Reactions of the Metallacycle $[(OC)(cp)\overline{FeC(SMe)SC(FeL_n)S}]^+$ with Nucleophiles. *X*-Ray Crystal Structures of the Complexes $[(OC)(cp)\overline{FeC(NC_5H_{10})SC(FeL_n)S}]SO_3CF_3$ and $[(OC)(cp)\overline{FeC\{(CN)(SMe)\}SC(FeL_n)S}]$ [FeL_n = Fe(cp)(CO)$_2$, cp = η-C_5H_5]†

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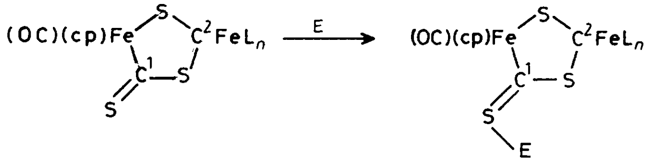
Reactions of the metallacyclic cation $[(OC)(cp)\overline{FeC(SMe)SC(FeL_n)S}]^+$ [FeL_n = Fe(cp)(CO)$_2$, cp = η-C_5H_5] with nucleophilic agents have been investigated. The results indicate that the carbene carbon atom bonded to the endocyclic iron is the site of addition of all the nucleophiles examined. Primary amines NH_2R (R = Me, C_6H_{11}, or Bu^n) form neutral isocyanide derivatives [(OC)(RNC)-(cp)FeSC(S)FeL_n] with opening of the FeC_2S_2 ring, whereas secondary amines such as NHR_2 (R = Me or Et) or $H\overline{N(CH_2)_nC}H_2$ (*n* = 3 or 4) produce stable cationic cyclic aminothiocarbenes. The structure of one of these, $[(OC)(cp)\overline{FeC(NC_5H_{10})SC(FeL_n)S}]SO_3CF_3$, has been determined by *X*-ray diffraction [triclinic, *a* = 11.570(2), *b* = 12.242(2), *c* = 10.552(2) Å, α = 104.60(2), β = 87.51(1), γ = 117.24(2)°, *Z* = 2, and space group $P\bar{1}$]. The cation contains the five-membered planar ring $\overline{FeSCSC}$ with the Fe(cp)(CO)$_2$ and NC_5H_{10} groups bonded to the carbon atoms. The C(carbene)–N interaction exhibits strong double-bond character [1.32(1) Å], typical for an iminium cation. Methanethiol, Li(BHEt$_3$), and KCN yield neutral $[(OC)(cp)\overline{FeCX(SMe)SC(FeL_n)S}]$ (X = SMe, H, or CN). In the hydride addition an isomeric mixture has been ascertained by i.r. and n.m.r. spectra, whereas the cyanide ion adds stereoselectively at the prochiral carbene centre to form only one diastereoisomer whose steric nature has been determined by *X*-ray diffraction [triclinic, *a* = 6.894(2), *b* = 10.057(1), *c* = 14.520(2) Å, α = 96.00(2), β = 96.17(1), γ = 106.31(1)°, *Z* = 2, and space group $P\bar{1}$]. In this derivative the $\overline{FeSCSC}$ ring undergoes substantial changes because the iron-bonded carbon atom becomes four-co-ordinate with loss of its carbenic character and significant out-of-plane displacement. A comparative analysis of the relevant geometric features of all the members of this family is reported. Propane-1,3-dithiol produces the neutral spirocyclic $[(OC)(cp)\overline{Fe\underline{C\{S(CH_2)_3S\}}SC(FeL_n)S}]$ which shows equivalence of the two diastereotopic SCH_2 carbons in the high-temperature ^{13}C n.m.r. spectrum and splitting of v(CO) in the i.r. spectrum. These spectroscopic features are discussed and interpreted.

We have recently described the synthesis of stable metallacyclic complexes (**1**) which have been obtained by metal-promoted CS_2–CS coupling.[1,2] The reaction with electrophiles (E) yielded the products (**2**) (Scheme 1) which were neutral or cationic depending on the nature of E.[2] The geometric evidence afforded by the *X*-ray crystallographic characterization of two of these complexes $[(OC)(cp)\overline{FeC(SEt)SC(FeL_n)S}]SO_3CF_3$ (**2b**) and $[(OC)(cp)\overline{FeC\{SW(CO)_5\}SC(FeL_n)S}]$ (**2c**), as well as spectroscopic studies, have shown that both ring carbon atoms C^1 and C^2 exhibit carbene character, C^1 more markedly.[2]

We report here the reactivity of $[(OC)(cp)\overline{FeC(SMe)SC(FeL_n)S}]SO_3CF_3$ (**2a**) towards nucleophilic agents. The results of these reactions show, in line with our predictions, that the carbon atom bonded to the endocyclic iron is the site of addition for all the nucleophiles employed.



(**1**) (**2**)

Scheme 1. E = M(CO)$_5$ (M = Cr, Mo, or W), Me$^+$, Et$^+$, HgX$_2$, Ag$^+$, H$^+$, or BF$_3$. FeL_n = Fe(cp)(CO)$_2$ where cp = η-C_5H_5

Our structural studies have paralleled the chemical characterizations and the structures of the products obtained from the reactions of (**2a**) with HNC_5H_{10} and CN^-: $[(OC)(cp)\overline{FeC(NC_5H_{10})SC(FeL_n)S}]SO_3CF_3$ and $[(OC)(cp)\overline{FeC\{(CN)(SMe)\}SC(FeL_n)S}]$ are described in detail. Correlations between chemical and stereochemical properties have helped to rationalize the chemistry of these new thioanhydride-like complexes.

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† 1,1,2-Tricarbonyl-1,2-di(η-cyclopentadienyl)-μ-[1′-(1″-piperidylidene-3′-thioxo-2′-thiapropane-1′,3′-diyl-$C^1(Fe^2)C^3(Fe^2)$ =$S(Fe^2)$]-di-iron trifluoromethanesulphonate and 1,1,2-tricarbonyl-μ-[1′-cyano-1′-methylthio-3′-thioxo-2′-thiapropane-1′,3′-diyl-$C^1(Fe^2)$-$C^3(Fe^1)$=$S(Fe^2)$]-di-iron.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

