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A new route to diiron bis(μ-thiocarbene) complexes: molecular structure of $[\{Fe[\mu\text{-}C(CN)SMe](cp)\}_2]$ (cp = $\eta\text{-}C_5H_5$) containing the unusually folded six-membered metallacycle $Fe_2C_2S_2$

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The bis(μ-thiocarbene) $[(cp)(OC)Fe\{\mu\text{-}C(CN)SMe\}\{\mu\text{-}C(SMe)X\}Fe(cp)]$ (X = H or CN; cp = $\eta\text{-}C_5H_5$) and all the intermediate species obtained from the thiocarbyne derivative *cis*-$[Fe_2(\mu\text{-}CS)\{\mu\text{-}C(SMe)\}(CO)_2(cp)_2][SO_3CF_3]$ *via* μ-C stereoselective addition of X^-, photochemical formation of $[(cp)Fe\{\mu\text{-}C(SMe)X\}(\mu\text{-}CS)Fe(CO)(cp)]$ followed by stepwise addition of $MeSO_3CF_3$ and $(NBu^n_4)CN$ at the bridging CS group have been prepared and characterized. Attempts to obtain the bis(μ-thiocarbene) $[\{Fe[\mu\text{-}C(CN)SMe](CO)(cp)\}_2]$ failed. The crystal structure of $[\{Fe[\mu\text{-}C(CN)SMe](cp)\}_2]$ which demonstrates the presence of two doubly bridging thiocarbene groups has been determined. The results show that bis(μ-thiocarbene) derivatives are stable when at least one of the ligands acts as a double bridge *via* a S–Fe bond.

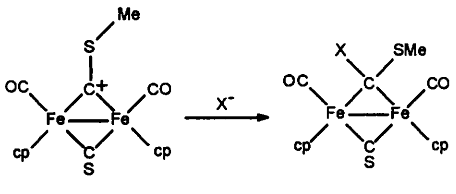
The recognition that the carbene fragment is an important surface species in several hetero- and homo-geneously catalysed reactions, like Fischer–Tropsch synthesis, metathesis and cyclopropanation of olefins, has prompted the study of a wide range of transition-metal dinuclear μ-carbene complexes. However, complexes with two bridging carbene ligands have been less studied[1] and among these only the following derivatives containing heteroatom-substituted carbene moieties have been prepared: $[Re_2\{\mu\text{-}C(OMe)Ph\}_2(CO)_8]$,[2] $[Mn_2(\mu\text{-}CF_2)_2(CO)_8]$[3] and $[Ru_2\{\mu\text{-}C(CN)N(Me)CH_2Ph\}_2(CO)_2(cp)_2]$[4] (cp = $\eta\text{-}C_5H_5$).

We have already reported that the stepwise N-alkylation ($MeSO_3CF_3$) and CN^- addition on both the isocyanide ligands in $[\{Ru(\mu\text{-}CNCH_2Ph)(CO)(cp)\}_2]$ leads to the formation of bis(μ-aminocarbene) derivatives, and that the same procedure does not afford the analogous iron complexes.[4] Since the stepwise transformation of μ-thiocarbonyl into a μ-thiocarbene ligand has also been shown to be a synthetically useful path[5,6] we have explored the possibility of applying this method to $[\{Fe(\mu\text{-}CS)(CO)(cp)\}_2]$ in order to obtain heteroatom-substituted bis(μ-carbene) complexes of iron.

In the present work we report the syntheses of $[(cp)Fe\{\mu\text{-}C(SMe)X\}\{\mu\text{-}C(CN)SMe\}Fe(CO)(cp)]$ (X = H or CN) and all the intermediate species obtained from the thiocarbyne derivative *cis*-$[Fe_2(\mu\text{-}CS)\{\mu\text{-}C(SMe)\}(CO)_2(cp)_2][SO_3CF_3]$[7,8] *via* μ-C stereoselective addition of X^-, photochemical formation of $[(cp)Fe\{\mu\text{-}C(SMe)X\}(\mu\text{-}CS)Fe(CO)(cp)]$ followed by the transformation of μ-CS into μ-C(SMe)X. We also describe the molecular structure of $[\{Fe[\mu\text{-}C(CN)SMe](cp)\}_2]$ for which spectroscopic evidence suggests the presence of two double-bridging thiocarbene groups.

Results and Discussion

Reactions of the known *cis*-$[Fe_2(\mu\text{-}CS)(\mu\text{-}CSMe)(CO)_2(cp)_2][SO_3CF_3]$ **1** with NBu^n_4X (X = H or CN) result in rapid hydride or cyanide attack at the carbon atom of the μ-CSMe thiocarbyne unit to generate the corresponding bridging carbene complexes *cis*-$[Fe_2(\mu\text{-}CS)\{\mu\text{-}C(SMe)X\}(CO)_2(cp)_2]$ (X = H **2** or CN **3**) in high yields (Scheme 1). The stereoselectivity of the addition reactions has been confirmed by the formation of the analogous *trans* isomers by treating *trans*-**1a**[8,9] with X^- (X = H **2a** or CN **3a**). In view of the observation that the geometry is retained in the S-alkylation and μ-C addition reactions, only the reactions involving *cis* isomers will be described.

