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THE PREPARATION, STRUCTURE AND FLUXIONAL BEHAVIOUR OF ISONITRILE DERIVATIVES OF $Cp_2Fe_2(CO)_{4-x}(CS)_x$ ($x = 1, 2$)

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Summary

The complexes $Cp_2Fe_2(CO)_2(CS)(CNR)$ ($R = Me$, Et, Pr^i, Bu^t; $Cp = \eta^5$-C_5H_5) exist in solution as interconverting $Cp(CO)Fe(\mu$-$CO)(\mu$-$CS)Fe(CNR)Cp \rightleftharpoons Cp(CO)Fe(\mu$-$CS)(\mu$-$CNR)Fe(CO)Cp$ isomers, with the proportion of the bridged isonitrile isomer increasing in the order $Bu^t < Pr^i < Et < Me$. A single crystal X-ray determination of the $CNPr^i$ derivative shows it to have a *cis*-$Cp(CO)Fe(\mu$-$CO)(\mu$-$CS)Fe(CNPr^i)Cp$ geometry in the solid state. $Cp_2Fe_2(CO)(CS)(CNMe)_2$ and $Cp_2Fe_2(CO)(CS)_2(CNMe)$ exist respectively as the single isomers $Cp(CO)Fe(\mu$-$CS)(\mu$-$CNMe)Fe(CNMe)Cp$ and $Cp(CO)Fe(\mu$-$CS)_2Fe(CNMe)Cp$ in solution. Interconversions of isomers are discussed in terms of the Adams–Cotton mechanism.

Introduction

In the area of transition metal cluster chemistry, there is a continuing interest in the bonding modes and site preferences of two electron ligands (CO, CS, PR_3, CNR) within the cluster, and in the ability of ligands other than carbon monoxide to participate in the fluxional processes which are a general feature of metal carbonyl clusters. $Cp_2Fe_2(CO)_4$ and its derivatives provide excellent examples for study, since synthetic routes to a wide variety of substituted complexes are available, and the mechanism of *cis* ⇌ *trans* isomerization and bridge ⇌ terminal carbonyl exchange has been well documented by the work of Adams and Cotton [1]. We [2a–d]

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and others [3a–c] have shown that isonitrile substituted derivatives $Cp_2M_2(CO)_{4-x}(CNR)_x$ (M = Fe, Ru; $x = 1$–3) exist as isomeric mixtures in which the isonitrile adopts both bridging and terminal coordination, with the proportion depending on both the steric and electronic properties of the isonitrile. In contrast, in the recently reported $Cp_2M_2(CO)_3(CS)$ and $Cp_2M_2(CO)_2(CS)_2$ complexes (M = Fe, Ru), the thiocarbonyl ligand is found to adopt exclusively bridging coordination [4a–d]. In order to further examine site preferences in these complexes, we describe here the preparation, structure, and fluxional behaviour of isonitrile substituted complexes of these two thiocarbonyl dimers. Subsequent to our previous communication of the preparation of $Cp_2Fe_2(CO)_2(CS)(CNBu^t)$ [2c], other authors have also reported the preparation of MeNC substituted derivatives of $Cp_2Fe_2(CO)_3(CS)$ [5].

Results

(a) Preparation

The substituted derivatives $Cp_2Fe_2(CO)_2(CS)(CNR)$ (IIIa–IIId; R = Me, Et, Pr^i, Bu^t) and $Cp_2Fe_2(CO)(CS)_2(CNMe)$ (V) were prepared by thermal substitution of $Cp_2Fe_2(CO)_3(CS)$ (I) and $Cp_2Fe_2(CO)_2(CS)_2$ (II), respectively. The disubstituted complex $Cp_2Fe_2(CO)(CS)(CNMe)_2$ (IV) was prepared by photochemical substitution of IIIa. Spectroscopic data are presented in Tables 1 to 3.

(b) Structure

Infrared and NMR spectra of (IIIa–IIId) indicate the presence of the four

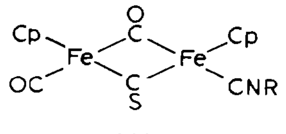
TABLE 1

INFRARED DATA (cm^{-1}) (hexane)

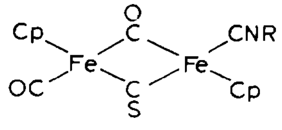
Complex	ν(CO(t)) [a]	ν(CO(b))	ν(CN(t))	ν(CN(b))	ν(CS(b))
$Cp_2Fe_2(CO)_4$	2007 (7.1)	1797 (9.7)			
	1964 (10.0)				
$Cp_2Fe_2(CO)_3(CS)$	2013 (9.2)	1811 (9 2)			1130
	1975 (10.0)				
$Cp_2Fe_2(CO)_2(CS)_2$	2012 (9.1)				1131
	1981 (10.0)				1124
$Cp_2Fe_2(CO)_2(CS)(CNMe)$	1999 (4.2)	1794 (8.6)	2149 (4.4)	1747 (2.3)	1119
	1971 (sh)				1113
	1963 (10.0)				
$Cp_2Fe_2(CO)_2(CS)(CNEt)$	2000 (3.2)	1795 (8.8)	2139 (4.5)	1747 (0.83)	1119
	1973 (2.5)		2107 (sh)		1113
	1965 (10.0)				
$Cp_2Fe_2(CO)_2(CS)(CNPr^i)$	2000 (1.6)	1794 (9.3)	2121 (4.5)	1747 (0.37)	1121
	1973 (sh)				1115
	1965 (10.0)				
$Cp_2Fe_2(CO)_2(CS)(CNBu^t)$	1963 (10.0)	1793 (9.3)	2123 (4.0)		1119
			2080 (sh)		1113
$Cp_2Fe_2(CO)(CS)(CNMe)_2$	1965 (7 2)		2147 (5 3)	1721 (7.0)	
	1955 (10.0)				
$Cp_2Fe_2(CO)(CS)_2(CNMe)$	1976 (10.0)		2157 (4 5)		1108

[a] (t) terminal group, (b) bridging group.

isomers **A** to **D** in solution.



