THE X-RAY STRUCTURAL CHARACTERIZATION AND SOLUTION DYNAMICS OF BIS[(μ-2,6-DIMETHYLPHENYLISOCYANIDE)-(CYCLOPENTADIENYL)(2,6-DIMETHYLPHENYLISOCYANIDE)IRON(I)]

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Summary

The X-ray structure of *trans*-[{Fe(η^5-C$_5$H$_5$)(CNC$_6$H$_3$Me$_2$-2,6)$_2$}$_2$] (**1a**) and the solution dynamics of both *cis*- and *trans*-[{Fe(η^5-C$_5$H$_5$)(CNC$_6$H$_3$Me$_2$-2,6)$_2$}$_2$] have been studied. The *trans*-isomer of **1a** crystallizes in the space group $P2_1/n$ with a 14.588(4), b 8.811(2) and c 14.847(4) Å, β 92.08(2)°. The molecule lies across a crystallographic centre of inversion with a *trans* arrangement of cyclopentadienyl ligands and a strictly planar bridging Fe$_2$C$_2$ ring. The Fe–Fe bond length is 2.518(1) Å and the bridging isocyanide ligands are symmetrically bonded to iron with a mean Fe–C(bridging) bond length of 1.928(3) Å. Solution ^{1}H NMR spectra of **1a** show the presence of both *cis*- and *trans*-isomers, and a 500 MHz ^{1}H NMR study at low temperature reveals two distinct exchange processes; the lower energy one results in the coalescence of the signals for the inequivalent methyl groups on the bridging isocyanide ligands of the *cis*-isomer, whereas the higher energy process brings about coalescence of the methyl signals for the bridging and terminal isocyanide ligands of the *trans*-isomer. At elevated temperatures all the methyl signals coalesce.

Introduction

The complex [{Fe(η^5-C$_5$H$_5$)(CO)$_2$}$_2$] was first synthesized by Cotton and Wilkinson [1] in 1954, and the crystal structure determination, reported shortly

afterwards, showed the molecule to be dimeric, consisting of two $\{Fe(\eta^5\text{-}C_5H_5)(CO)\}$ units bridged by two carbonyl groups [2]. Subsequent X-ray [3] and neutron diffraction [4] studies have shown that the molecule exists in the solid state in both *cis* and *trans* configurations. In solution, a dynamic interconversion of these isomers occurs, the mechanism of which was studied by Adams and Cotton who proposed a set of three postulates, the "Adams–Cotton rules", to explain the process [5]. Strong support for this mechanistic analysis was provided by the investigation [5,6] of the isonitrile derivative $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_2(CNMe)_2]$, which for the first time enabled the use of proton NMR to monitor the interchange of ligands other than cyclopentadienyl, in a complex closely related to $[\{Fe(\eta^5\text{-}C_5H_5)(CO)_2\}_2]$. With the recent discoveries of general, high yield synthetic routes to the fully substituted derivatives $[\{Fe(\eta^5\text{-}C_5H_5)(CNR)_2\}_2]$ (R = aryl [7], alkyl [8]), access has now been gained to detailed comparative investigations into the solution equilibria of the exact isocyanide analogue of $[\{Fe(\eta^5\text{-}C_5H_5)(CO)_2\}_2]$. Consequently we now report a solution and structural investigation of $[\{Fe(\eta^5\text{-}C_5H_5)(CNC_6H_3Me_2\text{-}2,6)_2\}_2]$ as a representative member of this series.

Experimental

The compounds $[\{Fe(\eta^5\text{-}C_5H_5)(CO)_2\}_2]$ and 2,6-dimethylphenyl isonitrile were purchased from Strem Chemicals and Fluka AG respectively. The complex $[\{Fe(\eta^5\text{-}C_5H_5)(CNC_6H_3Me_2\text{-}2,6)_2\}_2]$ was synthesized by the published procedure [7] and recrystallized from a dichloromethane/ethanol mixture to a constant analysis before use. The solvents were routinely dried and distilled. All ^1H NMR spectra were recorded using a Bruker WM500 (500 MHz) instrument except where indicated, in which case a Varian EM390 (90 MHz) instrument was used.

Crystal structure determination

Crystals suitable for X-ray examination were obtained from a chloroform/hexane solution.