Results and Discussion

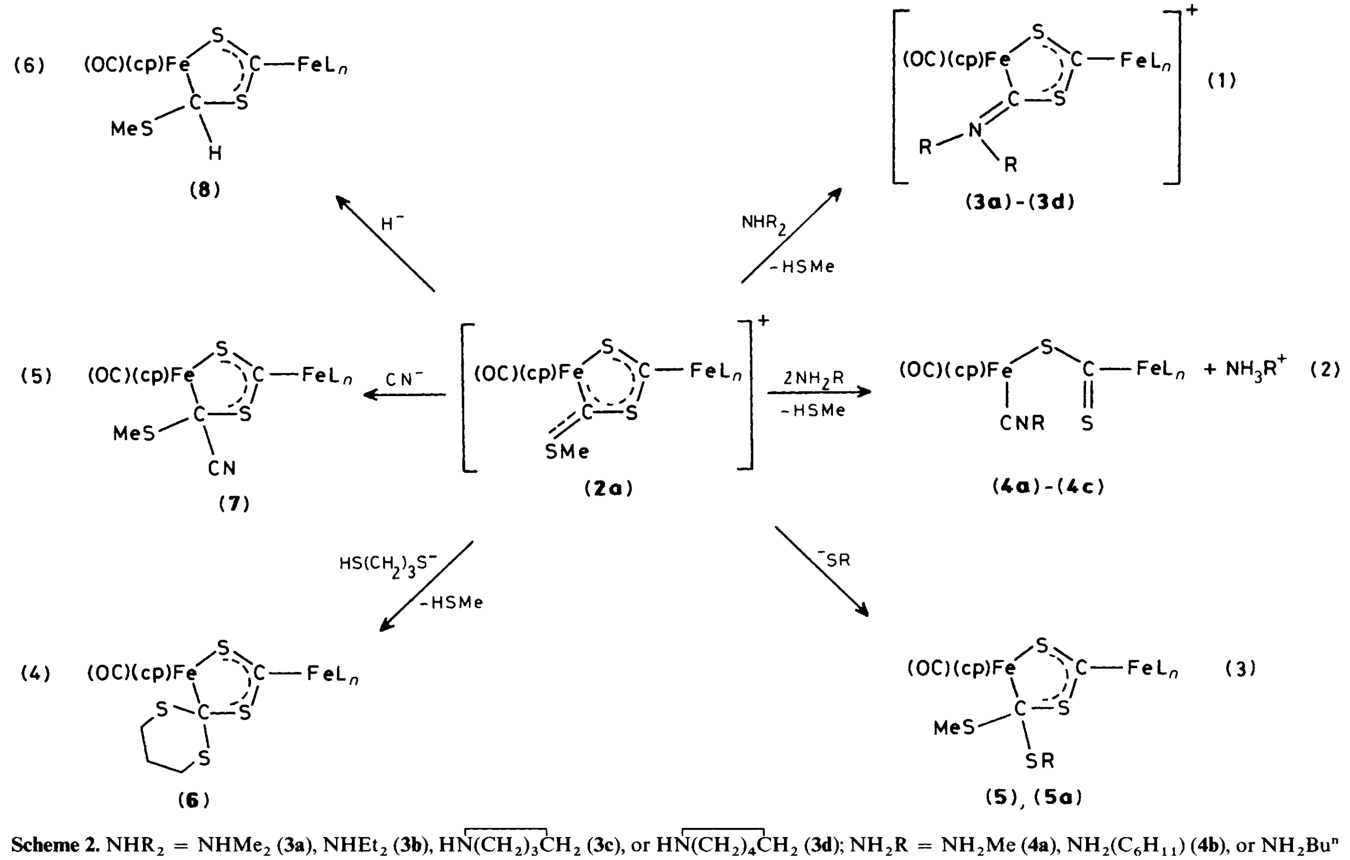
Reactions with Amines.—The reactions of complex (**2a**) with amines are similar to those already reported for $[\mathrm{FeL}_n\{\mathrm{C(SMe)}_2\}]^{+}$[3] and related acyclic dithiocarbene complexes.[4] Secondary amines readily replace the thiomethoxy group to produce cyclic aminothiocarbene derivatives (**3a**)—(**3d**) as shown in equation (1) of Scheme 2 in which all the reactions studied are collected. The reaction with primary amines [equation (2)], on the other hand, does not stop at the cationic aminothiocarbene adduct but rapidly proceeds to the formation of oily neutral acyclic isocyanide derivatives (**4a**)—(**4c**) with complete cleavage of the C–S bonds at the carbene-carbon addition centre. Both reactions occur at room temperature in $\mathrm{CH_2Cl_2}$ solvent and the reaction time is longer in the case of the bulkier $\mathrm{NHEt_2}$ or $\mathrm{NH_2Bu^n}$. In addition to the isolation of (**3a**)—(**3d**) (48—57%) and (**4a**)—(**4c**) (40—50% yield), green $[\mathrm{(OC)(cp)FeC(SMe)_2SC(FeL_{\mathit{n}})S}]$ (**5**) is obtained in variable yields, probably from a side reaction between the HSMe product [equations (1) and (2)] and (**2a**). The cationic metallacyclic derivatives (**3**) are stable in solution at room temperature, whereas (**4**) slowly decompose in chlorinated solvents to form the known $[\mathrm{(OC)(cp)FeSC(FeL_{\mathit{n}})S}]$[5] with elimination of the CNR ligand. Because of this side reaction, the formation of type (**4**) complexes may be accompanied by the chelate derivative to an extent depending on the reaction time. In these cases purification of (**4**) is achieved by column chromatography.

The spectroscopic properties of complexes (**3**) and (**4**) are reported in Table 1. A comparison between ν(CO) for (**3a**)—(**3d**) and (**2a**) shows a lowering of about 35 $\mathrm{cm^{-1}}$ of the lowest band, assigned to the carbonyl group bonded to the endocyclic iron, and almost no effect on the remaining two bands of the exocyclic FeL_n moiety. These differences indicate that the substitution of $\mathrm{NR_2}$ for SMe in (**2a**) causes a detectable increase in electron density at the endocyclic iron atom. The poorer π-acceptor ability of the aminothiocarbene $\mathrm{C(NR_2)SC}$ with respect to the dithiocarbene fragment C(SR)SC is attributable to the greater ability of nitrogen to donate π-electron density to the empty *p* orbital of the sp^2 carbene atom[6] bonded to the endocyclic iron atom (see also next section).

The i.r. spectra of complexes (**4a**)—(**4c**) show, in addition to the expected ν_{sym} and $\nu_{\mathrm{asym}}(\mathrm{CS_2})$ of the bridging $\mathrm{CS_2}$ at 1 000 and 730 $\mathrm{cm^{-1}}$,[7] three absorptions at 2 130—2 140 [ν(CN)], 2 014—2 010 and 1 965—1 970 $\mathrm{cm^{-1}}$ [ν(CO)].

In the ^{1}H n.m.r. spectra of complexes (**3a**)—(**3d**) (Table 1) singlets are found at 5.17—5.28 and 4.79—4.90 p.p.m. for the $\mathrm{C_5H_5}$ groups. The non-equivalence of the amine methyl or methylene protons of the $\mathrm{NR_2}$ groups is consistent both with their diastereotopic nature and with a strong $\mathrm{N}\rightarrow\mathrm{C}^1$ (carbene) π interaction. Accordingly, the ^{13}C n.m.r. spectrum of (**3d**) (Table 2) shows five resonances attributable to the piperidine ring carbons. The two low-field resonances at 289.4 and 260.9 p.p.m. present in the same spectrum are attributed to the carbons C^2 and C^1 respectively. A comparison between these resonances and those of the same carbon atoms in (**2a**) (286.1 and 312.1 p.p.m.) again indicates that replacement of $\mathrm{NR_2}$ for SR does not change the electronic environment at C^2, whereas the upfield shift of 51 p.p.m. of the C^1 resonance of (**3d**) clearly indicates a reduced electrophilic character of C^1.[8]

The Crystal and Molecular Structure of $[\mathrm{(OC)(cp)FeC(NC_5H_{10})SC\{Fe(cp)(CO)_2\}S}]^+$ (**3d**).—The crystals of (**3d**) as its $[\mathrm{SO_3CF_3}]^-$ salt contain discrete cations and anions. A view of the cation is shown in Figure 1 and bond distances and



Scheme 2. $\mathrm{NHR_2} = \mathrm{NHMe_2}$ (**3a**), $\mathrm{NHEt_2}$ (**3b**), $\mathrm{HN(CH_2)_3CH_2}$ (**3c**), or $\mathrm{HN(CH_2)_4CH_2}$ (**3d**); $\mathrm{NH_2R} = \mathrm{NH_2Me}$ (**4a**), $\mathrm{NH_2(C_6H_{11})}$ (**4b**), or $\mathrm{NH_2Bu^n}$ (**4c**); R = Me (**5**) or Et (**5a**)