(A)



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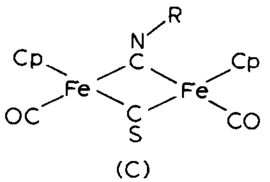
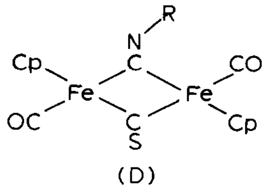


(C)



(D)

The bands at approximately 2100–2150, 1963, 1794 and 1110–1120 cm^{-1} are attributed to the terminal isonitrile, terminal carbonyl, bridging carbonyl, and bridging thiocarbonyl vibrations respectively of isomers **A/B**. The doubling of the thiocarbonyl and isonitrile (for IIIb, IIId) vibrations may be taken as an indication of the presence of both *cis* and *trans* isomers. Weaker bands at 2013 and 1975 cm^{-1} may be assigned to the terminal CO vibrations of isomers **C/D**, together with a weak bridging isonitrile vibration at 1747 cm^{-1}. The intensities of these weak bands relative to those for **A/B** decrease in the order Me > Et > Pr^i > Bu^t and, in fact, are completely absent for the Bu^tNC derivative. This decreasing population of the bridged isonitrile isomer is consistent both with the increase in steric interaction of the R group in a bridging position with the cyclopentadienyl ligands, and with the poorer π-acceptor (but better σ-donor) character of the isonitrile with increasing methyl substitution of the α-carbon. A parallel trend is observed in the Cp(CO)Fe(μ-

TABLE 2

^1H NMR DATA [a] (toluene-d_8)

Complex	Temperature (°C)	Cp		Other
$Cp_2Fe_2(CO)_2(CS)(CNR)$				
R = Me	−80	4.30	4.12	1.52 (l)
		4.28		3.30 (small)
R = Et	−40	4.34	4.22	CH_2 2.31 (q, *J* 7.4 Hz)
		4.33		CH_3 0.39 (t)
R = Pr^i	−40	4.34	4.21	CH_3 0.58 (d, *J* 6.5 Hz)
		4.32		0.59 (d, *J* 6.5 Hz)
				CH 2.79 (sept)
R = Bu^t	−30	4.34		CH_3 0.73 (s)
		4.31		
$Cp_2Fe_2(CO)(CS)_2(CNMe)$	0	4.40		CH_3 1.84
		4.39		
$Cp_2Fe_2(CO)(CS)(CNMe)_2$	20	4.42		CH_3-b 3.54
		4.47		CH_3-t 2.13

[a] Chemical shifts (δ, ppm) from TMS, l = large, q = quartet, t = triplet, d = doublet, s = singlet, sept = septet, t = terminal, b = bridging.

TABLE 3

^{13}C NMR DATA [a]

Complex	Temperature (°C)	CO	CS	CN	Other
$Cp_2Fe_2(CO)_3(CS)$	0	209.0 (t) 267.2 (μ)	378.3		92.2 90.3 } Cp[c]
$Cp_2Fe_2(CO)_2(CS)_2$	0	208.6	373.5 [b]		93.2 96 0 } Cp[c]
$Cp_2Fe_2(CO)_2(CS)CNBu^t$		211.8 274.2	391.0	157.8	88.8 89.1 } Cp CH_3 29.4
$Cp_2Fe_2(CO)_2(CS)(CNPr^i)$	0	212.1 274.5	391.5	157.7	89.3 89.0 } Cp CH 48.2 CH_3 22.6
$Cp_2Fe_2(CO)_2(CS)(CNEt)$	0	211.8 274.4	391.4	158.1	89.0 89.2 } Cp CH_2 39 3 CH_3 14.6
$Cp_2Fe_2(CO)_2(CS)(CNMe)$	0	211.7 274.4	391.4	157.7	88.6 89.2 } Cp CH_3 29.8
$Cp_2Fe_2(CO)(CS)_2(CNMe)$	0	211.6	385.3	156.8	92 8 92.5 } Cp CH_3 30.1
$Cp_2Fe_2(CO)(CS)(CNMe)_2$	0	212.1	394.1	256.1 159.5 161.6 } [c]	87.9 91.3 } Cp Me-t 29.5 Me-b 45.1

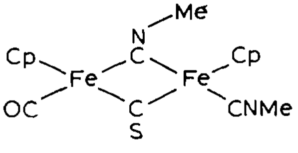
[a] CD_2Cl_2/CH_2Cl_2 solution; ppm from TMS. [b] The value reported in the literature [4b] is in error. [c] Unequal intensities; assigned to *cis* and *trans* isomers.

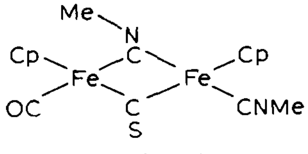
CO)(μ-CNR)Fe(CO)Cp $\rightleftharpoons$ Cp(CO)Fe(μ-CO)$_2$Fe(CNR)Cp equilibrium [2a,b] although the position of equilibrium is dramatically different. For IIIa, the (**A** + **B**) : (**C** + **D**) ratio (as determined by NMR; vide infra) is approximately 24 : 1, whereas the analogous ratio for the above equilibrium in toluene is 4 : 1.

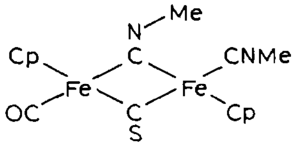
The *cis/trans* ratio C : D may be calculated [6] from the relative intensities of the two terminal CO absorptions, and yields a value of 57 : 43 for IIIa which may be compared with a ratio of 46 : 54 for the parent $Cp_2Fe_2(CO)_3(CS)$. As the value for $Cp_2Fe_2(CO)_4$ in the same solvent is 36 : 64 [6], this indicates a generally increasing population of the *cis* isomer with increasing substitution of the bridging carbonyl.

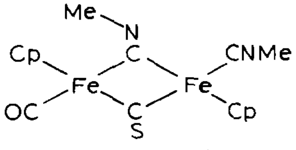
The infrared spectrum of IV shows no bridging carbonyl absorption, thus indicating the presence of only isomers **E**/**F**.

