Chemistry of Low-valent Metal Isocyanide Complexes. Part 3.[1] The Synthesis, Structure, and Dynamic Behaviour of Nonakis(ethyl and isopropyl isocyanide)di-iron and -ruthenium Complexes. Crystal Structure of $[Fe_2(\mu\text{-}CNEt)_3(CNEt)_6]$ *

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Ultra-violet irradiation of diethyl ether solutions of $[Fe(CNR)_5]$ (R = Et or Pr^i) affords the dinuclear complexes $[Fe_2(CNR)_9]$. In contrast, sodium amalgam reduction of *trans*-$[RuCl_2(CNPr^i)_4]$ in the presence of an excess of isopropyl isocyanide affords directly $[Ru_2(CNPr^i)_9]$. In order to establish the molecular structure of these dimetal complexes, an *X*-ray diffraction study was carried out on $[Fe_2(CNEt)_9]$, crystals of which are monoclinic, space group $P2_1/n$, $Z = 4$, in a unit cell with lattice parameters $a = 22.193(14)$, $b = 12.762(6)$, $c = 12.332(8)$ Å, and $\beta = 104.60(5)°$. The structure has been refined to R 0.08 (R' 0.11) for 3 062 observed intensities to $2.9 \leqslant 2\theta \leqslant 50°$ (Mo-K_α *X*-radiation) collected at 223 K. The structure is similar to that previously established for $[Fe_2(CO)_9]$, *i.e.* two iron atoms separated by 2.461(2) Å are spanned by three isocyanide ligands in bridging modes, while the remaining isocyanide molecules are terminally bound, three to each metal atom. Whereas for the terminal ligands the angles C–N–C range over 165—179°, for the bridging groups the angles C–N–C are 123(1)°. In the bridge system one ligand bends at its nitrogen atom in a direction *anti* with respect to the other two CNEt groups, with the Fe–C distances *syn* to the ethyl groups being *ca.* 0.03 Å longer than those which are *anti*. Examination of the ^1H and ^{13}C n.m.r. spectra of the di-iron and -ruthenium complexes at various temperatures reveals dynamic behaviour in solution involving bridge–terminal isocyanide exchange with $\Delta G_{Tc}^{\ddagger} = 63 \pm 1, 65 \pm 1$, and 61 ± 1 kJ mol^{-1} for $[Fe_2(CNEt)_9]$, $[Fe_2(CNPr^i)_9]$, and $[Ru_2(CNPr^i)_9]$ respectively, this process occurring *via* synchronous pair-wise exchange with inversion at nitrogen. Reaction of $[Fe_2(CNEt)_9]$ with methyl or ethyl iodide affords salts $[Fe_2(CNEt)_7\{CNEt(R)\}_2]I_2$ (R = Me or Et), which are formulated as having bridging carbyne ligands. Ultraviolet irradiation of solutions of $[Fe(CNBu^t)_5]$ yields *trans*-$[Fe(CN)_2(CNBu^t)_4]$, whereas in the presence of cyclo-octatetraene the complex $[Fe(CNBu^t)_3(\eta^4\text{-}C_8H_8)]$ is produced.

WE have previously described the synthesis of the compounds $[Fe(CNR)_5]$ (R = Et,Pr^i, Bu^t, or $C_6H_3Me_2$-2,6), $[Ru(CNBu^t)_5]$,[2] $[Co_2(CNBu^t)_8]$,[3] and $[Pt_3(CNBu^t)_6]$ [4] as part of a general study of the chemistry of low-valent transition-metal complexes. Of particular interest are comparative studies on isocyanide–metal complexes in those instances where binary carbonyl–metal compounds are known. We have already reported various aspects of the chemistry of $[Fe(CNBu^t)_5]$, the analogue of $[Fe(CO)_5]$. Moreover, the discovery [3] of $[Co_2(CNBu^t)_8]$ has allowed comparisons with $[Co_2(CO)_8]$. Thus, whereas knowledge of the molecular configurations of the latter in solution has been limited to inferences based on i.r. studies, variable-temperature ^{13}C n.m.r. measurements on the soluble species $[Co_2(CNBu^t)_8]$ has allowed insight into the dynamic processes occurring in this complex in solution. In a continuation of this research it became obvious that we should aim to synthesise dimetal complexes $[M_2(CNR)_9]$ (M = Fe, Ru, or Os). The discovery [5] of $[Fe_2(CO)_9]$ set the stage some 50 years later for the development of polynuclear metal carbonyl chemistry, yet only relatively recently has an accurate single-crystal *X*-ray diffraction study [6] been possible for this molecule. Moreover, the structural behaviour of nonacarbonyldi-iron in solution remains an enigma, its insolubility precluding n.m.r. experiments. The isolation and study of a complex $[Fe_2(CNR)_9]$ was thus well merited. A preliminary account of some aspects of our work has been given.[7]

RESULTS AND DISCUSSION

In view of the method used to prepare $[Fe_2(CO)_9]$, the obvious approach to the synthesis of complexes $[Fe_2(CNR)_9]$ was by u.v. light irradiation of the mononuclear iron species $[Fe(CNR)_5]$.[2] This technique was first applied to $[Fe(CNBu^t)_5]$ but, as described later in this paper, instead of formation of the desired nonakis(t-butyl isocyanide)di-iron a cyano-iron(II) complex was formed. However, u.v. irradiation of diethyl ether solutions of either of the compounds $[Fe(CNR)_5]$ (R = Et or Pr^i) affords orange crystals of the very air-sensitive complexes $[Fe_2(CNR)_9]$ (1, R = Et; 2, R = Pr^i). In contrast, sodium amalgam reduction of *trans*-$[RuCl_2(CNPr^i)_4]$ in the presence of an excess of isopropyl isocyanide afforded red crystals of $[Ru_2(CNPr^i)_9]$ (3) directly, without u.v. irradiation. These compounds all showed in their i.r. spectra bands which can be taken as indicative of both terminal and bridge-bonded CNR ligands, *e.g.* for complex (1), $\nu_{max.}$(NC) bands at 2 060vs, 1 920m(sh), 1 701m(sh), and 1 652vs cm^{-1}. However, the mono-iron and -ruthenium species $[M(CNR)_5]$ show i.r. bands at *ca.* 1 830 cm^{-1} which are attributable to ' bent ' CNR ligands.[2] Hence low-frequency absorptions cannot be inferred with certainty as being due to an isocyanide ligand bridging two metal atoms, although those in the range 1 650—1 700 cm^{-1} seemed very likely due to this mode of bonding. Fortunately, suitable crystals of (1) were available for an *X*-ray diffraction study.

The results of the crystallographic study are given in Tables 1 and 2, and are illustrated in Figure 1, which also shows the crystallographic numbering system, but with the Me groups omitted. It is at once apparent that compound (1) is indeed an analogue of $[Fe_2(CO)_9]$ in the sense that in both molecules nine ligands are disposed such that three adopt bridging modes, and the remaining six are terminally bonded, three to each iron atom.

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* Tris-μ-ethyl isocyanide-bis[tris(ethyl isocyanide)iron].

