 (M − 4CO − Cr, 32), 143 (M − 4CO − Cr − CH_2S, 37), 142 (M − 4CO − Cr − CH_3S, 78), 99 [$HC{=}NC(CH_3){=}CHS$, 15], 72 [$SCH{=}C(CH_3)$, 54], 71 ($SCH{=}C{=}CH_2$, 60), 52 (Cr, 74) and 45 (HCS, 71). δ_H 7.95 (1H, s, SCH), 3.09 (3H, s, SCH_3) and 2.80 (3H, s, $NCCH_3$). δ_C (−90 °C) 234.9 (s, *trans*-CO), 229.5 (s, *trans*-CO), 210.4 (s, *cis*-CO), 203.3 (s,CS_2CH_3), 167.5 (s, NCS), 159.1 (s, $NCCH_3$), 122.5 (s, SCH), 20.1 (s, SCH_3) and 19.5 (s, $NCCH_3$).

$[W(CO)_4\{S{=}C(SCH_3)C{=}NC(CH_3){=}CHS\}]$ 2. Compound **2** was prepared by employing the same method as used for **1** with $[W(CO)_6]$ (1.06 g, 3.0 mmol) and **I** (0.57 g, 3.0 mmol). The purple-black reaction mixture was reduced to dryness *in vacuo* after stirring for two hours and the residue purified by column chromatography at −20 °C on silica with diethyl ether–hexane (1:4) as eluent. The blue fraction containing the product was evaporated to dryness *in vacuo*. Dark blue crystals of **2** were obtained at −25 °C by layering a saturated solution of **2** in diethyl ether with hexane. Yield 0.40 g. MS: *m*/*z* 485 (M^+, 28%), 457 (M − CO, 21), 429 (M − 2CO, 27), 401 (M − 3CO, 33), 373 (M − 4CO, 90), 143 (M − 4CO − W − CH_2S, 17), 142 (M − 4CO − W − CH_3S, 25), 72 [$SCH{=}C(CH_3)$, 31], 71 ($SCH{=}C{=}CH_2$, 51) and 45 (HCS, 100). δ_H 8.04 (1H, s, SCH), 3.01 (3H, s, SCH_3) and 2.81 (3H, s, $NCCH_3$). δ_C (−90 °C) 216.1 (s, *trans*-CO), 211.1 (s, *trans*-CO), 203.7 (s,CS_2CH_3), 194.8 (s, *cis*-CO), 171.7 (s, NCS), 159.2 (s, $NCCH_3$), 124.0 (s, SCH), 21.2 (s, SCH_3) and 19.5 (s, $NCCH_3$).

$[Cr(CO)_4\{S{=}C(SCH_3)C{=}NC_6H_4S$-*o*$\}]$ 3. The method used for compound **1** was employed to prepare **3** from $[Cr(CO)_6]$ (0.66 g, 3.0 mmol) in THF (100 cm^3) and **II** (0.68 g, 3.0 mmol) in THF (30 cm^3). The dark green reaction mixture was purified in a similar fashion as that of **2**. Dark green, needle like crystals of **3** were obtained at −25 °C by layering a saturated CH_2Cl_2 solution of **3** with hexane. Yield 0.34 g. MS: *m*/*z* 389 (M^+, 28%), 305 (M − 3CO, 30), 277 (M − 4CO, 11), 225 (M − 4CO − Cr, 16), 179 (M − 4CO − Cr − CH_2S, 21), 178 (M − 4CO − Cr − CH_3S, 25), 135 ($HC{=}NC_6H_4S$-*o*, 10), 108 (C_6H_4S, 69), 91 (C_6H_4NH, 11), 52 (Cr, 100) and 45 (HCS, 20). δ_H 8.96 [1H, m, $NCCH(CH)_3CS$], 8.19 [1H, m, $NC(CH)_3CHCS$], 7.78 [2H, m, $NCCH(CH)_2CHCS$] and 3.18 (3H, s, SCH_3). δ_C (−90 °C) 237.6 (s, *trans*-CO), 229.3 (s, *trans*-CO), 211.4 (s, *cis*-CO), 203.1 (s, CS_2CH_3), 166.8 (s, NCS), 154.1 [s, $NC(CH)_4S$], 136.0 [s, $NC(CH)_4CS$], 130.9 [s, $NCCHCH(CH)_2CS$], 129.3 [s, $NC(CH)_2CHCHCS$], 125.1 [s, $NCCH(CH)_3CS$] 123.4 [s, $NC(CH)_3CHCS$] and 20.3 (s, SCH_3).