Table 1. I.r. and ^1H n.m.r. data

Complex	ν(CO)[a]/cm^{-1}	ν(CS)[b]/cm^{-1}	^1H N.m.r. (δ)[c]
(3a)	2 050s, 2 009s, 1 982ms	1 525m (CN), 1 031m, 778w	5.15 (s, cp), 4.80 (s, cp), 3.79 (s, CH_3), 3.70 (s, CH_3)
(3b)	2 050s, 2 009s, 1 981m		5.17 (s, cp), 4.81 (s, cp)
(3c)	2 050s, 2 006s, 1 981ms	1 490m (CN), 1 004m, 763w	5.17 (s, cp), 4.86 (s, cp), 4.0 (m, NCH_2), 2.2 (m, CH_2)
(3d)	2 050s, 2 009s, 1 980ms	1 506m (CN), 1 005m, 768mw	5.18 (s, cp), 4.79 (s, cp), 4.18 (m, NCH_2), 1.85 (m, CH_2)
(4a)	2 148m (CN), 2 014s, 1 970vs	997m, 732mw	4.80 (s, cp), 4.71 (s, cp), 3.38 (s, CH_3)
(4b)	2 142m (CN), 2 012s, 1 967vs	1 002m, 728mw	4.76 (s, cp), 4.68 (s, cp), 3.8 (m, CH), 1.6 (m, CH_2)
(4c)	2 160m (CN), 2 015s, 1 965vs	998m, 728mw	4.78 (s, cp), 4.67 (s, cp), 3.61 (t, NCH_2), 1.6 (m, C_3H_5)
(5)	2 040s, 1 999s, 1 940ms[d]	991m, 817w, 756w, 700w	4.90 (s, cp), 4.57 (s, cp), 2.46 (s, CH_3), 2.01 (s, CH_3)
(5a)	2 040s, 1 999s, 1 941ms[d]	984m, 820mw, 765w, 718w	4.89 (s, cp), 4.57 (s, cp), 3.1 (m, CH_2), 1.3 (m, CH_3)
(6)	2 040s, 1 997s, 1 956m, 1 940m[d]	978m, 816mw, 775w, 699w	4.89 (s, cp), 4.62 (s, cp), 2.8 (m, SCH_2), 2.2 (m, CH_2)
(7)	2 182w (CN), 2 043s, 1 998s, 1 945ms	1 001m, 826mw, 759w, 692w	4.93 (s, cp), 4.57 (s, cp), 2.35 (s, SCH_3)
(8)[e]	2 038s, 1 990s, 1 920ms	972m, 823mw, 746w, 695w	6.46 (s, H), *5.24* (s, H), 4.88 (s, cp), *4.55* (s, cp), 4.45 (s, cp), 2.29 (s, SCH_3), *2.10* (s, SCH_3)

[a] In CH_2Cl_2 solution. [b] In KBr pellets. [c] In $CDCl_3$ solution. [d] In n-hexane solution. [e] Mixture of *cis* and *trans* isomers (see text). The signals attributed to the *cis* isomer are italicized.

Table 2. Carbon-13 n.m.r. data (in CD_2Cl_2)

Complex	C^1	C^2	CO	cp	Others
(2a)	312.12	286.11	210.2, 210.1, 209.2	88.2, 87.9	29.8 (Me)
(3d)	260.91	289.42	213.63, 210.71 (1:2)	87.71, 84.92	63.85, 59.24 (NCH_2) 27.76 (CH_2), 26.82 (CH_2), 23.33 (CH_2)
(4a)		298.70	216.83, 214.07 (1:2)	87.21, 82.79	29.94 (CH_3)
(6)	79.63	273.28	220.49, 212.29, 212.11	87.10, 83.19	31.2 (br) (CH_2S) 26.83 (CH_2)
(7)	82.62	281.20	219.44, 211.56, 211.32	87.17, 83.84	126.08 (CN) 21.14(SCH_3)
(8)*	67.10	281.91	221.70, 212.67, 212.30	87.16, 82.98	23.80 (SCH_3)
	66.8			*82.71*	*19.44* (SCH_3)

* Mixture of *cis* and *trans* isomers. The signals attributed to the *cis* isomer are italicized.

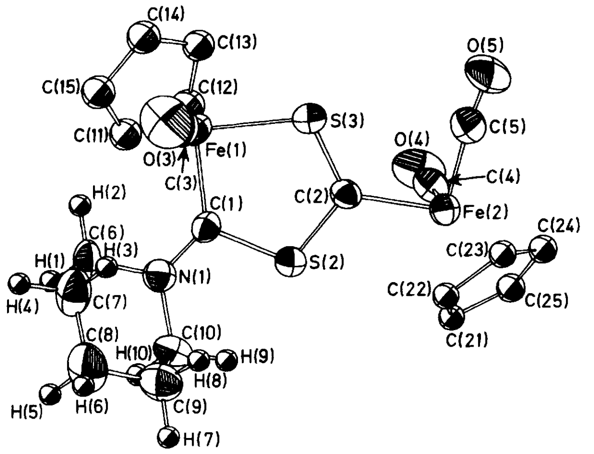


Figure 1. ORTEP view of the cation $[(OC)(cp)\overline{FeC(NC_5H_{10})SC(FeL_n)S}]^+$ (**3d**). Cyclopentadienyl hydrogen atoms have been omitted for clarity. Ellipsoids enclose 50% probability density

Table 3. Relevant bond distances (Å) and angles (°) with estimated standard deviations (e.s.d.s) in parentheses for complex (**3d**)

Fe(1)–S(3)	2.207(2)	Fe(1)–C(3)	1.72(1)
Fe(1)–C(1)	1.91(1)	C(3)–O(3)	1.15(1)
Fe(2)–C(2)	1.94(1)	Fe(2)–C(4)	1.771(7)
C(1)–S(2)	1.79(1)	C(4)–O(4)	1.13(1)
C(2)–S(2)	1.71(1)	Fe(2)–C(5)	1.78(1)
C(2)–S(3)	1.66(1)	C(5)–O(5)	1.13(1)
N(1)–C(1)	1.32(1)	C(16)–S(4)	1.79(1)
N(1)–C(6)	1.48(1)	S(4)–O(av.)	1.435(9)
N(1)–C(10)	1.49(1)	C(16)–F(av.)	1.327(1)
C(6)–C(7)	1.53(1)	C(cpl)–C(cpl)(av.)	1.38
C(7)–C(8)	1.49(2)	C(cp2)–C(cp2)(av.)	1.39
C(8)–C(9)	1.52(1)	Fe(1)–C(cpl)(av.)	2.10
C(9)–C(10)	1.52(1)	Fe(2)–C(cp2)(av.)	2.10
C(1)–Fe(1)–S(3)	89.3(2)	C(3)–Fe(1)–S(3)	93.8(3)
Fe(1)–S(3)–C(2)	107.4(3)	S(3)–C(2)–Fe(2)	125.1(5)
S(3)–C(2)–S(2)	117.5(5)	C(6)–N(1)–C(1)	122.3(8)
C(2)–S(2)–C(1)	103.0(4)	C(10)–N(1)–C(1)	126.0(7)
S(2)–C(1)–Fe(1)	118.0(4)	C(10)–N(1)–C(6)	111.6(7)
Fe(1)–C(1)–N(1)	130.0(6)	Fe(1)–C(3)–O(3)	179(1)
S(2)–C(1)–N(1)	111.9(7)	Fe(2)–C(4)–O(4)	177(1)
C(3)–Fe(1)–C(1)	93.3(5)	Fe(2)–C(5)–O(5)	175(1)

angles of interest are reported in Table 3. The structure will be discussed in comparison with the other members of this family with reference to the bond values in Table 4. The central unit of the cation is the five-atom ring $\overline{FeCSCS}$, in which carbon and sulphur atoms exhibit planar hybridization of their orbitals. The carbon atoms are three-co-ordinate and bear the outer groups $Fe(cp)(CO)_2$ and NC_5H_{10}. The endocyclic Fe(1) is a chiral centre bearing four ligands and completes its eighteen-electron configuration through electron-pair donations from S(3) and the carbonyl ligand C(3)–O(3), five-electron donation from η-C_5H_5, and a formal contribution of one electron from C(1). The ring is more puckered than in the species (**2b**) and (**2c**) and the distances from the plane defined by S(2)–C(2)–S(3) are as follows: Fe(1) −0.28, C(1) +0.19, N(1) +0.60, and Fe(2) −0.13 Å.