TABLE 1

Final positional (fractional co-ordinate) parameters for the non-hydrogen atoms in the complex $[Fe_2(CNEt)_9]$, with estimated standard deviations in parentheses

Atom	x	y	z
Fe(1)	0.101 26(7)	0.105 32(11)	0.270 35(13)
Fe(2)	0.168 65(7)	0.257 14(11)	0.337 69(12)
C(1)	0.066 2(5)	0.099 2(8)	0.117 4(10)
N(1)	0.044 8(5)	0.099 3(8)	0.019 6(9)
C(11)	0.026 7(7)	0.117 1(11)	−0.099 7(10)
C(12)	0.040 9(9)	0.228 4(13)	−0.126 7(16)
C(2)	0.031 6(6)	0.086 3(8)	0.320 2(11)
N(2)	−0.013 0(6)	0.079 7(9)	0.354 9(10)
C(21)	−0.063 8(9)	0.090 1(19)	0.411 2(18)
C(22)	−0.043 0(17)	0.174 6(3)	0.491 0(28)
C(3)	0.128 2(5)	−0.032 5(8)	0.291 4(9)
N(3)	0.142 1(4)	−0.119 7(7)	0.304 4(8)
C(31)	0.170 0(6)	−0.223 6(8)	0.329 0(14)
C(32)	0.125 0(7)	−0.311 5(10)	0.288 3(15)
C(4)	0.079 0(5)	0.254 6(9)	0.255 9(10)
N(4)	0.034 2(5)	0.310 6(8)	0.216 0(11)
C(41)	0.034 9(8)	0.426 4(14)	0.226 7(15)
C(42)	0.014 7(13)	0.465 2(23)	0.127 5(23)
C(5)	0.146 8(5)	0.138 3(8)	0.423 9(10)
N(5)	0.155 7(5)	0.098 8(8)	0.519 9(9)
C(51)	0.195 2(8)	0.150 6(13)	0.619 9(12)
C(52)	0.153 4(12)	0.178 6(20)	0.696 8(14)
C(6)	0.180 9(5)	0.146 4(8)	0.232 3(9)
N(6)	0.218 1(4)	0.122 2(7)	0.177 6(8)
C(61)	0.210 3(6)	0.030 1(9)	0.101 6(10)
C(62)	0.214 1(8)	0.064 4(12)	−0.012 7(12)
C(7)	0.180 2(6)	0.351 1(9)	0.232 1(10)
N(7)	0.188 7(5)	0.409 8(7)	0.162 9(9)
C(71)	0.198 3(8)	0.482 4(10)	0.078 9(12)
C(72)	0.189 1(11)	0.435 9(17)	−0.029 6(15)
C(8)	0.148 8(6)	0.349 8(10)	0.436 6(11)
N(8)	0.136 8(7)	0.405 9(10)	0.499 3(11)
C(81)	0.103 7(16)	0.478 1(27)	0.564 3(26)
C(82)	0.145 9(14)	0.510 0(24)	0.634 5(24)
C(9)	0.251 0(5)	0.250 4(8)	0.413 0(9)
N(9)	0.304 0(5)	0.250 8(8)	0.462 1(9)
C(91)	0.370 7(9)	0.256 3(18)	0.523 1(19)
C(92)	0.379 6(15)	0.295 6(25)	0.616 6(27)

When viewed down the Fe–Fe vector, in (1) there is almost complete eclipsing of the terminal ligands (ignoring the Me groups), while those in bridging positions are staggered with respect to them.

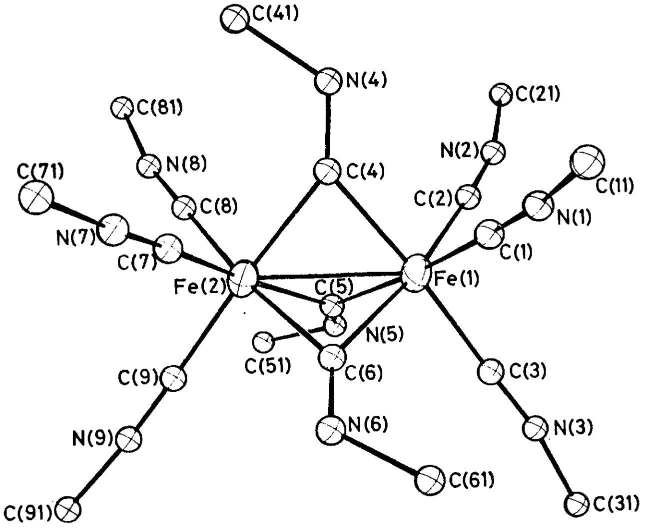


FIGURE 1 Molecular structure of the complex $[Fe_2(\mu\text{-}CNEt)_3(CNEt)_6]$ showing the crystallographic atom-numbering sequence, but with the methyl groups omitted

TABLE 2

Internuclear distances (Å) and bond angles (°) for $[Fe_2(CNEt)_9]$ with estimated standard deviations in parentheses

Fe(1)–Fe(2)	2.460 6(22)	Fe(2)–Fe(1)–C(1)	116.6(4)
		Fe(2)–Fe(1)–C(2)	119.2(4)
		Fe(2)–Fe(1)–C(3)	123.5(3)
		Fe(2)–Fe(1)–C(4)	52.0(3)
		Fe(2)–Fe(1)–C(5)	51.8(3)
		Fe(2)–Fe(1)–C(6)	51.5(3)
		Fe(1)–Fe(2)–C(4)	51.1(3)
		Fe(1)–Fe(2)–C(5)	50.8(3)
		Fe(1)–Fe(2)–C(6)	52.4(3)
		Fe(1)–Fe(2)–C(7)	117.2(3)
		Fe(1)–Fe(2)–C(8)	120.4(4)
		Fe(1)–Fe(2)–C(9)	125.3(3)
Fe(1)–C(1)	1.853(12)	C(1)–Fe(1)–C(2)	99.4(5)
Fe(1)–C(2)	1.818(14)	C(1)–Fe(1)–C(3)	98.1(5)
Fe(1)–C(3)	1.854(10)	C(1)–Fe(1)–C(4)	85.2(5)
Fe(1)–C(4)	1.965(12)	C(1)–Fe(1)–C(5)	167.9(5)
Fe(1)–C(5)	1.954(11)	C(1)–Fe(1)–C(6)	86.7(5)
Fe(1)–C(6)	2.009(12)	C(2)–Fe(1)–C(3)	95.6(5)
		C(2)–Fe(1)–C(4)	86.8(5)
		C(2)–Fe(1)–C(5)	88.7(5)
		C(2)–Fe(1)–C(6)	170.7(5)
		C(3)–Fe(1)–C(4)	175.5(4)
		C(3)–Fe(1)–C(5)	89.9(4)
		C(3)–Fe(1)–C(6)	90.5(5)
		C(4)–Fe(1)–C(5)	86.3(4)
		C(4)–Fe(1)–C(6)	86.6(5)
		C(5)–Fe(1)–C(6)	84.3(5)
Fe(2)–C(4)	1.991(11)	C(4)–Fe(2)–C(5)	84.8(5)
Fe(2)–C(5)	1.982(12)	C(4)–Fe(2)–C(6)	86.6(5)
Fe(2)–C(6)	1.984(11)	C(4)–Fe(2)–C(7)	87.2(5)
Fe(2)–C(7)	1.835(13)	C(4)–Fe(2)–C(8)	88.3(5)
Fe(2)–C(8)	1.831(14)	C(4)–Fe(2)–C(9)	176.4(5)
Fe(2)–C(9)	1.832(11)	C(5)–Fe(2)–C(6)	84.2(5)
		C(5)–Fe(2)–C(7)	167.9(5)
		C(5)–Fe(2)–C(8)	90.3(6)
		C(5)–Fe(2)–C(9)	92.3(5)
		C(6)–Fe(2)–C(7)	86.2(5)
		C(6)–Fe(2)–C(8)	172.8(6)
		C(6)–Fe(2)–C(9)	90.8(5)
		C(7)–Fe(2)–C(8)	98.7(6)
		C(7)–Fe(2)–C(9)	95.2(5)
		C(8)–Fe(2)–C(9)	94.0(5)
C(1)–N(1)	1.18(1)	Fe(1)–C(1)–N(1)	177(1)
N(1)–C(11)	1.44(2)	C(1)–N(1)–C(11)	169(1)
C(11)–C(12)	1.51(2)	N(1)–C(11)–C(12)	111(1)
C(2)–N(2)	1.17(2)	Fe(1)–C(2)–N(2)	176(1)
N(2)–C(21)	1.47(3)	C(2)–N(2)–C(21)	167(1)
C(21)–C(22)	1.45(4)	N(2)–C(21)–C(22)	104(2)
C(3)–N(3)	1.16(1)	Fe(1)–C(3)–N(3)	177(1)
N(3)–C(31)	1.46(1)	C(3)–N(3)–C(31)	171(1)
C(31)–C(32)	1.50(2)	N(3)–C(31)–C(32)	114(1)
C(4)–N(4)	1.22(1)	Fe(1)–C(4)–Fe(2)	76.9(4)
N(4)–C(41)	1.48(2)	Fe(1)–C(4)–N(4)	139.8(9)
C(41)–C(42)	1.29(3)	Fe(2)–C(4)–N(4)	143.3(9)
C(5)–N(5)	1.26(2)	C(4)–N(4)–C(41)	124(1)
N(5)–C(51)	1.48(2)	N(4)–C(41)–C(42)	108(2)
C(51)–C(52)	1.52(3)	Fe(1)–C(5)–Fe(2)	77.4(4)
C(6)–N(6)	1.23(2)	Fe(1)–C(5)–N(5)	138.4(9)
N(6)–C(61)	1.48(1)	Fe(2)–C(5)–N(5)	144.2(9)
C(61)–C(62)	1.50(2)	C(5)–N(5)–C(51)	122(1)
C(7)–N(7)	1.19(2)	N(5)–C(51)–C(52)	107(1)
N(7)–C(71)	1.45(2)	Fe(1)–C(6)–Fe(2)	76.1(4)
C(71)–C(72)	1.43(2)	Fe(1)–C(6)–N(6)	144.5(8)
C(8)–N(8)	1.13(2)	Fe(2)–C(6)–N(6)	139.4(8)
N(8)–C(81)	1.53(4)	C(6)–N(6)–C(61)	124(1)
C(81)–C(82)	1.18(4)	N(6)–C(61)–C(62)	110(1)
C(9)–N(9)	1.18(1)	Fe(2)–C(7)–N(7)	178(1)
N(9)–C(1)	1.48(2)	C(7)–N(7)–C(71)	179(1)
C(91)–C(92)	1.23(4)	N(7)–C(71)–C(72)	113(1)
		Fe(2)–C(8)–N(8)	179(1)
		C(8)–N(8)–C(81)	165(2)
		N(8)–C(81)–C(82)	101(3)
		Fe(2)–C(9)–N(9)	177(1)
		C(9)–N(9)–C(91)	177(1)
		N(9)–C(91)–C(92)	113(2)

