Synthesis, Reactions, and X-Ray Structures of the Functionalized Isocyanide Complexes [Fe₂{μ-CNC(O)SR}(μ-CO)(CO)₂(cp)₂](cp = η-C₅H₅, R = Me or Et) and of their Carbyne and Carbene Derivatives†

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The cyanate ion NCO^- inserts into the C–S bond of [Fe₂(μ-CSR)(μ-CO)(CO)₂(cp)₂]⁺ (cp = η-C₅H₅, R = Me or Et), to give the isocyanide-bridged complexes [Fe₂{μ-CNC(O)SR}(μ-CO)(CO)₂(cp)₂] (**1**). These derivatives exist in solution as a mixture of *cis* and *trans* isomers with the strong electron-withdrawing CNC(O)SR group bridging in both forms. The X-ray crystal structure of complex (**1b**; R = Et) [monoclinic, a = 9.418(3), b = 14.827(3), c = 12.793(4) Å, β = 97.28(3)°, Z = 4, space group $P2_1/n$] reveals the CO groups in *cis* position relative to the Fe–Fe bond. The nitrogen atom in (**1**) is alkylated or protonated to generate the cationic aminocarbyne complexes [Fe₂{μ-CN(R')C(O)SR}(μ-CO)(CO)₂(cp)₂]⁺ (**2**; R' = Me, Et, or H) which do not display *cis–trans* isomerization at room temperature. In accord with their carbyne nature, the μ-C atom in complexes (**2**) adds H⁻ or CN⁻ (X) to form the carbene derivatives [Fe₂{μ-C(X)N(R')C(O)SR}(μ-CO)(CO)₂(cp)₂] (**3**) which are not fluxional. The X-ray structure of (**3a**; X = CN, R' = R = Me) [orthorhombic, a = 9.238(3), b = 8.142(1), c = 24.712(2) Å, Z = 4, space group $P2_12_12_1$] shows that the molecule retains the *cis* geometry of the parent species (**1**) and (**2**), with the bulkier μ-carbon substituent N(Me)C(O)SMe on the less-hindered carbonyl face of the complex.

The instability of N-acyl isocyanides CNC(O)R, synthesized for the first time by Hofle and Lange[1] in 1977, has prevented an extensive study of their co-ordination ability towards transition metals. Only recently free acyl isocyanides have been trapped at metal centres either by reaction with an unsaturated iron(ɪɪ) porphyrin complex[2] or by displacement of CO ligands from [Co(CO)₂(cp)](cp = η-C₅H₅) to give [Co{CNC(O)Ph}₂-(cp)].[3] In all the other cases reported so far the chemistry of N-acyl isocyanide complexes has been studied by building up the co-ordinated CNC(O)R group through N-acylation of cyano-metalates.[4–6] The only examples of bridging acyl isocyanide complexes are the shortly described [Fe₂{μ-CNC(O)R}(μ-CO)(CO)₂(cp)₂] which have been prepared by acylation of the cyanometalate dimer [Fe₂(CO)₃(CN)(cp)₂]⁻.[7]

In the present paper we describe the synthesis of [Fe₂{μ-CNC(O)SR}(μ-CO)(CO)₂(cp)₂] (R = Me or Et) (**1**) which are the first complexes containing a μ-CNR ligand functionalized with a strong electron-withdrawing C(O)SR group. These derivatives have been obtained by an unusual insertion of NCO⁻ into the C–S bond of the μ-thiocarbyne cations [Fe₂(μ-CSR)(μ-CO)(CO)₂(cp)₂]⁺.[8] The novelty of type (**1**) complexes prompted us to investigate their spectroscopic properties and the X-ray molecular structure of (**1b**; R = Et). The protonation or alkylation of the nitrogen atom in (**1**) gives the cationic [Fe₂{μ-CN(R')C(O)SR}(μ-CO)(CO)₂(cp)₂]⁺ (**2**) which we here describe as functionalized μ-aminocarbyne complexes. Accordingly, these react with nucleophiles such as H⁻ or CN⁻ at the bridging carbon atom to give the corresponding carbene derivatives. The X-ray molecular structure of the CN⁻ adduct [Fe₂{μ-C(CN)N(Me)C(O)SMe}(μ-CO)(CO)₂(cp)₂] is discussed in order to clarify the stereochemical features of these new species.

Results and Discussion

Synthesis and Spectral Properties of [Fe₂{μ-CNC(O)SR}(μ-CO)(CO)₂(cp)₂] (R = Me *or* Et).—The room-temperature reaction between the cationic thiocarbyne derivatives [Fe₂(μ-CSR)(μ-CO)(CO)₂(cp)₂]⁺[9] and NBuⁿ₄NCO, in CH₂Cl₂, affords the neutral μ-carbothioalkoxy isocyanide [Fe₂{μ-CNC(O)SR}(μ-CO)(CO)₂(cp)₂][R = Me(**1a**) or Et(**1b**)](60%) together with minor amounts (5—10%) of the cyanato complexes [Fe₂(μ-CSR)(μ-CO)(CO)(NCO)(cp)₂]. The separation of the reaction products has been achieved by column chromatography.

The nature of complexes (**1a**) and (**1b**) has been ascertained by X-ray structure determination of (**1b**), whereas that of the red-brown air-stable cyanato derivatives has been established from the similarities of their spectral data with those of the analogous [Fe₂(μ-CSR)(μ-CO)(CO)X(cp)₂] (X = SCN or I)[9,10] in which X and a CO are terminal ligands in *cis* position in relation to the Fe–Fe bond. Furthermore the presence of the terminal N-bonded NCO group is confirmed by the occurrence of the two v_{sym} and v_{asym} bands at 1 313 and 2 240 cm⁻¹.

The formation of isocyanide derivatives may be seen as an insertion of the cyanate ion into the carbon–sulphur bond of the thiocarbyne precursor. The mechanism of this unprecedented reaction could imply a 1—2 cycloaddition of NCO⁻ at the C–S bond through attack of the cyanate ion at the electrophilic
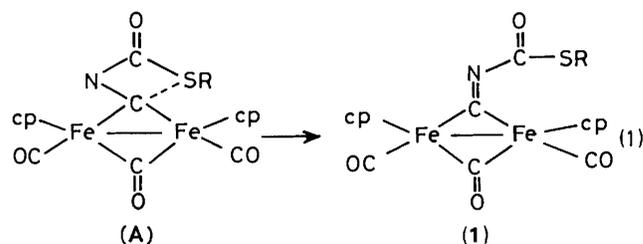
(A)　　　　　　(1)

μ-thiocarbyne-carbon centre, which is known to undergo nucleophilic addition by cyanide ion.[9]

Step (1) shows the strained spirocyclic intermediate (A) which undergoes ring opening via C–S bond breaking, to yield the functionalized isocyanide derivative (1).