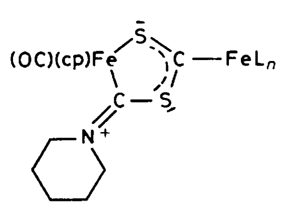
The cation can be divided into two almost independent

Table 4. Comparison of bond distances (Å) found within the FeSCSC ring

Compound	C(2)–S(2)	C(2)–S(3)	C(2)–Fe(2)	S(3)–Fe(1)	C(1)–Fe(1)	C(1)–S(1)	C(1)–S(2)
(2b) $[(OC)(cp)FeC(SEt)SC(FeL_n)S]^+$	1.722(5)	1.653(5)	1.940(4)	2.190(1)	1.862(5)	1.686(5)	1.739(5)
(2c) $[(OC)(cp)FeC\{SW(CO)_5\}SC(FeL_n)S]$	1.71(1)	1.65(1)	1.93(1)	2.181(3)	1.89(1)	1.67(1)	1.75(1)
(3d) $[(OC)(cp)FeC(NC_5H_{10})SC(FeL_n)S]^+$	1.71(1)	1.66(1)	1.94(1)	2.207(2)	1.91(1)		1.79(1)
(7) $[(OC)(cp)FeC\{(CN)(SMe)\}SC(FeL_n)S]$	1.704(3)	1.654(3)	1.956(3)	2.207(1)	2.045(3)	1.803(3)	1.853(3)

moieties, $S_2CFe(cp)(CO)_2$ and $(OC)(cp)FeC(NC_5H_{10})$. These fragments are connected by the bonds S(3)–Fe(1) [2.207(2) Å] and S(2)–C(1) [1.79(1) Å] which exhibit low if any multiple bond character in accord with the ring puckering (see Table 4). The bond distances in the $S_2CFe(cp)(CO)_2$ fragment remain unaltered in all the members of this family, and do not deserve further comment except that they are not sensitive either to chemical changes at C(1) or to rotation of the $Fe(cp)(CO)_2$ group around the C(2)–Fe(2) axis. The actual conformation of the $S_2C–Fe(cp)(CO)_2$ fragment can be described by the dihedral angle (41°) between the S_2C plane and the symmetry plane of $Fe(cp)(CO)_2$. This is 112° different from that found in **(2b)** and **(2c)** and almost midway between the conformations favouring π bonding, *i.e.* 0 or 180° and ±90°.[2] Therefore it is confirmed that the carbenic character of C(2) is weak and packing interactions easily force the $Fe(cp)(CO)_2$ group out of its preferred orientation.[5] The peculiarity of the present cation originates from the presence of the NC_5H_{10} fragment replacing the SE group in the related species **(2)**. The nitrogen atom exhibits strictly planar co-ordination geometry with bonds to two four-co-ordinate carbons [N(1)–C(6) and N(1)–C(10) 1.48(1) and 1.49(1) Å] and one three-co-ordinate carbon [N(1)–C(1) 1.32(1) Å]. The latter interaction shows strong double-bond character, as can be inferred not only by comparison with the two N(1)–C(sp^3) single bonds but also with the length of the double bond in the imine species $Bu^tN{=}CHC(OH)Bu^t(Ph)$ [1.253(3) Å].[9] The bond geometry around the nitrogen is typical for an iminium ion and therefore the molecular charge formally resides on that atom. A strictly equivalent bond length has been reported for the iminium-containing species $[Fe_2Ag(CO)_6\{CHC(=NHMe)Ph\}PPh_2]^+$ [1.311(9) Å].[10]

As for the related compounds, the carbenic character of C(1) is more pronounced than that of C(2), even though the bond C(1)–Fe(1) [1.91(1) Å] is longer than in **(2b)** and in **(2c)**. The lowering of the C(1)–Fe(1) π interaction is correlated to the high degree of double-bond character of C(1)–N(1), but some lengthening (0.07 Å) of the latter interaction with respect to the undisturbed double bond[9] is indicative of electron delocalization over the three atoms which provides a mechanism of charge equalization. The higher localization of the C(1)–N(1) π bond with respect to the C(1)–S(*exo*) interactions in the other species is due to the better overlap of the p_z orbitals between two atoms of the second period and to the higher electronegativity of the nitrogen. In conclusion, the electronic structure of this cation can be reasonably well represented by the following canonical formula. The NC_5H_{10} fragment adopts the expected chair conformation and points upwards, on the same side of C(3)–O(3), in order to minimize contacts with the cyclopentadienyl hydrogens.



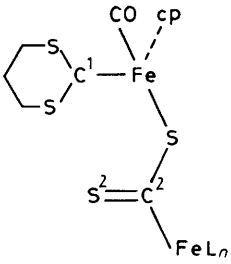
Reactions with Mercaptides.—The bis(methylthio) derivative $[(OC)(cp)FeC(SMe)_2SC(FeL_n)S]$ **(5)** was originally isolated as a side product in the reactions of **(2a)** with primary and secondary amines. According to the electrophilic nature of the C^1 carbon atom in **(2a)**, complex **(5)** and $[(OC)(cp)FeC(SEt)_2SC(FeL_n)S]$ **(5a)** are readily obtained by direct synthesis (Scheme 2). These tris(organothio) complexes **(5)** are stable only at low temperature (*ca.* −10 °C) in the solid state and solutions of **(5)** or **(5a)** in CH_2Cl_2 decompose at room temperature in a few hours affording $[(OC)(cp)FeSC(FeL_n)S]$ (30% yield). The formation of the chelate complex may indicate that the $:C(SR)_2$ group is lost during the decomposition in a reaction similar to that of the orthothioformate $HC(SPh)_3$ with LiBu which forms the sulphide Li(SPh) and the dithiocarbene fragment $:C(SPh)_2$.[11]

The reaction of complex **(2a)** with EtS^- produces a mixture of cyclic tris(organothio) complexes which probably contain **(5)**, **(5a)**, and the mixed derivatives $[(OC)(cp)FeC\{(SMe)(SEt)\}SC(FeL_n)S]$ **(5b)**. The complexity of this mixture prevented a study of the diastereomeric nature of **(5b)** in which two chiral centres are present, Fe(endocyclic) and C^1. Furthermore the presence of the symmetrically substituted **(5)** and **(5a)** indicate transfer of mercaptide groups between the two derivatives **(5b)**.

The i.r. spectra of complexes **(5)** and **(5a)** in n-hexane show three ν(CO) absorptions in the carbonyl-stretching region (Table 1). The absence of splitting of the i.r. bands observed for $[(OC)(cp)FeC(S)SC(FeL_n)S]$ **(1)** and the hexane-soluble complexes **(2)**[2] indicates that conformers arising from rotation about the Fe(*exo*)–C^2 bond are indistinguishable by i.r. spectroscopy. This behaviour is observed whenever C^1 becomes four-co-ordinate.

Complex **(2a)** reacts with propane-1,3-dithiol in the presence of NaH to give the spirocyclic complex $[(OC)(cp)FeC\{S(CH_2)_3S\}SC(FeL_n)S]$ **(6)** (74% yield). Its stability is by far greater with respect to that of the analogous tris(organothio) derivatives and may be related both to the less steric demand of the 1,3-dithiane group and to the formation of the six-membered ring.