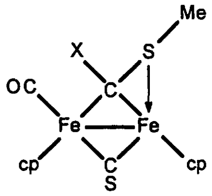


1

2 (*cis*), **2a** (*trans*) X = H
3 (*cis*), **3a** (*trans*) X = CN

Scheme 1

The IR spectra of complexes *cis*-**2** and **-3** show two ν(CO) (2008s, 1981m cm^{-1} for **3**), whereas only one band is observed for the corresponding *trans* isomers (1980s cm^{-1} for **3a**). Besides, a strong ν(μ-CS) absorption is observed in the 1150–1100 cm^{-1} range. The nature of the bridging ligands has been ascertained by the expected downfield signal of the μ-CS carbon atom (δ 370.6 for **3a**) and by the typical μ-C (carbene) resonance (δ 176.7 for **2**) in the ^{13}C NMR spectrum. The occurrence of a single cp signal in both ^1H (δ 4.85) and ^{13}C (δ 91.2 for **2**) NMR spectra indicates the formation of only one of the two possible *cis* isomers, very likely that with the small X substituent on the more hindered cp side (*cis-syn*).[5] Accordingly, both *trans* isomers (**2a** and **3a**) present two equally intense signals for both the cp and carbonyl ligands in the ^{13}C NMR spectra. The single resonance in the ^1H NMR spectrum attributed to the methine proton in the *cis* (δ 11.81) and *trans* (δ 11.02) isomers of **2** does not vary with time. This observation contrasts with that reported for the analogous $[Fe_2(\mu\text{-}CO)\{\mu\text{-}C(H)SMe\}(CO)_2(cp)_2]$[6] derivative, which exhibits a mixture of the three possible isomers in solution (two *cis* and one *trans*) at room temperature. We attribute the absence of isomerization to the higher rigidity of the molecular skeleton induced by the μ-CS ligand, as a consequence of the higher bond order of the Fe–(μ-CS) interactions.[9]

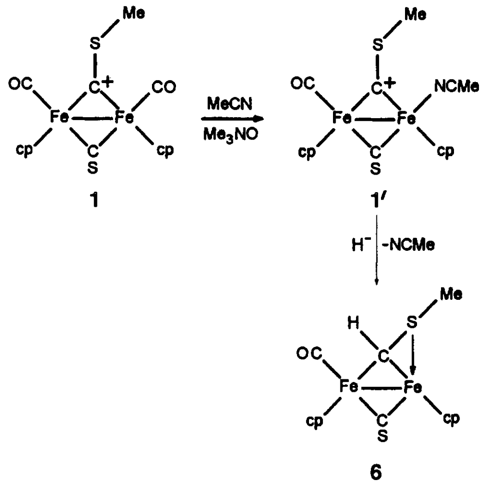


6 X = H
7 X = CN

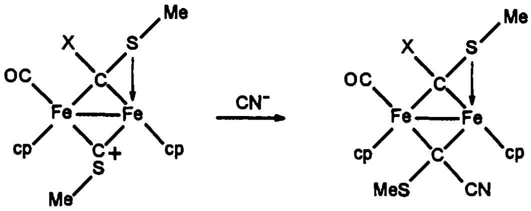
The reaction of an equimolar amount of $MeSO_3CF_3$ with complex **2** or **3** affords the corresponding crude thiocarbyne complexes $[Fe_2(\mu\text{-CSMe})\{\mu\text{-C(SMe)X}\}(CO)_2(cp)_2][SO_3CF_3]$ (X = H **4** or CN **5**). Although these derivatives have not been isolated as pure materials, the spectroscopic data strongly support S-methylation of the thiocarbonyl ligand. Their IR spectra are consistent with the formation of cationic complexes, the CO band pattern being considerably shifted to higher wavenumbers (2024s, 2001m cm^{-1} for **4**). Moreover, the absence of the $\nu(\mu\text{-CS})$ and the concomitant appearance of a strong absorption at 1031 cm^{-1} [$\nu(\mu\text{-C–SMe})$], together with the presence in the ^{1}H NMR spectrum of a resonance for the Me group at δ 3.26, suggests the formation of the bridging thiocarbyne ligand. Finally, the upfield signal for the methine proton at δ 13.03 (μ-CH) and the SMe resonance at δ 2.97 for **4** and δ 2.85 for **5** indicate that the μ-thiocarbene moiety is retained in the alkylation reactions.

Unexpectedly, neither **4** nor **5** reacts with $NBu^n{}_4X$ (X = H or CN) to give the desired bis(μ-carbene) complexes $[\{Fe[\mu\text{-C(SMe)X}](CO)(cp)\}_2]$. Our unsuccessful attempts to prepare these derivatives parallel our failure to obtain the bis(μ-aminocyanocarbene) diiron $[\{Fe[\mu\text{-C(CN)NMe}(CH_2Ph)](CO)(cp)\}_2]$.[4] Most likely the co-ordination of two bridging S- or N-substituted carbene ligands destabilizes the molecules, despite the presence of electron-withdrawing groups which are known to stabilize heteroatom-substituted μ-carbene derivatives.[10,11] Analogous conclusions can be drawn from the recently reported failure to convert the μ-CO into a carbene ligand in $[Fe_2(\mu\text{-CO})\{\mu\text{-C(OEt)Ph}\}(CO)_2(cp)_2]$.[12] Furthermore, molecules containing two bridging heteroatom-substituted carbene groups have been reported only for second- or third-row transition metals,[2,4] very probably because enough back-donation is provided by the heavier metals to keep two unsaturated moieties[13,14] anchored to the metal frame.

