Spectroscopic Study of the Structures of $[M_2(\eta\text{-}C_5H_5)_2(CO)_n(CNR)_{4-n}]$ Complexes (n = 1 or 2; M = Fe or Ru) in Solution. The Structure of *cis*-$[(\eta\text{-}C_5H_5)(OC)Fe(\mu\text{-}CO)(\mu\text{-}CNPr^i)Fe(CNPr^i)(\eta\text{-}C_5H_5)]$ † in the Solid State

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Various $[M_2(\eta\text{-}C_5H_5)_2(CO)_n(CNR)_{4-n}]$ complexes have been prepared [n = 2, M = Fe, R = Ph, p-$ClC_6H_4CH_2$, $PhCH_2$, p-$MeC_6H_4CH_2$, p-$MeOC_6H_4CH_2$, D(+)-Ph(Me)CH, Me, Et, Pr^n, Bu^n, Pr^i, C_6H_{11}, or Bu^t; M = Ru, R = Pr^i; n = 1, M = Fe, R = Me, Et, or Pr^i]. In solution, they exist as rapidly interconverting equilibrium mixtures of isomers; where n = 2, the RNC ligands are less likely to adopt bridged as opposed to terminal co-ordination as R is varied along the above series. The isomer distribution is a consequence of electron-withdrawing R favouring μ-CNR co-ordination and, less importantly, the more bulky R favouring terminal CNR. Where n = 1, only one predominant isomer is observed in solution. The crystal and molecular structure of *cis*-$[Fe_2(\eta\text{-}C_5H_5)_2(CO_t)(CNR_t)(CO_\mu)(CNR_\mu)]$ (R = Pr^i) has been determined by an X-ray diffraction study. It has been solved by the heavy-atom method from photographic data and refined by full-matrix least squares to R = 0.103 for 807 non-zero unique reflections. Crystals are monoclinic with space group $P2_1/c$ (no. 14), Z = 4, a = 13.881 ± 0.015, b = 10.755 ± 0.010, c = 15.262 ± 0.015 Å, and β = 112.5 ± 0.1°.

COMPLEXES of the type $[M_2(\eta\text{-}C_5H_5)_2(CO)_n(CNR)_{4-n}]$ (M = Fe or Ru; n = 1—4) are generally found as one isomer in the solid state but as a rapidly interconverting equilibrium mixture in solution. Previously we have reported [1-3] our spectroscopic studies on those complexes where n = 4 and 3; here we describe our investigation of the series where n = 2 and 1, together with an X-ray diffraction study of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNPr^i)_2]$ which has a molecular structure in the solid state that is of a previously undetermined isomer.

RESULTS AND DISCUSSION

Reaction of $[M_2(cp)_2(CO)_4]$ (M = Fe or Ru; cp = η-C_5H_5) with RNC in refluxing benzene, toluene, or related solvents gives $[M_2(cp)_2(CO)_n(CNR)_{4-n}]$ derivatives where n = 1—3. Where R is an alkyl group, the yields of disubstituted products are generally around 50%, but where R is phenyl or benzyl, they are often very low. Where R is alkyl, the trisubstituted derivatives may also be isolated in yields of around 15% (except where R = Bu^t). The complexes are isolated as air-stable crystalline solids whose solubility in common organic solvents depends on R. In the absence of air, solutions are normally stable, with the exception of those in carbon tetrachloride. Here for n = 2 the appearance of bands at 1 992 and 2 165 cm^{-1} (R = C_6H_{11}) is indicative of the formation of [Fe(cp)(CO)(CNR)Cl].[4,‡] The rate of chlorination depends markedly on R, increasing with the proportion of terminal RNC isomers in solution. The observation of the product resulting from only symmetrical scission is consistent with the reaction with I_2, which also yields only the [Fe(cp)(CO)(CNR)I] derivative.[5]

(*a*) $[M_2(cp)_2(CO)_2(CNR)_2]$ *Complexes*.—(*i*) *Infrared spectra*. The i.r. spectra of the complexes in solution generally show five absorption bands in the 1 600—2 200 cm^{-1} region (Table 1). Band A is attributed to ν(CN_μ), B to ν(CO_μ), C and D to ν(CO_t), and E to ν(CN_t) vibrations. With the exception of B and D, absorption bands are not simple and clearly contain more than one component. Band A is broad and usually asymmetric with an envelope which varies with both R and solvent. Band C may be resolved into two well separated components in heptane solution for all complexes except those of the p-$XC_6H_4CH_2$ ligands which are not sufficiently soluble in this solvent. Resolution is not possible using other solvents, but the presence of two components is usually apparent. Band E is very broad and asymmetric. In some instances (*e.g.* for R = C_6H_{11} or Pr^i) it clearly has two well defined shoulders at lower frequencies, and for R = Et a second resolved peak is also apparent. This seems to be real, but the spectra of this compound also show a band at *ca.* 1 725 cm^{-1} which could not be removed (*e.g.* by chromatography), but its intensity does vary from sample to sample. A similar absorption band occurs with some, but not all samples of other compounds. In these cases, it is clearly due to a removable impurity and so we assume that this is also true for the EtNC derivative. As there is no evidence for detectable concentrations of non-bridged isomers, the six isomers (1a) to (1f) are possible. A μ-co-ordinated isonitrile is not linear, but generally has an R–NC angle of *ca.* 130° and lies in the Fe_2C plane. Therefore there are two forms each of (1a) to (1d) which depend on the orientation of the μ-R group (Figure 1).

The successful interpretation of the i.r. spectra of metal

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† μ-Carbonyl-*b*-carbonyl-*ae*-dicyclopentadienyl-μ-isopropyl isocyanide-*f*-isopropyl isocyanidedi-iron.

‡ The complex $[Fe(cp)(CO)(CNPr^i)Cl]$ exhibits absorptions at 2 153 and 1 993 cm^{-1} (ref. 4).