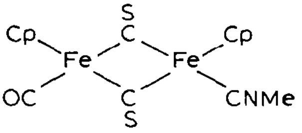
The doubling of the terminal carbonyl and bridging thiocarbonyl vibrations may be due to either (a) resolution of the CO$_t$ band of **E** from that of **F**, (b) resolution of the CO$_t$ bands of the *syn* and *anti* forms of either **E** or **F** (with one isomer being absent), or (c) a mixture of *syn* and *anti* forms of both **E** and **F** in which the bands are coincident. $Cp_2Fe_2(CO)_2(CNR)_2$ complexes exist in a Cp(CO)Fe(μ-CO)(μ-CNR)Fe(CNR)Cp $\rightleftharpoons$ Cp(CO)Fe(μ-CNR)$_2$Fe(CO)Cp equilibrium in which the former isomer is favoured even when R = Me [2d]. In the present case, it may be noted that the isomer Cp(CO)Fe(μ-CNR)$_2$Fe(CS)Cp would require CS to adopt a terminal coordination. Similarly, complex V exists in solution solely as isomers **G**/**H** containing terminally bound isonitrile. Although only one terminal carbonyl vibration is observed, coincidence of bands may mask the presence of both isomers.

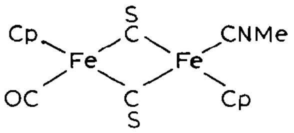

(E) *syn*


(E) *anti*


(F) *syn*


(F) *anti*


(G)


(H)

Thus, in none of these substituted complexes can detectable concentrations of isomers containing terminally bound thiocarbonyl be observed. The preference of CS for a bridging position may best be viewed in terms of the energies of its HOMO (σ-donor) and LUMO (π-acceptor) orbitals. Detailed molecular orbital calculations of the bonding in Cp$_2$Fe$_2$(CO)$_4$ have been made [7a–c]; in particular, the isolobal nature of Cp$^-$ and (CO)$_3$ may be noted, and these compounds may be related to the M$_2$L$_{10}$ bridged complexes which have been treated in detail by Hoffmann and coworkers [8]. The bonding feature of interest involves an overlap which is effectively in the M(μ-CO)$_2$M plane between π^*(CO) orbitals and frontier orbitals of the CpM(CO) fragment. Calculations indicate that whereas CO σ-donation is roughly comparable in bridging and terminal positions, population of the π^*(CO) orbitals is much more significant in the bridging interaction described above. In terms of ligand only molecular orbital calculations, CS may be seen as a better σ-donor than CO, but a much better π-acceptor [9]; therefore, its preference for a bridging position where its π-acceptor character is maximally utilised is not surprising. Spectroscopic properties (CO/CS stretching frequency and ^{13}C chemical shift) associated with the ligands in bridging positions show variations which are generally consistent with this interpretation. Thus, substitution of Cp(CO)Fe(μ-CO)$_2$Fe(CO)Cp to give Cp(CO)Fe(μ-CO)(μ-CS)Fe(CO)Cp results in an increase in ν(CO) and a decrease in δ(CO) of the remaining bridging carbonyl, consistent with less back donation to this carbonyl in competition with bridging CS. Replacement of terminal CO by the better σ-donating MeNC to give Cp(CO)Fe(μ-CO)(μ-CS)Fe(CNMe)Cp results in a decrease in both ν(CO) and ν(CS) and an increase in

(Continued on p. 234)

TABLE 4

BOND LENGTHS AND ANGLES WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES (Cp is the centroid of a cyclopentadienyl ring)

(a) Distances (Å)				(b) Angles (°)			
Fe(1)..Fe(2)	2.494(3)			C(BS)–Fe(1)–C(BO)	98(1)	C(BS)–Fe(2)–C(BO)	94(1)
Fe(1)–C(BS)	1.90(4)	Fe(2)–C(BS)	1.96(4)	C(BS)–Fe(1)–C(T1)	89(2)	C(BS)–Fe(2)–C(T2)	89(2)
Fe(1)–C(BO)	1.84(4)	Fe(2)–C(BO)	1.90(4)	C(BO)–Fe(1)–C(T1)	90(2)	C(BO)–Fe(2)–C(T2)	91(2)
Fe(1)–C(T1)	1.81(2)	Fe(2)–C(T2)	1.77(2)	C(BS)–Fe(1)–Cp(1)	124	C(BS)–Fe(2)–Cp(2)	124
Fe(1)–Cp(1)	1.74	Fe(2)–Cp(2)	1.75	C(BO)–Fe(1)–Cp(1)	123	C(BO)–Fe(2)–Cp(2)	125
Fe(1)..C(11)	2.13(2)	Fe(2)..C(21)	2.16(2)	C(T1)–Fe(1)–Cp(1)	124	C(T2)–Fe(2)–Cp(2)	123
Fe(1)..C(12)	2.18(3)	Fe(2)..C(22)	2.16(4)	Fe(1)–C(BS)–Fe(2)	81(2)	Fe(1)–C(BO)–Fe(2)	84(2)
Fe(1)..C(13)	2.08(3)	Fe(2)..C(23)	2.10(4)	Fe(1)–C(BS)–S	134(2)	Fe(1)–C(BO)–O(B)	143(2)
Fe(1)..C(14)	2.14(3)	Fe(2)..C(24)	2.09(5)	Fe(2)–C(BS)–S	140(2)	Fe(2)–C(BO)–O(B)	130(2)
Fe(1)..C(15)	2.11(3)	Fe(2)..C(25)	2.08(3)	Fe(1)–C(T1)–N	178(3)	Fe(2)–C(T2)–O(T2)	175(5)
C(BS)–S	1.50(4)	C(BO)–O(B)	1.51(5)	C(T1)–N–C(1)	177(2)	N–C(1)–C(2)	108(2)
C(T1)–N	1.18(2)	C(T2)–O(T2)	1.14(2)	C(2)–C(1)–C(3)	117(2)	N–C(1)–C(3)	108(3)
N–C(1)	1.45(3)			C(15)–C(11)–C(12)	110(2)	C(25)–C(21)–C(22)	105(2)
C(1)–C(2)	1.46(5)	C(1)–C(3)	1.49(6)	C(11)–C(12)–C(13)	102(2)	C(21)–C(22)–C(23)	108(3)
C(11)–C(12)	1.38(4)	C(21)–C(22)	1.45(5)	C(12)–C(13)–C(14)	112(3)	C(22)–C(23)–C(24)	109(4)
C(12)–C(13)	1.50(4)	C(22)–C(23)	1.40(6)	C(13)–C(14)–C(15)	100(3)	C(23)–C(24)–C(25)	109(4)
C(13)–C(14)	1.50(4)	C(23)–C(24)	1.37(4)	C(14)–C(15)–C(11)	115(3)	C(24)–C(25)–C(21)	109(3)
C(14)–C(15)	1.36(5)	C(24)–C(25)	1.39(6)				
C(15)–C(11)	1.42(5)	C(25)–C(21)	1.43(5)				