The μ-C(SR)X carbene grouping can also act as S-donor, becoming a bidentate ligand which increases the stability of the Fe_2C ring.[5,15] Therefore we have photochemically transformed **2** and **3** into the corresponding [(cp)(OC)Fe(μ-CS){μ-C(SMe)X}Fe(cp)] (X = H **6** or CN **7**) derivatives in which the thiocarbene ligand, while retaining the bridging geometry, coordinates through the S atom in the place of a CO group. The IR spectra show, as expected, a single carbonyl stretching (1962 cm^{-1} for **6**). The presence of the bridging carbene unit is supported by the resonance of the nitrile substituent at δ 125.3 for **7** in the ^{13}C NMR spectrum and by the signal at δ 11.5 for **6** in the ^{1}H NMR spectrum for μ-CH. For both species, NMR data reveal the formation of only one isomer in solution, probably the *cis-syn*, indicating that the photochemical reactions have not altered the stereogeometry of the parent compounds, in agreement with what is observed for the corresponding μ-CO complexes.[5] The conversion of a bridging carbene (as in **2**, **3**) into a bidentate ligand (as in **6**, **7**) produces a moderate upfield shift of the ^{13}C NMR signals attributed to cp (from δ 91 to *ca.* 83) and μ-C(carbene) (from δ 177 to *ca.* 172 for **6**) and a significant upfield shift of the ^{1}H NMR resonance of the methyl group (from δ 2.83 to 1.73).[5]



Scheme 2



8 X = H
9 X = CN

10 X = H
11a, **11b** X = CN

Scheme 3

Complex **6** has also been prepared by an alternative route consisting of the transformation of **1** into the acetonitrile complex **1′** followed by *in situ* treatment with an equimolar amount of $NaBH_4$ (Scheme 2). A determining factor of the second step in Scheme 2 could be the rotation of the SMe group imposed by the nucleophilic attack at the μ-C carbon. The iron atom is now closer to the sulfur atom, making possible ring closure, which is also driven by the entropically favoured elimination of one ligand. Nevertheless an alternative pathway involving Fe–H bond formation followed by hydride migration to μ-C cannot be ruled out.[16,17] The cation **1′**, which presents only one ν(CO) absorption, has been characterized by its ^{13}C NMR spectrum, which shows two non-equivalent cp signals and downfield resonances at δ 413.5 and 367.5 attributable to the bridging thiocarbyne and thiocarbonyl ligands, respectively.

Treatment of complexes **6** and **7** with $MeSO_3CF_3$ in dichloromethane solution gives the cationic derivatives $[(cp)(OC)Fe(\mu\text{-CSMe})\{\mu\text{-C(SMe)X}\}Fe(cp)][SO_3CF_3]$ [X = H **8** (85%) or CN **9** (71%)] containing bridging carbyne and carbene groups. The IR spectra show one ν(CO) band (2023 for **9** and 2008 cm^{-1} for **8**) shifted to higher wavenumbers with respect to the precursors. The ^{1}H NMR spectra exhibit two distinct signals for the non-equivalent cyclopentadienyl groups, while the different nature of the bridging ligands is unambiguously identified by the ^{13}C NMR signal of the bridging carbon atoms [δ 187.3, μ-*C*(H)SMe and δ 390.07, μ-*C*SMe for **8**].

The stabilizing effect of the sulfur co-ordination to one Fe is demonstrated by the formation of the first known examples of bis(μ-thiocarbene) complexes [(cp)(OC)Fe{μ-C(CN)SMe}{μ-C(SMe)X}Fe(cp)] (X = H **10** or CN **11**) (Scheme 3), obtained by CN$^-$ addition to the μ-carbyne carbon in **8** and **9**, respectively. Unless the signals are fortuitously coincident the NMR spectra of **10** indicate the presence of only one isomer in solution. Indeed the cyclopentadienyl ligands appear as a single broad signal in the ^{1}H NMR spectrum (δ 4.74) but as two distinct resonances in the ^{13}C spectrum. By contrast **11** shows, in addition to two pairs of cp signals (δ 91.4, 87.2, **11a**; δ 90.7, 87.4, **11b**), doubling of all the resonances with an intensity ratio 2:3. This observation is consistent with the presence of two isomers arising from CN$^-$ attack on either side of the C–SMe carbyne plane in **9** (Scheme 3). The signals have been assigned by comparison with the chemical shifts of the above described complexes. Therefore, the upfield resonances at δ 118.6 and 116.9 have been attributed to the μ-C of the doubly bridged ligand (see **7**), whereas those at δ 125.0 and 124.5 to the μ-C singly bridged ligand (see **4**). It should be noted that, while **11** is prepared as an unbalanced mixture of diastereoisomers, **11a** and **11b**, only one isomer of **10** is obtained, very likely the one bearing the CN$^-$ on the less-hindered side of the cp substituents, as in **11a**. Efforts to separate the two isomers of **11** have been unsuccessful.

The isomeric mixture of the bis(μ-carbene) [(cp)(OC)Fe{μ-C(CN)SMe}{μ-C(CN)SMe}Fe(cp)] **11** has been UV photolysed giving the complex [{Fe[μ-C(CN)SMe](cp)}$_2$] **12**, which has been isolated as air-stable yellow crystals in about 30% yield. The moderate yield can be explained by the observation that only one of the two possible isomers (**11a**) possesses the steric requirements to achieve cyclization. The spectroscopic properties indicate absence of carbonyl groups and presence of equivalent cp and SMe groups. Since this derivative represents a unique example of a bis(μ-carbene) complex containing two doubly bridging units, its nature has been unambiguously determined by a single-crystal X-ray diffraction study.