The ^1H n.m.r. spectrum of complex **(6)** exhibits two sharp singlets at 4.89 and 4.62 p.p.m., attributable to the cp groups and two multiplets centred at 2.8 and 2.2 p.p.m., respectively assigned to the SCH_2 and CH_2 protons. The room-temperature ^{13}C n.m.r. spectrum in CD_2Cl_2 shows, in addition to the expected resonances at 273.28 (C^2 sp^2 carbon), 220.49, 212.29, 212.11 (CO), 87.10, 83.19 (cp), 79.63 (C^1 sp^3 carbon), and 26.83 (CH_2 dithiane ring), a broad signal at 31.2 p.p.m. attributed to the S-bonded CH_2 ring carbons. However, in CD_2Cl_2 at low temperature (−60 °C), the signal due to SCH_2 is split into a pair of lines (32.4 and 28.4 p.p.m.) while the signals of the other carbon atoms remain unchanged. As the temperature is raised, these two singlets coalesce (+19 °C) and at 50 °C in $CDCl_3$ or 90 °C in $[^2H_8]$toluene a single line is observed (31.0 or 32.6 p.p.m., respectively). The equivalence of the two diastereotopic carbons in positions 4 and 6 of the dithiane ring, revealed by the variable-temperature ^{13}C n.m.r. experiment, may be explained by C^1–S^2 bond cleavage which affords a dithiocarbene intermediate. Rotation around the Fe–C^1 bond followed by ring closure at C^1 accounts for the observed equivalence. The depicted intramolecular mechanism is supported by the following facts: (*i*) the C^1–S^2 bond is the weakest among the C–S bonds in the molecule [see geometrical evidence in the structure of complex (**7**)]; (*ii*) the easy formation of the chelate dithiocarboxylate [(OC)(cp)FeSC(FeL$_n$)S] which always accompanies the reaction of (**2a**) with mercaptides; (*iii*) the previously reported stability of dithiocarbene complexes of the type [Fe(cp)(CO)$_2${CS(CH$_2$)$_n$S}]$^+$(n = 2 or 3).[12] Furthermore the absence of coalescence of the ^{13}C signals of the two diastereotopic CO groups in the exocyclic FeL$_n$ moiety rules out the possibility of cleavage at Fe^1–S in complex (**6**). Were this pathway to occur, inversion at the Fe^1 chiral centre would be expected and therefore equivalent signals for the two CO groups.



Another unusual feature of compound (**6**) is present in its i.r. spectrum in hexane which shows four rather than the expected three ν(CO) absorptions (Table 1). A similar effect has been noted for other metallacyclo complexes of this family and has been interpreted in terms of conformational isomers arising from restricted Fe(*exo*)–C^2 rotation.[2] However, the absence of i.r.-detectable conformers in the hexane-soluble tris(organothio) complex (**5**) suggests that the observed ν(CO) doubling originates from conformational isomerism within the flexible 1,3-dithiane group in the spirocyclic complex (**6**) because the two conformers obtained by chair-to-chair inversion of the dithiane ring can produce different interactions of the sulphur lone pairs with the π* orbitals of the CO ligand. This effect is limited at the iron-endocyclic region because the exocyclic FeL$_n$ moiety is not appreciably affected in the absence of π-delocalization within the metallacyclo ring [see structure of complex (**7**)].

Reactions with Cyanide and Hydride Ions.—Nucleophilic addition at the carbene carbon in carbene complexes of transition metals has been successfully studied by using a large variety of nucleophiles.[13] Despite this, cyanide-ion addition has never been reported. The only examples so far published which involved CN$^-$ are the substitution[14] or the insertion[15] reactions in Fischer-type carbene complexes [equations (7) and (8)].

$$[Cr(CO)_5\{CCl(NMe_2)\}] + KCN \longrightarrow [Cr(CO)_5\{C(CN)(NMe_2)\}] + KCl \quad (7)$$

$$[Cr(CO)_5\{C(OMe)Ph\}] + KCN \longrightarrow [Cr(CO)_5\{N{\equiv}CCH(OMe)Ph\}] + \ldots \quad (8)$$

In our case complex (**2a**) reacts in CH_2Cl_2 with KCN to form the dark brown air-stable nitrile derivative [(OC)(cp)-FeC{(CN)(SMe)}SC(FeL$_n$)S] (**7**) in a 78% yield [Scheme 2, equation (5)]. The spectroscopic properties of (**7**) (Table 1) are in agreement with the proposed formulation and indicate the presence of only one of the two diastereomers arising from a highly diastereoselective CN$^-$ addition at the prochiral C^1 atom.

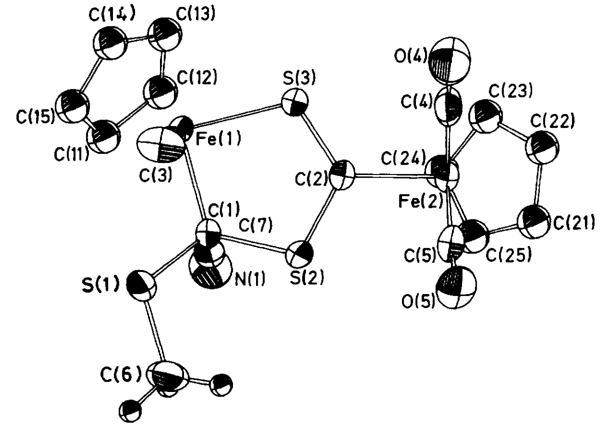


Figure 2. ORTEP view of the molecule [(OC)(cp)-FeC{(CN)(SMe)}SC(FeL$_n$)S] (**7**). Details as in Figure 1

Table 5. Relevant bond distances (Å) and angles (°) with e.s.d.s in parentheses for complex (**7**)

Fe(1)–S(3)	2.207(1)	N(1)–C(7)	1.142(4)
Fe(1)–C(1)	2.045(3)	C(1)–C(7)	1.458(4)
Fe(2)–C(2)	1.956(3)	Fe(1)–C(3)	1.751(3)
C(1)–S(1)	1.803(3)	C(3)–O(3)	1.147(4)
C(1)–S(2)	1.853(3)	Fe(2)–C(4)	1.778(4)
C(2)–S(2)	1.704(3)	C(4)–O(4)	1.130(4)
C(2)–S(3)	1.654(3)	Fe(2)–C(5)	1.769(3)
C(6)–S(1)	1.804(4)	C(5)–O(5)	1.139(4)
Fe(1)–C(cpl) (av.)	2.10	Fe(2)–C(cp2) (av.)	2.10
C(1)–Fe(1)–S(3)	89.9(1)	S(2)–C(2)–Fe(2)	116.9(2)
Fe(1)–S(3)–C(2)	108.8(1)	S(3)–C(2)–Fe(2)	123.4(2)
S(3)–C(2)–S(2)	119.5(2)	C(6)–S(1)–C(1)	104.8(2)
C(2)–S(2)–C(1)	104.0(1)	C(1)–C(7)–N(1)	179.9(1)
S(2)–C(1)–Fe(1)	113.5(1)	S(1)–C(1)–C(7)	109.3(2)
Fe(1)–C(1)–S(1)	107.2(1)	Fe(1)–C(3)–O(3)	176.7(3)
S(2)–C(1)–S(1)	110.8(2)	Fe(2)–C(4)–O(4)	179.0(4)
C(3)–Fe(1)–C(1)	92.3(1)	Fe(2)–C(5)–O(5)	176.9(3)
C(3)–Fe(1)–S(3)	92.5(1)		

In order to establish the steric nature of complex (**7**) an *X*-ray structural study was undertaken (see next section). It is worth mentioning that the nucleophilic addition of CN$^-$ at the carbene carbon seems to be a general feature of dithiocarbene complexes: [Fe(cp)(CO)$_2${C(SMe)$_2$}]$^+$[3] reacts with KCN to form [Fe(cp)(CO)$_2${C(SMe)$_2$(CN)}]. In addition we have also found that bridging thiocarbyne complexes of the type [(OC)(cp)Fe(μ-CO)(μ-CSR)Fe(cp)(CO)]$^+$[16] react with CN$^-$ to produce exclusively a neutral addition complex which contains the μ-C(SR)(CN) moiety.[17]

By analogy with other cationic carbene complexes such as [Fe(cp)(CO)$_2${C(SMe)$_2$}]$^+$[18] and [Fe(cp)(CO)$_2${CMe-(OMe)}]$^+$,[19] (**2a**) readily reacts with Li(BHEt$_3$) to produce the dark green hydride adduct [(OC)(cp)FeCH(SMe)SC(FeL$_n$)S] (**8**) [Scheme 2, equation (6)]. Its ^1H and ^{13}C n.m.r. spectra (Tables 1 and 2) clearly indicate that the hydride addition has formed a 5:1 mixture of the two diastereoisomers of (**8**). From the structural evidence of the nitrile derivative (**7**), the isomer in which hydrogen and CO are mutually *anti* can be supposed the prevalent one.