The described mechanism may also explain the conversion of co-ordinated CS into a CN group observed in an earlier study of the reaction (2) between $[Fe(CO)_2(CS)(cp)]^+$ and $NCO.^{-11}$ Also in this strictly related reaction mechanism the unstable cyclocarbene intermediate (B) decomposes to give the cyano complex by elimination of carbonyl sulphide.

$$\left[\begin{array}{c} CO \\ | \\ cp-Fe-CS \\ | \\ CO \end{array}\right]^+ \xrightarrow{+NCO^-} \begin{array}{c} CO \\ | \\ cp-Fe-C \\ | \\ CO \end{array}\begin{array}{c} S \\ \diagup \quad \diagdown \\ \quad\quad C=O \\ \diagdown \quad \diagup \\ N \end{array}$$

(B)

$$\diagup -COS$$

$$\begin{array}{c} CO \\ | \\ cp-Fe-CN \\ | \\ CO \end{array} \quad (2)$$
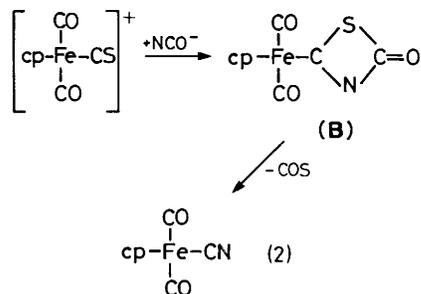
The low yield of $[Fe_2(\mu\text{-CSR})(\mu\text{-CO})(CO)(NCO)(cp)_2]$ is attributed to a competitive slower CO substitution process. The observation that the related CO substitution reactions of $[Fe_2(\mu\text{-CSR})(\mu\text{-CO})(CO)_2(cp)_2]^+$ with SCN^- or I^- occur in refluxing acetone or acetonitrile supports our view and indicates that the nucleophilic addition at the μ-thiocarbyne carbon, which promotes the formation of complex (1), is kinetically favoured under our experimental conditions.

In agreement with the cis configuration found in the solid state, the i.r. spectra of type (1) derivatives in KBr pellets show two terminal ν(CO) bands (1 995s and 1 957m cm⁻¹), a single bridging carbonyl absorption (1 808 cm⁻¹), and two bands at 1 665 and 1 625 cm⁻¹ which are attributed to the ν(CO) and ν(CN) of the bridging isocyanide group, respectively. The same

pattern is found in CH_2Cl_2 (Table 1), however the i.r. spectra in different solvents show that the relative intensities of the terminal ν(CO) bands vary in a consistent manner on increasing the solvent polarity (Table 2).

The ν(CO) solvent dependence, which is similar to those observed for $[Fe_2(CO)_4(cp)_2],^{12}$ $[Ru_2(CO)_4(cp)_2],^{13}$ and $[Fe_2(CO)_3(CS)(cp)_2],^{14}$ indicates the existence of a mixture of cis and trans isomers with the cis-(1) complexes favoured in polar solvents. Furthermore, the absence in all the solvents examined of an additional band in the 1 700—2 200 cm⁻¹ range, where the ν(CN) of the terminally bonded CNC(O)SR group is expected, suggests that the isocyanide ligand occupies the bridging position in both forms. Interconversion of the isomers can occur by the Adams–Cotton mechanism proposed for the isomerization of $[Fe_2(CO)_4(cp)_2].^{15}$

$$\begin{array}{cc} \text{cis - (1)} & \text{trans - (1)} \end{array}$$
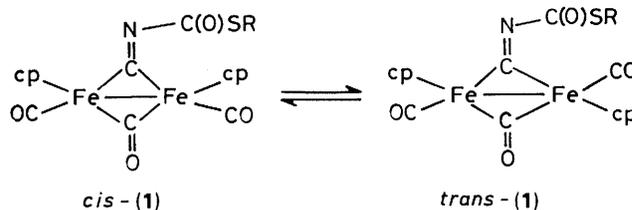
Type (1) complexes are, together with $[Fe_2\{\mu\text{-CNPh}\}(\mu\text{-CO})(CO)_2(cp)_2]$, the only di-iron monosubstituted-isocyanide derivatives in which the CNR ligand adopts the bridging position.[16]

Comparison of the ν(CO) frequencies of the cis-$[Fe_2(\mu\text{-L})(\mu\text{-CO})(CO)_2(cp)_2]$ [L = CO, CS, CNPh, CNC_6H_{11}, or CNC(O)SMe] derivatives (Table 3) reveals that the π/σ bonding properties of the μ-L group decrease in the order CS ~ CNC(O)SMe > CO > CNPh > CNR (R = alkyl). The high π/σ ratio of the μ-CNC(O)SR ligands, attributable to the powerful electron-withdrawing effect of the C(O)SR group, is typical of terminal acyl isocyanides which have been recently

Table 1. Analytical[a] and physical data

	Complex	M.p.[b] °C	Colour	Yield (%)	ν(CO)[c]/cm⁻¹	Analysis (%) C	H
(1a)	$[Fe_2\{\mu\text{-CNC(O)SMe}\}(\mu\text{-CO})(CO)_2(cp)_2]$	123—125	Red	63	2 004s, 1 966mw, 1 802m, 1 667m (sh), 1 632m	45.0 (45.0)	3.0 (3.1)
(1b)	$[Fe_2\{\mu\text{-CNC(O)SEt}\}(\mu\text{-CO})(CO)_2(cp)_2]$	115—117	Red	61	2 004s, 1 966mw, 1 802m, 1 666m (sh), 1 631m	46.3 (46.3)	3.3 (3.4)
(2a)	$[Fe_2\{\mu\text{-CN(Me)C(O)SMe}\}(\mu\text{-CO})(CO)_2(cp)_2]^+$	132—134	Dark red	79	2 036s, 2 003w, 1 843m, 1 717m, 1 460m [ν(CN)][d]	36.2 (36.6)	3.0 (2.7)
(2b)	$[Fe_2\{\mu\text{-CN(Me)C(O)SEt}\}(\mu\text{-CO})(CO)_2(cp)_2]^+$	128—130	Dark red	76	2 035s, 2 005w, 1 842m, 1 715m, 1 464m [ν(CN)][d]	37.8 (37.7)	3.3 (3.0)
(2c)	$[Fe_2\{\mu\text{-CN(Et)C(O)SMe}\}(\mu\text{-CO})(CO)_2(cp)_2]^+$	125—128	Dark red	61	2 035s, 2 001w, 1 840m, 1 710m, 1 475m [ν(CN)][d]	38.0 (37.7)	3.4 (3.0)
(2d)	$[Fe_2\{\mu\text{-CN(H)C(O)SMe}\}(\mu\text{-CO})(CO)_2(cp)_2]^+$	144—146	Dark red	54	2 043s, 2 013w, 1 842m, 1 728m, 1 492m [ν(CN)][d]	35.1 (35.4)	2.9 (2.4)
(3a)	$[Fe_2\{\mu\text{-C(CN)N(Me)C(O)SMe}\}(\mu\text{-CO})(CO)_2(cp)_2]$	173—175	Red	71	2 159w [ν(CN)], 2 009s, 1 970w, 1 806m, 1 647m	45.0 (44.8)	3.6 (3.5)
(3b)	$[Fe_2\{\mu\text{-C(CN)N(Me)C(O)SEt}\}(\mu\text{-CO})(CO)_2(cp)_2]$	156—158	Red	68	2 160w [ν(CN)], 2 008s, 1 971w, 1 806m, 1 647m	46.0 (46.0)	3.5 (3.7)
(3c)	$[Fe_2\{\mu\text{-C(CN)N(Et)C(O)SMe}\}(\mu\text{-CO})(CO)_2(cp)_2]$	165—167	Red	65	2 159w [ν(CN)], 2 010s, 1 970w, 1 806m, 1 642m	46.1 (46.0)	3.5 (3.7)
(3d)	$[Fe_2\{\mu\text{-C(H)N(Me)C(O)SMe}\}(\mu\text{-CO})(CO)_2(cp)_2]$	191—195	Red	53	1 970s, 1 934w, 1 780m, 1 630m	45.9 (46.1)	4.1 (3.9)
(3e)	$[Fe_2\{\mu\text{-C(H)N(Et)C(O)SMe}\}(\mu\text{-CO})(CO)_2(cp)_2]$	170—175	Red	48	1 970s, 1 935w, 1 777m, 1 626m	47.4 (47.3)	4.4 (4.2)

[a] Required values are given in parentheses. [b] With decomposition. [c] In dichloromethane. [d] In KBr pellets.