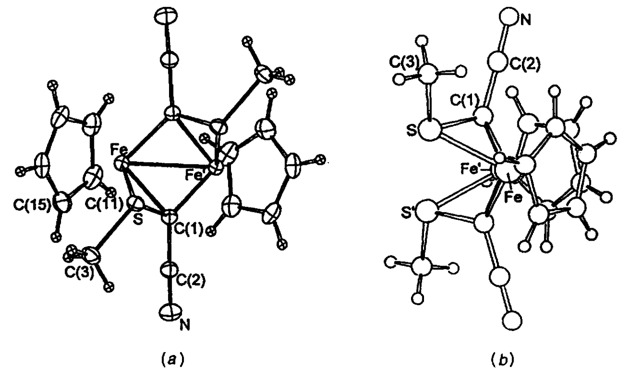


Fig. 1 Perspective drawings of the molecular structure of complex **12**: (*a*) down the two fold axis; (*b*) side-view illustrating the folding of the Fe$_2$(μ-C)$_2$ rhombus

Table 1 Selected bond lengths (Å) and angles (°) for [{Fe[μ-C(CN)SMe](cp)}$_2$]

Fe–C(1')	1.929(3)	C(3)–S	1.806(3)
Fe–C(1)	1.952(3)	C(1)–C(2)	1.422(4)
Fe–Fe'	2.510(1)	C(2)–N	1.147(4)
Fe–S	2.240(1)	Fe–C(cp)(average)	2.087
C(1)–S	1.791(3)		
C(1)–C(2)–N	178.3(3)	C(1)–S–Fe	56.6(1)
C(1)–S–C(3)	106.2(1)	Fe–C(1)–Fe'	80.6(1)
C(2)–C(1)–S	115.1(2)	Fe–C(1)–C(2)	129.8(2)
C(3)–S–Fe	110.8(1)	Fe'–C(1)–C(2)	123.4(2)

Molecular structure of complex 12

The solid-state structure of compound **12** is shown in Fig. 1 and selected bond lengths and angles are given in Table 1. The complex consists of two linked Fe(cp) units and two multiply bonded μ-C(CN)SMe ligands. The crystal contains a racemic mixture of chiral molecules which are positioned around crystallographic C_2 axes passing through the midpoint of the Fe–Fe bond. Each C(CN)SMe ligand binds the diiron unit through the bridging carbene carbon and the S atom. In this way two kinds of fused metallacycles Fe$_2$C and FeCS are formed, resulting in a folded six-membered Fe$_2$C$_2$S$_2$ unit. The cp ligands are in *cis* position with respect to the Fe–Fe vector and the bulky SMe groups point away from the cyclopentadienyl rings. The Fe$_2$(μ-C)$_2$ rhombus is highly folded around the bonded diagonal [Fe–Fe' distance 2.510(1) Å, dihedral angle 45.4(1)°]. This feature of the Fe$_2$(μ-C)$_2$ core is present in all the dinuclear complexes with the cp rings in *cis* configuration and has been rationalized on the basis of molecular orbital calculations.[18,19] It has been proposed that a highly folded rhombus will be adopted when one or both bridging ligands are alkylidenes.[20] In addition the folding of the Fe$_2$(μ-C)$_2$ core in **12** is enhanced by formation of the S–Fe bond, as can be inferred by the angles between the Fe$_2$(μ-C) planes in some related complexes (14° for [Fe$_2$(μ-CO){μ-C(CN)SMe}(CO)$_2$(cp)$_2$],[5] 29.4 and 29.3° (average) for [(cp)Fe{μ-C(CHO)SEt}(μ-CO)Fe(CO)(cp)][16] and [(cp)Fe{μ-C(CO$_2$Me)SMe}(μ-CO)Fe(CO)(cp)],[16] respectively). The least-folded conformation of the Fe$_2$(μ-C)$_2$ core is observed for [Fe$_2$(μ-CO){μ-C(CN)SMe}(CO)$_2$(cp)$_2$] where the sulfur is not bonded to the metal centre, whereas the maximum degree of folding is present in complex **12**, in which both sulfur atoms are co-ordinated to the two irons.

The Fe–S distance [2.240(1) Å] can be compared with the values reported for [(cp)Fe{μ-C(CHO)SEt}(μ-CO)Fe(CO)(cp)] and [(cp)Fe{μ-C(CO$_2$Me)SMe}(μ-CO)Fe(CO)(cp)] [2.273(1) and 2.268(1) (average) Å, respectively].[16] The angle between the metallacycles Fe, C(1), S and Fe, Fe', C(1) is of 55.2(1)°. The sulfur atoms exhibit pyramidal co-ordination, as can be appreciated in Fig. 1(*b*), and are in contact with each other [2.989(1) Å]. This value is well below the sum of the standard van der Waals radii (*ca.* 3.6 Å)[21] but the difference should not be overemphasized because some shrinkage of the atom surely results from its co-ordination to the iron. The short S···S contact is forced by the geometrical constraints introduced by the co-ordination of the sulfur to the iron atom which imposes a high degree of folding of the Fe$_2$(μ-C)$_2$ rhombus (see above). The most significant difference between the present bis(carbene) complex **12** and the aforementioned monothiocarbene species [(cp)Fe{μ-C(CHO)SEt}(μ-CO)Fe(CO)(cp)] and [(cp)Fe{μ-C(CO$_2$Me)SMe}(μ-CO)Fe(CO)(cp)] resides in the bond-length distribution in the Fe$_2$(μ-C)$_2$ core. The two Fe–μ-C distances are 1.952(3) and 1.929(3) Å, Fe–C(1) being longer than Fe–C(1'). On the other hand, in [(cp)Fe{μ-C(CHO)SEt}(μ-CO)Fe(CO)(cp)] and [(cp)Fe{μ-C(CO$_2$Me)SMe}(μ-CO)Fe(CO)(cp)] the Fe–μ-C (carbene) distances spanned by the SR groups are shorter [1.910(1) and 1.899 (average) Å, respectively] while the unbridged ones are longer [1.965(1) and 1.964(5) (average) Å]. The differences are small but significant and, while in the monoalkylidene species they reflect the non-equivalence of the iron atoms, in the present case they originate only in the bridging sulfur atom. We can suppose that the bridging sulfur would like to stretch the Fe–C(1) bond as much as possible, in order to widen the very acute Fe–S–C(1) angle [56.6(1)°]. The Fe–Fe interaction [2.510(1) Å] is slightly shorter than those in the parent complex *cis*-[{Fe(μ-CO)(CO)(cp)}$_2$] [2.531(2) Å][22] and in the monoalkylidene [Fe$_2$(μ-CO){μ-C(CN)SMe}(CO)$_2$(cp)$_2$] [2.540(1) Å].[5] It is comparable to the bond distances reported for [(cp)Fe{μ-C(CHO)SEt}(μ-CO)Fe(CO)(cp)] and [(cp)Fe{μ-C(CO$_2$Me)SMe}(μ-CO)Fe(CO)(cp)] [2.524(1) and 2.520(1) (average) Å]. The carbene unit μ-C(CN)SMe has the less-hindering CN group oriented *syn* to the cp ligands and, because of the co-ordination of the sulfur to the iron atom, it is not orthogonal to the Fe$_2$(μ-C) plane [dihedral angle between Fe, Fe', C(1) and C(2), C(1) S 58.0(1)°]. The C(2)–C(1)–S angle