The Fe–Fe distance [2.461(2) Å] is significantly shorter than that found [2.523(1) Å] by Cotton and Troup [6] for [$Fe_2(CO)_9$]. This shortening relates to the small angles at the bridging carbon atoms with Fe(1)–μ(C)–Fe(2) having a mean value of 76.8(4)°. The corresponding angle in [$Fe_2(CO)_9$] is 77.6(1)°. It thus seems that there is a strong metal–metal interaction in (1), indeed the separation is less than that found in the body-centred cubic structure of metallic iron (2.48 Å).[8]

If a direct iron–iron interaction is neglected, each metal atom can be regarded as occupying an octahedral co-ordination site as a consequence of the staggering of terminal and bridging carbon atoms referred to above. The two octahedra are joined at a common face defined by C(4), C(5), and C(6). While the molecule [$Fe_2(CNEt)_9$] does not possess the high symmetry of its carbonyl analogue, the atoms Fe(1), Fe(2), C(6), N(6), and C(61) can be described as defining an approximate mirror plane; this bridging isocyanide bending at the nitrogen in a direction *anti* with respect to the other two bridging ligands bonded at C(4) and C(5). Unfortunately, such symmetry is removed by the spatial orientation of the methyl groups which appears to be random within the confines of maintaining a tetrahedral angle at the carbon atoms of the methylene groups.

The contact-carbon atoms in the bridge system are asymmetrically bonded to Fe(1) and Fe(2), as observed in other molecules with this mode of ligand bonding.[3,4] The Fe–C distances [mean 1.99(1) Å] *syn* to the ethyl groups are *ca.* 0.03 Å longer than those which are *anti* [mean 1.96(1) Å]. These Fe–μ-C distances are as expected longer by on average 0.12—0.15 Å than the Fe–C bonds of the terminal ligands [mean 1.84(1) Å]. A similar effect is observed for the CO ligands in [$Fe_2(CO)_9$] where the Fe–C(bridge) bonds are *ca.* 0.18 Å longer than the Fe–C(terminal) bonds. The atoms Fe(1), Fe(2), C, N, and C of each bridging ligand form approximate planes inclined by *ca.* 120° to each other. For the μ-CNEt groups the C–N distances have a mean value of 1.24 (2) Å, showing a lengthening typical of this bonding mode with respect to the terminally bound CNEt groups [mean C–N 1.17(2) Å].

In the bridging system, the angles C–N–C [mean 123(1)°] are significantly smaller than those found in other structures with bridging isocyanide ligands.[3,4,9,10] For the terminal ligands in (1), the angles C–N–C range over 165—179°, the departure from linearity being very much less than that found (135°) [2] for the radial $CNBu^t$ ligands in [$Fe(CNBu^t)_5$]. The contents of the unit cell are shown in Figure 2.

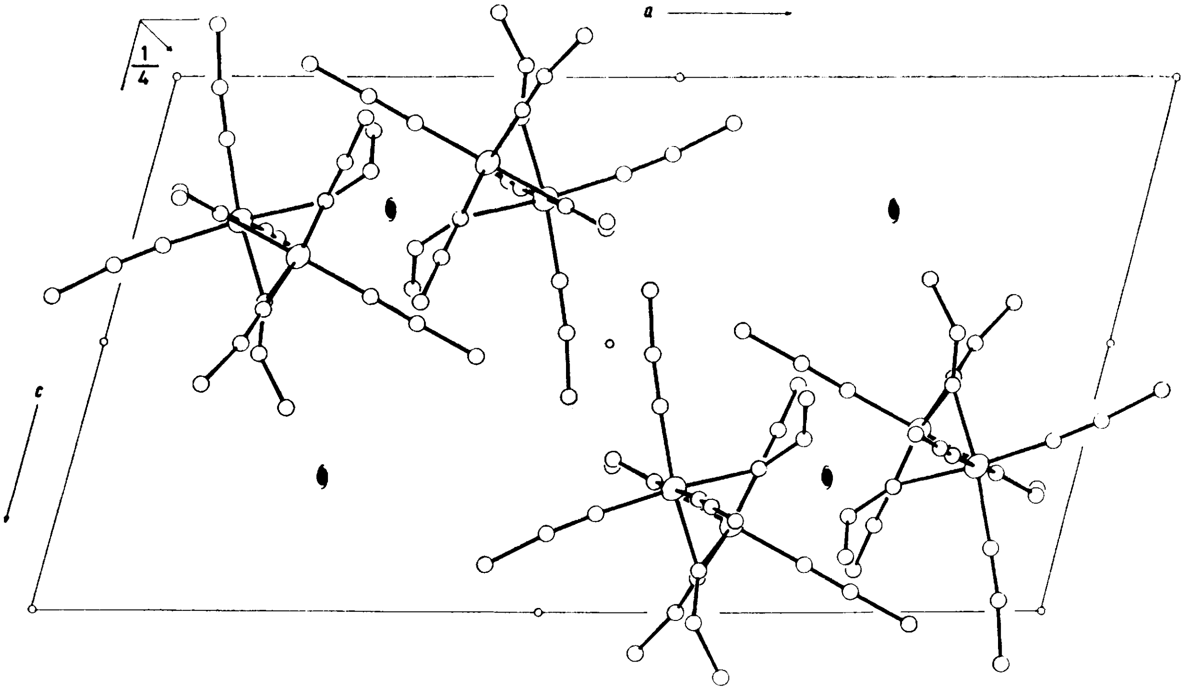


FIGURE 2 Contents of the monoclinic unit cell of complex (1) viewed down the *b* axis with methyl groups omitted for clarity

Examination of the ^1H n.m.r. spectrum of (1) in the temperature range −50 to 100 °C revealed dynamic behaviour (Figure 3) involving exchange of bridge and terminal isocyanide ligands, and inversion of the ethyl groups at the nitrogen atoms. At 100 °C the spectrum consisted of a triplet resonance at τ 8.76 [*J*(HH) 7 Hz] and a quartet signal at τ 6.61 [*J*(HH) 7 Hz] of relative intensity 27 : 18. At −50 °C the signals consisted of two quartets (relative intensity 6 : 12) at τ 5.96 and 7.14, and two triplets (relative intensity 9 : 18) at τ 8.23 and 9.19. Over the range of temperatures studied, the chemical environments of the CH_3 and CH_2 groups displayed no inequivalences within the two sets of bridging and terminal ligands. We ascribe this to rapid inversions at the nitrogen atoms of each bridging isocyanide *via* a lateral shift mechanism (‘ windscreen wiper effect ’), a

