Reaction of Bidentate Isonitrile Ligands with Iron Carbonyls

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Reaction of the bidentate isonitriles $CN(CH_2)_nNC$ (n = 2, 3, 4, or 6) with $[Fe_2(cp)_2(CO)_4]$ (cp = η-cyclopentadienyl) yields exclusively $[\{Fe_2(cp)_2(CO)_3\}_2\{CN(CH_2)_nNC\}]$ derivatives which are fluxional in solution and exist in three isomeric forms (bridged—bridged, bridged–terminal, and terminal–terminal with respect to the bonding mode of the bidentate isonitrile). The proportion of the isomers containing terminally bound isonitrile increases with the length of the alkyl chain. The complexes may be protonated to yield $[\{Fe_2(cp)_2(CO)_3\}_2\{CN(H)(CH_2)_n(H)NC\}][PF_6]_2$ salts (n = 2 or 6) and may be cleaved with I_2 to give $[Fe(cp)(CO)_2I]$ and $[\{Fe(cp)(CO)I\}_2\{CN(CH_2)_nNC\}]$ (n = 2 or 6). Reaction of $CN(CH_2)_nNC$ (n = 2 or 6) with $[Fe_2(CO)_9]$ or $[Fe_3(CO)_{12}]$ yields exclusively $[\{Fe(CO)_4\}_2\{CN(CH_2)_nNC\}]$ derivatives.

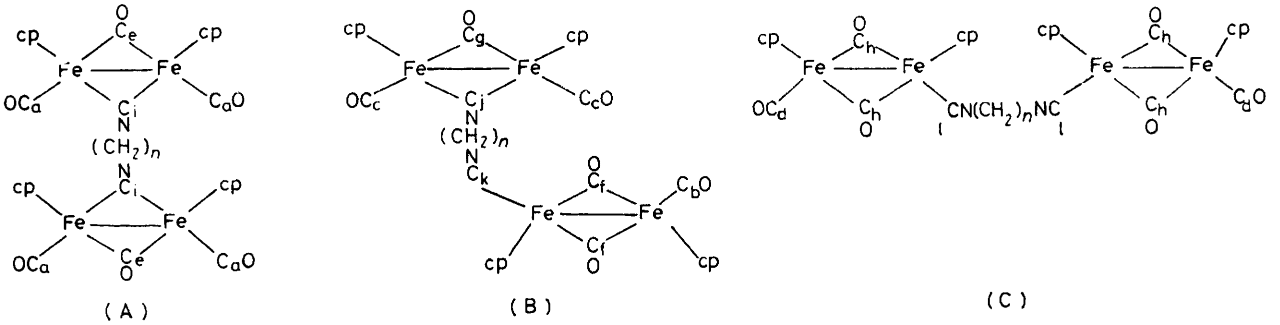
DURING the past decade it has become increasingly apparent that isonitriles may form one of the most versatile classes of ligand available to the transition-metal chemist. Despite the large number of studies on complexes of bi- and poly-dentate ligands of Groups 5 and 6, the chemistry of bi- and poly-dentate isonitriles remains almost unexplored, although the recent work of Gray and co-workers [1] and others [2] on the preparation and reactivity of $[Rh_2\{CN(CH_2)_nNC\}_4]^{2+}$ salts (n = 3—8) indicates the possibility of a rich and interesting chemistry. As part of our studies [3] of the reactions of isonitriles with transition-metal carbonyl clusters, we report here results on the reaction of the series $CN(CH_2)_nNC$ (n = 2, 3, 4, or 6) with the iron carbonyls $[Fe_2(cp)_2(CO)_4]$ (cp = η-cyclopentadienyl), $[Fe_2(CO)_9]$, and $[Fe_3(CO)_{12}]$.