[115.1(2)°] is wider than the corresponding angle in [Fe_2(μ-CO){μ-C(CN)SMe}$(CO)_2(cp)_2$],[5] as a consequence of the co-ordination of the sulfur at the Fe atom, but is still lower than expected for a sp^2 carbon. The two carbon–sulfur interactions are very similar [C(1)–S 1.791(3) and S–C(3) 1.806(3) Å]. The μ-C(1)–C(2) and C–N distances [1.422(4) and 1.147(4) Å] are strictly comparable with the equivalent interactions in [Fe_2(μ-CO){μ-C(CN)SMe}$(CO)_2(cp)_2$][5] [1.440(5) and 1.152(3) Å].

Experimental

All the reactions were carried out routinely under dinitrogen by standard Schlenk techniques. Solvents were distilled prior to use under dinitrogen from appropriate drying agents. Dichloromethane was distilled over CaH_2 and passed through a column of activated alumina to remove traces of ethanol. All the reagents were commercial products (Aldrich) of the highest purity available and used as received. The complexes *cis*-**1** and *trans*-[Fe_2(μ-CS)(μ-CSMe)$(CO)_2(cp)_2$][SO_3CF_3] **1a** were prepared as previously described.[7,9] Infrared spectra were recorded on a Perkin-Elmer 983G spectrophotometer, ^1H and ^{13}C NMR spectra on a Varian Gemini 200 spectrophotometer. The shiftless relaxation reagent [$Cr(acac)_3$] (acac = acetylacetonate) was added to solutions studied by ^{13}C NMR spectroscopy.

Syntheses

***cis*-[Fe_2(μ-CS){μ-C(H)SMe}$(CO)_2(cp)_2$] 2.** A mixture of complex *cis*-**1** (0.285 g, 0.52 mmol) and an equimolar amount of $NBu^n{}_4BH_4$ in CH_2Cl_2 (20 cm^3) was stirred at room temperature for 5 min, while the solution turned from green to deep violet. The solvent was evaporated under reduced pressure and the residue chromatographed on alumina. Elution with light petroleum (b.p. 40–60 °C)–CH_2Cl_2 (2:1 v/v) developed a violet band which provided, after crystallization from CH_2Cl_2–hexane at −20 °C, the deep violet complex **2** (0.149 g, 70%), m.p. 170–172 °C (Found: C, 44.9; H, 3.6. $C_{15}H_{14}Fe_2O_2S_2$ requires C, 44.8; H, 3.5%); $\tilde{\nu}_{max}/cm^{-1}$ (CH_2Cl_2) 1990s, 1960m (CO); (KBr) 1113s (CS); 1061m (CSMe); $\delta_H(CDCl_3)$ 11.81 [1 H, s, μ-C(SMe)*H*], 4.85 (10 H, s, C_5H_5) and 2.83 (3 H, s, SMe); $\delta_C(CD_2Cl_2)$ 382.2 (μ-CS), 212.3 (CO), 176.7 [μ-*C*(SMe)H], 91.2 (C_5H_5) and 27.9 (SMe).

***trans*-[Fe_2(μ-CS){μ-C(H)SMe}$(CO)_2(cp)_2$] 2a.** This complex was prepared as described above from *trans*-**1a** (0.285 g, 0.52 mmol). Crystallization from CH_2Cl_2–hexane at −20 °C yielded deep blue crystals of **2a** (0.134 g, 64%); $\tilde{\nu}_{max}/cm^{-1}$ (CH_2Cl_2) 1956s (CO); $\delta_H(CDCl_3)$ 11.02 [1 H, s, μ-C(SMe)*H*], 4.89 (5 H, s, C_5H_5), 4.84 (5 H, s, C_5H_5) and 2.94 (3 H, s, SMe); $\delta_C(CD_2Cl_2)$ 383.0 (μ-CS), 214.3, 212.6 (CO), 96.9 (br, C_5H_5), 177.8 (μ-C) and 29.2 (SMe).