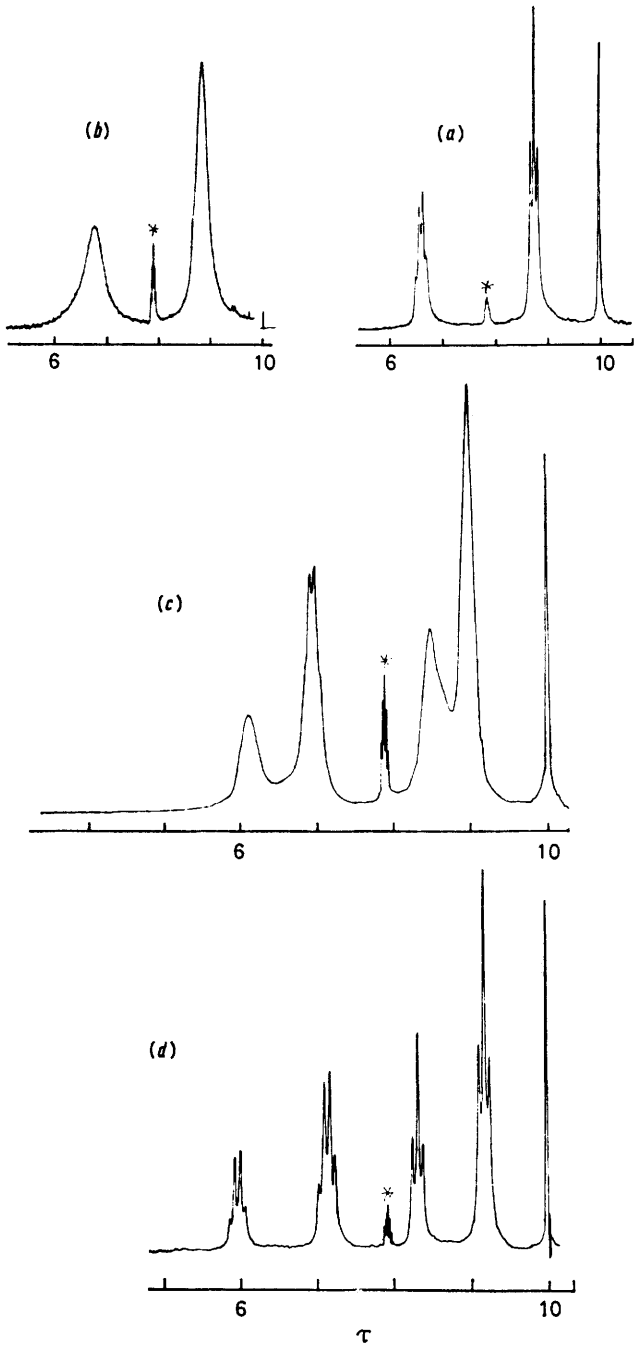


FIGURE 3 Hydrogen-1 n.m.r. spectra of complex (1) measured in [$^2H_8$]toluene: solvent peaks are indicated by an asterisk, resonance at τ 10 is due to $SiMe_4$. (*a*) 100; (*b*) 50; (*c*) 30; and (*d*) −50 °C

process having a low activation energy.[11] However, from the estimated coalescence temperature for terminal–bridging ligand-site exchange it was possible to obtain [12] a value of $\Delta G_{T_c}^{\ddagger}$ for this process of 63 ± 1 kJ mol^{-1} [$\Delta\nu(CH_3) = 86 \pm 2$ Hz, $T_c(CH_3) = 313 \pm 5$ K; $\Delta\nu(CH_2) = 118 \pm 2$ Hz, $T_c(CH_3) = 328 \pm 5$ K; $p_A = \frac{2}{3}$, $p_B = \frac{1}{3}$].

The variable-temperature ^1H spectra of compounds (2) and (3) showed similar features to the spectrum of (1), and were thus also consistent with the presence in solution of the triply bridged structure. Estimated activation energies for terminal–bridge site exchange were for (2) $\Delta G_{T_c}^{\ddagger}$ 65 ± 1 kJ mol^{-1} [$\Delta\nu(CH_3) = 50 \pm 2$ Hz, $T_c(CH_3) = 313 \pm 5$ K; $\Delta\nu(CH) = 57 \pm 2$ Hz, $T_c(CH) = 323 \pm 5$ K] and for (3) $\Delta G_{T_c}^{\ddagger}$ 61 ± 1 kJ mol^{-1} [$\Delta\nu(CH_3) = 48 \pm 2$ Hz, $T_c(CH_3) = 293 \pm 5$ K; $\Delta\nu(CH) = 78 \pm 2$ Hz, $T_c(CH) = 308 \pm 5$ K]. Thus within the dimetal isocyanide complexes the activation energy sequence Fe > Ru apparently occurs.

A study of the ^{13}C n.m.r. spectra provided corroborative evidence for the dynamic behaviour observed in the ^1H spectra. At room temperature the spectrum of (1) showed the expected broad resonances, but upon cooling to −50 °C signals were observed which could be assigned to each carbon atom of the terminal and bridging sets of ligands, *viz.*, δ (p.p.m.) 255.7 (μ-*C*NEt), 178.0 (*C*NEt), 55.8 (CH_2 bridging), 39.2 (CH_2 terminal), 17.7 (Me bridging), and 17.0 (Me terminal). However, the resonance at 178 p.p.m., assigned to the contact-carbon atoms of the terminally bonded ethyl isocyanide groups, was significantly broader than the corresponding resonance of the bridging ligands. On cooling to −90 °C (low-temperature limit for the solvent used) this signal became resolved into four separate resonances at 173.8, 175.7, 176.9, and 178.9 p.p.m. in an approximate 1 : 2 : 2 : 1 ratio of intensities. This was initially thought to be the result of coupling with ^{14}N (I = I) producing two overlapping 1 : 1 : 1 triplets. However, this hypothesis was discounted because ^{14}N–^{13}C coupling has not been previously observed with low-valent metal isocyanide complexes, and moreover the chemical shift separations were not uniform.

A more plausible explanation for this observation is that the four separate resonances arise from a slowing down [$\Delta G_{T_c}^{\ddagger} = 42 \pm 2$ kJ mol^{-1}; $\Delta\nu = 30 \pm 2$ Hz; $T_c = 200$ K, $p_A = p_B$] of the ' windscreen wiper ' motion so that in effect the chemical shifts of the contact-carbon atoms of the terminal isocyanide ligands are dependent on the orientation or *trans* influence of the alkyl group on a bridging ligand. This is illustrated in Figure 4, from which it may be seen that a 1 : 2 : 2 : 1 distribution of resonances would be expected, as is observed.

An apparent weakness in this analysis is that the three contact-carbon atoms of the bridging *C*NEt ligands from

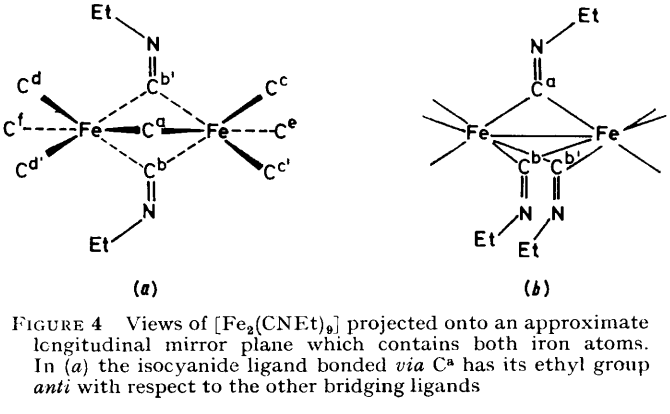
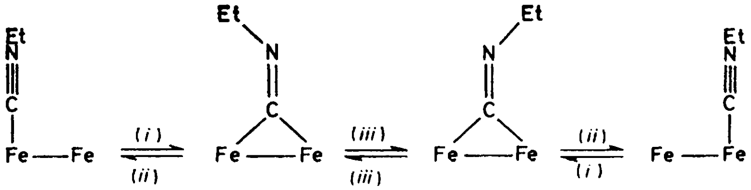