DISCUSSION

We have found the most satisfactory synthesis of the $CN(CH_2)_nNC$ series (1a—d; n = 2, 3, 4, or 6) to involve the elimination of water from the disubstituted formamide $OHCHN(CH_2)_nNHCHO$ using phosgene, $COCl_2$, in the presence of triethylamine.[4]

Reaction of (1a)—(1d) with $[Fe_2(cp)_2(CO)_4]$ in benzene at room temperature, followed by chromatography, yields exclusively red-purple crystalline complexes which analytical (Table 1) and other data show to have the composition $[\{Fe_2(cp)_2(CO)_3\}_2\{CN(CH_2)_nNC\}]$ (2a—d; n = 2, 3, 4, or 6). Yields are not as satisfactory as those obtained in the preparation of unidentate ligand derivatives $[Fe_2(cp)_2(CO)_3(CNR)]$ and the formation of amounts of insoluble polymeric material is undoubtedly responsible. No products were isolated which involved chelation within a single Fe_2 moiety.

As isonitriles are known to function as both bridging and terminal ligands, the three isomeric structures (A)—(C) are possible. In the drawing, the cp groups are represented as having a *cis* configuration, although the possibility of *cis–trans* isomerism of the $Fe_2(cp)_2(CO)_3$ moieties raises the total number of isomers to ten [three each for (A) and (C) and four for (B)]. In common with work on the monosubstituted $[Fe_2(cp)_2(CO)_3(CNR)]$ complexes, it does not appear possible to differentiate between *cis* and *trans* isomers by n.m.r. spectroscopy (if indeed, more than one isomer is present), and the discussion which follows is in terms of the structural isomers (A)—(C) only.



(2a)—(2d) n = 2,3,4 or 6

Carbon-13 and ^1H n.m.r. studies (Tables 2 and 3) show that all three isomers may be present, with the proportions dependent on the alkyl chain length, n, and that the molecules are fluxional in solution, undergoing isomer interchange accompanied by both CO and $CNCH_2$ bridge–terminal exchange, and cyclopentadienyl site exchange. Thus, the limiting low-temperature proton spectrum of (2a) (Figure 1) shows the expected four cyclopentadienyl signals due to a mixture of isomers (A) and (B) in the ratio 1 : 4. On the basis of intensities and characteristic trends in chemical shifts,[3] the resonance at δ 4.88 may be assigned to the equivalent cyclopentadienyl ligands of (A) while the three other peaks at δ 4.86, 4.70, and 4.59 in the ratio of 2 : 1 : 1 may be assigned to (B). In the CH_2 region a singlet is observed at δ 4.34 due to (A), while the multiplet at δ 3.71 may be assigned to (B), which may be regarded as an unsymmetrical 1,2-disubstituted ethane. Such compounds are known to exhibit AA'BB' spectra,[5] and the experimental spectrum may be simulated exactly using values of $\delta_A = 3.67$ and $\delta_B = 3.78$, with geminal and vicinal coupling constants of −14 and 6 Hz respectively. A rather large natural linewidth of *ca.* 3 Hz must be assumed; broadness of the alkyl resonances is a feature characteristic of the other complexes (2b)—(2d) and may be due to incompletely resolved resonances from *cis* and *trans* isomers.

TABLE 1

Analytical data (%)

Complex	Found C	Found H	Found N	Calc. C	Calc. H	Calc. N
(2a)	48.9	3.30	4.10	49.2	3.30	3.85
(2b)	49.8	3.45	4.30	49.9	3.50	3.75
(2c)	50.3	3.60	3.90	50.5	3.70	3.70
(2d)	52.1	4.25	3.75	51.8	4.05	3.55
(3a)	35.6	2.55	3.50	35.2	2.55	2.75
(3b)	37.3	3.15	2.80	37.8	3.15	2.60
(4a)	30.6	2.10	4.75	30.4	2.20	4.45
(4b)	34.8	3.15	3.60	34.9	3.20	4.05
(5a)	34.9	1.00	7.65	34.6	0.95	6.75
(5b)	41.3	2.60	6.55	40.7	2.55	5.95