Crystal data. $C_{46}H_{46}Fe_2N_4$, $M = 766.60$. Monoclinic, space group $P2_1/n$ (alt. $P2_1/c$, No. 14), a 14.588(4), b 8.811(2), c 14.847(4) Å, β 92.08(2)°, U 1909.7 Å^3 (by least-squares refinement on diffractometer angles of 24 automatically centred reflections, λ 0.71069 Å), $Z = 2$, D_c 1.333 g cm^{-3}. Dark green air-stable tablets. Crystal dimensions $0.3 \times 0.2 \times 0.08$ mm, μ(Mo-K_α) 7.79 mm^{-1}.

Data collection and processing. Philips PW1100 diffractometer, $\omega/2\theta$ mode with ω scan width of 1.20°, ω scan speed of 0.04° s^{-1}, graphite monochromatized Mo-K_α radiation; 2585 unique reflections measured ($3 \leqslant \theta \leqslant 23°$, $\pm h$, $+k$, $+l$) giving 1951 with $I > 2\sigma(I)$. No observable decay, no absorption corrections.

Structure analysis and refinement. Normal heavy atom procedures. Full-matrix least-squares refinement (two blocks for final anisotropic cycles) using SHELX [9], with all non-hydrogen atoms anisotropic. All hydrogen positions were located using difference synthesis and were refined with three common isotropic temperature factors. Using a weighting scheme $w = 1/\sigma^2(F_0)$, the final $R[= \Sigma\Delta/\Sigma F_0$, $\Delta = |F_0 - F_c|]$ and $R_w[= \Sigma w\Delta/\Sigma w F_0]$ are 0.0397 and 0.0333. Complex neutral-atom scattering factors [10] were used for all atoms. The final atom fractional coordinates are given in Table 1. Selected bond lengths and angles are given in Table 2. Figure 1 is a

TABLE 1

FRACTIONAL COORDINATES ($\times 10^4$, $\times 10^5$ for Fe, $\times 10^3$ for H) AND EQUIVALENT ISO-TROPIC TEMPERATURE FACTORS (Å^2, $\times 10^3$, $\times 10^4$ for Fe) FOR **1a**

Atom	x	y	z	U_{eq}
Fe	47101(3)	−10377(5)	4980(3)	333(3)
C(1)	5729(3)	−2772(5)	642(4)	54(3)
C(2)	5069(4)	−3203(4)	−12(3)	46(3)
C(3)	4230(3)	−3280(4)	406(3)	48(3)
C(4)	4379(3)	−2899(4)	1316(3)	52(3)
C(5)	5304(4)	−2584(4)	1464(3)	55(3)
C(11)	5611(2)	521(4)	736(2)	35(2)
N(1)	6176(2)	1022(3)	1304(2)	40(2)
C(12)	6362(3)	630(4)	2213(2)	40(2)
C(13)	5778(3)	1101(5)	2883(3)	49(2)
C(14)	4940(4)	2005(6)	2649(3)	69(3)
C(15)	6019(4)	743(6)	3772(3)	67(3)
C(16)	6809(4)	−46(6)	3992(4)	75(4)
C(17)	7382(4)	−459(6)	3330(4)	75(3)
C(18)	7184(3)	−116(5)	2437(3)	57(3)
C(19)	7861(5)	−458(10)	1733(6)	94(5)
C(21)	3757(3)	50(4)	847(2)	36(2)
N(2)	3115(2)	764(3)	1066(2)	48(2)
C(22)	2200(3)	1215(5)	1109(2)	43(2)
C(23)	2000(4)	2703(5)	1355(2)	49(2)
C(24)	2736(4)	3828(6)	1580(4)	71(3)
C(25)	1070(3)	3100(6)	1377(3)	62(3)
C(26)	398(3)	2065(7)	1192(3)	66(3)
C(27)	610(3)	596(6)	970(3)	65(3)
C(28)	1521(3)	134(5)	907(2)	50(2)
C(29)	1766(4)	−1448(6)	642(4)	69(3)
H(1)	635(2)	−266(4)	58(2)	46(5)[a]
H(2)	514(2)	−342(4)	−62(2)	46(5)[a]
H(3)	367(2)	−347(4)	12(2)	46(5)[a]
H(4)	393(2)	−285(4)	173(2)	46(5)[a]
H(5)	559(2)	−229(4)	202(2)	46(5)[a]
H(141)	450(3)	155(5)	223(3)	95(6)[a]
H(142)	508(3)	288(5)	231(3)	95(6)[a]
H(143)	456(3)	216(5)	315(3)	95(6)[a]
H(15)	563(3)	114(5)	422(3)	95(6)[a]
H(16)	696(3)	−24(5)	463(3)	95(6)[a]
H(17)	791(3)	−94(5)	344(3)	95(6)[a]
H(191)	768(3)	−43(6)	116(3)	95(6)[a]
H(192)	842(3)	−49(6)	196(3)	95(6)[a]
H(193)	778(4)	−129(6)	157(5)	95(6)[a]
H(241)	310(3)	404(5)	107(3)	84(5)[a]
H(242)	254(3)	467(5)	176(3)	84(5)[a]
H(243)	316(3)	352(5)	198(3)	85(5)[a]
H(25)	99(3)	414(5)	156(3)	84(5)[a]
H(26)	−22(3)	233(5)	121(3)	84(5)[a]
H(27)	17(3)	−9(5)	79(3)	84(5)[a]
H(291)	132(3)	−204(5)	46(3)	84(5)[a]
H(292)	216(3)	−149(5)	15(3)	84(5)[a]
H(293)	216(3)	−205(4)	115(3)	84(5)[a]