***cis*-[Fe_2(μ-CS){μ-C(CN)SMe}$(CO)_2(cp)_2$] 3.** To a CH_2Cl_2 (15 cm^3) solution of complex **1** (0.440 g, 0.80 mmol) was added an excess of $NBu^n{}_4CN$ (0.200 g, 1.49 mmol) dissolved in the same solvent (10 cm^3); the bright green solution immediately turned deep green. The solvent was removed *in vacuo* and the residue chromatographed on an alumina column (8 × 3 cm). Elution with CH_2Cl_2–light petroleum (2:1 v/v) produced a green fraction which was evaporated to dryness. The residue was washed with light petroleum and crystallized from CH_2Cl_2–hexane, to give green crystals of complex **3** (0.260 g, 76%), m.p. 165–168 °C (Found: C, 44.5; H, 3.4; N, 3.2; S, 14.5. $C_{16}H_{13}Fe_2NO_2S_2$ requires C, 45.0; H, 3.1; N, 3.3; S, 15.0%); $\tilde{\nu}_{max}/cm^{-1}$ (CH_2Cl_2) 2008s, 1981m (CO); 2158w (CN); (KBr) 1146s (CS); $\delta_H(CDCl_3)$ 4.85 (10 H, s, C_5H_5) and 2.66 (3 H, s, SMe); $\delta_C(CD_2Cl_2)$ 370.0 (μ-CS), 209.9 (CO), 132.0 (CN), 129.0 [μ-*C*(SMe)CN], 94.6 (C_5H_5) and 25.6 (SMe).

***trans*-[Fe_2(μ-CS){μ-C(CN)SMe}$(CO)_2(cp)_2$] 3a.** A CH_2Cl_2 (25 cm^3) solution of complex **1a** (0.440 g, 0.80 mmol) and $NBu^n{}_4CN$ (0.200 g, 1.49 mmol) was worked up as described for the synthesis of **3** to give deep green **3a** (150 mg, 74%); $\tilde{\nu}_{max}/cm^{-1}$ (CH_2Cl_2) 1980s (CO) and 2158w (CN); (KBr) 1138s (CS); $\delta_H(CDCl_3)$ 4.94 (5 H, s, C_5H_5), 4.85 (5 H, s, C_5H_5), and 2.76 (3 H, s, SMe); $\delta_C(CD_2Cl_2)$ 370.6 (μ-CS), 210.4, 209.3 (CO), 130.8 (CN), 129.9 [μ-*C*(SMe)CN], 96.3, 96.1 (C_5H_5) and 25.3 (SMe).

[Fe_2(μ-CSMe){μ-C(SMe)X}$(CO)_2(cp)_2$][SO_3CF_3] (X = H 4 or CN 5). To a cooled (−20 °C) CH_2Cl_2 (20 cm^3) solution of complex **2** (0.240 g, 0.60 mmol) or **3** (0.100 g, 0.23 mmol) was slowly added, with stirring, an equimolar amount of $MeSO_3CF_3$. After 1 h, addition of Et_2O (20 cm^3) followed by filtration afforded a dark green powder. Further purification of these derivatives was precluded by extensive decomposition. [Fe(μ-CSMe){μ-C(H)SMe}$(CO)_2(cp)_2$][SO_3CF_3] **4**: yield 0.150 g, (45%); $\tilde{\nu}_{max}/cm^{-1}$ (CH_2Cl_2) 2024s, 2001m (CO); (KBr) 1031m (CSMe); $\delta_H(CD_3NO_2)$ 13.03 [1 H, s, μ-C(SMe)*H*], 5.24 (10 H, s, C_5H_5), 3.26 (3 H, s, SMe) and 2.97 (3 H, s, SMe). [Fe(μ-CSMe){μ-C(CN)SMe}$(CO)_2(cp)_2$][SO_3CF_3] **5**: yield 0.75 g, (56%); $\tilde{\nu}_{max}/cm^{-1}$ (CH_2Cl_2) 2015s, 2010 (sh) (CO); 2180m (CN); (KBr), 1031s (CSMe); $\delta_H(CD_3NO_2)$ 5.29 (10 H, s, C_5H_5), 3.20 (3 H, s, SMe) and 2.85 (3 H, s, SMe).

[(cp)(OC)Fe(μ-CS){μ-C(H)SMe}Fe(cp)] 6. An acetonitrile solution (100 cm^3) of complex **2** (0.560 g, 1.39 mmol) was irradiated under nitrogen with a low-pressure ultraviolet lamp for 2 h. The resulting brown solution was dried under vacuum and the residue chromatographed on an alumina column eluting with light petroleum–CH_2Cl_2 (2:1 v/v). The first fraction containing traces of the precursor **2** was followed by a brown fraction which was dried under vacuum. Crystallization from CH_2Cl_2–hexane afforded the brown complex **6** (0.240 g, 46%), m.p. 143–145 °C (Found: C, 45.2; H, 3.6. $C_{11}H_{14}Fe_2OS_2$ requires C, 44.95; H, 3.8%); $\tilde{\nu}_{max}/cm^{-1}$ (CH_2Cl_2) 1962s (CO); (KBr) 1108s (CS) and 1047w (CSMe); $\delta_H(CD_3NO_2)$ 11.52 [1 H, s, μ-C(SMe)*H*], 4.75 (10 H, s, br, C_5H_5), and 1.73 (3 H, s, SMe); $\delta_C(CD_3NO_2)$ 383.3 (μ-CS), 212.0 (CO), 172.3 [μ-*C*(SMe)H] 82.0, 84.2 (C_5H_5), and 25.1 (SMe).