The chemical properties of complex (**8**) are quite different from those of the related [FeL$_n${CH(SMe)$_2$}] derivatives. In contrast with the latter which easily produce the secondary thiocarbene [FeL$_n${CH(SR)}]$^+$ by removal of HSR,[19] all attempts to obtain the secondary cyclic carbenes [(OC)(cp)FeCHSC(FeL$_n$)S] failed.

The Crystal and Molecular Structure of [(OC)(cp)FeC{(CN)(SMe)}SC(FeL$_n$)S] (**7**).—The crystals of (**7**) contain discrete molecules whose overall geometry is shown in Figure 2. Bond distances and angles of interest are reported in Table 5. The central unit of the molecule, the five-atom ring Fe(1)C(1)S(2)C(2)S(3), is the same as in the related species but with an important difference for C(1), which is now four-co-ordinate, having undergone the nucleophilic addition of the CN$^-$ ion. This atom is now a chiral centre contiguous to the pre-existing centre of asymmetry, Fe(1). The handedness of Fe(1) drives that of C(1), selectively favouring the approach of the entering group from the direction opposite to that occupied by the ligand C(3)–O(3) (see Figure 2). No mixture of diastereoisomers has been observed, except when the entering group is the small H$^-$ ion (see previous section). The ring is substantially puckered and C(1) is displaced downwards (−0.38 Å) with respect to the plane defined by S(2)–C(2)–S(3), while Fe(1) deviates upwards very slightly (0.04 Å).

The Fe(1)–C(1) distance [2.045(3) Å] is now that of a pure single bond and a comparison with the Fe–C values of related species, which are on average 0.15 Å shorter, confirms the carbenic character of all the C(sp^2)–Fe interactions. The C(1)–Fe(1) single bond gives the opportunity of estimating the actual covalent radius of Fe(1) (1.28 Å), assuming 0.77 Å for C(1).

The strictly equivalent carbon–sulphur distances, C(1)–S(1) and S(1)–C(6)(methyl) 1.803(3) and 1.804(4) Å, also allow calculation of the radius 1.03 Å for the sulphur atom, a value coincident with that found for elemental sulphur.[20] These covalent radii give an indication of partial double-bond character for the Fe(1)–S(3) interaction which is 0.1 Å shorter than expected for a single bond. The C(1)–S(2) interaction, on the other hand, is 0.05 Å longer than the sum of the covalent radii and the longest among the corresponding values reported in Table 4. The destabilization of this interaction is to be ascribed to the C(1) atom which, no longer kept coplanar with the other ring atoms by bonding, is placed out-of-plane in order to bring the Fe(1)–C(1)–S(2) angle [113.5(1)°] nearer to the tetrahedral value. The displacement of C(1) lowers the orbital overlap with S(2) with consequent destabilization of the bond. The weakening of the C(1)–S(2) interaction is expected to be present in all the derivatives in which C(1) is four-co-ordinate and can explain the peculiarities of the ^{13}C n.m.r. spectrum of the 1,3-dithiane derivative (see below).

The CN group is strictly linear [C(1)–C(7)–N(1) 179.9(1)°] with C(1)–C(7) and C(7)–N(1) distances 1.458(4) and 1.142(4) Å, respectively, in very good agreement with the expected values.

The geometry of the fragment S$_2$C–Fe(cp)(CO)$_2$ confirms once more its substantial independence from changes in the remaining part of the molecule. The dihedral angle between the S$_2$C plane and the symmetry plane of the group Fe(cp)(CO)$_2$ is *ca.* 89°, one of the conformations favouring π bonding, but no shortening of the C(2)–Fe(2) interaction is observed.

Experimental

All solvents were appropriately dried and degassed prior to use under dinitrogen and reactions were routinely carried out by using standard Schlenk techniques under dinitrogen. All reagent-grade chemicals were used as received. Liquid amines were distilled prior to their use. The compounds [(OC)(cp)FeC(SR)SC(FeL$_n$)S]SO$_3$CF$_3$[2] (R = Me or Et) and [FeL$_n${C(SMe)$_2$}]SO$_3$CF$_3$[3] were prepared by the reported procedures.

Table 6. Crystal data and intensity collection parameters[a]

Complex	(**3d**)	(**7**)
Formula	$C_{21}H_{20}F_3Fe_2NO_6S_3$	$C_{17}H_{13}Fe_2NO_3S_3$
M	647.28	487.18
Crystal size (mm)	0.05 × 0.15 × 0.1	0.12 × 0.2 × 0.15
a/Å	11.570(2)	6.894(2)
b/Å	12.242(2)	10.057(1)
c/Å	10.552(2)	14.520(2)
α/°	104.60(2)	96.00(1)
β/°	87.51(1)	96.17(1)
γ/°	117.24(2)	106.31(1)
U/Å^3	1 281.5	951.0
D_c/g cm^{-3}	1.68	1.70
F(000)	656	492
μ(Mo-K_α)/cm^{-1}	14.24	18.6
ω scan width (°)	0.8 + 0.35 tanθ	0.5 + 0.35 tanθ
Prescan rate (° min^{-1})	8	5
Maximum scan time (s)	120	150
Reflections collected	4 768 (±h, ±k, l)	3 480 (±h, ±k, l)
Unique observed reflections [$F_o > 5\sigma(F_o)$]	1 997	2 740
No. of refined parameters	283	175
R, R'[b]	0.0451, 0.0463	0.031, 0.035

[a] Details common to both: triclinic, space group $P\bar{1}$; $Z = 2$; scan mode ω—2θ; 2θ limits 2.5—25°; prescan acceptance criterion, $I = 2\sigma(I)$; criterion for observed reflections $I = 10\sigma(I)$; three standard reflections measured periodically, no decay. [b] $R = \Sigma|F_o - |F_c||/\Sigma F_o$, $R' = \Sigma|F_o - |F_c||w^{\frac{1}{2}}/\Sigma F_o w^{\frac{1}{2}}$.

Infrared spectra were recorded on a Perkin-Elmer 983-G spectrometer as KBr pellets or in solution using a pair of matched 1.0-mm NaCl cells. The observed frequencies (±1 cm^{-1}) were calibrated with the band of water vapour at 1 673 cm^{-1}. Hydrogen-1 and ^{13}C-{^{1}H} n.m.r. spectra were recorded on a Varian XL100 spectrometer using SiMe$_4$ as internal standard; [Cr(acac)$_3$] (acac = acetylacetonate) (0.1 mol dm^{-3}) was added to the ^{13}C samples to reduce data collection time. Elemental analyses were by Pascher Microanalytical Laboratorium (Bonn, Germany). Melting points are uncorrected.

Reactions of [(OC)(cp)FeC(SMe)SC(FeL$_n$)S]SO$_3$CF$_3$ (**2a**).—*With secondary amines.* These derivatives were prepared by a general procedure which is here described for (**3d**).

Piperidine (100 μl, 1.01 mmol) was added to complex (**2a**) (0.30 g, 0.49 mmol) in dichloromethane (25 cm^3). After 60 min, at room temperature, the solution was filtered through Celite and evaporated to dryness under vacuum. The red oily residue was washed with Et$_2$O (50 cm^3). Crystallization from CH$_2$Cl$_2$–hexane (2:1) at −20 °C afforded bright red-orange crystals of (**3d**). Yield 66% (0.21 g, 0.32 mmol), m.p. 136—138 °C (decomp.) (Found: C, 38.25; H, 3.15. $C_{21}H_{20}F_3Fe_2NO_6S_3$ requires C, 38.95; H, 3.1%).