FIGURE 4 Views of $[Fe_2(CNEt)_9]$ projected onto an approximate longitudinal mirror plane which contains both iron atoms. In (*a*) the isocyanide ligand bonded *via* C^a has its ethyl group *anti* with respect to the other bridging ligands



SCHEME 1 Bridge–terminal site exchange indicated for one ligand in complex (1): (*i*) *anti* movement, (*ii*) *syn* movement, (*iii*) fast lateral inversion at nitrogen

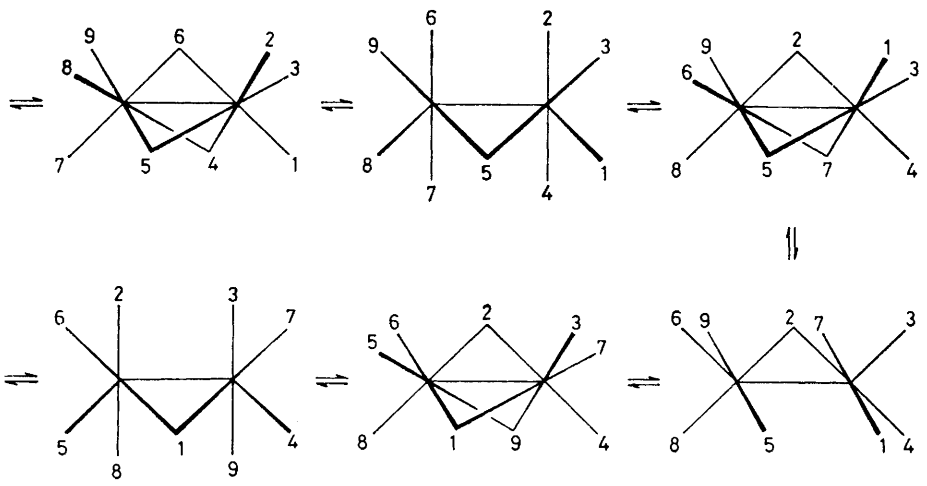
the spectrum appear equivalent. However, this could arise from accidental coincidence since in the corresponding ^{13}C spectra (−100 °C) of (2) and (3) which also show four resonances (1 : 2 : 2 : 1) for the terminally bonded contact-carbon atoms, two different environments (ratio 1 : 2) are in fact observed for the $Pr^iN\textit{C}Fe_2$ and $Pr^iN\textit{C}Ru_2$ bridging contact carbons.

Comparable free energy of activation barriers to inversion at nitrogen were obtained for the complexes $[Fe_2(CO)(CNMe)_3(\eta\text{-}C_5H_5)_2]$ (*ca.* 43 ± 2 kJ mol^{-1}) and $[Fe_2(CO)_2(CNMe)_2(\eta\text{-}C_5H_5)_2]$ (*ca.* 46 ± 4 kJ mol^{-1}).[13] It is interesting that the slowing down of this type of dynamic behaviour, which is a necessary part of bridge–terminal ligand exchange,[12] has not been observed for the other recently discovered binary isocyanide metal complexes $[Pt_3(CNBu^t)_6]$ and $[Co_2(CNBu^t)_8]$. However, it has been suggested [13] that the magnitude of the energy barrier to this inversion process is inversely proportional to the degree of triple-bond character in the C–N bond, and as the N–C distances for the bridging ligands average to *ca.* 1.21 Å in both $[Pt_3(CNBu^t)_6]$ and $[Co_2(CNBu^t)_8]$, compared with 1.24 Å in $[Fe_2(CNEt)_9]$, it is not difficult to rationalise why a slow exchange limit for inversion was not observed in the platinum and cobalt complexes.

Bridging–terminal isocyanide exchange occurs *via* an intramolecular process in the dinuclear complex $[Co_2(CNBu^t)_8]$,[3] whereas an intermolecular process has been demonstrated for $[Pt_3(CNBu^t)_6]$.[4] In order to clarify this question with regard to the iron and ruthenium dinuclear species the ^{13}C n.m.r. spectrum (room temperature) of a solution of $[Fe_2(CNEt)_9]$ in $[^2H_6]$acetone to which ethyl isocyanide had been added was observed. The spectrum showed distinct resonances (1 : 1 : 1 pattern due to ^{14}N coupling) due to the added EtN*C* (156.8 p.p.m.) and the $CH_2\textit{C}H_2NC$ (36.9 p.p.m.) carbons. Also, although the resonances due to the contact carbons of the co-ordinated isocyanides were not observed, because of rapid site exchange, the $CH_3\textit{C}H_2NCFe$ (44.5 p.p.m.) and $\textit{C}H_3CH_2NCFe$ (17.2 p.p.m.) resonances were present in the spectrum as broad signals. Thus any intermolecular exchange processes must be slow even at room temperature. Similar observations were made with the ^{13}C n.m.r. spectra of $[Fe_2(CNPr^i)_9]$ and $[Ru_2(CNPr^i)_9]$. Therefore, the exchange process, which results in an averaging of terminal and bridging isocyanide environments in (1)—(3), can be discussed in terms of an intramolecular process.

A likely reaction path for synchronous pair-wise bridge–terminal exchange is illustrated in Schemes 1 and 2. As is shown (Scheme 1), an essential step [3,13] requires a reversal of configuration at the nitrogen atoms of the bridging ligands in conjunction with migration of the ligand between the two metal centres *via* the *syn* or *anti* movements. The lateral shift at the nitrogen atoms has a lower energy barrier, and is consistent with our observations indicating that this process occurs more readily than ligand migration.

It is interesting that in such a degenerate process the conversion occurs of a triply bridged species *via* singly bridged intermediates. Examination of a molecular model suggested that such a transformation might require torsional twisting of the two iron co-ordination spheres. Moreover, an *X*-ray crystal-structure determination of the complex $[Fe_2(CO)_8(\mu\text{-}C{=}CPh_2)]$ has

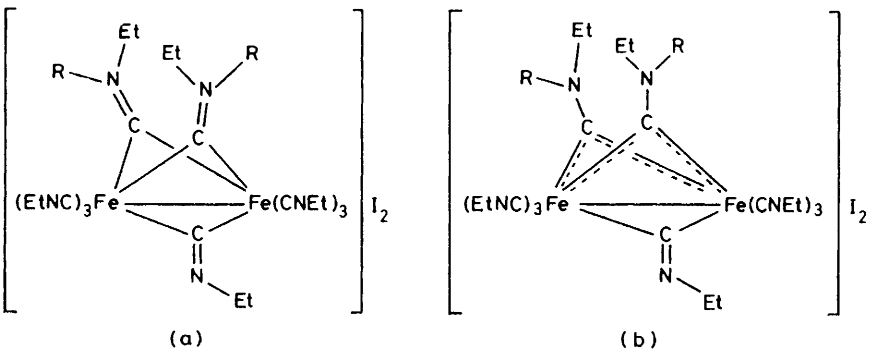


SCHEME 2 Overall ligand migration processes in complex (1)

shown [14] that such a singly bridged species need not have a plane of symmetry, and that the co-ordination spheres around each iron atom can be twisted with respect to each other.

As shown earlier,[1] mononuclear zerovalent isocyanide complexes of iron readily undergo oxidative reactions with various substrate molecules. As a first step in the exploration of the chemistry of the dinuclear complexes, the reaction with alkyl halides was examined. Addition at room temperature of methyl or ethyl iodide to a solution of (1) in tetrahydrofuran afforded, respectively, the bright red crystalline complexes (4) and (5). Elemental analyses showed that these products were 2 : 1 adducts, and their solubility behaviour suggested that they were ionic adducts.