Crystallographic studies have shown that a bridging isonitrile ligand is not linear, but generally has an R–N–C angle of *ca.* 130°. The equivalence of the cyclopentadienyl ligands of isomer (A) and those of the $Fe_2(cp)_2(CO)_3$ residue of isomer (B) containing the bridging isonitrile group implies that nitrogen inversion is rapid on the n.m.r. time scale at −20 °C. On cooling to −80 °C, considerable broadening of these resonances is observed. This implies a slowing of the inversion at this temperature, although spectra at lower temperatures could not be obtained due to solubility problems. Analogous spectra of the bridged isonitrile isomer in the series $[Fe_2(cp)_2(CO)_3(CNR)]$ (R = alkyl or phenyl) show no temperature dependence down to −105 °C,[3] indicating that the bulk of the substituent on a bridging isonitrile is perhaps an important factor in determining the barrier to nitrogen inversion.

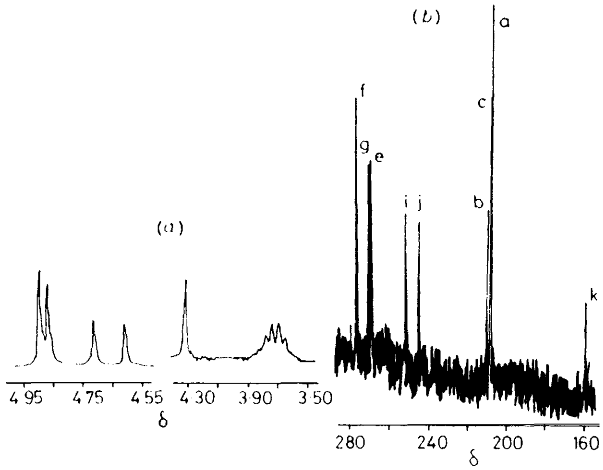


FIGURE 1 Proton (*a*) and ^{13}C (*b*) n.m.r. spectra of (2a) in CD_2Cl_2 at −20 °C

On warming to room temperature, both the cyclopentadienyl and CH_2 resonances broaden, and in $[^2H_8]$toluene a limiting high-temperature spectrum consisting of single cyclopentadienyl and CH_2 resonances can be obtained at 80 °C. This demonstrates the presence of both (A) $\rightleftharpoons$ (B) exchange and cyclopentadienyl site

TABLE 2

Proton n.m.r. spectra [a]

Complex	cp		Other			Ratio (A) : (B) : (C)
(2a) [b]	4.88 (A)		4.34 (s) CH_2(A)			1 : 4 : 0
	4.86 4.70 4.59	(B)	3.71 (m) CH_2(B)			
(2b) [b]	4.86 (B)		3.81 (t, J = 5.7) 3.42 (t, J = 5.8) 3.19 (t, J = 7.0)	CH_2(B,b) CH_2 (B,te) CH_2(C)	α	0 : 4 : 1
	4.70 4.59 4.57	(B + C)	0.83—1.80 (m) β-CH_2(B + C)			
(2c) [b]	4.83 (B)		3.84 (t,br) 3.48 (t,br) 3.18 (t,br)	CH_2(B,b) CH_2(B,te) CH_2(C)	α	0 : 1 : 2
	4.69 4.58	(B + C)	1.16—1.80 (m) β-CH_2(B + C)			
(2d) [b]	4.83 (B)		3.87 (t, J = 7.4) 3.35 (t,br) 3.19 (t, J = 5.9)	CH_2(B,b) CH_2(B,te) CH_2(C)	α	0 : 1 : 7
	4.69 4.58	(B + C)	0.53—1.74 (m) β,γ-CH_2(B + C)			
(4a) [c]	4.83 4.81		4.10 (s) CH_2			
(4b) [c]	4.73		3.77 (t, J = 6.2) α-CH_2 1.41—1.99 (m) β,γ-CH_2			