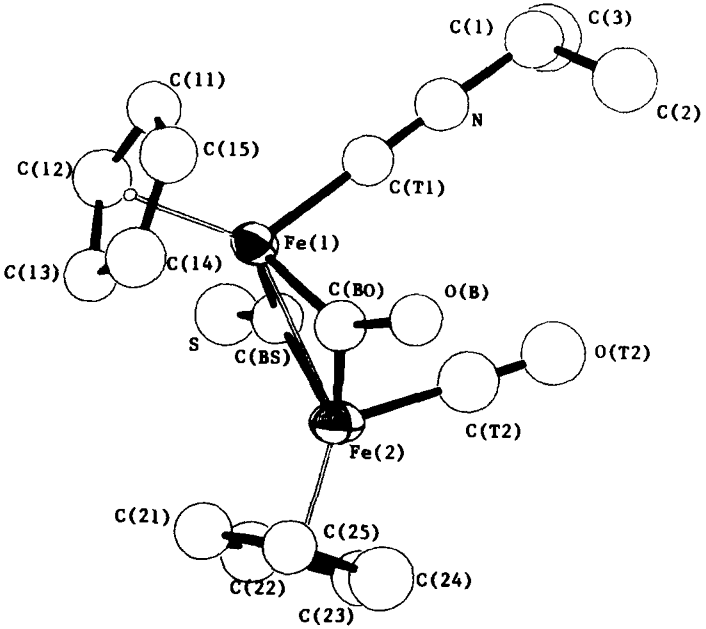


Fig. 1. Perspective drawing of the molecule with atom labelling scheme. Thermal ellipsoids are drawn to include 35% probability.

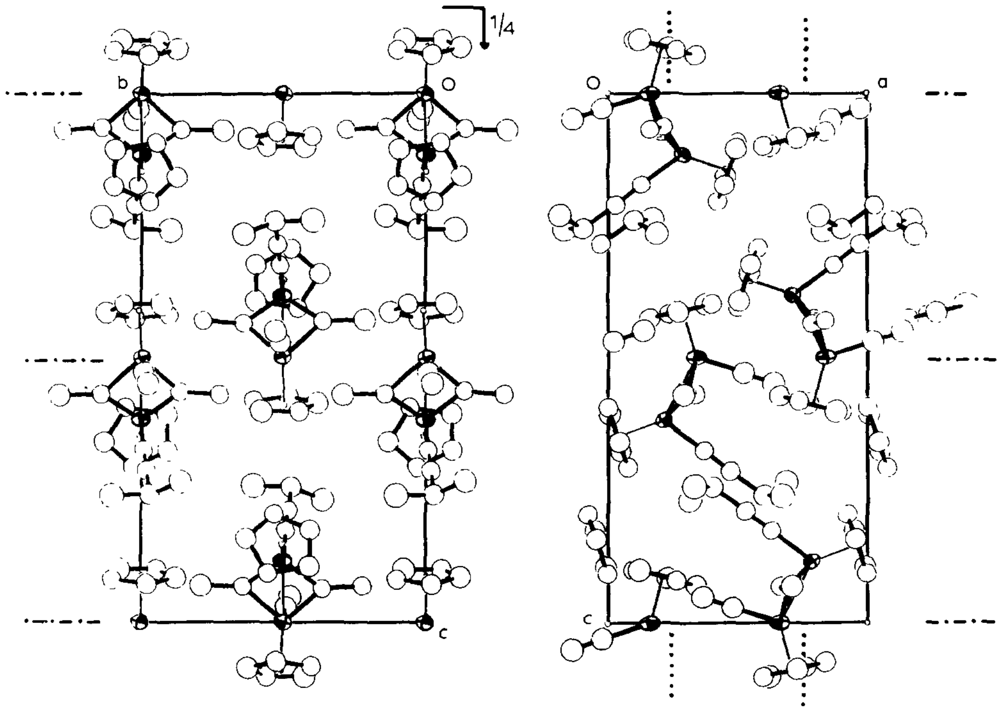


Fig. 2. The packing in the crystal with the positions of the pseudo-glide planes being indicated.

both δ(CO) and δ(CS), consistent with increased back donation to the bridging CO and CS ligands. The much greater shifts of ν(CS) and δ(CS) may perhaps indicate a greater back donation to the thiocarbonyl. Similar, though larger, shifts have been observed in Cp(CO)Fe(μ-CO)(μ-CS)Fe($\mathrm{PEt_3}$)Cp [5]. Further substitution of the bridging carbonyl to give Cp(CO)Fe(μ-CS)(μ-CNMe)Fe(CNMe)Cp results in a further, though much smaller, downfield shift of δ(CS). We have recently shown [10] that the π-acceptor character of RNC depends substantially on molecular geometry; as the CNR angle decreases, the π-acceptor character increases markedly (surpassing that of CO), while the σ-donor character remains essentially constant. It is well established [2d,11a,b] that bridging isonitriles in complexes of this type are substantially bent (CNR angle 125°). Thus, the smaller shift in δ(CS) observed for IV probably reflects the better π-accepting character of the bridging isonitrile.