TABLE 1

I.r. spectral data

		Absorption bands [a]				
(a) $[M_2(cp)_2(CO)_2(CNR)_2]$ M = Fe, R = p-$ClC_6H_4CH_2$	Sovent [b]	A	B	C	D	E
	Xylene	1 695(6.2)	1 774(1.3)	1 945(3.8)	1 984(10)	2 116(1.1)
	thf	1 691(6.4)	1 773(1.0)	1 940(3.1)	1 981(10)	2 117(0.7)
$C_6H_5CH_2$	Xylene	1 702(7.3)	1 774(2.4)	1 942(4.9)	1 982(10)	2 121(1.7)
	thf	1 699(6.3)	1 775(2.4)	1 940(4.1)	1 979(10)	2 121(1.3)
p-$MeC_6H_4CH_2$	Xylene	1 699(6.7)	1 773(2.1)	1 942(5.1)	1 983(10)	2 120(1.8)
	thf	1 696(7.1)	1 773(2.2)	1 941(4.7)	1 976(10)	2 121(1.5)
p-$MeOC_6H_4CH_2$	Xylene	1 696(8.3)	1 772(2.1)	1 942(5.2)	1 983(10)	2 122(0.8)
	thf	1 698(6.9)	1 772(2.3)	1 940(4.9)	1 977(10)	2 120(1.7)
Me	Xylene	1 713(11.1)	1 775(5.1)	1 938(8.9)	1 982(10)	2 139(4.2)
	C_7H_{16}	1 720(7.1)	1 784(3.5)	1 944(5.1) 1 952(4.4)	1 990(10.0)	2 127(1.2)
	mull	1 697s, br		1 926s	1 971s, br	
Et	Xylene	1 691(10.0)	1 771(8.5)	1 937(12.1)	1 981(10.0)	2 102(4.9) 2 128(6.2)
Pr^n	Xylene	1 702(13.1)	1 771(10)	1 936(15.0)	1 981(10)	2 122(8.1)
	thf	1 697(12.9)	1 771(10.2)	1 936(15.3)	1 976(10)	2 124(7.6)
	C_7H_{16}	1 706(7.6)	1 783(8.3)	1 943(10.2) 1 950(10.6)	1 989(10)	2 118(4.2)
	MeCN	1 694(19.6)	1 758(12.5)	1 936(23.3)	1 972(10)	2 127(15.0)
Bu^n	Xylene	1 706(17.3)	1 772(11.2)	1 937(18.8)	1 979(10)	2 125(11.2)
Pr^i	Xylene	1 696(25.1)	1 773(16.8)	1 936(21.8)	1 979(10)	2 111(11.9)
C_6H_{11}	Xylene	1 696(37.2)	1 772(27.6)	1 935(41.5)	1 978(10)	2 115(23.4)
	C_7H_{16}	1 697(21.5)	1 783(21.3)	1 941(28.5) 1 951(15.1)	1 987(10)	2 062 (sh) 2 090 (sh) 2 111(11.4)
Bu^t	C_7H_{16}	1 715(2.6)	1 750(10) 1 779(3.0)	1 935(5.0) 1 945(4.3)		2 050(3.3) 2 099 (sh)
Ph(Me)CH	Xylene	1 689(9.5)	1 774(3.9)	1 942(7.3)	1 983(10)	2 112(2.7)
Ph	CS_2	1 683(9.0)		1 945(7.0)	1 985(10)	
M = Ru, R = Pr^i	C_7H_{16}	1 694(7.8)	1 786(1.8)	1 955(4.2) 1 958(4.0) 1 947(7.9)	1 992(10)	2 116(0.4)
(b) $[Fe_2(cp)_2(CO)(CNR)_3]$						
R = Me	C_7H_{16}	1 702(10)		1 954(3.5) 1 944(7.7) 1 934(5.8)		2 120(4.0)
Et	C_7H_{16}	1 678(10 1 686 (sh)		1 958(4.6) 1 941(9.6) 1 930(7.0)		2 115 (sh) 2 095(4.9)
Pr^i	C_7H_{16}	1 682(10) 1 686 (sh)		1 950 (sh) 1 940(8.9) 1 930(6.6)		2 145(2.7) 2 104 (sh) 2 044 (sh)

[a] Peak positions (cm^{-1}) with relative peak heights in parentheses; s = strong, br = broad, w = weak, sh = shoulder. [b] thf = Tetrahydrofuran, C_7H_{16} = heptane.

carbonyls has been aided by the suppositions that (*a*) $\nu(CO_t)$ and $\nu(CO_\mu)$ modes do not interact significantly with other molecular vibrations or each other, (*b*) that $\nu(CO_t)$–$\nu(CO_t)$ or $\nu(CO_\mu)$–$\nu(CO_\mu)$ interaction constants are positive, and (*c*) that C–O stretching dipole gradient vectors are directed along the C–O bond and, for a normal mode of vibration, may be summed by the usual methods of vector addition. It is assumed that (*a*), (*b*), and (*c*) are applicable to ν(CN) vibrations and that (*d*) ν(CN)–ν(CO) interactions are negligible and (*e*) the specific intensities of the absorption band per CO or CNR ligand are comparable for the four types of vibration that we are considering, even though the bands due to isocyanide modes tend to be much broader. Using these assumptions, it is possible to predict the spectra of the various isomers (Figure 2), and in relating the observed spectra to those predicted we assume that changes in the relative intensities of the absorption bands reflect changes in the relative amounts of isomers present in solution.

Where R = Ph, bands B and E are not observed, and therefore the complex exists solely as a (1a)/(1b) mixture in solution. From the relative intensities of bands C and D, a *cis* : *trans* ratio of 59 : 41 may be calculated. Analogous values for $[Fe_2(cp)_2(CO)_3(CNPh)]$ (which also exists in solution solely as the μ-CNR isomer) [6] and $[Fe_2(cp)_2(CO)_4]$ [3] of 49 : 51 and 43 : 57 respectively in CS_2 indicate an increasing proportion of *cis* isomer with increasing PhNC substitution. Varying R also has its consequences, as the *cis* isomer (1a) is overwhelmingly the most important to be found in solutions of $[Fe_2(cp)_2(CO)_2(CNCH_2C_6H_4Cl\text{-}p)_2]$ and only small amounts of (1b) (perhaps), (1c), and (1d) are present. For complexes other than R = Ph or Bu^t, appearance of bands B and E indicates the appearance of isomers (1c) and (1d). Where R = Bu^t, only isomers (1c) to (1f) are present [as evidenced by the lack of band D and the presence of the $\nu(CO_\mu)$ band at 1 750 cm^{-1} due to (1e) and (1f)]. Only for this complex can isomers (1e) and (1f) be detected in significant concentration, and consistent with this two $\nu(CN_t)$ absorptions bands are observed. Although calculation of the (1e) : (1f) ratio from these bands is not possible due to broadness and a contribution from isomers (1c) and (1d), n.m.r. results (see below) show that the *cis* : *trans* ratio in CH_2Cl_2 at −80 °C is 66 : 33.

Spectra of the other complexes are consistent with the presence of significant amounts of isomers (1a) to (1d) with the proportion of [(1c) + (1d)] increasing in the order R = p-$ClC_6H_4CH_2$ < $C_6H_5CH_2$ < p-$MeC_6H_4CH_2$ < p-$MeOC_6H_4CH_2$ < $C_6H_5(Me)CH$ < Me < Et < Pr^n < Bu^n < Pr^i < C_6H_{11}. In terms of solvent, the proportion of [(1c) + (1d)] increases in the order heptane < xylene < tetrahydrofuran < acetonitrile where R = alkyl; when R = p-$XC_6H_4CH_2$, the positions of xylene and tetrahydrofuran are reversed.

Where R = alkyl, band C clearly consists of two components, while band E is asymmetric and may actually be resolved into two components where R = Et.