[a] Isotropic temperature factor.

TABLE 2

SELECTED BOND LENGTHS (Å) AND ANGLES (°)[a,b]

Fe–Fe′	2.518(1)	Fe–C(1)	2.137(4)
Fe–C(11)	1.924(3)	Fe–C(2)	2.125(4)
Fe–C(11′)	1.931(3)	Fe–C(3)	2.099(4)
Fe–C(21)	1.781(4)	Fe–C(4)	2.108(4)
Fe–Cp	1.759(4)	Fe–C(5)	2.140(4)
C(11)–N(1)	1.240(4)	C(21)–N(2)	1.184(5)
N(1)–C(12)	1.412(5)	N(2)–C(22)	1.396(5)
Cp–Fe–C(11)	121.1(2)	C(11)–Fe–C(11′)	98.4(2)
Cp–Fe–C(11′)	118.4(2)	C(11)–Fe–C(21)	95.6(2)
Cp–Fe–C(21)	126.5(2)	C(11′)–Fe–C(21)	89.1(2)
Cp–Fe–Fe′	139.5(1)	C(11)–Fe–Fe′	49.4(1)
C(21)–Fe–Fe′	93.7(1)	C(11′)–Fe–Fe′	49.1(1)
Fe–C(11)–Fe′	81.6(2)	Fe′–C(11)–N(1)	134.1(3)
Fe–C(11)–N(1)	144.3(3)	Fe–C(21)–N(1)	178.8(3)
C(11)–N(1)–C(12)	131.7(3)	C(21)–N(1)–C(22)	158.6(3)

[a] Cp is the centroid of the cyclopentadienyl ring. [b] Primed atoms refer to the symmetry position $1 - x$, $- y$, $- z$.

perspective view of the complex showing the atom numbering scheme. A full list of bond lengths and angles and lists of thermal parameters and structure factors are available from the authors.
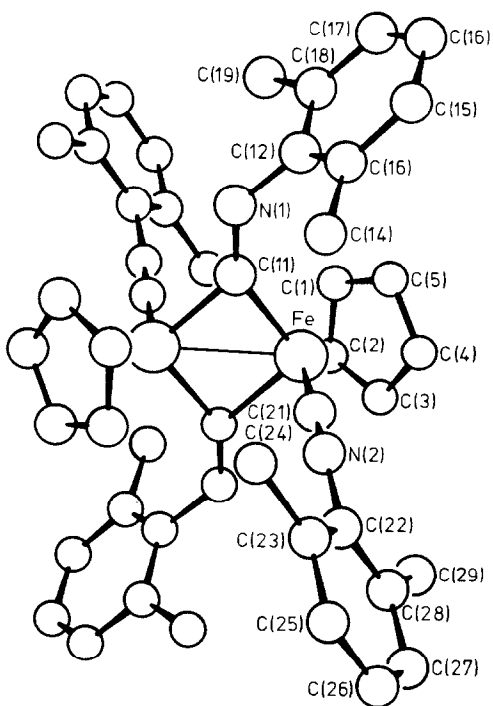