Examination of the ^{13}C n.m.r. spectra of these compounds revealed resonances typical of terminal and bridging isocyanide contact-carbon atoms, and in addition showed strong signals at **317.2** and **317.7** p.p.m. for (4) and (5), respectively. These shifts are characteristic [15] of either bridging carbene (alkylidene) or carbyne (alkylidyne) ligands; formulations (a) and (b), respectively. Species (4) and (5) could arise by alkylation of two of the bridging isocyanide ligands. The ^{1}H n.m.r. spectra were complex with overlapping signals but were consistent with these structures, although there was no evidence for the formation of isomers of (4), which could arise through restricted rotation about the carbon–nitrogen double bond. This leads us to prefer structures (4b) and (5b) involving a bridging carbyne system, which would also be more consistent with the low chemical shift [15] mentioned above. Bridging ligands of this type have been observed before in the complexes [$Fe_2(CO)_6(\mu\text{-}CNEt_2)_2$],[16] [$Fe_3H(\mu\text{-}CNMe_2)(CO)_{10}$],[17] and [$Fe_2(\mu\text{-}CNMe_2)(CO)_3(\eta\text{-}C_5H_4Me)_2$]I.[18]



(4, R = Me)
(5, R = Et)

In contrast to the behaviour of [$Fe(CNR)_5$] (R = Et or Pr^{i}) upon u.v. irradiation, similar treatment of [$Fe(CNBu^{t})_5$] afforded a yellow crystalline air-stable complex *trans*-[$Fe(CN)_2(CNBu^{t})_4$] (6). Although consistent microanalytical data could not be obtained for this product probably due to solvation effects [19] the i.r. and ^{1}H and ^{13}C n.m.r. spectra were consistent with the proposed formulation. Similar complexes have been previously prepared by conventional methods, and have been structurally identified by *X*-ray crystallography.[19] Compound (6) was also formed on heating [$Fe(CNBu^{t})_5$] in toluene. Evidently pentakis(t-butyl isocyanide)iron readily undergoes a redox reaction [$Fe^{0} \longrightarrow Fe^{II}$] involving cleavage of the carbon–carbon bonds of CNBu^{t} ligands. Interestingly the cyano-complex [$Fe(CN)_2(CNMe)_4$] is formed by heating [$Fe(CNMe)_6Cl_2$],[20] in another reaction involving cleavage of the C–C bonds of isocyanide ligands, although in this process a change in oxidative state of the iron is not readily apparent.

Although u.v. irradiation of [$Fe(CNBu^{t})_5$] by itself in various solvents afforded (6), in the presence of cyclo-octatetraene the complex [$Fe(CNBu^{t})_3(\eta^{4}\text{-}C_8H_8)$] (7) is formed in moderate yield, and characterised by microanalysis, and by ^{1}H and ^{13}C n.m.r. spectroscopy. The same complex has been prepared by addition of an excess of CNBu^{t} to bis(cyclo-octatetraene)iron.[21] The ^{1}H and ^{13}C n.m.r. spectra at room temperature showed the expected equivalence of the eight protons and carbon atoms of the co-ordinated cyclo-octatetraene. At −150 °C, in CF_2Cl_2 as solvent, the C_8H_8 protons appeared as two broad resonances suggesting that the 1,2-shift process had still not been completely stopped, whereas at this temperature two sharp singlets (ratio 2 : 1) were observed for the CN*Bu^{t}* protons demonstrating that there was no rotation of the $Fe(CNBu^{t})_3$ unit relative to the C_8 ring. Similar behaviour has been noted with the tricarbonyl analogue, which in its ^{13}C n.m.r. spectrum at −120 °C shows two signals for the CO ligands with intensity ratio 2 : 1.[22]

EXPERIMENTAL

The instrumentation used for i.r., n.m.r., and mass spectral studies was as described in Part 1 of this series.[2] Experiments were carried out using Schlenk-tube techniques under a dry oxygen-free nitrogen atmosphere, with solvents dried and distilled under nitrogen prior to use. Light petroleum refers to that fraction with b.p. 40—60 °C.

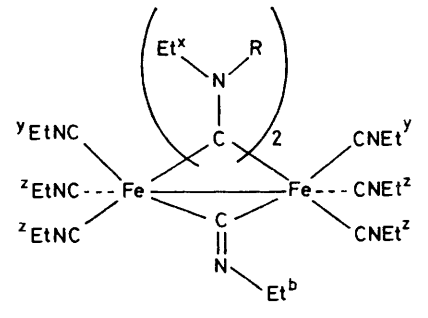
Preparation of Nonakis(ethyl isocyanide)di-iron.—Ultraviolet irradiation (36 h, 250-W medium-pressure lamp) of a diethyl ether solution (30 cm^3) of [$Fe(CNEt)_5$] (2.0 g, 6 mmol) contained in a quartz tube (100 cm^3) afforded orange crystals. After cooling (−78 °C) the supernatant liquid was removed using a syringe, to give, after washing with cold diethyl ether–light petroleum (1 : 1), very air-sensitive orange *crystals* of $[\mathrm{Fe_2(\mu\text{-}CNEt)_3(CNEt)_6}]$ (1) (1.1 g, 61%) (Found: C, 52.5; H, 7.7; N, 20.2. $\mathrm{C_{27}H_{45}Fe_2N_9}$ requires C, 53.4; H, 7.4; N, 20.8%), $\nu_{\max.}$ (tetrahydrofuran) at 2 060vs, 1 920m(sh), 1 701m(sh), 1 652vs, and 715s cm^{-1}. N.m.r. resonances: ^{1}H ($[^2\mathrm{H}_8]$toluene, −50 °C), τ 5.96 [q, 6 H, $\mathrm{CH_2}$ bridge, ^3J(HH) 7], 7.14 [q, 12 H, $\mathrm{CH_2}$ terminal, J(HH) 7], 8.32 [t, 9 H, $\mathrm{CH_3}$ bridge, J(HH) 7], and 9.19 [t, 18 H, $\mathrm{CH_3}$ terminal, J(HH) 7]; ^{1}H ($[^2\mathrm{H}_8]$toluene, 100 °C), τ 6.61 [q, 18 H, $\mathrm{CH_2}$, J(HH) 7] and 8.76 [t, 27 H, $\mathrm{CH_3}$, J(HH) 7 Hz]; ^{13}C ($[^2\mathrm{H}_6]$acetone, −90 °C), δ (p.p.m.) 17.0 ($\mathrm{CH_3}$ terminal), 17.7 ($\mathrm{CH_3}$ bridging), 39.2 ($\mathrm{CH_2}$ terminal), 55.8 ($\mathrm{CH_2}$ bridging), 173.8, 175.7, 176.9, 178.9 (*C*NEt terminal), and 256.6 (*C*NEt bridging); ^{13}C ($[^2\mathrm{H}_6]$acetone, 25 °C, CNEt added), δ (p.p.m.) 17.2 ($\mathrm{CH_3}$), 36.9 [t, $\mathrm{CNCH_2CH_3}$ (uncomplexed), J(NC) 6 Hz], 44.5 (br, $\mathrm{CH_2}$), and 156.8 [t, *C*NEt (uncomplexed), J(NC) 4 Hz].

Preparation of Nonakis(isopropyl isocyanide)di-iron.—Similarly, irradiation (40 h) of a solution of $[\mathrm{Fe(CNPr^i)_5}]$ (2.4 g, 6 mmol) in diethyl ether (30 cm^3) afforded orange crystals. Extraction with light petroleum followed by filtration and cooling (−30 °C) gave orange *crystals* of $[\mathrm{Fe_2(\mu\text{-}CNPr^i)_3(CNPr^i)_6}]$ (2) (1.1 g, 50%) [Found: C, 58.2; H, 9.0; N, 16.9%; *M*, 734 (mass spec.). $\mathrm{C_{36}H_{63}Fe_2N_9}$ requires C, 58.9; H, 8.7; N, 17.2%; *M*, 734], m.p. 75 °C, $\nu_{\max.}$ (hexane) at 2 065s(sh), 2 025s, 1 740vw, 1 702s, 800s, and 704s cm^{-1}. N.m.r. resonances: ^{1}H ($[^2\mathrm{H}_8]$toluene, 0 °C), τ 6.07 [septet, 3 H, CH bridge, J(HH) 6], 6.38 [septet, 6 H, CH terminal, J(HH) 6], 8.42 [d, 18 H, $\mathrm{CH_3}$ bridge, J(HH) 6], and 8.81 [d, 36 H, $\mathrm{CH_3}$ terminal, J(HH) 6 Hz]; ^{1}H ($[^2\mathrm{H}_8]$toluene, 80 °C), τ 6.32 [septet, 9 H, CH, J(HH) 6] and 8.69 [d, 54 H, $\mathrm{CH_3}$, J(HH) 6 Hz]; ^{13}C ($[^2\mathrm{H}_8]$toluene, −85 °C), δ (p.p.m.) 22.9, 24.8, 45.6, 60.7 [$\mathrm{CH(CH_3)_2}$, bridging and terminal], 172.1, 174.7, 177.8, 181.5 (N*C*Fe terminal), 207.6, and 208.7 (N*C*$\mathrm{Fe_2}$ bridging); ^{13}C ($[^2\mathrm{H}_8]$toluene, 28 °C), δ (p.p.m.) 23.3 ($\mathrm{CH_3}$ terminal), 24.6 ($\mathrm{CH_3}$ bridging), 46.0 (CH terminal), 60.7 (CH bridging), 180.3 (NC terminal), and 211.1 (N*C*$\mathrm{Fe_2}$ bridging).