[a] Chemical shifts in p.p.m. from $SiMe_4$, J values in Hz; s = singlet, t = triplet, m = multiplet, te = terminal, b = bridging. [b] In CD_2Cl_2 solution at −40 °C. [c] In $CDCl_3$ solution.

exchange in isomer (B). In terms of the Adams–Cotton mechanism, these processes are related. Thus, independent bridge–terminal isonitrile exchange at each $Fe_2(cp)_2(CO)_3$ moiety results in (A) $\rightleftharpoons$ (B) $\rightleftharpoons$ (C) exchange [although (C) is depopulated below the limits of observation for $n = 2$], while it has been shown [3,6] that cyclopentadienyl site exchange in the terminally bound isomer is an automatic consequence of bridge–terminal isonitrile exchange.

TABLE 3

Carbon-13 n.m.r. spectra [a]

	CO_{te}				CO_b				CN_b		CN_{te}			
Complex	a	b	c	d	e	f	g	h	i	j	k	l	cp	Other
(2a) [b]	209.9	212.1	210.4		271.1	278.6	272.3		253.6	246.7	160.8		86.6 86.3 85.5	60.9 CH_2(A) 57.5 CH_2(B,b) 45.0 CH_2(B,te)
(2b) [b]		209.5	209.5	211.7		277.6	271.6	278.3		247.7	161.0	158.4	86.2 85.9 85.1	53.9 [c] CH_2(B,b) α 41.2 CH_2(B,te) α 39.7 CH_2(C) α 29.2 CH_2(B) β 27.7 CH_2(C) β
(2c) [b,d]				211.0				278.5					86.3 86.1 85.3	42.9 α-CH_2(C) 22.9 β-CH_2(C)
(2d) [b,e]				211.6				278.7				158.4	85.0 85.8	43.2 α-CH_2(C) 27.6 β-CH_2(C) 23.8 γ-CH_2(C)
(3a) [f]			207.5				254.9			320.1			89.6	58.2 CH_2
(3b) [f]			207.9 208.2				254.9			319.6			89.7 90.3	59.9 α-CH_2 28.9 β-CH_2 26.4 γ-CH_2
(5a) [b]			210.9									160.8		45.6 CH_2
(5b) [b]			212.3									154.4		45.6 α-CH_2 28.4 β-CH_2 25.2 γ-CH_2

[a] Chemical shifts in p.p.m. from $SiMe_4$; b = bridging, te = terminal. [b] In CH_2Cl_2–CD_2Cl_2 solution; spectra of (2a)—(2d) at −30 °C. [c] Obscured by solvent peak. [d] Limited solubility; only carbonyl resonances of isomer (B) detectable. [e] Resonances of minor isomer (B) not detected. [f] In CH_3CN–CD_3CN solution.

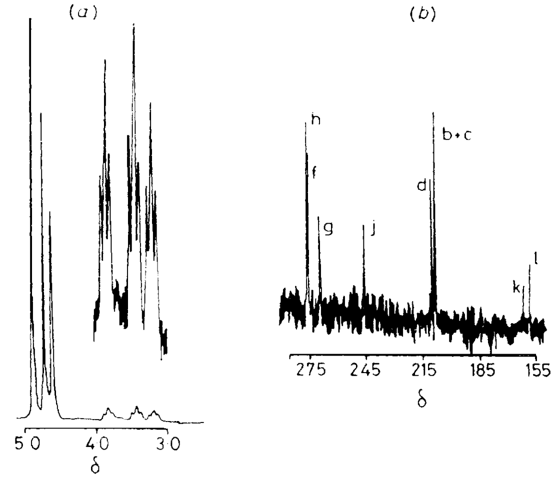


FIGURE 2 Proton (*a*) and ^{13}C (*b*) n.m.r. spectra of (2b) in CD_2Cl_2 at −20 °C

The ^{13}C spectrum of (2a) at −20 °C (Figure 1) in the CO and CN region shows the nine resonances expected for a mixture of isomers (A) and (B). The assignment shown is made on the basis of intensity and on chemical shifts found for the related $[Fe_2(cp)_2(CO)_3(CNR)]$ series.[3] Some of the assignments are not unambiguous; thus, the two resonances at 271.1 and 272.3 p.p.m. may be reversed. Some overlap of resonances is observed in the cyclopentadienyl region, but the expected three CH_2 resonances can be clearly seen (Table 3).