Fig. 1. A perspective view of 1a showing the atom numbering scheme.
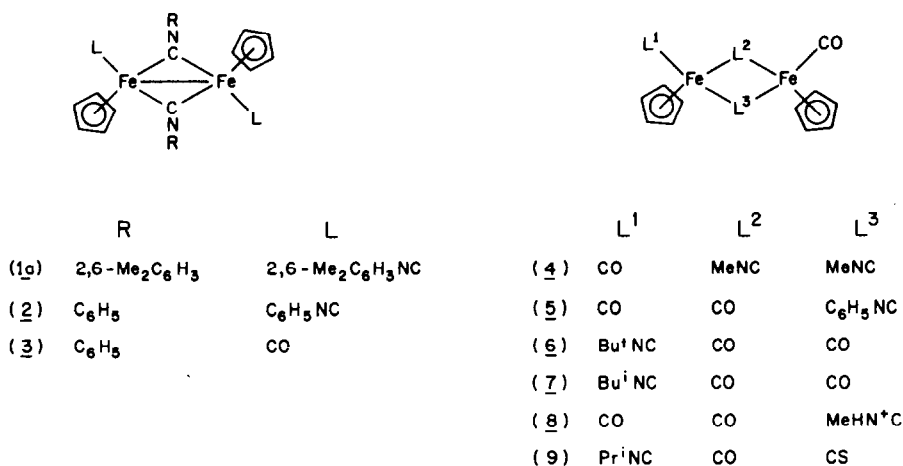
Results and discussion

Crystal structure of trans-[{Fe(η^5-C$_5$H$_5$)(CNC$_6$H$_3$Me$_2$-2,6)$_2$}$_2$] (1a)

The binuclear complex **1a** consists of isolated molecules lying across a centre of inversion. The coordination sphere of each iron atom comprises a pentahapto-cyclopentadienyl ligand and two bridging and one terminal 2,6-dimethylphenyl isocyanide ligands. As the complex has $\bar{1}$ symmetry, the bridging Fe$_2$C$_2$ ring is strictly planar, and the two cyclopentadienyl groups have a *trans* configuration.

The structures of a number of bis(cyclopentadienyliron) complexes containing bridging and/or terminal isocyanide ligands have been determined. These are depicted in Scheme 1 and relevant bond lengths and bond angles are given in Table 3. Complexes **2** (with bridging and terminal phenylisocyanide ligands) and **3** (with bridging phenylisocyanide and terminal carbonyl ligands) also have $\bar{1}$ symmetry, whereas in the other complexes **4–9** the cyclopentadienyl rings have a *cis* configuration and the bridging Fe$_2$C$_2$ rings are not planar with the two Fe–C–Fe moieties folded along the Fe–Fe axis away from the cyclopentadienyl ligands.

The iron–iron distance of 2.518(1) Å in **1a**, although slightly shorter than those reported for the other complexes in Table 2 (with the exception of **9** which has a bridging CS ligand), is not significantly different from the mean Fe–Fe distance of 2.527(6) Å in complexes **2–8**. The Fe–C bond lengths in **1a** all lie within the range of previously reported values (Table 3). The two independent Fe–C (bridging) bond lengths in **1a** are not significantly different (difference 0.007(5) Å) whereas in the phenylisocyanide analogue **2** the bridging Fe–C bonds are significantly asymmetric (difference 0.029(8) Å) with the longer bond *syn* to the phenyl group. In **4**, which contains two crystallographically independent bridging methyl isocyanide ligands, the Fe–C bonds *syn* to the methyl groups are also both longer than the *anti* bonds; the difference is, however, significant for only one of the two bridging ligands.