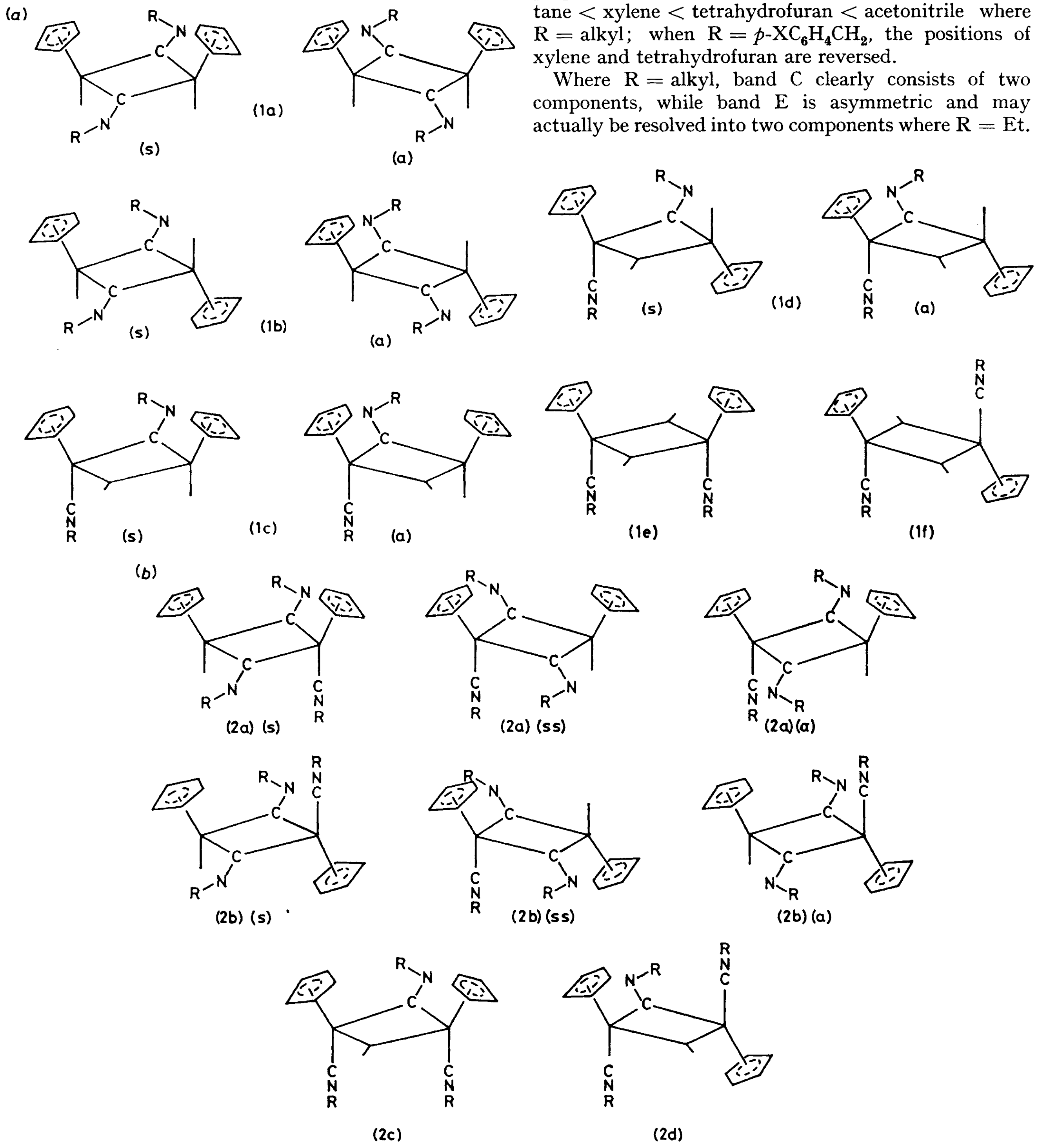

FIGURE 1 The possible isomers of (*a*) $[M_2(\eta\text{-}C_5H_5)_2(CO)_2(CNR)_2]$ (M = Fe or Ru) and (*b*) $[M_2(\eta\text{-}C_5H_5)_2(CO)(CNR)_3]$ with M atoms and CO ligands omitted for clarity; (s) and (ss) are *syn* forms. (a) are *anti* forms

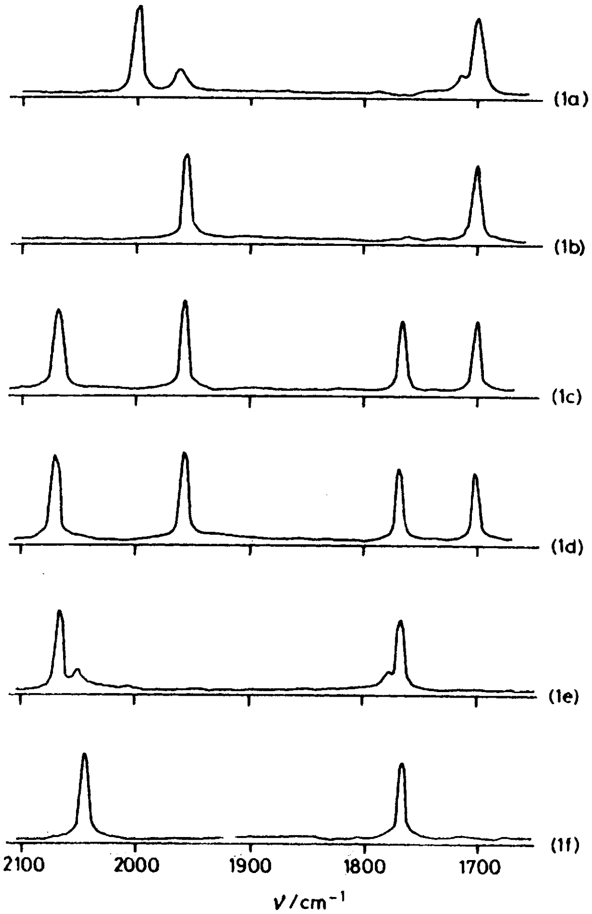

FIGURE 2 Infrared spectra predicted for the various $[M_2(\eta\text{-}C_5H_5)_2(CO)_2(CNR)_2]$ isomers in the $\nu(CN)/\nu(CO)$ regions

This may be due to either (*a*) the resolution of the $\nu(CO_t)$ absorption band of (1c) from that of (1d) or (*b*) resolution of the $\nu(CO_t)$ bands of the two forms of either (1b) or (1d) (with one isomer being absent) or a mixture of (1c) and (1d) in which the bands are coincident. If (*b*) is correct, one might also expect that the two forms of (1a) would also have different $\nu(CO_t)$ frequencies, and that band D would have two resolvable components separated by an amount comparable to the splitting in C (*i.e. ca.* 10 cm^{-1}). This is not observed, and while it is possible that only one form of (1a) is present in solution, n.m.r. results on $[Ru_2(cp)_2(CO)_2(CNPr^i)_2]$ indicate that both forms are present.