Although RNC competes effectively with CO for the bridging position in IIIa–IIIc, and IV, it still compares poorly with CS as a π-accepting ligand. Thus, monosubstitution of Cp(CO)Fe(μ-CS)$_2$Fe(CO)Cp yields exclusively Cp(CO)Fe(μ-CS)$_2$Fe(CNMe)Cp, and is accompanied by the expected downfield shift of δ(CS).

(c) Crystal and molecular structure of IIIc

The infrared spectra of solid samples of IIIa–IIId dispersed in KBr or CsBr discs are similar and consistent with the presence of isomer **A** or **B** only. Thus, absorption bands for IIIc are found at 1110, 1783, 1924 and 2118 $\mathrm{cm^{-1}}$ due respectively to the stretching vibrations of the μ-CS, μ-CO, t-CO and t-$\mathrm{CNPr^i}$ ligands. A single crystal X-ray diffraction study has shown that $\mathrm{Cp_2Fe_2(CO)_2(CS)(CNPr^i)}$ exists as isomer **A** in the solid state. The molecular geometry is illustrated together with the atom

TABLE 5

LEAST-SQUARES PLANES AND THEIR EQUATIONS IN THE FORM $lX+mY+nZ-p=0$ WHERE X, Y, Z ARE THE COORDINATES IN Å (The deviations (Å) of the most relevant atoms from the planes are given in square brackets)

	l	*m*	*n*	*p*
Plane (1): Fe(1), C(BO), C(BS)	0.7866	−0.0692	−0 6136	0.7062
Plane (2): Fe(2), C(BO), C(BS)	0.9502	−0.0715	−0.3034	1.4052
Plane (3). C(11)–(15)	0.9522	−0.0221	0.3045	4 9290
(C(11) −0.018; C(12) 0.012, C(13)–0.003; C(14) −0.008; C(15) 0.016)				
Plane (4): C(21)–C(25)	0.2461	−0.0100	−0.9692	2.1006
(C(21) 0.005; C(22) 0.006; C(23) −0.015; C(24) 0.018; C(25) −0.013)				
Plane (5): C(BS),Fe(1),Fe(2),S	0.8827	−0.0903	−0.4611	1 2616
[C(BS) −0.16; Fe(1),Fe(2) 0.04; S 0.08]				
Plane (6): C(BO),Fe(1),Fe(2),O(B)	0.8686	0 1976	−0 4544	1.3143
[C(BO) 0.12; Fe(1) −0.04; Fe(2) −0.03, O(B) −0.06]				

Dihedral Angles (°)

1 : 2	20.2	3 . 4	93.5
1 : 3	55.7	5 . 6	16.6
2 : 4	58.1		

labelling scheme in Fig. 1 [12] while Fig. 2 shows the packing in the crystal. The shortest intermolecular contact is 3.46(5) Å from O(**B**) to C(3) at $\bar{x}$, $\frac{1}{2}+y$, $\frac{1}{2}-z$ and all other contacts are > 3.5 Å. With disorder in the bridging groups, a pseudo *c*-glide perpendicular to *a* and a pseudo *n*-glide perpendicular to *c* are apparent (see Fig. 2). The latter glide occurs since the molecule has approximately *m* symmetry and is oriented such that the mirror plane is both closely perpendicular to *b* and at $y = 0$. These pseudo symmetry elements would account for the observed absences in the 0*kl* and *hk*0 zones. The bond lengths and angles are listed in Table 4 and relevant mean planes data are given in Table 5. The structure has the expected Fe(CO)(CS)Fe bridging system, with disorder between the bridging carbonyl and thiocarbonyl groups, and with the cyclopentadienyl rings in a *cis* configuration. The disorder of

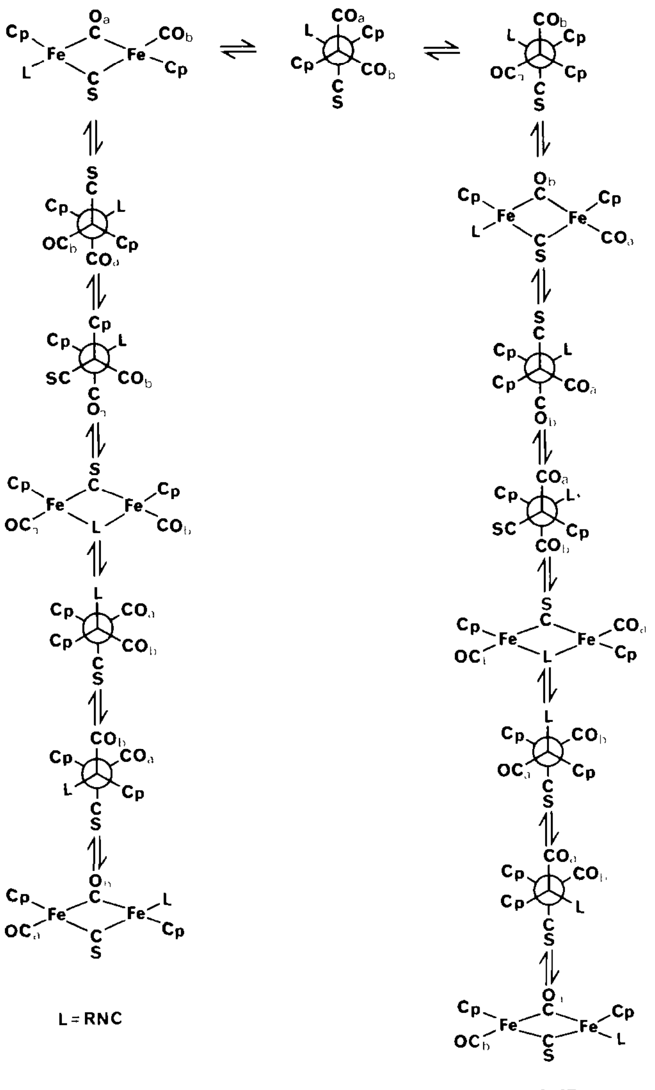


Fig. 3. Adams–Cotton mechanism for $Cp_2Fe_2(CO)_2(CS)(CNR)$.

the bridging CO and CS ligands reflects the presence of the two enantiomers of IIIc in equal amounts in the crystal. In common with other dimers of *cis* geometry [2d,3a,b,11a,13a–e] the bridging ligands are bent away from the cyclopentadienyl ligands such that the angle between the two FeC_bC_b planes is 20.2°. Other structural features of the molecule resemble those of $Cp_2Fe_2(CO)_3(CS)$ [14] and its alkylated derivative $[Cp_2Fe_2(CO)_3(CSEt)]^+$ [4d]. In particular, the Fe-----Fe distance of 2.494(3) Å may be seen to be intermediate between that of *cis*-$Cp_2Fe_2(CO)_4$ (2.531 Å) [13b] and that of $Cp_2Fe_2(CO)_2(CS)_2$ (2.482 Å) [4b]. The geometry and bond lengths of the coordinated terminal isonitrile are unexceptional [2d,3a,13c].