Preparation of trans-*Dichlorotetrakis(isopropyl isocyanide) ruthenium.*—Solid $\mathrm{RuCl_3{\cdot}3H_2O}$ (1 g, 4 mmol) was added to a suspension of zinc amalgam (3 g, in excess) in ethanol (50 cm^3) and isopropyl isocyanide (3 cm^3, *ca.* 20 mmol). The mixture was stirred at room temperature for 24 h during which time a deep yellow solution was formed. The solvent was removed *in vacuo*, the residue extracted with dichloromethane (100 cm^3), and the resultant extract filtered through an alumina packed column (15 × 2 cm). Removal of the solvent afforded yellow *crystals* of *trans*-$[\mathrm{RuCl_2(CNPr^i)_4}]$ (1.7 g, 94%) (Found: C, 42.0; H, 6.3; N, 12.4. $\mathrm{C_{16}H_{28}Cl_2N_4Ru}$ requires C, 42.9; H, 6.3; N, 12.5%), $\nu_{\max.}$ (Nujol) at 2 145vs, 1 320m, 1 162w, 1 130w, 1 114m, 727w, and 695w cm^{-1}. Hydrogen-1 n.m.r. ($[^2\mathrm{H}_1]$chloroform), τ 5.9 [septet, 4 H, CH, J(HH) 6] and 8.52 [d, 24 H, $\mathrm{CH_3}$, J(HH) 6 Hz].

Preparation of Nonakis(isopropyl isocyanide)diruthenium.—A slurry of *trans*-dichlorotetrakis(isopropyl isocyanide)-ruthenium (1.7 g, 3.8 mmol) and isopropyl isocyanide (1 cm^3, *ca.* 7 mmol) in tetrahydrofuran (40 cm^3) was added to sodium amalgam (50 g, 1%). After stirring at room temperature for 48 h, the volatile material was removed *in vacuo*, and the residue extracted with hexane (60 cm^3). Filtration, followed by cooling (−20 °C) gave deep red *crystals* of $[\mathrm{Ru_2(\mu\text{-}CNPr^i)_3(CNPr^i)_6}]$ (3) (0.83 g, 53%) (Found: C, 52.3; H, 7.8; N, 14.7. $\mathrm{C_{36}H_{63}N_9Ru_2}$ requires C, 52.5; H, 7.7; N, 15.3%), m.p. 85 °C decomp., $\nu_{\max.}$ (diethyl ether) at 2 090(sh), 2 070vs, 2 045s, 1 643s, 795m, and 693s cm^{-1}. N.m.r. resonances: ^{1}H ($[^2\mathrm{H}_8]$toluene, −10 °C), τ 6.29 [septet, 3 H, CH bridge, J(HH) 7], 6.52 [septet, 6 H, CH terminal, J(HH) 7], 8.43 [d, 18 H, $\mathrm{CH_3}$, bridge, J(HH) 7], and 8.90 [d, 36 H, $\mathrm{CH_3}$ terminal, J(HH) 7 Hz]; ^{1}H ($[^2\mathrm{H}_8]$toluene, 60 °C), τ 6.47 [septet, 9 H, CH, J(HH) 6] and 8.74 [d, 54 H, $\mathrm{CH_3}$, J(HH) 6 Hz]; ^{13}C ($[^2\mathrm{H}_8]$-toluene, −100 °C), δ (p.p.m.) 23.4, 25.7, 46.8, 67.7 [$\mathrm{CH(CH_3)_2}$ bridging and terminal], 159.8, 161.3, 162.7, 165.8 (N*C*Ru terminal), 233.3, and 236.9 (N*C*$\mathrm{Ru_2}$ bridging); ^{13}C ($[^2\mathrm{H}_8]$toluene, −30 °C), δ (p.p.m.) 24.1, 26.1, 47.0, 65.2 [$\mathrm{CH(CH_3)_2}$ bridging and terminal], 165.0 (N*C*Ru terminal), and 222.2 (N*C*$\mathrm{Ru_2}$ bridging); ^{13}C ($[^2\mathrm{H}_8]$toluene, 28 °C), δ (p.p.m.) 24.7, 47.3 [$\mathrm{CH(CH_3)_2}$]; ^{13}C ($[^2\mathrm{H}_8]$toluene, 70 °C), δ (p.p.m.) 25.0 and 48.1 [$\mathrm{CH(CH_3)_2}$].

Reactions of Nonakis(ethyl isocyanide)di-iron.—(*a*) *With methyl iodide.* To a stirred solution at room temperature of (1) (0.6 g, 1 mmol) in tetrahydrofuran (20 cm^3) was added methyl iodide (0.2 cm^3, 3.2 mmol) dropwise. After 10 min bright red microcrystals separated. The solution was cooled (−78 °C) and the supernatant liquid separated from the crystals. Recrystallisation (−20 °C) from dichloromethane–diethyl ether afforded red *prisms* of $[\mathrm{Fe_2(CNEt)_7\{CN(Me)Et\}_2]I_2}$ (4) (0.5 g, 56%) (Found: C, 38.7; H, 6.0; N, 13.8. $\mathrm{C_{29}H_{51}Fe_2I_2N_9}$ requires C, 39.1; H, 5.7; N, 14.1%), $\nu_{\max.}$ (Nujol) at 2 170s(sh), 2 150vs, 1 803s, 1 576s, 1 395w, 1 340m, 1 320w, 1 275w, 1 260w(sh), 1 182w, 1 160w, 1 090w, 1 030w, 862w, 830w, 800w, and 762m cm^{-1}. N.m.r. resonances: ^{1}H ($[^2\mathrm{H}_6]$acetone, 25 °C), τ 5.86 [q, $\mathrm{CH_2}$, J(HH) 7.5], 6.14 and 6.18 [overlapping quartets, $\mathrm{CH_2}$, J(HH) 7.5], 6.22 (s, $\mathrm{NCH_3}$), 8.57, 8.61, and 8.70 [overlapping triplets, $\mathrm{CH_3}$, J(HH) 7.5]; ^{13}C ($[^2\mathrm{H}_3]$acetonitrile, 25 °C), δ (p.p.m.) 14.5 [$\mathrm{CH_3}$ (b,x)], 15.9 [$\mathrm{CH_3}$ (y,z)], 40.8 [$\mathrm{CH_2}$ (y,z)], 48.4 [CN(*C*$\mathrm{H_3}$)Et], 49.5 [$\mathrm{CH_2}$ bridging (b)], 60.6 [$\mathrm{CH_2}$ (x)], 159.6 [*C*NEt (z)], 168.6 [*C*NEt (y)], 288.5 [*C*NEt (b)], and 317.2 [*C*N($\mathrm{CH_3}$)Et].