The i.r. spectra of the solid samples of these complexes are of three types. Where R = Me, Et, or p-$XC_6H_4CH_2$, two absorption bands are observed in the $\nu(CO_t)$ region and one or two in the $\nu(CN_\mu)$ region which are attributable to isomer (1a). Where R = Pr^n, Pr^i, Bu^n, or C_6H_{11}, four absorption bands due to $\nu(CN_\mu)$, $\nu(CN_t)$, $\nu(CO_t)$, and $\nu(CO_\mu)$ are observed which are attributable to (1c) or (1d), although for R = Pr^i, the configuration is definitely *cis* (1c) (see below). Where R = Bu^t, $\nu(CO_\mu)$ and $\nu(CN_t)$ bands are observed due to either (1e) or (1f). Absorption band splitting is observed for all compounds except where R = Pr^n.

We have previously suggested[1] that the isonitrile ligand may be encouraged to adopt a bridged as opposed to a terminal co-ordination by increasing the electron-withdrawing ability of R (electronic effect) or by decreasing its bulk (steric effect). If ligand bulk is varied by exchanging α protons for electron-donating methyl groups, the two effects reinforce one another. On the other hand, if it is varied by exchanging α protons for electron-withdrawing phenyl groups, the two effects are in opposition, and under such circumstances the electronic effect seems to be most important. Thus isomers (1a) and (1b) are overwhelmingly important for the strongly electron-withdrawing p-$ClC_6H_4CH_2$, while replacing the p-chloro-group by more electron-donating groups such as H, Me, or OMe brings about a noticeable increase in the importance of isomers having terminal CNR co-ordination. Even more effective in this respect is the replacement of an α proton by Me in Ph(Me)CH and then the Ph by Me in $MeCH_2$. It is noticeable that the steric effect of R depends not only on the cone angle at RNC which is a consequence of the number of substituents on the α carbon, but also on its effective bulk which increases with increasing chain length. This is not surprising, as the important steric interactions are those of R with the $Fe(cp)L_t$ moiety which are, to a certain extent, going to be a function of intramolecular contacts involving substituents on the β and subsequent carbon atoms. This accounts, at least partially, for $[Fe_2(cp)_2(CO)_2(CNR)_2]$ having the structure (1a) in the solid state when R = Me or Et but (1c) or (1d) when R = Pr^n or Bu^n.

Comparison of the spectra of $[M_2(cp)_2(CO)_2(CNPr^i)_2]$ (M = Fe or Ru) shows that the proportion of isomers [(1a) + (1b)] in solution is greater for ruthenium than for iron. A similar trend was observed in the $[M_2(cp)_2(CO)_3(CNR)]$ (M = Fe or Ru) series.[2]

(*ii*) *Structure of* $[Fe_2(cp)_2(CO)_2(CNPr^i)_2]$. A structural determination was undertaken in order to clarify

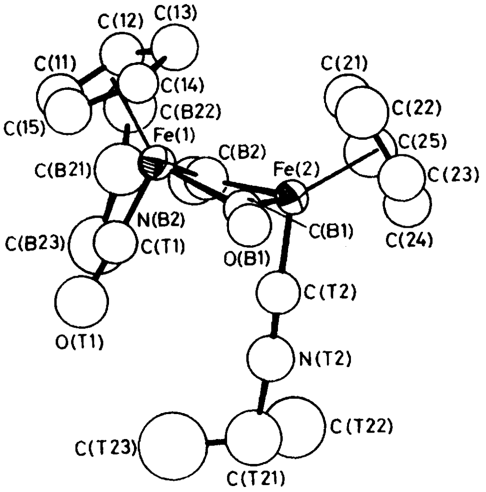

FIGURE 3 Perspective drawing of the $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNPr^i)_2]$ molecule and the atom-labelling system. Thermal ellipsoids are scaled to include 35% probability

the stereochemistry of either a (1c) or (1d) isomer. This molecule has the expected CO,CNR bridging system, but is a (1c) (*cis*) isomer rather than (1d) (*trans*). The molecular geometry is illustrated together with the labelling of the atoms in Figure 3 while Figure 4 shows the packing in the crystal. There are some intermolecular contacts of <3.4 Å; C(23) · · · C(23) {1 − *x*, *y*, *z*} at 3.30 Å, O(B1) · · · C(T21){1 − *x*, ½ + *y*, ½ − *z*} at 3.39 Å. Final atomic parameters are given in Table 2.

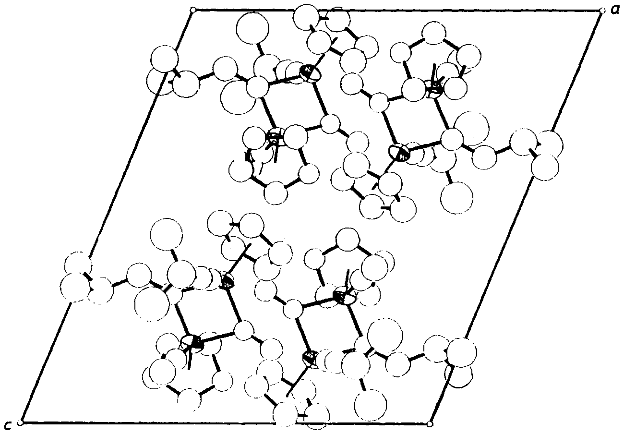

FIGURE 4 The packing of $[\mathrm{Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNPr^i)_2}]$ in the crystal

TABLE 2

Final atomic fractional co-ordinates (× 10^3) with estimated standard deviations in parentheses

Atom	*x*/*a*	*y*/*b*	*z*/*c*
Fe(1)	338.4(3)	41.9(3)	308.6(3)
Fe(2)	350.4(3)	−22.1(3)	154.3(3)
O(B1)	537(2)	−68(2)	321(1)
O(T1)	294(2)	−187(2)	376(2)
N(B2)	139(2)	10(2)	143(2)
N(T2)	291(2)	−289(2)	149(2)
C(B1)	451(2)	−39(2)	276(2)
C(B2)	236(3)	13(3)	187(2)
C(T1)	314(2)	−89(3)	347(2)
C(T2)	317(2)	−180(3)	152(2)
C(B21)	59(3)	32(3)	181(3)
C(B22)	−19(3)	135(3)	119(3)
C(B23)	−5(3)	−94(4)	172(3)
C(T21)	241(3)	−420(4)	141(4)
C(T22)	199(4)	−431(5)	213(5)
C(T23)	164(4)	−405(5)	44(4)
C(11)	280(3)	155(3)	389(3)
C(12)	280(3)	222(3)	311(3)
C(13)	380(3)	231(3)	308(3)
C(14)	450(2)	174(2)	397(2)
C(15)	388(3)	131(3)	445(2)
C(21)	341(3)	141(3)	78(3)
C(22)	443(3)	116(3)	124(3)
C(23)	461(3)	4(3)	90(3)
C(24)	362(3)	−38(3)	23(3)
C(25)	284(3)	50(3)	17(3)