The spectra of $[\{Fe_2(cp)_2(CO)_3\}_2\{CN(CH_2)_3NC\}]$ (2b) indicate a mixture of isomers (B) and (C) (Figure 2). Only four of the five expected cyclopentadienyl absorptions can be seen, although a clear shoulder is observable on the resonance at δ 4.71. Thus, the resonance at δ 4.86 is assigned to the equivalent cyclopentadienyl groups of the $Fe_2(cp)_2(CO)_3$ residue of (B) containing a bridging isonitrile and the remaining four resonances are assigned to the terminal $Fe_2(cp)_2(CO)_3$ residue of (B) and isomer (C). In the α-CH_2 region the expected three triplets can be clearly seen. The ^{13}C spectrum at −40 °C in the CO and CN region (Figure 2) shows eight of the nine resonances expected. The most probable assignments shown are based on intensity and chemical shift; in particular, the intensity of the resonance at 209.5 p.p.m. indicates a coincidence of carbonyls (b) and (c). On warming to room temperature, both CO and CN resonances broaden, indicating both CO and CN bridge–terminal exchange. A high-temperature-limiting spectrum could not be obtained because of limited solubility in other solvents and slow decomposition at higher temperatures.

Spectra of (2c) and (2d) may be interpreted on the same basis (Tables 2 and 3) and clearly show a decrease in the amount of isomer (B) relative to (C).

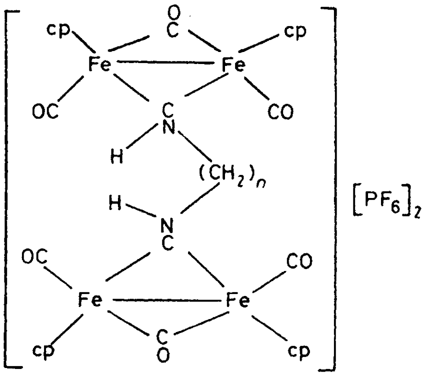
Infrared spectra (Table 4) are also in accord with this interpretation. Thus, the band at *ca.* 1 990 cm^{-1} may be assigned to the coincident symmetric terminal CO vibrations of (A) and the $Fe_2(cp)_2(CO)_3$ residue of (B) containing a bridging isonitrile, while the band at *ca.* 1 945 cm^{-1} may be assigned to coincident asymmetric terminal CO vibrations of (A) and the $Fe_2(cp)_2(CO)_3$ residue of (B) containing a bridging isonitrile and the terminal CO vibrations of (C) and the $Fe_2(cp)_2(CO)_3$ residue of (B) containing a terminal isonitrile. In the bridging CO region, the band at *ca.* 1 785 cm^{-1} may be assigned to (A) and the $Fe_2(cp)_2(CO)_3$ residue of (B) containing a bridging isonitrile, while that at *ca.* 1 755 cm^{-1} is due to (C) and the $Fe_2(cp)_2(CO)_3$ residue of (B) containing a terminal isonitrile. The presence of two bridging CN vibrations in the spectrum of (2a) confirms the presence of isomers (A) and (B).