Table 2. Carbonyl stretching bands (cm^{-1}) for [Fe$_2${μ-CNC(O)SMe}(μ-CO)(CO)$_2$(cp)$_2$] in Various Solvents at Room Temperature

Solvent	v(CO)*
Cyclohexane	2 010(10), 1 971(9.7)
CS$_2$	2 006(10), 1 967(7.8)
CHCl$_3$	2 010(10), 1 971(5.2)
CH$_2$Cl$_2$	2 005(10), 1 966(4.1)
MeCN	2 000(10), 1 961(2.3)

* Intensities in absorbance units relative to the high-frequency absorption are given in parentheses.

Table 3. I.r. data, v(CO)/cm^{-1} in CS$_2$, for binuclear iron compounds

Complex	
cis-[Fe(CO)$_2$(cp)]$_2$[a]	2 001, 1 957, 1 785
cis-[Fe$_2$(CO)$_3$(CS)(cp)$_2$][b]	2 006, 1 969, 1 811
cis-[Fe$_2${CNC(O)SMe}(CO)$_3$(cp)$_2$]	2 006, 1 967, 1 808
	2 010, 1 971, 1 813[c]
cis-[Fe$_2$(CNC$_6$H$_{11}$)(CO)$_3$(cp)$_2$][d]	1 987, 1 948, 1 757
cis-[Fe$_2$(CNPh)(CO)$_3$(cp)$_2$][e]	1 997, 1 954, 1 807[c]

[a] Ref. 13. [b] Ref. 14. [c] In cyclohexane. [d] Ref. 18. [e] Ref. 16.

Table 4. Proton N.m.r. data[a]

Complex	^{1}H (δ)[b]
(1a)	4.88, 4.82 (10 H, s, C$_5$H$_5$), 2.49, 2.46 (3 H, s, CH$_3$)[c]
(1b)	4.86, 4.82 (10 H, s, C$_5$H$_5$), 3.03 (2 H, q, CH$_2$CH$_3$), 1.42 (3 H, t, CH$_2$CH$_3$)
(2a)	5.3 (10 H, s, br, C$_5$H$_5$), 4.52 (3 H, s, NCH$_3$), 2.61 (3 H, s, SCH$_3$)
(2b)	5.3 (10 H, s, br, C$_5$H$_5$), 4.48 (3 H, s, NCH$_3$), 3.17 (2 H, q, CH$_2$CH$_3$), 1.46 (3 H, t, CH$_2$CH$_3$)
(2c)	5.70 (5 H, s, C$_5$H$_5$), 5.51 (5 H, s, C$_5$H$_5$), 5.16 (2 H, q, CH$_2$CH$_3$), 2.86 (3 H, s, SCH$_3$), 1.67 (3 H, t, CH$_2$CH$_3$)[d]
(2d)	5.26 (10 H, s, C$_5$H$_5$), 2.56 (3 H, s, CH$_3$)[e]
(3a)	4.92 (10 H, s, C$_5$H$_5$), 3.58 (3 H, s, NCH$_3$), 2.30 (3 H, s, SCH$_3$)
(3b)	4.91 (10 H, s, C$_5$H$_5$), 3.55 (3 H, s, NCH$_3$), 2.97 (2 H, q, CH$_2$CH$_3$), 1.23 (3 H, t, CH$_2$CH$_3$)
(3c)	4.91 (10 H, s, C$_5$H$_5$), 4.07 (2 H, q, NCH$_2$CH$_3$), 2.29 (3 H, s, SCH$_3$), 1.70 (3 H, t, NCH$_2$CH$_3$)
(3d)	12.91[1 H, s, μ-CHN(R)C(O)SR], 4.83 (10 H, s, C$_5$H$_5$), 3.10 (3 H, s, NCH$_3$), 2.51 (3 H, s, SCH$_3$)
(3e)	12.61 [1 H, s, μ-CHN(R)C(O)SR], 4.82 (10 H, s, C$_5$H$_5$), 3.34 (2 H, q, NCH$_2$CH$_3$), 2.48 (3 H, s, SCH$_3$), 1.31 (3 H, t, NCH$_2$CH$_3$)

[a] Chemical shifts (δ) referred to SiMe$_4$. [b] measured in CDCl$_3$. [c] Signals due to the *trans* isomer are italicized. [d] In CD$_3$COCD$_3$. [e] In CD$_3$CN.

demonstrated to act as strong π-acceptor ligands.[3,17] The preference for the bridging site of the carbothioalkoxy isocyanide group in type (1) derivatives may be a consequence of their good π-acceptor ability.[18]

Infrared spectra in solution at room temperature reveal that the cis-(1) ⇌ trans-(1) equilibrium is established very rapidly since there is no change in the v(CO) intensities with time. Accordingly, the ^{1}H n.m.r. spectrum of complex (1a) in CDCl$_3$ solvent (Table 4) shows two cp and two SMe singlets attributable to the two isomers present in solution with a cis-(1a): trans-(1a) ratio of about 3:1. The ^{13}C n.m.r. spectrum in CD$_2$Cl$_2$ solution again indicates the presence of two isomers. The lowest-field resonances at 273.3 [trans-(1a)] and 271.8 p.p.m. [cis-(1a)], with an intensity ratio of about 1:3.5, are assigned to the carbon of the bridging CO groups, whereas those at 268.0 [trans-(1a)] and 267.7 p.p.m. [cis-(1a)] are attributed to the bridging carbons of the isocyanide ligand in

Table 5. Relevant bond distances (Å) and angles (°) for complex (1b)