TABLE 3

Bond lengths and angles with estimated standard deviations in parentheses *

(*a*) Distances (Å)

Fe(1) · · · Fe(2) 2.521(7)

Fe(1)–C(B1)	2.01(3)	Fe(2)–C(B1)	1.86(3)
Fe(1)–C(B2)	1.89(3)	Fe(2)–C(B2)	1.88(4)
Fe(1)–C(T1)	1.61(3)	Fe(2)–C(T2)	1.76(3)
Fe(1)–Cp(1)	1.75	Fe(2)–Cp(2)	1.74
C(T1)–O(T1)	1.21(3)	C(B1)–O(B1)	1.17(3)
C(B2)–N(B2)	1.26(3)	C(T2)–N(T2)	1.22(3)
N(B2)–C(B21)	1.45(4)	N(T2)–C(T21)	1.55(4)
C(B21)–C(B22)	1.58(4)	C(T21)–C(T22)	1.44(7)
C(B21)–C(B23)	1.59(5)	C(T21)–C(T23)	1.46(6)
C(11)–C(12)	1.38(4)	C(21)–C(22)	1.35(4)
C(12)–C(13)	1.41(4)	C(22)–C(23)	1.37(4)
C(13)–C(14)	1.47(4)	C(23)–C(24)	1.43(4)
C(14)–C(15)	1.39(4)	C(24)–C(25)	1.42(4)
C(15)–C(11)	1.44(4)	C(25)–C(21)	1.37(4)

(*b*) Angles (°)

cp(1)–Fe(1)–C(T1)	125	cp(2)–Fe(2)–C(T2)	126
cp(1)–Fe(1)–C(B1)	123	cp(2)–Fe(2)–C(B1)	121
cp(1)–Fe(1)–C(B2)	125	cp(2)–Fe(2)–C(B2)	125
C(B1)–Fe(1)–C(B2)	93(1)	C(B1–Fe(2)–C(B2)	98(1)
C(B1)–Fe(1)–C(T1)	90(1)	C(B1)–Fe(2)–C(T2)	91(1)
C(B2)–Fe(1)–C(T1)	92(1)	C(B2)–Fe(2)–C(T2)	87(1)
Fe(1)–C(B1)–Fe(2)	91(1)	Fe(1)–C(B2)–Fe(2)	84(1)
Fe(1)–C(B1)–O(B1)	133(2)	Fe(1)–C(B2)–N(B2)	142(3)
Fe(2)–C(B1)–O(B1)	145(3)	Fe(2)–C(B2)–N(B2)	134(3)
Fe(1)–C(T1)–O(T1)	178(3)	Fe(2)–C(T2)–N(T2)	179(3)
C(B2)–N(B2)–C(B21)	128(3)	C(T2)–N(T2)–C(T21)	171(3)
N(B2)–C(B21)–C(B22)	110(3)	N(T2)–C(T2)–C(T22)	108(4)
N(B2)–C(B21)–C(B23)	108(3)	N(T2)–C(T21)–C(T22)	97(4)
C(B22)–C(B21)–C(B23)	109(3)	C(T22)–C(T21)–C(T23)	115(4)
C(15)–C(11)–C(12)	105(3)	C(25)–C(21)–C(22)	116(3)
C(11)–C(12)–C(13)	113(3)	C(21)–C(22)–C(23)	107(3)
C(12)–C(13)–C(14)	104(3)	C(22)–C(23)–C(24)	106(3)
C(13)–C(14)–C(15)	108(3)	C(23)–C(24)–C(25)	110(3)
C(14)–C(15)–C(11)	110(3)	C(24)–C(25)–C(21)	102(3)

(*c*) Dihedral angles (°) between planes

Fe(1)–C(B1)–C(B2) Fe(2)–C(B1)–C(B2)	159
Fe(1)–Fe(2)–C(B1)–O(B1) Fe(1)–Fe(2)–C(B2)–N(B2)	161
Fe(1)–C(B1)–C(B2) C(11)–C(15)	54
Fe(2)–C(B1)–C(B2) C(21)–C(25)	57

* cp is the centroid of a cyclopentadienyl ring.

Bond lengths and bond angles within the molecule are given in Table 3 and details of the mean-plane calculations in Table 4. The dimensions within the molecule agree well with those observed in similar isonitrile containing complexes such as $[\mathrm{(cp)(OC)Fe(\mu\text{-}CNR)_2Fe(CO)(cp)}]$ (R = Me[7] and Ph[8]) and summarized in ref. 8 and $[\mathrm{(cp)(OC)Fe(\mu\text{-}CO)_2Fe(CNR)(cp)}]$ (R = $\mathrm{Bu^t}$[9] or $\mathrm{Bu^i}$[10]). The dihedral angle between the two $\mathrm{FeC_{\mu}Fe}$ planes of 161° is intermediate in the range 162—166° found for compounds containing terminal CNR ligands and the 158° found for the bis(μ-CNMe) derivative.

(*iii*) *Nuclear magnetic resonance spectra.* Hydrogen-1 and ^{13}C spectral data for the series $[\mathrm{M_2(cp)_2(CO)_2(CNR)_2}]$ (M = Fe, R = Me, Et, $\mathrm{Pr^i}$, or $\mathrm{Bu^t}$; M = Ru, R = $\mathrm{Pr^i}$) are summarized in Tables 4 and 5. Nuclear magnetic resonance data for the R = Me derivative have previously been reported.[11] In terms of exchange between isomers (1a) to (1f), limiting low-temperature spectra are obtained at *ca.* −10 °C where M = Fe and −30 °C where M = Ru. With the exception of the t-butyl complex, resonances due to *cis* and *trans* forms are not resolved (if indeed both are present in $\mathrm{CH_2Cl_2}$ at low temperature). The ^{1}H spectrum of the isopropyl derivative in the cp region, which is typical, is shown in

TABLE 4

Hydrogen-1 n.m.r. spectral data [a]