TABLE 4

Infrared data (cm^{-1})

Complex	CN_{te}	CO_{te}	CO_b	CN_b
(2a) [a]		1 990 (100) [b]	1 790 (43)	1 706 (35)
		1 946 (65)	1 750 (59)	1 722 (31)
(2b) [a]		1 987 (100)	1 787 (37)	1 711 (52)
		1 967 (sh)	1 759 (100)	
		1 943 (97)		
(2c) [a]		1 987 (62)	1 783 (24)	1 711 (22)
		1 943 (80)	1 755 (100)	
(2d) [a]		1 984 (38)	1 779 (20)	1 715 (sh)
		1 947 (82)	1 755 (100)	
(3a) [c]		2 015	1 825	1 525
		1 990		
(3b) [c]		2 010	1 820	1 570
		1 980		
(4a) [d]	2 149	1 980		
(4b) [d]	2 163	1 975		
(5a) [d]	2 171	2 060		
		2 003		
		1 979		
(5b) [d]	2 175	2 057		
		1 995		
		1 969		

[a] 10% CH_2Cl_2–CS_2 solution; CN_{te} obscured by solvent absorption but can be seen at *ca.* 2 130 cm^{-1} in CH_2Cl_2 solution. [b] Relative intensities in parentheses. [c] In Nujol mull. [d] In hexane solution.



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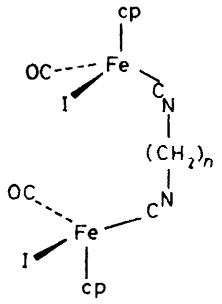

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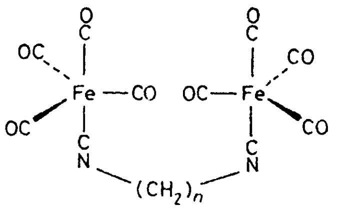

(5)

(a) $n = 2$, (b) $n = 6$

We believe that the increase in the amounts of isomers (A) and (B) with decreasing alkyl chain length can be explained primarily on steric grounds. Inspection of molecular models shows that, for $n = 2$, the structural form (A) provides the least amount of steric interaction between the $Fe_2(cp)_2(CO)_3$ moieties (and therefore the least hindrance to $H_2C–CH_2$ rotation). As the length of the chain increases and this interaction becomes less relevant, isomers (B) and particularly (C) become progressively more abundant because the steric interaction between the cyclopentadienyl ligands and the α-CH_2 of the alkyl chain is minimized.

These complexes exhibit a reactivity similar to that of the $[Fe_2(cp)_2(CO)_3(CNR)]$ derivatives. Thus, protonation of (2a) or (2d) with aqueous HPF_6 yields the non-fluxional bridged iminium complexes (3a) or (3b).[7] Characteristic of these salts are the bridging CN vibration at 1 520—1 570 cm^{-1} and the considerably deshielded CN resonance at *ca.* 315 p.p.m. in the ^{13}C spectrum. Reaction of (2a) or (2d) with iodine results in cleavage to yield $[Fe(cp)(CO)_2I]$ and $[\{Fe(cp)(CO)I\}_2\{CN(CH_2)_nNC\}]$ [(4a; $n = 2$) or (4b; $n = 6$)]. This is a reaction characteristic of $[Fe_2(cp)_2(CO)_4]$ and $[Fe_2(cp)_2(CO)_3(CNR)]$ derivatives, but, interestingly, only poor yields of the $[Fe(cp)(CO)I(L)]$ complexes are obtained on cleavage of $[Fe_2(cp)_2(CO)_3L]$ complexes where L = $P(OR)_3$, PR_3, or CS.[8,9] The ^1H n.m.r. spectrum of (4a) shows two cyclopentadienyl resonances of equal intensity consistent with the presence of two diastereoisomers (one *meso*, one DL).

Reaction of (1a) or (1d) with either $[Fe_2(CO)_9]$ or $[Fe_3(CO)_{12}]$ yields exclusively the $[\{Fe(CO)_4\}_2\{CN(CH_2)_nNC\}]$ complexes (5a; $n = 2$) or (5b; $n = 6$) isolated as light yellow solids, but decomposing slowly to $[Fe_3(CO)_{12}]$ in the solid state. The i.r. spectrum is typical, in terms of intensities of the bands, of an axially substituted trigonal-bipyramidal $[Fe(CO)_4L]$ complex,[10] and the singlet ^{13}C carbonyl resonance observed down to −90 °C is consistent with the low activation energy for intramolecular exchange commonly found in similar five-coordinate species.