Fe(1)–Fe(2)	2.514(1)	C(3)–O(3)	1.13(1)
Fe(1)–C(1)	1.93(1)	N–C(4)	1.24(1)
Fe(2)–C(1)	1.93(1)	N–C(5)	1.40(1)
Fe(1)–C(2)	1.74(1)	C(5)–O(4)	1.19(1)
Fe(2)–C(3)	1.75(1)	C(6)–C(7)	1.51(1)
Fe(1)–C(4)	1.92(1)		
Fe(2)–C(4)	1.90(1)	mean Fe–C(cp)	
S–C(5)	1.74(1)	Fe(1)–C(8—12)A	2.14(2)
S–C(6)	1.83(1)	Fe(1)–C(8—12)B	2.11(4)
C(1)–O(1)	1.16(1)	Fe(2)–C(13—17)A	2.12(3)
C(2)–O(2)	1.14(1)	Fe(2)–C(13—17)B	2.13(3)
Fe(1)–C(1)–O(1)	140(1)	Fe(1)–C(4)–Fe(2)	83(1)
Fe(2)–C(1)–O(1)	138(1)	C(4)–N–C(5)	130(1)
Fe(1)–C(2)–O(2)	180(1)	N–C(5)–O(4)	125(1)
Fe(2)–C(3)–O(3)	179(1)	N–C(5)–S	112(1)
Fe(1)–C(4)–N	141(1)	S–C(5)–O(4)	122(1)
Fe(2)–C(4)–N	137(1)	C(5)–S–C(6)	100(1)
Fe(1)–C(1)–Fe(2)	82(1)	S–C(6)–C(7)	109(1)

the two isomers. The latter are the lowest chemical shifts yet observed for a μ-CNR group in di-iron complexes.[19]

The Molecular Structure of cis-[Fe$_2${μ-CNC(O)SEt}(μ-CO)-(CO)$_2$(cp)$_2$] (1b).—The geometry of the molecule is shown in Figure 1, bond distances and angles in Table 5. The molecule exhibits the same basic structure as in the parent cation cis-[Fe$_2$(μ-CSEt)(μ-CO)(CO)$_2$(cp)$_2$]$^+$.[20] The differences derive from the unprecedented insertion of a cyanate ion into the μ-CSEt bond. The entering group binds through its N end to the bridging carbon [C(4)] while the SEt group is bonded to C(5). The new ligand can be rationalized in terms of two fragments. The atom sequence around C(5) can be regarded as a derivative of the S-ethyl ester of the monothiocarbamic acid, while the metal-bonded termination is an isocyanide group adopting a bridging co-ordination to two metal centres. Typically, the bridging isocyanide exhibits bent geometry at the nitrogen atom [C(4)–N–C(5) 130(1)°]. In spite of the planar hybridization of all the atoms in the ligand (except the terminal ethyl), the isocyanide and the thiocarbamate moieties have separated π-bond systems. In fact no conjugation takes place through the N–C(5) interaction because the O(4)–C(5)–S and Fe$_2$C(4)N groupings adopt an almost orthogonal orientation in the crystal [torsion angle around N–C(5) 73°]. Electronically favoured all-planar conformations are hindered by steric factors. The molecule is chiral but the crystal contains the racemic mixture. An inspection of Figure 1 shows that the SEt group is located *syn* to the CO ligands, similarly to the SMe group in [Fe$_2${μ-C(CN)SMe}(μ-CO)(CO)$_2$(cp)$_2$].[9] This may indicate that the directions of attack of NCO$^-$ and CN$^-$ are the same (see above) and that the SMe groups does not leave the previously occupied region of space upon NCO$^-$ insertion. Electron delocalization in the O(4)C(5)S system is evidenced by a comparison of the C(5)–S and S–C(6) (alkyl) bonds [1.74(1) and 1.83(1) Å] and by the in-plane position of C(6) [O(4)–C(5)–S–C(6) torsion angle 3°]. The two N–C bonds [N–C(4) and N–C(5), 1.24(1) and 1.40(1) Å] clearly show the double-bond character of N–C(4). Although the C(4)–Fe distances [1.90(1) and 1.92(1) Å] are not significantly different, some opening of the C(4)–N–C(5) angle [130(1)°] indicates unbalanced steric pressure caused by the bent ligand geometry. All the described values are comparable with those found in a host of similar molecules and fragments. A typical comparison can be made with the geometry of [Fe$_2$(μ-CNPh)$_2$(CNPh)$_2$(cp)$_2$] [Fe-Fe 2.523(1), Fe-(μ-C) 1.905, 1.934(6), (μ-C)–N 1.242(8), and N–C(phenyl) 1.414(7) Å; (μ-C)–N–C(phenyl) 126.4(5)].[21] The
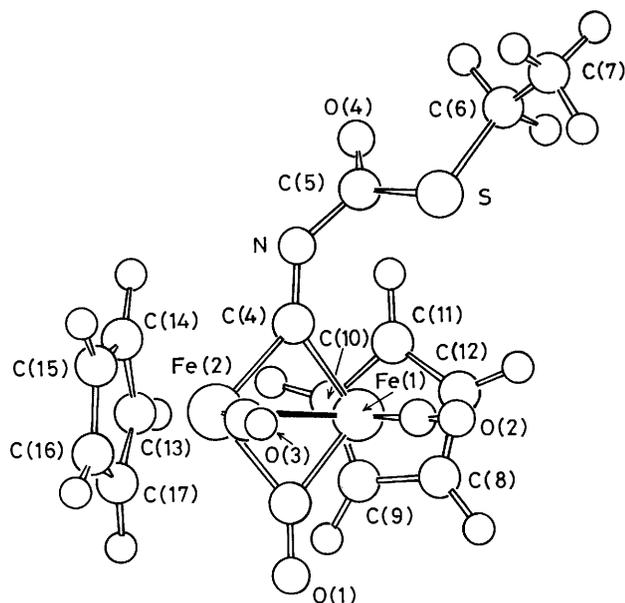
Figure 1. Perspective drawing of the molecule (**1b**)

mode of bonding of the bridging C(4) can be rationalized in line with that adopted for cis-[Fe$_2${μ-C(CN)SMe}(μ-CO)(CO)$_2$(cp)$_2$].[9] Peculiar to the present species is the linear hybridization of the C(4) orbitals so that the p_y and p_z orbitals can be used for bonding to N and Fe$_2$. Another feature is the expected folding of the bridging ligands towards the terminal CO groups (dihedral angle 165°).

Reactions of [Fe$_2${μ-CNC(O)SR}(μ-CO)(CO)$_2$(cp)$_2$].—It is known that the nitrogen atoms of the CNR ligands (R = alkyl or aryl) in [Fe$_2$(CO)$_3$(CNR)(cp)$_2$] are very susceptible to protonation[22] or alkylation.[23] The cationic products of these reactions contain the μ-CN(R')R group (R' = H or alkyl). A similar acylation reaction with ClC(O)R' (R' = alkyl) has been found to afford [Fe$_2${μ-CN(R)C(O)R'}(μ-CO)(CO)$_2$(cp)$_2$] $^+$, described to be unstable.[24]
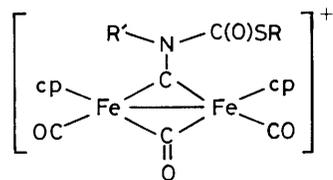
	R	R'
(2a)	Me	Me
(2b)	Et	Me
(2c)	Me	Et
(2d)	Me	H