Complex	θ$_c$/°C	Isomer	cp	Other	Ratio (1a) + (1b) : (1c) + (1d)
(*a*)[Fe$_2$(cp)$_2$(CO)$_2$(CNR)$_2$]					
R = Me	−10	(1a)/(1b)	4.84	CH$_3$ 3.61 (s)	0.35 : 1
		(1c)/(1d)	4.71 4.50	μ-CH$_3$ 3.67 (s) te-CH$_3$ 2.89(s)	
		(1e)/(1f)	4.44	CH$_3$ 2.95 (s)	
R = Et	−10	(1a)/(1b)	4.82	CH$_3$ 1.36 (t, J = 7.3) CH$_2$ 3.92 (m)	0.15 : 1
		(1c)/(1d)	4.71 4.56	μ-CH$_3$ 1.38 (t, J = 7.2) te-CH$_3$ 0.99 (t, J = 7.1) μ-CH$_2$ 3.92 (m) te-CH$_2$ 3.18 (q)	
		(1e)/(1f)	4.45		
R = Pr^i	−10	(1a)/(1b)	4.80	CH$_3$ [b] CH 3.95 (sept)	0.06 : 1
		(1c)/(1d)	4.70 4.53	μ-CH$_3$ $\left.\begin{matrix}1.40\\1.34\end{matrix}\right\}$ (d, J = 6.5) te-CH$_3$ $\left.\begin{matrix}1.01\\0.99\end{matrix}\right\}$ (d, J = 6.5) μ-CH 3.92 (sept) te-CH 3.50 (sept)	
		(1e)/(1f)	4.44		
R = Bu^t	−20	(1e)/(1f)	4.37 4.47	CH$_3$ 1.20 (s)	
(*b*) [Ru$_2$(cp)$_2$(CO)$_2$(CNPr^i)$_2$]	−40	(1a)/(1b)	5.29	CH$_3$ 1.18 (d, J = 6.3) CH 3.36 (sept)	1 : 3.5
		(1c)/(1d)	5.21 5.06	μ-CH$_3$ 1.21 (d, J = 6.4) te-CH$_3$ $\left.\begin{matrix}1.07\\1.09\end{matrix}\right\}$ (d, J = 6.4) μ-CH 3.68 (sept) te-CH [b]	
(*c*) [Fe$_2$(cp)$_2$(CO)(CNR)$_3$]					
R = Me	0	(2a)/(2b)	4.58 4.76	μ-CH$_3$ 3.68 te-CH$_3$ 2.88	
		(2c)/(2d)	4.53		
R = Et	0	(2a)/(2b)	4.51 4.71	μ-CH$_3$ 1.36 (t, J = 6.7) te-CH$_3$ 0.97 (t, J = 7.4) μ-CH$_2$ 3.90 (m) te-CH$_2$ 3.15 (q)	
		(2c)/(2d)	4.51		
R = Pr^i	0	(2a)/(2b)	4.55 4.75	μ-CH$_3$ $\left.\begin{matrix}1.29\\1.36\end{matrix}\right\}$ (d, J = 6.5) te-CH$_3$ 0.96 (d, J = 6.5) μ-CH 3.94 (sept) te-CH 3.49 (sept)	
		(2c)/(2d)	4.45		

[a] Chemical shifts (δ) from SiMe$_4$ in CD$_2$Cl$_2$ solvent; s = singlet, d = doublet, t = triplet, sept = septet, q = quartet, μ = bridging, te = terminal. [b] Not detected.

Figure 5. From an integration of the peaks assigned as shown, a ratio of (1a) + (1b) to (1c) + (1d) can be obtained. As (1c)/(1d) are inherently chiral, the isopropyl resonances assigned exhibit diastereotopic methyl groups. In addition, a small resonance at *ca.* δ 4.45 is observed for all the iron complexes. The chemical shift (by comparison with the t-butyl complex) and the lack of temperature-dependent behaviour at lower temperatures is consistent with an assignment to (1e)/(1f), but because of its low intensity (less than 5% of the integrated intensity) an impurity may be responsible. Warming to 80 °C in [^{2}H$_8$]toluene results in coalescence to yield single broad cp and alkyl resonances indicative of both isomer interconversion and bridge–terminal isonitrile exchange.

This interconversion is thought to proceed *via* non-bridged species and has been discussed in detail by Adams and Cotton.[12] If the mechanism is restricted to symmetrical non-bridged species of the type [(cp)(RNC)(OC)FeFe(CO)(CNR)(cp)] then (*a*) the six isomers are divided into the two groups (1a), (1d), and (1e) and (1b), (1c), and (1f), (*b*) interconversion of isomers within each group is possible *via* a bridge opening and closing mechanism, and (*c*) it is not possible for the two groups to interconvert. Infrared and n.m.r. data show here, however, that (1f) $\rightleftharpoons$ (1e) interconversion takes place for the t-butyl derivative, and that (1c) (solid) $\rightleftharpoons$ (1a) (solution) interconversion occurs for the isopropyl complex. As explained in more detail elsewhere,[13] this implies the existence of an unsymmetrical [(cp)(RCN)$_2$FeFe(CO)$_2$(cp)] intermediate which allows linking of the two groups of isomers.

On cooling below −10 °C, further changes consistent with the slowing of nitrogen inversion occur. At −90 °C, the resonances due to (1c)/(1d) have now split into two unequal pairs in a ratio of *ca.* 2.5 : 1 assignable to the

TABLE 5

Carbon-13 spectral data [a]

Complex	Isomer	CO_t	CN_t	CO_μ	CN_μ	cp	Other	
(*a*) $[Fe_2(cp)_2(CO)_2(CNR)_2]$ [b]								
R = Me	(1a)/(1b)	211.0			248.5	84.5	CH_3	45.2
	(1c)/(1d)	212.4	161.4	280.1	257.5	84.5 85.2	μ-CH_3 t-CH_3	45.2 29.7
R = Et	(1a)/(1b)	211.0			245.4	85.3	CH_2 CH_3	*c* 15.7
	(1c)/(1d)	212.4	161.4	280.0	254.0	84.3 85.0	μ-CH_2 t-CH_2 μ-CH_3 t-CH_3	*c* 38.7 16.1 14.4
R = Pr^i	(1c)/(1d)	212.8	161.1	280.5	250.6	84.7 85.1	μ-CH_3 t-CH_2 μ-CH t-CH	23.9 22.6 62.1 47.5
R = Bu^t [d]	(1e)/(1f)		166.1 172.0	285.8 287.3		84.6 86.0	CH_3 C	30.0 30.2 *c*
(*b*) $[Ru_2(cp)_2(CO)_2(CNPr^i)_2]$								
	(1a)/(1b)	198.0			227.4	87.3	CH_3 CH	23.0 63.1
	(1c)/(1d)	200.7	142.2	252.8	221.2	86.3 86.8	μ-CH_3 t-CH_3 μ-CH t-CH	23.0 21.7 63.1 46.6
(*c*) $[Fe_2(cp)_2(CO)(CNR)_3]$ [b]								
R = Me	(2a)/(2b)	213.0	163.8		258.8	84.1 83.7	μ-CH_3 t-CH_3	45.0 29.2
R = Et	(2a)/(2b)	213.7	165.2		255.9	84.7 84.2	μ-CH_3 t-CH_3 μ-CH_2 t-CH_2	16.5 15.0 *c* 38.9
R = Pr^i	(2a)/(2b)	213.8	163.8		252.3	84.3 84.1	μ-CH_3 t-CH_3 μ-CH t-CH	23.8 22.6 61.5 47.1

[a] Chemical shifts in p.p.m. from $SiMe_4$; t = terminal, μ = bridging. [b] Disubstituted complexes at −10 °C (M = Fe) or −40 °C (M = Ru), trisubstituted complexes at 0 °C (CD_2Cl_2–CH_2Cl_2 solvent). [c] Not detected; may be under solvent resonance at 53.8 p.p.m. [d] Resonances due to *cis*/*trans* isomers.