($\mathrm{R = CH_3}$ or $\mathrm{CH_2CH_3}$)

(*b*) *With ethyl iodide.* A similar reaction of (1) with ethyl iodide afforded red *crystals* of (5) $[\mathrm{Fe_2(CNEt)_7(CNEt_2)_2]I_2}$ (60%) (Found: C, 43.0; H, 6.2; N, 14.3. $\mathrm{C_{31}H_{55}Fe_2I_2N_9}$ requires C, 43.1; H, 6.4; N, 14.6%), $\nu_{\max.}$ (Nujol) at 2 135vs(br), 1 801s, 1 546s, 1 340s, 1 330(sh), 1 268m, 1 170m, 1 140m, 1 090w, 1 035w, 930w, 850w, 827w, and 755m cm^{-1}. N.m.r. resonances: ^{1}H ($[^2\mathrm{H}_3]$acetonitrile, 25 °C), τ 6.02 [q, 2 H, $\mathrm{CH_2}$, J(HH) 7.5], 6.14, 6.22, and 6.42 [overlapping quartets, $\mathrm{CH_2}$, J(HH) 7.5], 8.64, 8.72, 8.75, and 8.78 [overlapping triplets, $\mathrm{CH_3}$, J(HH) 7.5 Hz]; ^{13}C ($[^2\mathrm{H}_3]$acetonitrile, 25 °C), δ (p.p.m.) 14.4 [$\mathrm{CH_3}$ (b)], 14.8 [$\mathrm{CH_3}$ (y)], 15.9 [$\mathrm{CH_3}$ (x)], 16.4 [$\mathrm{CH_3}$ (z)], 40.7 [$\mathrm{CH_2}$ (z)], 43.5 [$\mathrm{CH_2}$ (y)], 54.6 [$\mathrm{CH_2}$

(y)], 55.9 [CH_2 (x)], 160.1 [CNEt (z)], 169.0 [CNEt (y)], 229.4 [CNEt (b)], and 317.7 ($CNEt_2$).

Ultraviolet Irradiation of Pentakis(t-butyl isocyanide)iron.—A solution contained in a quartz tube of [$Fe(CNBu^t)_5$] (1.5 g, 3.2 mmol) in tetrahydrofuran (30 cm^3) was irradiated at room temperature for 48 h. The reaction mixture was filtered through a short (1 cm) alumina pad and the solvent removed *in vacuo*. The residue was recrystallised (−20 °C) from dichloromethane–light petroleum (6 cm^3) to give light yellow *crystals* of [$Fe(CN)_2(CNBu^t)_4$] (6) (0.3 g, 21%), $\nu_{max.}$ (Nujol) at 2 200m(sh), 2 150vs, 2 110s, 2 058w(sh), 1 259w, 1 234m, 1 205s, 802w, 710w, and 575m cm^{-1}. N.m.r. resonances: ^1H ($CHClF_2$, −130 °C), τ 8.53 (s); ^1H ([$^2H_1$]-chloroform, 28 °C), τ 8.47 (s); ^{13}C ([$^2H_1$]chloroform, 25 °C), δ (p.p.m.) 29.5 (CH_3), 56.2 (CMe_3), and 143.5 (Fe-CN).

Preparation of 1—4-η-Cyclo-octatetraenetris(t-butyl isocyanide)iron.—A solution of [$Fe(CNBu^t)_5$] (0.6 g, 1.3 mmol) and cyclo-octatetraene (1 cm^3, 9 mmol) in light petroleum (30 cm^3) was irradiated (72 h) at room temperature. The volatile material was removed *in vacuo*, and the residue recrystallised (−20 °C) from light petroleum to give red *crystals* of *1—4-η-cyclo-octatetraenetris(t-butyl isocyanide)-iron* (7) (0.37 g, 69%) (Found: C, 66.9; H, 8.7; N, 10.1. $C_{23}H_{35}FeN_3$ requires C, 67.4; H, 8.6; N, 10.3%); m.p. 103—105 °C, $\nu_{max.}$ (Nujol) at 2 130s, 2 020vs, 1 548w, 1 365m, 1 228m, 1 210s, 1 035w, 877w, 847w, 738w, 719w, 707w, and 692m cm^{-1}. The mass spectrum showed peaks at *m/e* 409 (*P*, 2%), 326 ($P - CNBu^t$, 3%), 305 ($P - C_8H_8$, 2%), 243 ($P - 2CNBu^t$, 4%), 222 ($P - C_8H_8 - CNBu^t$, 16%), and 160 ($P - 3CNBu^t$, 13%). N.m.r. resonances: ^1H ([$^2H_1$]chloroform, 25 °C), τ 5.50 (s, 8 H, C_8H_8) and 8.57 (s, 27 H, Bu^t), ^1H (CF_2Cl_2, −150 °C), τ 4.17 (br, 4 H, C_8H_8), 4.65 (br, 4 H, C_8H_8), 8.61 (s, 18 H, Bu^t), and 8.85 (s, 9 H, Bu^t); ^{13}C ([$^2H_8$]toluene–CCl_2F_2, −148 °C), δ (p.p.m.) 31.3 (Me), 55.3, 55.8 (CMe_3), 85.9 (C_8H_8), and 177.0 (Fe-CN); ^{13}C ([$^2H_8$]toluene, 25 °C), δ (p.p.m.) 32.3 (CH_3), 56.7 (CMe), 97.8 (C_8H_8), and 177.5 (FeCN).

Crystal Structure Determination of Nonakis(ethyl isocyanide)di-iron.—Attempts to recrystallise samples of (1) from solvents such as diethyl ether or toluene–hexane afforded long flat orange needles of proportions unsuitable for *X*-ray crystallographic investigation. However, the u.v. irradiation of a solution of [$Fe(CNEt)_5$] in diethyl ether of *ca.* 0.2 mol dm^{-3} concentration provided conditions for the growth of single crystals from the reaction mixture. One such crystal, an approximately equidimensional parallelepiped (*ca.* 0.4 mm), was mounted inside a Lindemann tube filled with nitrogen. Rigorous precautions were taken to exclude oxygen.

Intensity data were recorded at 233 K on a Syntex $P2_1$ four-circle diffractometer in the range $2.9 \leqslant 2\theta \leqslant 50.0°$, using methods described earlier.[23] From a total of 6 161 measured intensities, 3 106 satisfied the observability criterion of $I \geqslant 2\sigma(I)$, $\sigma(I)$ being the standard deviation of the measured intensity based on counting statistics. Corrections were applied to compensate for some observed decay, and for Lorentz and polarisation but not for *X*-ray absorption effects.

Crystal data. $C_{27}H_{45}Fe_2N_9$, $M = 607.4$, Monoclinic, space group $P2_1/n$, $a = 22.193(14)$, $b = 12.762(6)$, $c = 12.332(8)$ Å, $\beta = 104.60(5)°$, $U = 3\ 380.2$ Å^3, $D_m = 1.23$ g cm^{-3}, $Z = 4$, $D_c = 1.19$ g cm^{-3}, $F(000) = 1\ 288$, Mo-K_α *X*-radiation, graphite monochromator ($\lambda = 0.710\ 69$ Å) $\mu(\text{Mo-}K_\alpha) = 40.6\ cm^{-1}$.

Structure solution and refinement. Following location of the iron atoms by a Patterson synthesis, a refinement of the fractional positional co-ordinates and two successive difference-Fourier syntheses gave the positions of the reremaining non-hydrogen atoms. Refinement of these atomic positions, together with anisotropic thermal motion parameters for the iron atoms and isotropic parameters for all other atoms, resulted in an agreement factor of *R* 0.11. At this stage, the observability criterion was increased to $I \geqslant 2.5\sigma(I)$ and refinement was continued with anisotropic temperature factors for all atoms except C(22), C(41), C(42), C(81), and C(92). With these atoms having isotropic temperature factors, an unstable refinement was obtained for C(41), C(42), and C(82). Attempts to fit a disordered model for the ethyl group bonded to N(4), and for the methyl carbon C(82), were unsuccessful, and final refinement of the structure was carried out with thermal parameters for these atoms [C(41), C(42), and C(82)] held invariant. A scheme for applying individual weights was of the form $w^{-1} = \sigma^2(F_o) - 0.15\,|F_o|$, where σ is the estimated standard deviation in $|F_o|$ based on counting statistics only. Full refinement using 3 062 weighted data satisfying the criterion $I \geqslant 2.5\sigma(I)$ resulted in convergence at *R* 0.08 (*R'* 0.11), the mean and maximum shift-to-error ratios being 0.01 and 0.4 respectively. The final electron-density difference synthesis revealed no residuals less than −0.3 e Å^{-3} nor greater than 0.9 e Å^{-3} except for that discussed above. Scattering factors were from ref. 24 for C and N and ref. 25 for Fe, including corrections for effects of anomalous dispersion for Fe. Computational work was carried out using the '*X*-Ray' system of programs[26] at the University of London Computing Centre. The observed and calculated structure factors, equations of some least-squares planes, and the thermal parameters are listed in Supplementary Publication No. SUP 22862 (20 pp.).*

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