We have found that the reaction of complex (**1**) with R'OSO$_2$CF$_3$ (R' = Me or Et) in CH$_2$Cl$_2$ solution forms red derivatives (**2a**)—(**2c**) in about 80% yield. These complexes can be stored under nitrogen for several months, but they slowly decompose in CH$_2$Cl$_2$ solution. The N-alkylation reaction takes 4 h to go to completion, but with the weaker alkylating agent MeI no reaction occurs even on refluxing the reactants for 12 h in CH$_2$Cl$_2$. The known N-methylation of [Fe$_2$(CO)$_3$(CNR)(cp)$_2$] (R = Me, Et, Pr^i, or CH$_2$Ph) with MeI[23] and the fact that some of the μ-CNR derivatives (R = Me, Et, or Pr^i) are readily alkylated (30 min) with MeSO$_3$CF$_3$

or [OEt$_3$][BF$_4$][18,23] suggest that the electron-withdrawing C(O)SR group decreases the N atom nucleophilicity and then the reactivity towards the electrophilic addition of R$^+$ or that of the nucleophilic substitution on MeI. The low basicity of the nitrogen atom is confirmed by its reaction with acids. Only the strong trifluoromethanesulphonic acid is capable of partially forming [Fe$_2${μ-CN(H)C(O)SMe}(μ-CO)(CO)$_2$(cp)$_2$] $^+$ (**2d**) in equilibrium with the unprotonated species in CH$_2$Cl$_2$. Complex (**2d**) has been isolated by carrying out the protonation reaction in CH$_2$Cl$_2$—Et$_2$O (1:1). Dissolution of the precipitated hygroscopic solid, which has been characterized by i.r. spectroscopy in KBr pellets, reproduces the equilibrium mixture.

The spectroscopic properties of derivatives (**2a**)—(**2d**) are in agreement with a *cis* structure and comparable with those of the related [Fe$_2${μ-CN(R)R'}(μ-CO)(CO)$_2$(cp)$_2$] $^+$ (R = R' = alkyl) which have been found also to adopt *cis* geometry both in solution and in the solid state.[16,17] The v(CO) band patterns of (**2**), which are similar both in the solid state and in solution (Table 1), do not change either on standing at room temperature in solution or by varying the solvent polarity. This observation indicates that *cis*-(**2a**)—(**2d**) are not detectably converted into the *trans* isomers. Although *trans*-(**1**) is approximately 33% abundant in CH$_2$Cl$_2$, no *trans*-(**2**) is produced upon alkylation. This may be attributed to a rapid isomerization of the *trans* isomer possibly formed from *trans*-(**1**). Further stereochemical information on the cationic derivatives (**2**) comes from their ^{1}H n.m.r. spectra (Table 4). The cp resonances appear as broad (**2a**; R = R' = Me) or separate singlets of equal intensities (**2b**; R' = Me, R = Et). The nonequivalence of the cp groups is attributed to hindered rotation about the C–N bond of the bridging ligand (see previous section).

The v(CN) of type (**2**) complexes occurs 100—130 cm^{-1} to lower wavenumber with respect to that of the related cation [Fe$_2${μ-CN(R)C(O)R'}(μ-CO)(CO)$_2$(cp)$_2$] $^+$ (R = R' = alkyl)[24] and 180—230 cm^{-1} lower than for the iminium cations [R$_2$C=NR$_2$] $^+$.[25] Such shifts are consistent with a strong decrease in the C=N bond order due to the C(O)SR group bonded to the sp^2-hybridized N atom which causes extensive π-electron delocalization in the presumably planar Fe$_2$[μ-CN(R')C(O)SR] fragment. These observations suggest that the bridging group may be regarded as a carbyne ligand. Accordingly the ^{13}C n.m.r. spectrum of complex (**2a**) shows the μ-C resonance at δ 343.29 p.p.m. This signal is about 60 p.p.m. upfield with respect to that found for [Fe$_2$(μ-CSR)(μ-CO)(CO)$_2$(cp)$_2$] $^+$,[10] but about 25 p.p.m. downfield of that for [Fe$_2${μ-CN(R')R}(μ-CO)(CO)$_2$(cp)$_2$] $^+$.[23] The reactivity of (**2**) with nucleophiles confirms our prediction. The bridging aminocarbyne is converted by CN$^-$ or H$^-$ into the aminocarbene μ-
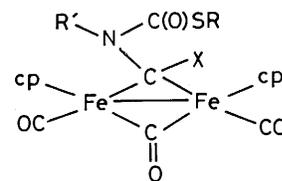
	X	R'	R
(3a)	CN	Me	Me
(3b)	CN	Me	Et
(3c)	CN	Et	Me
(3d)	H	Me	Me
(3e)	H	Me	Et

[C(X)N(R')C(O)SR] (X = CN or H) group *via* nucleophilic addition at the carbyne carbon atom.

The air-stable neutral derivatives [Fe$_2${μ-C(X)N(R')C(O)-

Table 6. Relevant bond distances (Å) and angles (°) for complex (**3a**)

Fe(1)–Fe(2)	2.506(1)	N(1)–C(6)	1.463(5)
Fe(1)–C(1)	1.886(3)	O(4)–C(5)	1.209(5)
Fe(2)–C(1)	1.924(3)	S–C(5)	1.785(4)
Fe(2)–C(2)	1.758(4)	S–C(8)	1.786(7)
Fe(1)–C(3)	1.758(4)	C(4)–C(7)	1.438(5)
Fe(1)–C(4)	1.995(3)	N(2)–C(7)	1.149(5)
Fe(2)–C(4)	1.991(3)		
C(1)–O(1)	1.184(4)	Mean Fe–C(cp)	
C(2)–O(2)	1.139(5)		
C(3)–O(3)	1.145(5)	Fe(1)–C(9—13)	2.110(4)
C(4)–N(1)	1.492(4)	Fe(2)–C(14—18)	2.103(4)
N(1)–C(5)			
		Mean C–C(cp)	
		C(9—13)	1.405(4)
		C(14—18)	1.394(4)
Fe(1)–C(1)–O(1)	140.1(3)	C(4)–N(1)–C(6)	117.9(3)
Fe(2)–C(1)–O(1)	137.6(3)	C(4)–N(1)–C(5)	118.1(3)
Fe(2)–C(2)–O(2)	177.2(4)	C(5)–N(1)–C(6)	119.6(3)
Fe(1)–C(3)–O(3)	178.2(3)	N(1)–C(5)–O(4)	124.3(3)
Fe(1)–C(4)–Fe(2)	77.9(1)	N(1)–C(5)–S	114.1(3)
N(1)–C(4)–C(7)	105.3(3)	S–C(5)–O(4)	121.4(3)
C(4)–C(7)–N(2)	177.2(4)	C(5)–S–C(8)	98.7(3)

Figure 2. Perspective drawing of the molecule (**3a**)

SR}(μ-CO)(CO)₂(cp)₂] (**3**) are obtained in about 60% yield, but if traces of water are present or added to the reaction mixture the yield is reduced because of the concomitant formation of the isocyanide complexes [Fe₂(CO)₃(CNR′)(cp)₂] (R′ = Me or Et). The latter have been characterized by i.r. spectroscopy after separation by column chromatography. Their formation is due to the hydrolysis of the N–C bond in R′N–C(O)SR which liberates the thiolcarbonate HOC(O)SR. The quantitative yield in [Fe₂(CO)₃(CNR′)(cp)₂] from (**2a**)— (**2c**) and methoxide ion in methanol demonstrates our view and suggests an alternative route to the synthesis of di-iron isocyanide complexes.