$[Fe(CO)_3\{S{=}C(SCH_3)C{=}NC(CH_3){=}CHS\}]$ 4. A solution of compound **I** (0.42 g, 2.2 mmol) in THF (80 cm^3) was slowly added with stirring to $[Fe_2(CO)_9]$ (0.80 g, 2.2 mmol). The dark blue solution was stirred for two hours, evaporated to dryness *in vacuo* and the residue purified by column chromatography at −20 °C on silica and eluted with diethyl ether–hexane (1:4). The intensely coloured purple-blue fraction yielded microcrystalline **4** upon evaporation to dryness *in vacuo*. Yield 0.19 g. MS: *m*/*z* 329 (M^+, 10%), 301 (M − CO, 12), 273 (M − 2CO, 40), 245 (M − 3CO, 50), 189 (M − 3CO − Fe, 57), 143 (M − 3CO − Fe − CH_2S, 58), 142 (M − 3CO − Fe − CH_3S, 100), 99 [$HC{=}NC(CH_3){=}CHS$, 5], 72 [$SCH{=}C(CH_3)$, 23], 71 ($SCH{=}C{=}CH_2$, 28), 56 (Fe, 9) and 45 (HCS, 33). δ_H 7.45 (1H, s, SCH), 2.90 (3H, s, SCH_3) and 2.77 (3H, s, $NCCH_3$). δ_C (−90 °C) 213.3 (s, 3CO), 165.1 (s, CS_2CH_3), 155.4 (s, $NCCH_3$), 152.6 (s, NCS), 115.8 (s, SCH), 19.4 (s, SCH_3) and 18.7 (s, $NCCH_3$).

$[Fe(CO)_3\{S{=}C(SCH_3)C{=}NC_6H_4S$-*o*$\}]$ 5. Compound **5** was prepared and purified in the same way as **4** from **II** (0.59 g, 2.6 mmol) in THF (100 cm^3) and $[Fe_2(CO)_9]$ (0.95 g, 2.6 mmol). The dark blue reaction mixture yielded blue crystals of **5**

after purification. Yield 0.26 g. MS: m/z 365 (M^+, 5%), 337 (M − CO, 10), 309 (M − 2CO, 24), 281 (M − 3CO, 100), 225 (M − 3CO − Fe, 10), 179 (M − 3CO − Fe − CH_2S, 15), 178 (M − 3CO − Fe − CH_3S, 28), 108 (C_6H_4S, 5), 56 (Fe, 11) and 45 (HCS, 5). δ_H 8.79 [1H, m, NCC*H*(CH)$_3$CS], 7.98 [1H, m, NC(CH)$_3$C*H*CS], 7.60 [2H, m, NCCH(C*H*)$_2$CHCS] and 2.77 (3H, s, SCH_3). δ_C (−90 °C) 212.7 (s, 3CO), 163.6 (s, *C*S$_2$CH$_3$), 154.0 [s, N*C*(CH)$_4$S], 152.2 (s, NCS), 132.1 [s, NC(CH)$_4$*C*S], 128.7 [s, NCCHCH(CH)$_2$CS], 127.6 [s, NC-(CH)$_2$*C*HCHCS], 125.4 [s, NC*C*H(CH)$_3$CS], 121.3 [s, NC-(CH)$_3$*C*HCS] and 19.0 (s, SCH_3).

Crystal data

[Cr(CO)$_4${S=C(SCH$_3$)C=NC(CH$_3$)=CHS}] 1. $C_{10}H_7CrNO_4S_3$, $M = 353.35$, monoclinic, space group $P2_1/n$, $a = 8.948(2)$, $b = 16.647(3)$, $c = 9.4732(18)$ Å, $\beta = 97.854(19)°$, $U = 1397.9(5)$ Å^3, $T = 293(2)$ K, $Z = 4$, μ(Mo-Kα) = 1.27 mm^{-1}, 2535 reflections, 1941 unique [$R_{int} = 0.016$], $R1 = 0.050$ and $wR2 = 0.093$ (all data).

[Fe(CO)$_3${S=C(SCH$_3$)C=NC$_6$H$_4$S-*o*}] 5. $C_{12}H_7FeNO_3S_3$, $M = 365.23$, monoclinic, space group $P2_1$, $a = 9.312(2)$, $b = 7.317(3)$, $c = 10.741(4)$ Å, $\beta = 94.38(2)°$, $U = 729.6(4)$ Å^3, $T = 293(2)$ K, $Z = 4$, μ(Mo-Kα) = 1.448 mm^{-1}, 2752 reflections, 1845 unique [$R_{int} = 0.033$], $R1 = 0.034$ and $wR2 = 0.031$ [$I > 2\sigma(I)$].

CCDC reference number 186/2093.

See http://www.rsc.org/suppdata/dt/b0/b004251j/ for crystallographic files in .cif format.

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