Alternatively, an acetonitrile (20 cm^3) solution of complex **1** (0.255 g, 0.46 mmol) was treated with an equimolar amount of Me_3NO. Immediately the solution turned from bright green to yellow-green. The reaction was continued until the disappearance of the two ν(CO) bands of **1** and the formation of a band at 2013 cm^{-1} due to [Fe_2(μ-CS){μ-CSMe}(CO)(NCMe)$(cp)_2$][SO_3CF_3] **1′**. After 30 min the solution was concentrated under reduced pressure (10 cm^3), filtered on a Celite pad and treated with $NaBH_4$ (0.019 g, 0.50 mmol) for 15 min. The resulting brown solution was evaporated to dryness and the residue worked up as above to give after crystallization **6** (0.060 g, 35%).

[(cp)(OC)Fe(μ-CS){μ-C(CN)SMe}Fe(cp)] 7. The complex was prepared from **3** (0.260 g, 0.61 mmol) following the procedure described for **6**. Crystallization from CH_2Cl_2–hexane afforded the red-brown complex **7** (0.141 g, 54%) (Found: C, 44.8; H, 3.4; N, 3.3; S, 15.6. $C_{15}H_{13}Fe_2NOS_2$ requires C, 45.1; H, 3.3; N, 3.5; S, 16.1%), m.p. 160–165 °C; $\tilde{\nu}_{max}/cm^{-1}$ (CH_2Cl_2) 1979s (CO) and 2157m (CN); (KBr) 1123s (CS) and 1055w (CSMe); $\delta_H(CD_3NO_2)$ 4.78 (5 H, s, C_5H_5), 4.72 (5 H, s, C_5H_5) and 1.83 (3 H, s, SMe); $\delta_C(CD_3NO_2)$ 374.7 (μ-CS), 210.5 (CO), 125.3 (CN), 121.7 [μ-*C*(SMe)CN], 85.3, 84.5 (C_5H_5) and 22.7 (SMe).

[(cp)(OC)Fe(μ-CSMe){μ-C(H)SMe}Fe(cp)][SO_3CF_3] 8. To a CH_2Cl_2 (20 cm^3) solution of complex **6** (0.150 g, 0.40 mmol) was added an equimolar amount of $Me_3SO_3CF_3$. The reaction mixture was stirred for 15 min and the solvent evaporated to dryness. The residue, washed several times with Et_2O, was crystallized from CH_2Cl_2–hexane to give yellow-brown **8** (0.184 g, 85%) (Found: C, 35.9; H, 3.3. $C_{16}H_{17}F_3Fe_2O_4S_3$ requires C, 35.7; H, 3.2%); $\tilde{\nu}_{max}/cm^{-1}$ (CH_2Cl_2) 2008s (CO); $\delta_H(CD_3NO_2)$ 12.35 [1 H, s, μ-C(SMe)*H*], 5.29 (5 H, s, C_5H_5), 5.18 (5 H, s, C_5H_5), 3.46 (3 H, s, μ-CSMe) and 2.11 [3 H, s, μ-C(S*Me*)H]; $\delta_C(CD_3NO_2)$ 390.7 (μ-CSMe), 206.15 (CO), 187.3 [μ-*C*(SMe)H], 84.8, 83.1 (C_5H_5), 29.3 and 23.8 (Me).

[(cp)(OC)Fe(μ-CSMe){μ-C(CN)SMe}Fe(cp)][SO_3CF_3] 9. To a CH_2Cl_2 (20 cm^3) solution of complex **7** (0.141 g, 0.35 mmol) was added an equimolar amount of $Me_3SO_3CF_3$. The reaction mixture was stirred for 30 min and the solvent evaporated to dryness. The residue, washed several times with Et_2O, was crystallized from CH_2Cl_2–hexane to give orange-yellow complex **9** (0.140 g, 71%) (Found: C, 36.0; H, 2.7. $C_{17}H_{16}F_3Fe_2NO_4S_3$ requires C, 36.3; H, 2.9%); $\tilde{\nu}_{max}/cm^{-1}$ (CH_2Cl_2) 2023s (CO) and 2171m (CN); $\delta_H(CD_3CN)$ 5.40 (5 H, s, C_5H_5), 5.35 (5 H, s, C_5H_5), 3.45 (3 H, s, μ-CSMe) and 2.21 [3 H, s, C(SMe)CN]; $\delta_C(CD_3NO_2)$ 393.6 (μ-CS), 200.4 (CO), 147.5 (CN), 89.6, 88.1 (C_5H_5), 33.0 and 26.7 (SMe).

[(cp)(OC)Fe{μ-C(CN)SMe}{μ-C(H)SMe}Fe(cp)] 10. A CH_2Cl_2 (20 cm^3) solution of complex **8** (0.136 g, 0.25 mmol) and $NBu^n{}_4CN$ (0.197 g, 0.73 mmol) were stirred at room temperature for 5 min. The solvent was evaporated under reduced pressure and the residue chromatographed on an alumina column (5 × 2 cm). Elution with CH_2Cl_2–light petroleum (1 : 1 v/v) developed a green-brown band which was collected and evaporated to dryness. Crystallization from dichloromethane–hexane yielded green-brown complex **10** (0.64g, 62%) (Found: C, 46.8; H, 4.5. $C_{16}H_{17}Fe_2NOS_2$ requires C, 46.3; H, 4.1%); ν_{max}/cm^{-1} (CH_2Cl_2) 1976s (CO) and 2152m (CN); $\delta_H(CD_3CN)$ 11.78 [1 H, s, μ-C(SMe)*H*], 4.74 (10 H, s, br, C_5H_5), 2.73 (3 H, s, SMe) and 1.66 (3 H, s, FeSMe); $\delta_C(CD_3NO_2)$ 214.9 (CO), 174.5 [μ-*C*SMe(H)], 129.2 [μ-*C*(CN)SMe], 84.2 (br, C_5H_5), and 23.9, 18.09 (Me).