(d) Fluxional behaviour

^1H NMR spectra of complexes IIIa–IIId in toluene-d_8 from room temperature down to −80°C typically show two resonances at δ 4.30 and 4.28 ppm assignable to the inequivalent Cp ligands of of **A** and/or **B** [15], together with a much smaller single resonance at δ 4.12 ppm assignable to isomers **C** and/or **D** (assuming that nitrogen inversion at the bridged isonitrile ligand is rapid on the NMR time scale). The absence of this small resonance in the spectrum of Id is consistent with infrared studies which show the absence of detectable concentrations of the bridged isonitrile isomers **C**/**D**.

As infrared studies indicate that all four isomers **A**–**D** are present in cyclohexane, the observation of only three cyclopentadienyl resonances implies that either (i) the resonances due to **A**/**B** and **C**/**D** are coincident, or (ii) only one isomer of each pair is present in toluene or (iii) $\mathbf{A} \rightleftharpoons \mathbf{B}$ and $\mathbf{C} \rightleftharpoons \mathbf{D}$ exchange is rapid even at low temperature but is not accompanied by $\mathbf{A}/\mathbf{B} \rightleftharpoons \mathbf{C}/\mathbf{D}$ interconversion. The possibilities for interconversion can be visualised in terms of the Adams–Cotton mechanism, and are outlined in Fig. 3. This scheme is simplified in that pathways leading to bridged dimers containing terminally bound thiocarbonyl have been disregarded; as such complexes cannot be detected in solution, exchange pathways proceeding through these complexes clearly require higher activation energies than those in which the bridging coordination of the thiocarbonyl is maintained.

Examination of Fig. 3 leads to the following predictions: (a) If exchange processes are restricted to those involving only $Cp(CS)(CNR)FeFe(CO)_2Cp$ rotamers, exchange only between **A** and **B** is possible. This must be accompanied by bridge-terminal carbonyl exchange but not by exchange of CNR between the metal atoms. Although a rapid *cis* ⇌ *trans* isomerization by this process has been postulated to account for the two resonances assignable to **A**/**B** [5], the absence of any line broadening in the room temperature ^{13}C spectrum shows that this is not accompanied by the required bridge-terminal CO exchange. Thus, the observation of only one set of resonances (apparent also in the ^{13}C spectrum) is most probably due to a coincidence of signals.

(b) If only rotamers of the type Cp(CO)(CS)FeFe(CNR)(CO)Cp are allowed, then exchange can occur between either **A** and **D** or between **B** and **C**. This must be accompanied by bridge-terminal CO exchange and by scrambling of CNR between the two metal atoms. This process is certainly evident in higher temperature ^1H NMR spectra. Thus, warming of IIIa (Fig. 4) results in a broadening and coalescence to yield a single broadened cyclopentadienyl resonance at 100°C. A similar broadening of the MeNC resonances is observed, although because of the larger chemical shift difference coalescence is not observed. For the same reason, the ^{13}C

spectra show no line broadening up to 110°C, above which temperature, decomposition ensues. Resonances due to the minor isomers **C**/**D** were not detected in the ^{13}C spectrum.

Since we have not been able to observe independently the *cis* ⇌ *trans* isomerization, it is not possible to determine whether process (a) or (b) above represents the lower energy exchange pathway. We have previously shown, however, that they can be distinctly different; for the complex $Cp_2Fe_2(CO)_2(CNBu^t)_2$, exchange processes which involve rotamers of the type $Cp(CO)_2FeFe(CNR)_2Cp$ do have a higher activation energy than that for the process involving only the symmetrical rotamers Cp(CNR)(CO)FeFe(CO)(CNR)Cp [2c].

The ^1H NMR spectrum of IV in toluene-d_8 shows two resonances assignable to the non-equivalent cyclopentadienyl ligands of **E** and/or **F** which show no reversible broadening at temperatures up to 100°C. Thus, in common with the $Cp_2Fe_2(CO)_{4-x}(CNR)_x$ series ($x = 1$–3), increasing isonitrile substitution raises substantially the barrier to isomer exchange. The coalescence temperature of the *cis*