The spectroscopic properties of the substituted μ-methylene derivatives (**3**) are in agreement with the structure of the cyanide adduct (**3a**) established by X-ray crystallography. The molecule [Fe₂{μ-C(CN)N(Me)C(O)SMe}(μ-CO)(CO)₂(cp)₂] retains the *cis* geometry of the precursor (**1**) and, like the previously reported addition of CN⁻ to carbyne carbon atoms,[9] the cyanide ion diastereoselectively adds *syn* to the cp ligands (see next section). The ability of CN⁻ specifically to add at electrophilic carbon centres is confirmed by the lack of CO-substituted derivatives. The only ν(CN) observed in the reaction mixture is that attributable to a cyano group bonded to a *sp*² carbene-carbon atom of cyanocarbene derivatives.[9,26] The i.r. spectra of

type (**3**) carbene derivatives do not evidence, as in the case of complexes (**2**), *cis–trans* isomerization in solution. Furthermore, the appearance of single signals for both methylene protons in (**3d**) and (**3e**) and for cp groups in (**3a**)—(**3e**) in their ¹H n.m.r. spectra (Table 1) confirms the presence of only the *cis* isomer in solution at room temperature.

The Molecular Structure of cis-[Fe₂{μ-C(CN)N(Me)C(O)S-Me}(μ-CO)(CO)₂(cp)₂] (**3a**).—This species precipitates in two types of red crystals, one is monoclinic with a blade-like habit, the other orthorhombic with stubby multifaceted crystals. As the presence of stereoisomers was possible, the structures of both crystals were determined. Either the crystals contain the same chiral molecule crystallized as a racemic mixture in the monoclinic species or as separate enantiomers in the ortho-rhombic modification. Here we describe only the molecule in the rhombic crystals because this structure was more accurate.

The crystal used in the diffraction experiment contains molecules of the same chirality whose absolute configuration is shown in Figure 2; bond distances and angles are listed in Table 6. This species derives from the just described *cis-*[Fe₂{μ-CNC(O)SR}(μ-CO)(CO)₂(cp)₂] by methylation of N(1) and nucleophilic addition of a CN⁻ ion at C(4). The geometry of the Fe₂(μ-CO)(CO)₂(cp)₂ moiety is unchanged. It is noteworthy that the Fe–Fe distance [2.506(1) Å] is almost equal to that in the parent compound [2.514(1) Å], in spite of the substantial changes at the bridging C(4) that now bears a CN group and has lost the double-bond character of the C(4)–N(1) interaction [1.492(4) against 1.24(1) Å in the parent species]. The C(4)–Fe bonds, on the other hand, are significantly elongated [1.993(3) against 1.91(1) Å] as a consequence of the increased co-ordination number of C(4), and comparable to that in *cis-*[Fe₂{μ-C(CN)SMe}(μ-CO)(CO)₂(cp)₂][9] [1.994(5) Å]. The geometry of the CN group bonded to C(4) is substantially equivalent to that in *cis-*[Fe₂{μ-C(CN)SMe}(μ-CO)(CO)₂-(cp)₂] [C–C and C–N 1.438(5) and 1.149(5) against 1.440(5) and 1.152(3) Å, respectively]. Atom N(1) is the second atom at which substantial change has occurred, not only as a consequence of the methylation but also because of the just

cited single-bond character of the C(4)–N(1) interaction. It exhibits planar co-ordination geometry and its lone pair is delocalized into the orbitals of the N(1)–C(5)–O(4) unit. The double-bond character of the N(1)–C(5) interaction is demonstrated by its length [1.367(5) Å] which is some 0.1 Å shorter than the other N(1)–C bonds. There is no evidence of double-bond character in S–C(5) [compare C(5)–S 1.785(4) with S–C(8) (methyl) 1.786(7) Å], probably because interactions are preferentially established among O(4), C(5), and N(1). The bond at C(5) should be compared with the corresponding one in the parent species. Small but concerted changes, *i.e.* lengthening of C(5)–S (0.04 Å) and shortening of C(5)–N(1) (0.03 Å), originate from the actual conformation of the C(5)–N(1)–O(4)–S grouping, allowing the p_z orbital of N(1) to interact with those of C(5) and O(4). In conclusion this heteroatom grouping could be described, as in the parent molecule, as a monothiocarbamate unit, but it is significant that the atoms involved in the stronger bonds define a methyl isocyanate sequence.

Experimental

All the 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. The compounds [Fe$_2$(μ-CSR)(μ-CO)(CO)$_2$(cp)$_2$][SO$_3$CF$_3$] (R = Me or Et) were prepared by the reported procedures.[8]

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 wavenumbers (± 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 determined by Pascher Microanalytical Laboratorium (Bonn, Germany). Melting points were uncorrected. Analytical data and physical properties of the complexes are in Table 1.

Synthesis of the Complexes.—[Fe$_2${μ-CNC(O)SR}(μ-CO)(CO)$_2$(cp)$_2$] [R = Me (1a) *or* Et (1b)]. A dichloromethane solution (5 cm^3) of NBu$^n_4$NCO (0.32 g, 1.12 mmol) was added dropwise to the complex [Fe$_2$(μ-CSMe)(μ-CO)(CO)$_2$(cp)$_2$]-[SO$_3$CF$_3$] (0.48 g, 0.90 mmol) in CH$_2$Cl$_2$ (30 cm^3). The mixture was stirred for 30 min then the solvent was removed *in vacuo* and the residue chromatographed on an alumina column (4 × 15 cm). Gradient elution with CH$_2$Cl$_2$—light petroleum (b.p. 40—60 °C) (1:2 increasing to 1:1) gave first a red band containing a small amount of the complex [{Fe(CO)$_2$(cp)}$_2$]. A second red band was collected and evaporated to dryness. The residual solid was dissolved in CH$_2$Cl$_2$ (2 cm^3), layered with n-pentane, and cooled to −20 °C affording red crystals of complex (1a) (0.24 g, 63%). A third brown fraction was collected, dried under high vacuum, and the residue, recrystallized from CH$_2$Cl$_2$–Et$_2$O mixture at −20 °C, gave [Fe$_2$(μ-CSMe)(μ-CO)(CO)(NCO)(cp)$_2$] (0.04 g, 11%), m.p. 126—128 °C (decomp.) (Found: C, 45.2; H, 3.5 C$_{15}$H$_{13}$Fe$_2$NO$_3$S requires C, 45.2; H, 3.3%); ν(CO) 2 004s, 1 821s, ν$_{asym}$ (NCO) 2 240s cm^{-1} (CH$_2$Cl$_2$ solution). δ$_H$(CD$_2$Cl$_2$) 4.90 (5 H, s, C$_5$H$_5$), 4.78 (5 H, s, C$_5$H$_5$), and 3.70 (3 H, s, CH$_3$).