The C(11)–N(1)–C(12) bond angle in the bridging isocyanide ligand of 131.7(3)° compares well with the range of 124.1(6)–131° for the equivalent angles in **2–5**. It is

	R	L		L^1	L^2	L^3
(**1a**)	2,6-Me$_2$C$_6$H$_3$	2,6-Me$_2$C$_6$H$_3$NC	(**4**)	CO	MeNC	MeNC
(**2**)	C$_6$H$_5$	C$_6$H$_5$NC	(**5**)	CO	CO	C$_6$H$_5$NC
(**3**)	C$_6$H$_5$	CO	(**6**)	Bu^{t}NC	CO	CO
			(**7**)	Bu^{i}NC	CO	CO
			(**8**)	CO	CO	MeHN$^+$C
			(**9**)	Pr^{i}NC	CO	CS

SCHEME 1

TABLE 3

COMPARISON OF GEOMETRIES OF COMPLEXES RELATED TO $trans$-$[\{Fe(\eta^5\text{-}C_5H_5)\text{-}(CNC_6H_3Me_2\text{-}2,6)_2\}_2]$ (1a) [a] (see Scheme 1 for the key to the complex numbering)

	1a	2[b]	3[c]	4[d]	5[e]	6[f]	7[g]	8[h]	9[i]
Fe–Fe	2.518(1)	2.523(1)	2.53	2.538(1)	2.53	2.523(2)	2.524(3)	2.521(3)	2.494(3)
Fe–C(N)$_b$	1.924(3)	1.905(6)	1.93[j]	1.947(7)	1.90			1.87(1)	
	1.931(3)	1.934(6)		1.937(7)				1.88(1)	
				(1.948(7))					
Fe–C(N)$_t$	1.782(3)	1.775(6)				1.81(1)	1.85(2)		1.81(2)
Fe–Cp	1.758(4)	1.757[j]	–	1.749	–	1.74	1.74(2)	1.75	1.74
				1.758		1.74	1.76(2)	1.73	1.75
C$_b$–N	1.240(4)	1.242(8)	–	1.216(8)	–			1.28(1)	
				1.226(8)					
C$_t$–N	1.183(4)	1.161(8)				1.16(1)	1.13(2)		1.18(2)
Fe–C(N)$_b$–Fe	81.5(2)	82.2(3)	81.7	81.63(3)	84			84.6(4)	
C$_t$–N–C	131.8(3)	126.4(5)	129	124.1(6)	131			124(1)	
				126.8(7)					
Fe–C$_t$–N	178.8(3)	178.4(4)				178.5(8)	178(1)		178(3)
C$_t$–N–C	158.5(3)	171.1(6)				171.5(9)	176(2)		177(2)
D	0	0	0	22.2(3)	14	17.7	14.4	18.5	17.8

[a] Distances in Å, angles in degrees. The subscripts b and t refer to bridging and terminal ligands respectively. Cp is the centroid of the cyclopentadienyl ring. D is the dihedral angle between the two Fe–C$_b$–Fe bridging planes. [b] W.P. Fehlhammer, A. Mayr and W. Kehr, J. Organomet. Chem., 197 (1980) 327. [c] J.A.S. Howell, M.J. Mays, I.D. Hunt, and O.S. Mills, J. Organomet. Chem., 128 (1977) C29. [d] F.A. Cotton and B.A. Frenz, Inorg. Chem., 13 (1974) 253. [e] K.K. Joshi, O.S. Mills, P.L. Pauson, B.W. Shaw, and W.H. Stubbs, Chem. Commun., (1965) 181. [f] R.D. Adams, F.A. Cotton, and J.M. Troup, Inorg. Chem., 13 (1974) 257. [g] I.L.C. Campbell and F.S. Stephens, J. Chem. Soc., Dalton Trans., (1975) 982. [h] S. Willis, A.R. Manning, and F.S. Stephens, J. Chem. Soc., Dalton Trans., (1979) 23. [i] J. Howell, P. Mathur, R. Kumar, A.R. Manning, and F.S. Stephens, J. Organomet. Chem., 262 (1984) 227. [j] Value calculated from the published data.