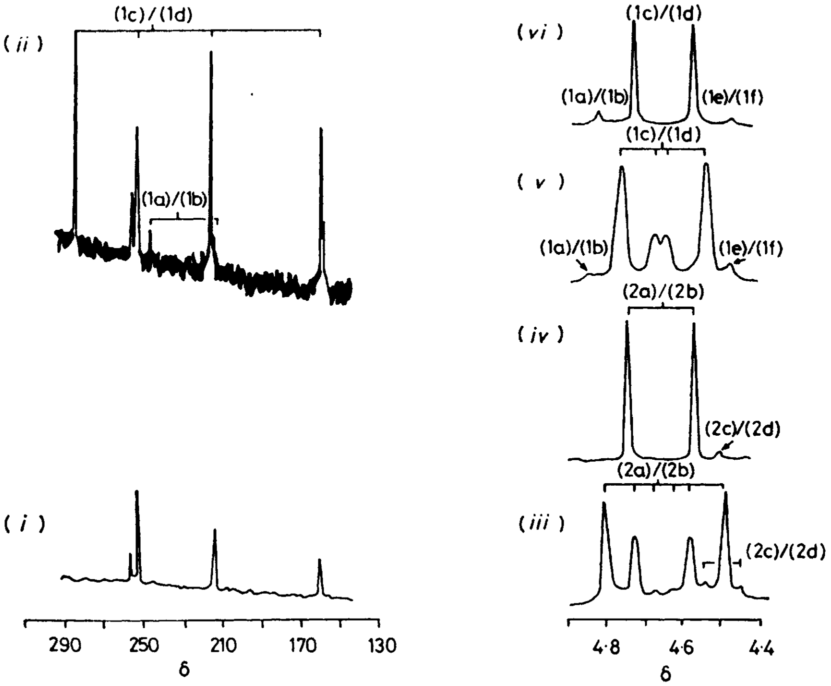

FIGURE 5 N.m.r. spectra for $[Fe_2(cp)_2(CO)_n(CNR)_{4-n}]$ (n = 1 or 2, R = Pr^i) (CD_2Cl_2 solvent): ^{13}C, − 80 °C, n = 1 (*i*) or 2 (*ii*); ^1H, n = 1, − 80 (*iii*) or 0 °C (*iv*), n = 2, − 80 (*v*) or − 20 °C (*vi*)

syn and *anti* isomers having the two possible orientations of the R group. An unambiguous assignment is not possible, although on steric grounds it seems likely that the most abundant isomer is the *anti*, the structure adopted in the solid state. Within experimental error, the same *syn* : *anti* ratio is maintained for R = Me and Et complexes, and for the ruthenium complex, for which a similar spectrum may be obtained at −60 °C. The broadness of the resonance assigned to (1a)/(1b) at −80 °C implies that nitrogen inversion is freezing out, and this resonance may actually be resolved into its components at −80 °C in the case of the ruthenium complex. While the resonances overlap somewhat, the results indicate a greater abundance of *anti* over *syn*. Both $[Fe_2(cp)_2(CO)_2(CNR)_2]$ (R = Me or Ph)[7,8] are known to adopt the *anti* structure in the solid state. In common with the $[M_2(cp)_2(CO)_3(CNR)]$ series (M = Fe or Ru), the ruthenium complexes exhibit a lower activation energy for isomer interconversion, but a higher activation energy for nitrogen inversion.

The ^{13}C spectrum of the R = Pr^i, M = Fe derivative (Figure 5) in the CO/CN region at −80 °C is consistent with the above. Assignments given in Table 5 are based on chemical shifts and intensities. In particular, the resolution of CN_μ and CO_t resonances associated with the *syn* and *anti* isomers may be noted in a ratio consistent with ^1H results. A similar splitting of the cp resonances into two unequal pairs is also found. On warming to −10 °C the CO_t and CN_μ resonances coalesce to single peaks, while at room temperature, significant broadening of all resonances is observed consistent with both CO and CNR bridge–terminal exchange.

(*b*) $[Fe_2(cp)_2(CO)(CNR)_3]$ *Complexes*.—(*i*) *Infrared spectra*. Spectra (Table 1) of all the complexes studied (R = Me, Et, or Pr^i) show only $\nu(CN_t)$, $\nu(CO_t)$, and $\nu(CN_\mu)$ absorptions, indicating that of the eight possible isomers (Figure 1) only (2a) and/or (2b) are present in solution. Both the $\nu(CN_t)$ and $\nu(CN_\mu)$ bands are broad, but the presence of more than one component is apparent, particularly in the ethyl and isopropyl derivatives. A band of varying intensity at *ca.* 1 725 cm^{-1} is also observed and is attributed to an impurity (see earlier discussion). The $\nu(CO_t)$ is clearly resolved into three components. The most likely explanation would seem to be resolution of the three isomeric forms of (2a)/(2b) (Figure 1), as the relative intensities of the bands roughly parallel the distribution of these isomers determined by n.m.r. (see below). Either resolution of (2a) from (2b) does not occur, or only one isomer is present in solution. In the spectrum of the M = Pr^i complex, a weak band at 2 044 cm^{-1} may possibly be attributed to the $\nu(CN_t)$ band of (2c) and/or (2d).

(*ii*) *Nuclear magnetic resonance spectra*. Spectra at room temperature show the two cp resonances expected for a (2a)/(2b) mixture. For all complexes, a small resonance at δ 4.44 is also observed which may be assigned to a small amount of isomers (2c) and/or (2d) in view of its behaviour at lower temperature. On warming to 100 °C in $[^2H_8]$toluene, only a slight broadening of resonances occurs. The activation energy for bridge–terminal exchange thus increases with increasing isonitrile substitution. On cooling to −80 °C, the pair of cyclopentadienyl resonances broadens and reforms as three pairs of resonances of unequal intensity (Figure 5) in the ratio 1 : 0.6 : 0.15 consistent with the three possible isomeric forms of (2a)/(2b). Previous results[13] on the R = Me complex found only two pairs of resonances, although the presence of the third was inferred from the difficulties encountered in the fit of simulated to experimental spectra. On the basis of the methyl resonances of the MeNC complex, the most abundant isomer is *syn* [either (s) or (ss), but most probably (s)] while an unambiguous assignment to the minor isomers is not possible. The same isomer distribution is found for the R = Me and Et complexes.