Complex (1b) and [Fe$_2$(μ-CSEt)(μ-CO)(CO)(NCO)(cp)$_2$] were analogously prepared from [Fe$_2$(μ-CSEt)(μ-CO)(CO)$_2$-(cp)$_2$][SO$_3$CF$_3$]: (1b) (0.24 g, 61%); δ$_C$ (CD$_2$Cl$_2$), *cis*-(1b) 271.8 (μ-CO), 267.7 (μ-CNCOSEt), 210.4 (CO), 173.2 (COSEt), 82.5 (C$_5$H$_5$), 25.6 (CH$_2$CH$_3$), and 15.35 (CH$_2$CH$_3$); *trans*-(1b) 273.3 (μ-CO), 268.0 (μ-CNCOSEt), 210.8 (CO), 173.2 (COSEt), 90.2 (C$_5$H$_5$), 30.0 (CH$_2$CH$_3$), and 15.3 (CH$_2$CH$_3$) p.p.m.; [Fe$_2$(μ-

CSEt)(μ-CO)(CO)(NCO)(cp)$_2$] (0.03 g, 8%), m.p. 108—110 °C (decomp.) (Found: C, 46.6; H, 3.8. C$_{16}$H$_{15}$Fe$_2$NO$_3$S requires C, 46.5; H, 3.7%); ν(CO) 2 003s, 1 822s, ν$_{asym}$(NCO) 2 240s cm^{-1} (CH$_2$Cl$_2$ solution); δ$_H$ (CDCl$_3$) 4.85 (5 H, s, C$_5$H$_5$), 4.76 (5 H, s, C$_5$H$_5$), 4.12 (2 H, s, CH$_2$CH$_3$), and 1.63 (3 H, s, CH$_2$CH$_3$).

[Fe$_2${μ-CN(R′)C(O)SR}(μ-CO)(CO)$_2$(cp)$_2$][SO$_3$CF$_3$] [R′ = R = Me (2a); R′ = Me, R = Et (2b); R′ = Et, R = Me (2c)]. Stoicheiometric amounts of CF$_3$SO$_3$Me were added to a CH$_2$Cl$_2$ solution (20 cm^3) of complex (1a) (0.30 g, 0.70 mmol). The mixture was stirred for 2 h at room temperature, then the solvent was removed *in vacuo*. The red oily residue was washed with Et$_2$O (2 × 5 cm^3) and crystallized from CH$_2$Cl$_2$—Et$_2$O at −20 °C, affording red microcrystals of (2a) (0.33 g, 79%); δ$_C$ (CD$_2$Cl$_2$) 343.3 (μ–C), 253.5 (μ-CO), 208.5 (CO), 174.6 (COSMe), 92.3 (C$_5$H$_5$), 53.0 (NMe), and 15.4 p.p.m. (SMe).

The preparation of the complexes (2b) and (2c) differed only in the reaction times, 3 and 6 h respectively.

[Fe$_2${μ-CN(H)C(O)SMe}(μ-CO)(CO)$_2$(cp)$_2$][SO$_3$CF$_3$] (2d). A dichloromethane solution (15 cm^3) of complex (1a) (0.25 g, 0.47 mmol) was stirred with a slight excess of CF$_3$SO$_3$H (0.09 g, 0.60 mmol) for 1 h. The solution was then evaporated to dryness under high vacuum and the red oily residue was washed with Et$_2$O (2 × 5 cm^3) and redissolved in CH$_2$Cl$_2$. Addition of Et$_2$O afforded a red microcrystalline precipitate of complex (2d) (0.15 g, 54%).

[Fe$_2${μ-C(CN)N(Me)C(O)SR}(μ-CO)(CO)$_2$(cp)$_2$] [R = Me (3a) *or* Et (3b)]. The crude complex (2a) (0.62 g, 1.05 mmol) was allowed to react with a slight excess of NBu$^n_4$CN (0.30 g, 1.10 mmol) in dichloromethane (15 cm^3). The mixture was stirred for 15 min, the solvent removed *in vacuo*, and the residue chromatographed on an alumina column (3 × 15 cm). Gradient elution with CH$_2$Cl$_2$–light petroleum (b.p. 40—60 °C)

Table 7. Summary of crystal data and intensity collection parameters[a]

Complex	(1b)	(3a)
Formula	C$_{17}$H$_{15}$Fe$_2$NO$_4$S	C$_{18}$H$_{16}$Fe$_2$N$_2$O$_4$S
M	441.1	467.8
Crystal size/mm	0.2 × 0.05 × 0.1	0.30 × 0.34 × 0.37
System	Monoclinic	Orthorhombic
Space group	$P2_1/n$	$P2_12_12_1$
a/Å	9.418(3)	9.238(3)
b/Å	14.827(3)	8.142(1)
c/Å	12.793(4)	24.712(2)
β/°	97.28(3)	—
U/Å^3	1 772.02	1 858.72
F(000)	896	952
D$_c$/g cm^{-3}	1.65	1.67
μ(Mo-K$_a$)/cm^{-1}	17.7	17.1
θ range/°	2.5—25	2.5—28
ω scan width/°	1.6 + 0.35 tan θ	0.9 + 0.35 tan θ
Requested counting σ(I)/I	0.01	0.01
Maximum scan time/s	150	140
Octants explored in reciprocal space	±h, +k, +l	+h, +k, +l
Measured reflections	3 531	2 512
Unique observed reflections [I$_o$ > 2.5σ(I$_o$)]	1 726	2 132
R, R'[b]	0.053, 0.057	0.028, 0.031
K, g[b]	0.25, 0.02	1.7, 0.0001
Residual peaks/e Å^{-3}	0.8	0.5
Minimum, maximum absorption correction factors[c]	0.7—1	0.85—1

[a] Details common to both structures: scan mode ω—2θ; pre-scan rate 6° min^{-1}; acceptance criterion σ(I)/I = 0.5; Z = 4. [b] R′ = Σ(F$_o$ − F$_c$)w$^{\frac{1}{2}}$/Σ(F$_o$w$^{\frac{1}{2}}$), where w = K/[σ^2(F) + |g|F^2]. [c] Applied by the Walker and Stuart method.

Table 8. Fractional atomic co-ordinates of complex (1b)

Atom	x	y	z	Atom	x	y	z
Fe(1)	0.396 9(1)	0.144 6(1)	0.875 0(1)	C(A11)	0.458 2(14)	0.179 7(7)	0.725 2(7)
Fe(2)	0.163 1(1)	0.188 4(1)	0.936 3(1)	C(A12)	0.570 2(14)	0.131 9(7)	0.786 3(7)
S	0.594 3(3)	0.390 6(2)	0.935 4(2)	C(B8)	0.445 7(22)	0.031 1(6)	0.787 2(11)
C(1)	0.268 8(7)	0.076 8(5)	0.950 7(5)	C(B9)	0.330 2(22)	0.076 9(6)	0.727 5(11)
O(1)	0.257 6(7)	0.005 5(4)	0.986 1(5)	C(B10)	0.376 3(22)	0.165 7(6)	0.707 5(11)
C(2)	0.511 9(7)	0.162 9(5)	0.990 6(6)	C(B11)	0.520 4(22)	0.174 7(6)	0.754 7(11)
O(2)	0.586 7(6)	0.175 2(4)	1.066 8(4)	C(B12)	0.563 3(22)	0.091 6(6)	0.804 0(11)
C(3)	0.222 1(7)	0.210 4(7)	1.068 6(7)	C(A13)	0.013 7(9)	0.163 8(8)	0.799 6(5)
O(3)	0.259 1(7)	0.224 2(7)	1.154 7(5)	C(A14)	0.011 2(9)	0.255 5(8)	0.831 3(5)
C(4)	0.310 5(6)	0.260 0(5)	0.890 3(5)	C(A15)	−0.028 9(9)	0.258 3(8)	0.934 6(5)
N	0.331 3(7)	0.340 9(4)	0.874 7(7)	C(A16)	−0.051 1(9)	0.168 3(8)	0.966 8(5)
C(5)	0.447 5(10)	0.384 4(6)	0.838 8(8)	C(A17)	−0.024 8(9)	0.109 9(8)	0.883 4(5)
O(4)	0.446 1(9)	0.419 3(5)	0.755 0(7)	C(B13)	0.022 1(14)	0.205 9(12)	0.791 9(8)
C(6)	0.714 5(12)	0.458 9(8)	0.865 5(8)	C(B14)	−0.000 1(14)	0.278 2(12)	0.860 8(8)
C(7)	0.813 7(18)	0.511 6(10)	0.945 3(9)	C(B15)	−0.042 7(14)	0.241 0(12)	0.954 2(8)
C(A8)	0.518 2(14)	0.044 7(7)	0.807 3(7)	C(B16)	−0.046 9(14)	0.145 7(12)	0.943 0(8)
C(A9)	0.374 1(14)	0.038 7(7)	0.759 3(7)	C(B17)	−0.006 8(14)	0.124 0(12)	0.842 7(8)
C(A10)	0.337 0(14)	0.122 1(7)	0.708 6(7)				