interesting to note that protonation of the nitrogen atom in **8** has very little effect on the C–N–C bond angle (124(1)°). For the terminal isocyanide ligand in **1a** the Fe–C(21)–N(2) bond angle is approximately linear (178.8(3)°), as are the equivalent angles in **2**, **6** and **7**, but whereas in these latter complexes the bond angles at nitrogen are also close to linear (> 171°), the C(21)–N(2)–C(22) angle in **1a** is 158.5(3)°. This bending at N(2) may be ascribed to a steric interaction between the C(24) methyl group on the terminal isocyanide ligand and the C(14) methyl group on the bridging isocyanide ligand (see Fig. 2). The C(14) · · · C(24) distance (3.882(7) Å) is shorter than the sum of the Van der Waals radii (4.0 Å) for two methyl groups. An increase of the angle at N(2) to between ca. 171 to 180° would result in a decrease of the C(14) · · · C(24) distance to between ca. 3.3 to 2.9 Å resulting in considerable steric strain. The Fe–Fe–C(21) plane is not perpendicular to the Fe$_2$C$_2$ bridging plane but is angled so that the Fe–C(21) bond is bent away from the closest dimethylphenyl group of the bridging isocyanide ligands (Fig. 2) with a dihedral angle of 85.7° between the Fe$_2$C$_2$ bridging plane and the Fe–Fe–C(21) plane.

^{1}H NMR study of $[\{Fe(\eta^5\text{-}C_5H_5)(CNC_6H_3Me_2\text{-}2,6)_2\}_2]$ (1)

Considerable evidence now supports the mechanism proposed by Adams and Cotton [5] to account for the fluxional behaviour of $[\{Fe(\eta^5\text{-}C_5H_5)(CO)_2\}_2]$. This
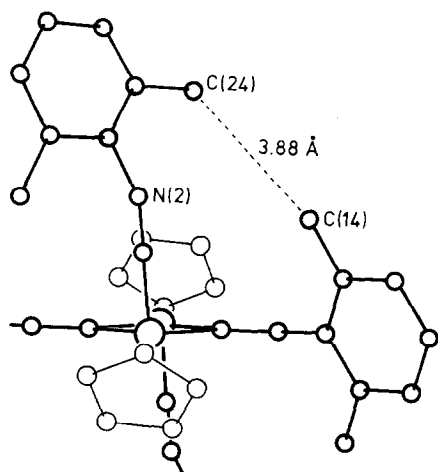
Fig. 2. A partial view of **1a** showing the short intramolecular contacts.

involves initial pairwise opening of the bridging groups to yield an intermediate which may undergo rotation about the iron–iron bond. Thus the complex [{Fe(η^5-C$_5$H$_5$)(CO)$_2$}$_2$] exists in solution as a mixture of *cis*- and *trans*-isomers and NMR studies are consistent with the postulates that (i) *cis–trans* interconversion is slow, (ii) bridge–terminal carbonyl exchange in the *cis*-isomer is slow, and, (iii) bridge–terminal interconversion in the *trans*-isomer is rapid. In terms of the Adams–Cotton mechanism, bridge–terminal exchange in the *trans*-isomer may take place without iron–iron bond rotation in the bridged intermediate, while bridge–terminal exchange in the *cis*-isomer requires iron–iron bond rotation which also results in *cis–trans* interconversion. The significantly higher activation energy for the latter process is ascribed to the need for bond rotation.

The room temperature (303 K) ^{1}H NMR spectrum of **1** consists of non-interconverting *cis*- and *trans*-isomers, and the spectrum may be assigned [7] on the basis of its superficial similarity to that of the ^{13}C and ^{1}H variable temperature NMR spectra reported for [{Fe(η^5-C$_5$H$_5$)(CO)$_2$}$_2$] [5]. Variable temperature ^{1}H NMR studies of **1** in dichloromethane-d_2 and toluene-d_8 confirm these assignments and also lend strong support to the Adams–Cotton mechanism [5] for bridge–terminal, *cis–trans* isomerization which has been reported for related systems.