The resonance associated with (2c)/(2d) also broadens and reforms as two resonances of approximately equal intensity; at room temperature, rapid nitrogen inversion in the single possible isomer would result in equilibration of the cp resonances.

The ^{13}C spectrum at −80 °C (Figure 5) is consistent with this; again, resolution of the CN_μ resonance may be observed although only two of the expected four resonances are observed, probably due to coincidence of signals. At room temperature, a single CN_μ resonance is found.

The adoption of the (2a)/(2b) structure irrespective of R seems surprising in view of the results obtained on the mono- and di-substituted derivatives.

EXPERIMENTAL

Literature methods were used to prepare the various organoisocyanides.[14,15] Other chemicals were purchased. Reactions were carried out under an atmosphere of nitrogen in solvents which had been purified by refluxing over calcium hydride and distilled prior to use.

(*a*) $[Fe_2(cp)_2(CO)_2(CNR)_2]$ *Complexes*.—The complex $[Fe_2(cp)_2(CO)_4]$ (1.0 g) and the appropriate isocyanide (1.0 cm^3) were refluxed in benzene (50 cm^3) until complete disappearance of the monosubstituted $[Fe_2(cp)_2(CO)_3(CNR)]$ derivative, as determined by i.r. monitoring of the reaction mixture. The only exception is $[Fe_2(cp)_2(CO)_2(CNBu^t)_2]$ which is formed only in small amounts. This complex can be prepared in high yield, however, by the reaction of $[Fe_2(cp)_2(CO)_3\{P(OPh)_3\}]$[16] with excess of Bu^tNC in benzene at room temperature,[17] followed by purification as described below.

Solvent was removed and the residue was chromatographed on grade IV alumina using dichloromethane–light petroleum as eluant. After elution of a small amount of $[Fe_2(cp)_2(CO)_3(CNR)]$, the disubstituted complex was eluted and recrystallized from dichloromethane–light petroleum. Yields were generally in the region of 50%, but were generally lower for the phenyl and benzyl complexes.

(*b*) $[Fe_2(cp)_2(CO)(CNR)_3]$ *Complexes*.—These derivatives were prepared only for R = Me, Et, and Pr^i. Refluxing was continued as described above until i.r. monitoring indicated an unchanging mixture of the $[Fe_2(cp)_2(CO)_2(CNR)_2]$ and $[Fe_2(cp)_2(CO)(CNR)_3]$ complexes. Purification as above gave these two derivatives in yields of *ca.* 50% and 15% respectively.

The complex $[Ru_2(cp)_2(CO)_2(CNPr^i)_2]$ was prepared in the same way using refluxing xylene. Analytical data are given in Table 6.

TABLE 6

Analytical data

	Found (%)			Calc. (%)		
Complex	C	H	N	C	H	N
(*a*) $[M_2(cp)_2(CO)_2(CNR)_2]$						
M = Fe, R = Me	50.0	4.15	7.20	50.5	4.20	7.35
Et	52.9	4.95	7.15	52.9	4.90	6.85
Pr^i	54.4	5.45	6.50	55.0	5.50	6.40
Bu^t	56.5	5.95	6.25	56.9	6.05	6.05
Ph	62.3	4.20	6.10	61.8	3.95	5.55
p-$ClC_6H_4CH_2$	55.8	3.70	4.80	55.9	3.65	4.65
p-$MeC_6H_4CH_2$	63.9	4.85	4.60	64.3	5.00	5.00
p-$MeOC_6H_4CH_2$	61.2	4.75	4.95	60.8	4.75	4.75
$PhCH_2$	62.8	4.6	5.1	63.2	4.5	5.3
Ph(Me)CH	63.8	5.3	5.0	64.3	5.00	5.00
Bu^n	56.3	6.0	6.00	56.7	6.00	6.00
Pr^n	55.1	5.60	6.90	55.0	5.50	6.40
C_6H_{11}	59.6	6.1	5.5	60.5	6.0	5.4
M = Ru, R = Pr^i	45.8	4.55	5.50	45.6	4.55	5.30
(*b*) $[Fe_2(cp)_2(CO)(CNR)_3]$						
R = Me	52.2	4.75	10.6	51.9	4.85	10.7
Et	55.1	5.45	10.2	55.2	5.75	9.65
Pr^i	58.2	6.75	9.0	57.9	6.50	8.80

Infrared spectra were recorded on a Perkin-Elmer 257 or a Perkin-Elmer 337 spectrometer equipped with a Perkin-Elmer readout recorder, and were calibrated with DCl and water vapour so that peak positions are accurate to ± 1 cm^{-1} for sharp absorption bands and ± 2 cm^{-1} for those which are broader. Hydrogen-1 and ^{13}C n.m.r. spectra were run on a JEOL FX-100 n.m.r. spectrometer, the latter in the presence of $[Cr(acac)_3]$ (acac = acetylacetonate).

Crystal Data.—$C_{20}H_{24}Fe_2N_2O_2$, $M = 436.1$, Monoclinic, $a = 13.881 \pm 0.015$, $b = 10.755 \pm 0.010$, $c = 15.262 \pm 0.015$ Å, $\beta = 112.5 \pm 0.1°$, $U = 2\,105.0$ Å^3, $D_m = 1.38$ (by flotation), $Z = 4$, $D_c = 1.376$ g cm^{-3}, $F(000) = 904$, $\mu(\text{Mo-}K_\alpha) = 14.3$ cm^{-1}. Systematic absences $0k0$ if $k \neq 2n$ and $h0l$ if $l \neq 2n$, space group $P2_1/c$ (no. 14).

Cell parameters were determined from precession photographs using Mo-K_α radiation. Intensities were estimated visually from precession photographs for the layers 0—2 about [100], [001], and [011]. 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 807 non-zero unique reflections obtained. Scattering factors were taken from ref. 18, and all calculations were carried out on a UNIVAC 1106 computer with programs written by Dr. F. S. Stephens.

The structure was solved by the heavy-atom method. Refinement was by full-matrix least squares in which $\Sigma w\Delta^2$ was minimised. Weights were initially unity and in the final stages $w = (10.0 + 0.3|F_o| + 0.01|F_o|^2)^{-1}$. Reflections were omitted from a refinement cycle if $|F_c| < 0.2|F_o|$. The refinement was terminated when the maximum shift in any parameter was $< 0.02\sigma$. Only two reflections were omitted from the final cycle. The final value of R, based on 807 reflections, was 0.103 and R' [$= (\Sigma w\Delta^2/\Sigma w|F_o|^2)^{\frac{1}{2}}$] was 0.139. A final difference map showed no features $> |0.7|$e Å^{-3}. The final atomic parameters are given in Table 2. Lists of structure factors and thermal parameters are available as Supplementary Publication No. SUP 23029 (8 pp.).*

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1980, Index issue.