[(cp)(OC)Fe{μ-C(CN)SMe}{μ-C(CN)SMe}Fe(cp)] 11. The complex was prepared as described above from **9** (0.254 g, 0.47 mmol) and $NBu^n{}_4CN$. Crystallization from dichloromethane–hexane produced, as described in the text, a mixture of geometrical isomers: **11a** and **11b** (0.130 g, 63%) (Found: C, 46.0; H, 3.6; N, 6.3; S, 14.5. $C_{17}H_{16}Fe_2N_2OS_2$ requires C, 46.4; H, 3.7; N, 6.4; S, 14.6%); $\tilde{\nu}_{max}/cm^{-1}$ (CH_2Cl_2) 1985s (CO) and 2152m (CN); $\delta_H(CD_3CN)$ 4.89 (10 H, s, br, C_5H_5), 2.75 [3 H, s, br, μ-C(SMe)CN] and 1.66 {3 H, s, Fe[μ-C(SMe)CN]}; $\delta_C(CD_3NO_2)$ **11a**, 217.8 (CO), 129.9 (br, CN), 125.0 {FeFe[μ-*C*(CN)SMe]}, 118.6 {FeFe[μ-*C*(CN)SMe]}, 91.4, 87.2 (C_5H_5), 26.8 and 24.3 (Me); **11b**, 215.8 (CO), 131.2 (br, CN), 124.5 {Fe[μ-*C*(CN)SMe]}, 116.9 {Fe[μ-*C*(CN)SMe]} 90.7, 87.4 (C_5H_5), 25.7 and 23.9 (Me).

[{Fe[μ-C(CN)SMe](cp)}$_2$] 12. An acetonitrile (20 cm^3) solution of complex **11** (0.130 g, 0.30 mmol) was irradiated with a 500 W low-pressure ultraviolet lamp for 30 min. The resulting yellow solution was evaporated under reduced pressure and the residue chromatographed on an alumina column (5 × 2 cm) eluting with CH_2Cl_2–light petroleum (3 : 1 v/v). The deep yellow fraction was collected, evaporated to dryness and crystallized from CH_2Cl_2–hexane at −20 °C to give yellow crystals of complex **12** (0.037 g, 30%), m.p. 190–192 °C (Found: C, 46.7; H, 4.0. $C_{16}H_{16}Fe_2N_2S_2$ requires C, 46.6; H, 3.9%); $\tilde{\nu}_{max}/cm^{-1}$ (CH_2Cl_2) 2148m (CN); $\delta_H(CDCl_3)$ 4.64 (10 H, s, C_5H_5) and 1.90 (3 H, s, SMe).

Crystallography

Crystal data and details of the data collection for complex **12** are given in Table 2. The diffraction experiments were carried out on a fully automated Enraf-Nonius CAD4 diffractometer at room temperature by using graphite-monochromated Mo-Kα radiation (λ 0.710 67 Å). The unit-cell parameters were determined from 25 randomly selected reflections by using automatic search, indexing and least-squares routines. Intensity measurements were corrected for Lorentz-polarization effects and an empirical absorption correction was applied by using the azimuthal scan method.[23] The structure was solved in the space group *C*2/*c* by direct methods using SHELXS 86[24] which revealed the positions of the metal atoms. All remaining non-hydrogen atoms were located from subsequent refinement and Fourier-difference syntheses. The methyl hydrogen atoms were located in the Fourier map but calculated positions were used. The structure model was refined on F^2 by full-matrix least-squares calculations, thermal motion being treated anisotropically for all non-hydrogen atoms. The methyl hydrogen atoms were assigned an isotropic thermal parameter 1.5 times that of the attached carbon atom. The final difference map showed peaks not exceeding 0.47 e Å^{-3} in the vicinity of the Fe atoms. All calculations were carried out using the program SHELXL 93.[25]

Table 2 Crystal data and experimental details for [{Fe[μ-C(CN)SMe](cp)}$_2$]

Formula	$C_{16}H_{16}Fe_2N_2S_2$
M	412.13
Crystal size/mm	0.10 × 0.075 × 0.275
Crystal symmetry	Monoclinic
Space group	*C*2/*c* (no. 15)
a/Å	9.648(3)
b/Å	15.197(4)
c/Å	11.715(2)
β/°	108.67(2)
U/Å^3	1627.2(8)
Z	4
D_c/Mg m^{-3}	1.682
F(000)	840
μ(Mo-Kα)/mm^{-1}	2.035
Scan mode	ω
θ limits/°	2–27
ω Scan width/°	0.7 + 0.35 tan θ
Prescan rate/° min^{-1}	4
Prescan acceptance, σ(*I*)/*I*	0.5
Required σ(*I*)/*I*	0.02
Maximum scan time/s	70
Standard reflections	3, measured periodically no decay
Reflections collected	1977 (±*h*, +*k*, +*l*)
Unique observed reflections [$F_o > 4\sigma(F_o)$]	1779
No. refined parameters	92
*R*1(*F*), *wR*2(F^2)*	0.0309, 0.0777
Goodness of fit on F^2	1.148

* $w^{-1} = \sigma^2(F_o{}^2) + (0.0434P)^2 + 1.2435P$, where $P = \frac{1}{3}(2F_c{}^2 + F_o{}^2)$.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/173.

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