The methyl resonances of **1** (193–303 K, CD$_2$Cl$_2$) are shown in Fig. 3 and chemical shift data for **1** in this solvent are given in Table 4. The intensity ratio of the three resonances in the methyl region of the spectrum recorded at 303 K is ca. 1.2/1/1.1 (Fig. 3 a,d/b,c/e) and these resonances are assigned to the *cis*-bridging, *trans*-terminal and -bridging, and *cis*-terminal methyl groups of the isocyanide ligands, respectively. This assignment is in agreement with the interpretation of the spectra recorded at lower temperatures. Similar results are obtained in toluene-d_8. Two cyclopentadienyl resonances (ratio 2.4/1) are also observed at 303 K and are accordingly assigned to the *cis*- and *trans*-isomers of **1** respectively. As was observed in toluene [7], the *cis*-isomer is thus the major isomer in the mixture. At higher temperatures (in toluene-d_8) all the methyl group resonances broaden simultaneously and coalescence occurs at ca. 80°C (90 MHz). This suggests that
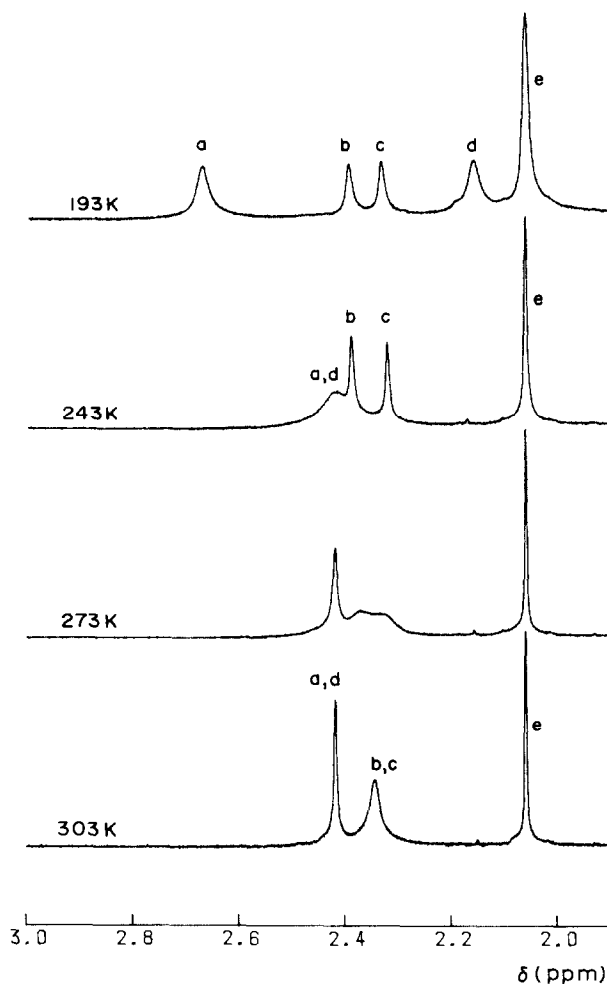
Fig. 3. Selected low temperature ^{1}H NMR spectra at 500 MHz of the methyl signals of [{Fe(η^5-C$_5$H$_5$)(CNC$_6$H$_3$Me$_2$-2,6)$_2$}$_2$] (1) in CD$_2$Cl$_2$.

bridge–terminal isocyanide interchange of the *cis*-isomer occurs at the same time as *cis–trans* isomerization, consistent with the Adams–Cotton mechanism. However, it is the variable temperature NMR data at temperatures lower than 303 K which provide mechanistic information on lower energy processes which are not readily

TABLE 4

^{1}H NMR CHEMICAL SHIFT VALUES^a FOR METHYL AND CYCLOPENTADIENYL SIGNALS FOR [{Fe(η^5-C$_5$H$_5$)(CNC$_6$H$_3$Me$_2$-2,6)$_2$}$_2$]

Me	2.06, 2.16, 2.33, 2.39, 2.67
C$_5$H$_5$	4.60, 4.65

^{a} In CD$_2$Cl$_2$ solution at 193 K referenced to CHDCl$_2$ signal 5.32 ppm at 303 K.
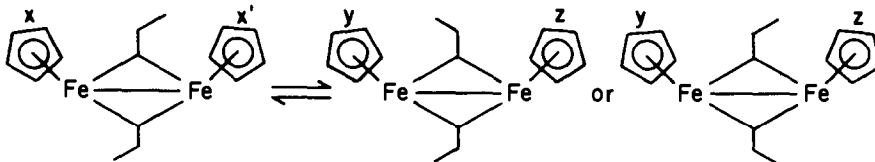
Fig. 4. Nitrogen inversion of the bridging isocyanide ligands in cis-[{Fe(η^5-C$_5$H$_5$)(CNC$_6$H$_3$Me$_2$-2,6)$_2$}$_2$].

accessible for the [{Fe(η^5-C$_5$H$_5$)(CO)$_2$}$_2$] system. Thus, between 303 and 273 K, the b,c resonance broadens and at ca. 273 K re-emerges as two resonances, b and c, assigned from their chemical shifts [5] as the bridging and terminal isocyanides of the *trans*-isomer respectively. Also below 303 K, the a,d resonance broadens and at temperatures below 243 K the resonance re-emerges as two resonances, a and d. At 193 K the intensity ratio of the cyclopentadienyl resonances has changed to approximately 5/1 and the ratio of the *cis* methyl resonances (a, d, e) to the *trans* methyl resonances (b, c) is also approximately 5/1, confirming the peak assignments. This would suggest that the *trans*-isomer is being precipitated from solution in CD$_2$Cl$_2$ at this temperature in preference to the *cis*-isomer.