Table 9. Fractional atomic co-ordinates for complex (3a)

Atom	x	y	z	Atom	x	y	z
Fe(1)	0.259 7(1)	0.222 8(1)	0.181 8(1)	C(5)	0.410 0(5)	0.489 9(5)	0.086 5(2)
Fe(2)	0.027 7(1)	0.231 3(1)	0.129 3(1)	O(4)	0.503 3(3)	0.411 9(4)	0.109 2(2)
S	0.446 1(2)	0.687 5(1)	0.058 3(1)	C(8)	0.632 6(7)	0.704 5(8)	0.076 5(3)
C(1)	0.066 2(3)	0.233 9(5)	0.205 8(1)	C(9)	0.444 4(4)	0.078 3(5)	0.166 7(2)
O(1)	−0.001 1(3)	0.238 3(4)	0.246 6(1)	C(10)	0.465 9(4)	0.176 2(2)	0.212 3(2)
C(2)	−0.018 8(4)	0.439 5(5)	0.136 4(2)	C(11)	0.361 0(5)	0.132 0(7)	0.251 5(2)
O(2)	−0.954 5(4)	0.572 4(4)	0.141 6(2)	C(12)	0.276 4(4)	0.004 5(6)	0.228 9(2)
C(3)	0.276 9(4)	0.432 1(5)	0.198 0(1)	C(13)	0.327 6(4)	−0.027 3(5)	0.176 8(2)
O(3)	0.288 8(4)	0.567 3(4)	0.209 9(1)	C(14)	−0.047 1(6)	0.116 5(6)	0.058 5(2)
C(4)	0.228 3(3)	0.276 6(4)	0.103 9(1)	C(15)	−0.159 8(6)	0.197 8(7)	0.083 9(3)
C(7)	0.285 6(5)	0.160 9(5)	0.065 6(2)	C(16)	−0.177 3(6)	0.125 1(9)	0.135 3(3)
N(2)	0.329 6(6)	0.072 7(5)	0.033 2(2)	C(17)	−0.074 6(6)	0.001 1(7)	0.140 4(2)
N(1)	0.268 7(3)	0.441 6(4)	0.082 4(1)	C(18)	−0.006 1(6)	0.004 5(5)	0.092 9(2)
C(6)	0.176 1(6)	0.514 2(6)	0.040 8(2)				

gave first a red band containing [Fe$_2$(CO)$_3$(CNMe)(cp)$_2$] (0.02 g). The second red fraction was collected and evaporated to dryness under high vacuum. The residue, dissolved in dichloromethane (3 cm^3) was layered with n-pentane and cooled to −20 °C affording dark red crystals of complex (3a) (0.34 g, 71%); δ$_C$ (CD$_2$Cl$_2$) 264.3 (μ-CO), 209.9 (CO), 170.0 (COSMe), 139.3 (μ-C), 92.0 (C$_5$H$_5$), 44.4 (NMe), and 13.8 p.p.m. (SMe); CN not observed. Complex (3b) was prepared in a similar manner (68%).

[Fe$_2${μ-C(H)N(R′)C(O)SR}(μ-CO)(CO)$_2$(cp)$_2$] [R′ = R = Me (3d); R′ = Me, R = Et (3e)]. Stoicheiometric amounts of NaBH$_4$ were added to a MeCN solution (15 cm^3) of complex (2a) (0.50 g, 0.85 mmol). After stirring for 15 min the solution was evaporated to dryness and the residue redissolved in CH$_2$Cl$_2$, filtered through an alumina pad (3 × 3 cm), and dried in vacuo. Crystallization from CH$_2$Cl$_2$ layered with n-pentane at −20 °C afforded dark red crystals of (3d) (0.20 g, 53%). The red complex (3e) was analogously prepared from (2c).

Reaction of [Fe$_2${μ-CN(Me)C(O)SMe}(μ-CO)(CO)$_2$(cp)$_2$]-[SO$_3$CF$_3$] (2a) with NaOMe.—The compound (2a) (0.30 g, 0.50 mmol) in methanol (10 cm^3) was treated with stoicheiometric amounts of sodium methoxide and the mixture was stirred for 10 min at room temperature. The solvent was then removed in vacuo and the residue, redissolved in benzene, was filtered on an alumina column (3 × 3 cm). Removal of the solvent and crystallization from CH$_2$Cl$_2$—Et$_2$O afforded red crystals of [Fe$_2$(CO)$_3$(CNMe)(cp)$_2$] (0.09 g, 47%).

X-Ray Data Collection and Structure Determinations.— Crystal data for complexes (1b) and (3a) are reported in Table 7. The diffraction experiments were carried out on a CAD-4 diffractometer equipped with Mo-$K_α$ radiation, at room temperature. The unit-cell parameters were determined by least-squares refinement of the setting angles of 25 well centred high θ reflections. Diffraction intensities were corrected for Lorentz and polarization factors. Absorption correction was applied by the Walker and Stuart method[27] once the complete structural models were known and all atoms refined isotropically. The structures were solved by direct methods and refined by full-matrix least squares using the SHELX 76[28] package of crystallographic programs. All atoms except hydrogens were allowed to vibrate anisotropically; H atoms were added in calculated positions (C–H 1.08 Å) and refined 'riding' on their corresponding C atoms. The approximate H atom positions in the alkyl groups, detected in a Fourier difference synthesis, were used to define the model orientation. Orientational disorder of the cp ligands was detected in complex (1b); site occupation factors were refined independently for the two ligands yielding the values 0.56 and 0.44 for atoms C(8)—C(12) (A and B) and 0.64 and 0.36 for atoms C(13)—C(17) (A and B). Isotropic thermal parameters were refined for these atoms.

The absolute configuration of complex (3a) was determined by refining two structural models related by inversion. The rejected model gave the following agreement indices: $R = 0.030$, $R′ = 0.033$ versus $R = 0.028$, $R′ = 0.031$ for that accepted. The

co-ordinates of all non-hydrogen atoms are reported in Tables 8 and 9 for (**1b**) and (**3a**), respectively.

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

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