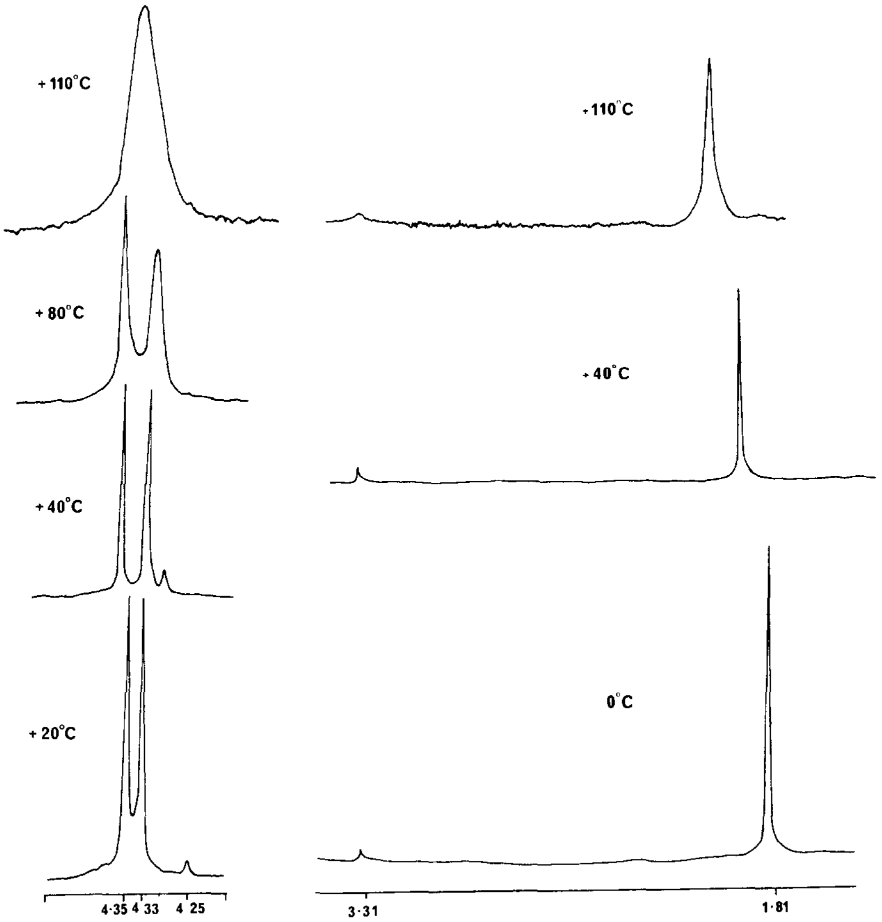


Fig. 4. (a) ^1H NMR spectrum of $Cp_2Fe_2(CO)_2(CS)(CNMe)$; Cp region; toluene-d_8. (b) ^1H NMR spectrum of $Cp_2Fe_2(CO)_2(CS)(CNMe)$; toluene-d_8; Me region only.

and *trans* cyclopentadienyl signals for $Cp_2Fe_2(CO)_3(CS)$ of 61°C in this solvent is itself about 100°C higher than that found for $Cp_2Fe_2(CO)_4$. The increased barrier to bridge opening may again be understood in terms of the strong preference of CS for a bridging coordination.

Cis $\rightleftharpoons$ *trans* isomerization of $Cp_2Fe_2(CO)_2(CS)_2$ is sufficiently slow that the complexes may be separated by chromatography, and up to 100°C, no line broadening of the inequivalent cyclopentadienyl resonances of $Cp(CO)Fe(\mu\text{-}CS)_2Fe(CNMe)Cp$ (V) may be observed. Application of the Adams–Cotton mechanism to the *cis* $\rightleftharpoons$ *trans* isomerization of $Cp_2Fe_2(CO)_2(CS)_2$ shows that the process must proceed via the intermediacy of isomers of the type $Cp(CO)Fe(\mu\text{-}CO)(\mu\text{-}CS)Fe(CS)Cp$; although there is no infrared evidence for detectable concentrations of such isomers in solution, this does not preclude their intermediacy in the exchange process. It might be expected, however, that their intermediacy would raise substantially the barrier to *cis* $\rightleftharpoons$ *trans* exchange, compared to $Cp_2Fe_2(CO)_3(CS)$ and its derivatives, for which such intermediates are not required.

Experimental

All reactions were performed in freshly distilled solvents under nitrogen. The isonitriles were prepared as described in the literature [16a–c]. $Cp_2Fe_2(CO)_{4-x}(CS)_x$ ($x = 1, 2$) were prepared by published methods [4a–d] from commercial $Cp_2Fe_2(CO)_4$. Infrared and NMR spectra were run on Perkin–Elmer 257 and JEOL FX-100 instruments respectively. Proton decoupled ^{13}C spectra were run in the presence of $Cr(acac)_3$.

(a) $Cp_2Fe_2(CO)_2(CS)(CNMe)$ (IIIa)

$Cp_2Fe_2(CO)_3(CS)$ (0.6 g, 1.7 mmol) and MeNC (0.2 cm^3, 3.5 mmol) were refluxed in benzene (30 ml) until infrared monitoring indicated complete consumption of starting material (1 h). Solvent and excess ligand were removed under vacuum and the dark green residue was chromatographed on Grade IV alumina. Elution with petroleum ether(40–60°C) : CH_2Cl_2 (95 : 5) yielded $Cp_2Fe_2(CO)_2(CS)(CNMe)$ as green crystals after recrystallization from petroleum ether/dichloromethane (65% yield). Complexes (IIIb–IIId) were obtained in the same way.

Complex V was obtained as green black crystals (63% yield) in a similar way by refluxing of $Cp_2Fe_2(CO)_2(CS)_2$ with MeNC in benzene for 70 h followed by chromatography on Grade III alumina using petroleum ether(40–60°C) : CH_2Cl_2 (50 : 50).

Analytical data

Complex	Found (%)			Calculated (%)		
	C	H	N	C	H	N
IIIa	47.1	3.52	3.75	47.0	3 34	3.65
b	48.2	3.86	3.64	48.4	3.78	3.53
c	49.5	4.19	3 37	49 0	4.14	3.41
d	50.4	4.36	3.55	50.8	4.47	3.29
IV	48.2	4.00	7.00	48.3	4.00	7.00
V	45.1	3.29	3.67	45 1	3.26	3.51

Complex IV was prepared by photolysis of $Cp_2Fe_2(CO)_2(CS)(CNMe)$ in the presence of MeNC in benzene until infrared monitoring indicated complete consumption of starting material (10 h). Chromatography on Grade III alumina using CS_2 : diethyl ether (9 : 1) gave the product in 32% yield after recrystallization from diethyl ether/hexane.

(b) Structure determination of IIIb

Crystal data: $C_{17}H_{17}N_2O_2SFe_2$, $M_r = 411.1$. Orthorhombic, a 9.220(5), b 10.126(5), c 18.953(10) Å, U 1769.5 Å^3, D_c 1.543 g cm^{-3}, $F(000) = 840$, μ(Mo-K_α) = 17.8 cm^{-1}. Systematic absences: $h00$ if $h \neq 2n$, $0k0$ if $k \neq 2n$ and $00l$ if $l \neq 2n$, space group $P2_12_12_1$ (No. 19).