The appearance of two resonances for the bridging *cis* methyl groups but not for the terminal *cis* methyl groups can be explained in either of two ways. Firstly, in line with previous arguments by Adams and Cotton, nitrogen inversion, as shown in Fig. 4 is possible. However, only the two original cyclopentadienyl resonances are observed under the conditions in which the nitrogen inversion process is supposed to be frozen out. Three cyclopentadienyl resonances [x (or x'), y and z] would be expected unless fortuitous overlap of resonances occurs. A second explanation involves rotation of the isocyanide ligand phenyl ring about the C–N bond. Two
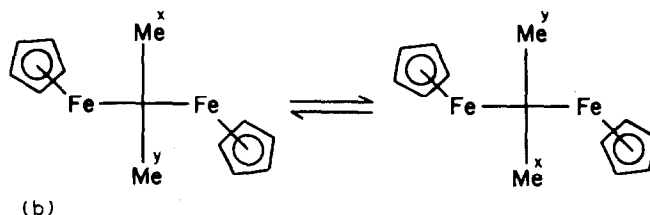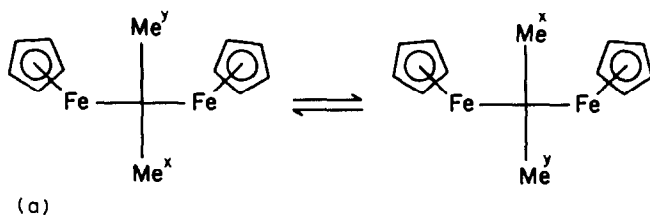

(a)

(b)

Fig. 5. (a) Rotation of the bridging isocyanide ligand phenyl ring about the C–N bond in cis-[{Fe(η^5-C$_5$H$_5$)(CNC$_6$H$_3$Me$_2$-2,6)$_2$}$_2$] (only one ligand shown, in edge view). (b) Rotation of the bridging isocyanide ligand phenyl ring about the C–N bond in trans-[{Fe(η^5-C$_5$H$_5$)(CNC$_6$H$_3$Me$_2$-2,6)$_2$}$_2$] (only one ligand shown, in edge view).

TABLE 5

DYNAMIC NMR DATA[a] AND FREE ENERGIES OF ACTIVATION FOR [{Fe(η^5-C$_5$H$_5$)(CNC$_6$H$_3$Me$_2$-2,6)$_2$}$_2$]

Process	$\Delta\nu$ (Hz)	T_c [b] (K)	k (s^{-1})	ΔG^* (kJ mol^{-1})
C$_p$ ⇌ C$_p$[c]	14	350	31	76
Me$_b$ ⇌ Me$_c$	40	280	91	58
Me$_a$ ⇌ Me$_d$	210	240	476	46

[a] 350 K; toluene-d_8 solution, 90 MHz. 280 and 240 K; methylene chloride-d_2 solution 500 MHz.
[b] Coalescence temperature (± 5 K). [c] Cp = cyclopentadienyl.

methyl resonances together with a single cyclopentadienyl resonance would be expected for the *cis*-isomer (Fig. 5a), consistent with our experimental data. For the *trans*-isomer, even if the exchange process was limiting, only one methyl and one cyclopentadienyl resonance would be expected (Fig. 5b). Indication that restricted bond rotation is feasible comes from the X-ray crystal structure data in which methyl–methyl interactions between the isocyanide ligands have been detected.

Table 5 summarizes the rate constants and corresponding free energies of activation at the coalescence point for the identified processes. These data were obtained from the coalescence temperature and the use of the expressions $k = \pi\Delta\nu/2$ and $\Delta G^\ddagger = 8.31T_c[23.76 + \ln(T_c/k)]$ [19].

Acknowledgements

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