The red complexes (**3b**) (48%) and (**3c**) (61%) were prepared analogously and characterized by their spectroscopic properties (Table 1). In the synthesis of (**3a**), NHMe$_2$ was slowly bubbled into a stirred CH$_2$Cl$_2$ solution of (**2a**) for 30 min and the resulting solution was worked up as described above (yield 59%).

With primary amines. The isocyanide derivative [(OC)(MeNC)(cp)FeSC(S)FeL$_n$] (**4a**) was prepared by bubbling gaseous NH$_2$Me for 20 min through a CH$_2$Cl$_2$ solution (20 cm^3) of (**2a**) (0.30 g, 0.49 mmol). After stirring for another 15 min the resulting red solution was evaporated under vacuum and the residue was chromatographed on an alumina column (10 × 3 cm), with light petroleum (b.p. 40—70 °C)–CH$_2$Cl$_2$

Table 7. Fractional atomic co-ordinates for complex (**3d**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Fe(1)	0.247 77(10)	0.229 71(11)	0.723 70(11)	C(9)	0.047 0(9)	0.276 7(10)	0.321 3(9)
Fe(2)	−0.169 06(10)	0.205 84(10)	0.907 04(11)	C(10)	0.111 2(9)	0.369 2(8)	0.454 2(8)
S(2)	0.025 5(2)	0.309 1(2)	0.701 4(2)	O(6)	0.750 3(7)	0.385 7(6)	0.266 3(7)
S(3)	0.072 7(2)	0.150 2(2)	0.830 4(2)	O(7)	0.595 3(6)	0.378 7(6)	0.431 0(7)
S(4)	0.628 4(2)	0.310 4(2)	0.316 6(2)	O(8)	0.523 3(6)	0.226 4(6)	0.219 5(6)
N(1)	0.184 0(6)	0.320 8(5)	0.518 2(6)	F(1)	0.571 3(7)	0.132 3(6)	0.433 3(7)
C(1)	0.159 7(6)	0.288 0(6)	0.629 8(7)	F(2)	0.699 8(7)	0.133 6(7)	0.281 9(7)
C(2)	−0.020 3(7)	0.215 9(6)	0.809 4(7)	F(3)	0.772 6(6)	0.272 4(7)	0.466 5(7)
C(16)	0.670 8(10)	0.208 3(10)	0.377 9(11)	C(11)	0.419 4(9)	0.402 8(9)	0.754 6(10)
C(3)	0.202 5(9)	0.089 4(9)	0.604 0(10)	C(12)	0.365 0(10)	0.393 2(9)	0.872 8(10)
O(3)	0.174 5(8)	−0.003 5(7)	0.523 6(8)	C(13)	0.362 2(9)	0.287 8(8)	0.901 6(10)
C(4)	−0.056 8(8)	0.340 2(8)	1.027 1(8)	C(14)	0.412 5(9)	0.231 4(10)	0.800 9(9)
O(4)	0.018 9(6)	0.426 8(6)	1.099 9(6)	C(15)	0.449 2(10)	0.304 9(9)	0.711 6(11)
C(5)	−0.167 8(8)	0.092 0(8)	0.983 4(8)	C(21)	−0.254 7(8)	0.280 8(7)	0.803 8(7)
O(5)	−0.176 9(6)	0.017 2(6)	1.033 1(7)	C(22)	−0.287 9(7)	0.155 0(7)	0.735 7(8)
C(6)	0.286 1(7)	0.306 0(8)	0.436 3(7)	C(23)	−0.356 3(8)	0.078 5(8)	0.818 9(8)
C(7)	0.223 5(9)	0.215 2(9)	0.300 8(9)	C(24)	−0.364 5(8)	0.155 7(7)	0.937 8(9)
C(8)	0.145 0(9)	0.255 0(11)	0.231 7(8)	C(25)	−0.300 9(8)	0.281 0(8)	0.928 6(8)

Table 8. Fractional atomic co-ordinates for complex (**7**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Fe(1)	0.419 86(7)	0.666 42(4)	0.375 67(3)	C(13)	0.277 4(3)	0.736 3(2)	0.484 4(1)
Fe(2)	−0.056 02(6)	0.215 94(4)	0.191 14(3)	C(14)	0.490 5(3)	0.769 0(2)	0.514 0(1)
S(1)	0.684 93(12)	0.720 5(9)	0.216 13(6)	C(15)	0.593 7(3)	0.858 5(2)	0.453 9(1)
S(2)	0.305 86(13)	0.474 51(8)	0.170 78(6)	C(21)	−0.295 4(4)	0.136 6(2)	0.079 9(1)
S(3)	0.176 56(13)	0.464 71(8)	0.354 19(5)	C(22)	−0.367 9(4)	0.107 0(2)	0.165 7(1)
C(1)	0.422 5(4)	0.654 0(3)	0.234 3(2)	C(23)	−0.337 9(4)	0.236 2(2)	0.223 2(1)
C(2)	0.153 9(4)	0.390 5(3)	0.244 8(2)	C(24)	−0.246 9(4)	0.345 8(2)	0.173 1(1)
C(3)	0.612 9(5)	0.585 4(3)	0.390 5(2)	C(25)	−0.220 7(4)	0.284 3(2)	0.084 5(1)
O(3)	0.740 2(4)	0.534 3(3)	0.404 7(2)	C(11P)	0.313 6(12)	0.845 2(10)	0.392 4(8)
C(4)	−0.006 6(5)	0.133 9(3)	0.290 1(3)	C(12P)	0.247 9(12)	0.754 7(10)	0.459 0(8)
O(4)	0.022 0(5)	0.081 1(3)	0.353 0(2)	C(13P)	0.424 1(12)	0.745 1(10)	0.515 1(8)
C(5)	0.105 1(5)	0.149 3(3)	0.124 6(2)	C(14P)	0.598 7(12)	0.829 7(10)	0.483 1(8)
O(5)	0.201 2(4)	0.103 1(3)	0.079 0(2)	C(15P)	0.530 4(12)	0.891 6(10)	0.407 3(8)
C(6)	0.674 9(6)	0.711 9(5)	0.090 9(3)	C(21P)	−0.342 7(10)	0.094 1(7)	0.119 8(5)
C(7)	0.303 7(5)	0.737 2(3)	0.192 5(2)	C(22P)	−0.369 6(10)	0.160 5(7)	0.206 7(5)
N(1)	0.210 4(5)	0.802 4(4)	0.159 9(2)	C(23P)	−0.300 1(10)	0.307 5(7)	0.206 5(5)
C(11)	0.444 3(3)	0.881 2(2)	0.387 2(1)	C(24P)	−0.230 2(10)	0.331 9(7)	0.119 6(5)
C(12)	0.248 8(3)	0.805 6(2)	0.406 0(1)	C(25P)	−0.256 5(10)	0.200 0(7)	0.065 9(5)

(1:4) to separate the first fraction containing [(OC)(cp)FeSC(FeL$_n$)S]. The second fraction, eluted with CH_2Cl_2, was collected and evaporated to dryness under high vacuum, producing (**4a**) as a red oil. Yield 50% (0.11 g, 0.24 mmol) (Found: C, 43.9; H, 3.05. $C_{16}H_{13}Fe_2NO_3S_2$ requires C, 43.35, H, 2.95%).

The oily complexes (**4b**) (yield 45%) and (**4c**) (42%) were prepared using the same procedures. In the case of liquid primary amines a slight variation was required. A three-fold excess of the amine was added to the CH_2Cl_2 solution of complex (**2a**). The resulting solution was reduced in volume (to *ca.* 5 cm^3) and chromatographed on an alumina column. Attempts to crystallize the oily derivatives (**4a**)—(**4c**) failed.