Until cell parameters were determined from precession photographs using Mo-K_α radiation. Intensities were estimated visually from precession photographs for the layers 0–3 about [100], [010], and [100]. They were corrected for Lorentz and polarisation effects but not for absorption or extinction. The structure factors were placed on a common scale by internal correlation, and 904 non-zero unique reflections were obtained. Scattering factors were taken from ref. 17 and all calculations were carried out on a UNIVAC 1106 computer with programmes written by F.S. Stephens.

Initial investigations showed absences for $0kl$ if $l \neq 2n$ and for $hk0$ if $h + k \neq 2n$ which suggests the space groups to be $Pc2_1n$ (non-standard $Pna2_1$ (No. 33)) or $Pcmn$ [non-standard $Pnma$ (No. 62)]. For the latter with $Z = 4$, the molecules must possess $\bar{1}$ or m symmetry, neither of which is chemically feasible without invoking some kind of disorder *. Although the Patterson synthesis yielded a solution in the space group $Pc2_1n$ for the iron atoms and the bridging groups, the packing of these units in the lattice indicated that some of the intermolecular contacts would be extremely short, and a complete solution of the structure was not attainable. If the observed absences for the principal zones were fortuitous, then the space group of next lowest symmetry would be $P2_12_12_1$. The choice of this space group permitted a complete solution of the structure. Initially, both bridging groups were treated as carbonyls. During the Fourier refinement, one of the groups was assigned as the thiocarbonyl on the basis of a longer interatomic distance (ca. 1.5 Å) and the higher electron density. However, later refinement showed these groups to be disordered. Eleven of the seventeen hydrogen atoms, whose positions could be calculated from molecular geometry, were included in the calculations, assuming C–H to be 1.0 Å. Difference maps calculated at various stages of refinement failed to yield positions for the methyl hydrogen atoms. Refinement was by least squares procedures in which $\Sigma w\Delta^2$

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* A referee has pointed out that the refinement did, in fact, reveal disorder which would be consistent with the centric space group which we ruled out. However, the refinement further showed that the molecule has only an approximate mirror plane and the deviations from m symmetry are believed significant. If m symmetry is assumed, nine atoms of the molecule must lie in the plane and those atoms in the refinement show deviations of up to 0.3 Å. The deviations between atoms which would be symmetry-related are even higher, up to 0.6 Å for C(2), C(3). Resorting to the centric group, in which origin shift is 0, $\frac{1}{4}$, $\frac{1}{4}$, will give the average of those structures with the approximate m symmetry. Refinement in this group gives results which show significantly higher thermal parameters, as expected if we were averaging structures with closely m symmetry. We therefore believe that the structure has been refined in the appropriate space group. Because of the closeness to m symmetry the overall molecular geometry will be similar for refinement in either space group.

TABLE 6

FINAL ATOMIC PARAMETERS ($\times 10^4$) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES (Anisotropic Thermal parameters in the form $\exp-\{h^2b_{11}+k^2b_{22}+l^2b_{33}+2hkb_{12}+2hlb_{13}+2klb_{23}\}$)

	x	y	z	B (Å^2)
Fe(1)	2858(2)	6(9)	1175(1)	–
Fe(2)	1610(3)	19(9)	7(10)	–
S	2078(10)	–2879(10)	705(5)	7.3(2)
O(B)	1622(18)	2787(19)	698(9)	5.1(4)
O(T2)	–1368(18)	252(25)	499(8)	7.6(4)
N	298(16)	199(28)	2132(7)	5.4(4)
C(BS)	1938(34)	–1404(42)	686(18)	5.0(8)
C(BO)	2141(37)	1381(42)	645(18)	4.9(7)
C(T1)	1296(18)	109(48)	1747(8)	4.9(4)
C(T2)	–218(25)	104(61)	297(11)	6.9(5)
C(1)	–982(25)	285(33)	2576(11)	6.3(5)
C(2)	–1862(35)	1393(28)	2327(18)	7.8(8)
C(3)	–1690(41)	–1040(46)	2591(19)	8.9(9)
C(11)	4231(21)	–292(28)	2061(10)	5.4(5)
C(12)	4553(34)	–1287(36)	1586(17)	6.4(7)
C(13)	4979(28)	–529(27)	940(13)	5.3(6)
C(14)	4929(37)	933(36)	1065(18)	6.7(8)
C(15)	4504(34)	959(37)	1754(16)	6.1(7)
C(21)	3388(21)	–220(37)	–726(10)	6.1(5)
C(22)	2297(40)	–1228(39)	–856(19)	7.0(9)
C(23)	986(37)	–585(40)	–1011(19)	5.7(9)
C(24)	1211(49)	751(53)	–1008(25)	7.7(12)
C(25)	2636(35)	1003(33)	–816(16)	5.5(7)

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Fe(1)	109(3)	129(3)	23(1)	–10(8)	7(1)	0(5)
Fe(2)	178(4)	107(3)	23(1)	11(8)	–1(1)	–5(4)

TABLE 7

HYDROGEN ATOM PARAMETERS ($\times 10^3$)[a]

H(1)	–65	40	308
H(11)	386	–44	255
H(12)	451	–227	166
H(13)	526	–95	48
H(14)	515	168	74
H(15)	439	180	202
H(21)	443	–35	–60
H(22)	245	–220	–84
H(23)	4	–103	–111
H(24)	47	143	–113
H(25)	307	190	–75

[a] For all hydrogen atoms $B = 7.0$ Å^2.

was minimised. Initially, the weight for each reflection was unity and in the final cycles given by $w = (0.9 + 0.05|F_0| + 0.0023|F_0|^2)^{-1}$. In the final stages of refinement, only the iron atoms were allowed to vibrate anisotropically. Refinement was terminated when the minimum function shifted by $< 0.05\%$ between successive cycles. The final value for R was 0.071 and for R' $[= (\Sigma w\Delta^2/\Sigma w|F_0|^2)^{1/2}]$ was 0.100. A final difference map showed no features $> |0.6| \text{e Å}^{-3}$. The final atomic parameters are given in Tables 6 and 7. Observed and calculated structure factors may be obtained from the authors.

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