Preparations.—[(OC)(cp)FeC(SMe)$_2$SC(FeL$_n$)S] (**5**). Gaseous methanethiol was bubbled through a tetrahydrofuran (thf) solution of n-butyl-lithium (20 cm^3, 0.16 mol dm^{-3}) for 5 min. Part (3.3 cm^3, 0.53 mmol) of this solution was added with a syringe to complex (**2a**) (0.30 g, 0.49 mmol) previously dissolved in thf (30 cm^3). The mixture, which immediately turned dark green, was stirred for 15 min at room temperature. Volatile material was removed *in vacuo* and the residue was extracted with light petroleum (100 cm^3). The volume was then reduced to *ca.* 50 cm^3 and black crystals of (**5**) were obtained by crystallization at −20 °C. Yield 88% (0.22 g, 0.43 mmol); m.p. 116—118 °C (decomp.) (Found: C, 39.85; H, 3.15. $C_{17}H_{16}Fe_2O_3S_4$ requires C, 40.15; H, 3.15%).

[(OC)(cp)FeC(SEt)$_2$SC(FeL$_n$)S] (**5a**). This compound was prepared as described above from Li(SEt) and [(OC)(cp)FeC(SEt)SC(FeL$_n$)S]SO_3CF_3 (**2b**). Yield 83% (0.22 g, 0.41 mmol), m.p. 112—114 °C (decomp.) (Found: C, 42.1; H, 3.6. $C_{19}H_{20}Fe_2O_3S_4$ requires C, 42.55; H, 3.75%).

[(OC)(cp)FeC{S(CH$_2$)$_3$S}SC(FeL$_n$)S] (**6**). Propane-1,3-dithiol (50 µl, 0.50 mmol) was added to a suspension of NaH (24 mg, 1.0 mmol) in thf (10 cm^3). The mixture was stirred until evolution of gas ceased and treated with a solution of complex (**2a**) (0.30 g, 0.49 mmol) in thf (20 cm^3). The mixture, which rapidly turned dark green, was stirred for another 30 min. The solvent was then evaporated *in vacuo* and the residue was chromatographed on an alumina column (2 × 15 cm). Elution with CH_2Cl_2–light petroleum (1:2) gave a dark green band which was collected and evaporated to dryness. Crystallization of the residue at −20 °C from light petroleum–CH_2Cl_2 gave black crystals of (**6**). Yield 74% (0.19 g, 0.36 mmol); m.p. 134—136 °C (decomp.) (Found: C, 40.9; H, 3.1; S, 24.1. $C_{18}H_{16}Fe_2O_3S_4$ requires C, 41.55; H, 3.1; S, 24.65%).

[(OC)(cp)FeC{(CN)(SMe)}SC(FeL$_n$)S] (**7**). An acetone solution (25 cm^3) of complex (**2a**) (0.30 g, 0.49 mmol) was stirred with a ten-fold excess of KCN (0.32 g, 4.90 mmol) for 2 h. The solution was then evaporated to dryness and the residue filtered on an alumina pad (3 × 3 cm). Crystallization from CH_2Cl_2–light petroleum afforded black crystals of (**7**). Yield 78% (0.19 g, 0.38 mmol); m.p. 158—160 °C (decomp.) (Found: C, 42.05; H, 2.75; S, 19.4. $C_{17}H_{13}Fe_2NO_3S_3$ requires C, 41.9; H, 2.7; S, 19.7%).

$[Fe(cp)(CO)_2\{C(CN)(SMe)_2\}]$. A dichloromethane solution (20 cm^3) of the complex $[FeL_n\{C(SMe)_2\}]SO_3CF_3$ (0.40 g, 0.92 mmol) was stirred with a two-fold excess of KCN (0.12 g, 1.84 mmol) for 2 h. The solvent was then evaporated to dryness and the residue chromatographed on an alumina column (3 × 15 cm). Elution with CH_2Cl_2–light petroleum (1:2) gave a yellow band which was collected and evaporated to dryness. Crystallization of the residue afforded yellow crystals of $[Fe(cp)(CO)_2\{C(CN)(SMe)_2\}]$. Yield 76% (0.22 g, 0.70 mmol), m.p. 114—116 °C (decomp.) (Found: C, 42.75; H, 3.5; S, 21.0. $C_{11}H_{11}FeNO_2S_2$ requires C, 42.75; H, 3.6; S, 20.75%). I.r. (dichloromethane): ν(CO) 2 035s, 1 988s; ν(CN) 2 190w cm^{-1}. ^1H N.m.r. ($CDCl_3$): 5.15 (s, 5 H, C_5H_5) and 2.43 (s, 6 H, CH_3).

$[(OC)(cp)\overline{FeCH(SMe)SC(FeL_n)S}]$ (**8**). Stoicheiometric amounts of $Li(BHEt_3)$ (0.50 cm^3, 1.0 mol dm^{-3} in thf) were added by a syringe to a thf solution (30 cm^3) of complex (**2a**) (0.30 g, 0.49 mmol). After stirring for 15 min, the solution was evaporated to dryness and the residue redissolved in CH_2Cl_2, filtered through an alumina pad (3 × 2 cm), and dried *in vacuo*. Crystallization from CH_2Cl_2–light petroleum at −20 °C afforded dark green crystals of the required complex. Yield 67% (0.15 g, 0.33 mmol), m.p. 122—124 °C (decomp.) (Found: C, 41.5; H, 3.2; S. 20.1. $C_{16}H_{14}Fe_2O_3S_3$ requires C, 41.6; H, 3.05; S, 20.8%).

X-*Ray Data Collection*.—Crystal data and details of the data collection for compound (**3d**) as its $[SO_3CF_3]^-$ salt and (**7**) are given in Table 6. The diffraction experiments for both compounds were carried out at room temperature on a fully automated Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.710 67 Å). The unit cell was determined from 25 randomly selected strong reflections by using the automatic search, indexing, and least-squares routines. Data were corrected for Lorentz-polarization effects. Empirical absorption corrections were applied by using the Walker and Stuart method[21] for compound (**3d**) and by using the azimuthal scan method for compound (**7**).[22] All calculations were performed using the SHELX 76 system of programs.[23]

Structure determination and refinement. The structures were solved by direct methods which allowed location of Fe and S atoms. All additional non-hydrogen atoms were located in Fourier maps phased with the heavy atoms. The two structures were refined by full-matrix least-squares methods in the space group $P\bar{1}$ (no. 2). In the least-squares calculations the weighting factor used was $w = k/[\sigma^2(F) + |g|F^2]$ where $k = 2.66$ and $g = 0.000\,21$ for (**3d**), 7.67 and 0.000 05 for (**7**). Hydrogen atoms were added in calculated positions (d_{CH} = 1.08 Å) and their co-ordinates were not refined but continuously updated with respect to their carbon atoms. Bond-length constraints for the C–C distances in the cyclopentadienyl rings were introduced (distances equal within an estimated error of 0.01 Å) for complex (**3d**). The cyclopentadienyl ligands in complex (**7**) showed weak second images indicating disorder over two sites and were refined as rigid groups. The second images gave occupancy factors of *ca*. 13 and 20% for the groups bonded to the endocyclic and exocyclic iron atoms, respectively. The final refinement of all positional and thermal parameters proceeded using anisotropic thermal parameters, except for the cyclopentadienyl atoms which were refined isotropically with hydrogens having their thermal parameters fixed at $U = 0.08$ $Å^2$. The final Fourier difference map was featureless with residual peaks in the range ±0.70 e $Å^{-3}$. The final positional parameters of the atoms are listed in Tables 7 and 8.

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

Acknowledgements

We thank the C.N.R. and Ministero della Pubblica Istruzione for financial support.

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Received 18*th May* 1987; *Paper* 7/873