It is interesting to compare these results with the reaction of $[Fe_2(CO)_9]$ with $Ph_2P(CH_2)_2PPh_2$ which yields both the related $[\{Fe(CO)_4\}_2\{Ph_2P(CH_2)_2PPh_2\}]$ and the chelated $[Fe(CO)_3\{Ph_2P(CH_2)_2PPh_2\}]$ in the ratio of 1 : 1.[11] No chelate complexes have been isolated in this work, and other workers have shown [12,13] that the alkyl chain must be at least eight carbons long before chelate behaviour is observed due to the particular requirements of the linear CN–R linkage. We are currently examining syntheses of potentially chelating di-isonitriles, and are also investigating the possibility of the preparation of polymer-supported complexes.

EXPERIMENTAL

The compounds $[Fe_2(CO)_9]$ and $[Fe_3(CO)_{12}]$ were prepared from $[Fe(CO)_5]$;[14] all other starting materials were obtained commercially. Reactions involving metal carbonyls were carried out under nitrogen in purified solvents. N.m.r. and i.r. spectra were recorded on JEOL FX-100 and Perkin-Elmer 257 instruments respectively. Carbon-13 n.m.r. spectra were run on *ca.* 0.06 mol dm^{-3} solutions in the presence of $[Cr(acac)_3]$ (acac = acetylacetonate) under nitrogen.

1,6-*Di-isocyanohexane* (1d).—Triethylamine (320 cm^3) and *NN'*-diformyl-1,6-diaminohexane (86 g, 0.5 mol) (prepared from 1,6-diaminohexane and ethyl formate [15]) were dissolved in CH_2Cl_2 (450 cm^3). With magnetic stirring, phosgene (99 g, 1.0 mol) was bubbled into the solution through a wide-bore tube sufficiently rapidly to cause reflux. The reaction was allowed to cool to room temperature and ammonia (40 g) then bubbled into the solution over 1 h. After filtration and removal of solvent, the residue was distilled to yield 1,6-di-isocyanohexane (40 g, 59%), b.p. 100—110 °C (0.01 mmHg).* N.m.r. spectra: ^1H 3.19 [m, J(N–H) = 1.9, J(H–H) = 6.4, α-CH_2], 1.26 (m, β-,γ-CH_2); ^{13}C, 155.2 [J(CN) = 6.1, CN], 41.3 [J(CN) = 6.1 Hz, α-CH_2], 28.7 (β-CH_2), 25.4 p.p.m. (γ-CH_2). The following isonitriles were prepared similarly: 1,2-*di-isocyanoethane* (1a), b.p. 60—65 °C (0.01 mmHg) {n.m.r.: ^1H 3.71 (br s, CH_2); ^{13}C, 158.6 [J(CN) = 3.0, CN], 36.3 p.p.m. [J(CN) = 5.6 Hz, CH_2]}; 1,3-*di-isocyanopropane* (1b), b.p. 70—80 °C (0.01 mmHg) {n.m.r.: ^1H, 3.55 [m, J(NH) = 1.9, J(HH) = 6.2, α-CH_2], 1.96 [m, J(NH) = 1.8, β-CH_2]; ^{13}C, 157.0 [J(CN) = 5.9, CN], 37.9 [J(CN) = 7.3 Hz, α-CH_2], 27.7 p.p.m. (β-CH_2)}; and 1,4-*di-isocyanobutane* (1c), b.p. 80—90 °C (0.01 mmHg) {n.m.r.: ^1H, 3.41 [J(NH) = 2.0, α-CH_2], 1.78 (m, β-CH_2); ^{13}C, 156.0 [J(CN) = 5.7, CN], 40.4 [J(CN) = 5.9 Hz, α-CH_2], 25.4 p.p.m. (β-CH_2)}.

CAUTION: Explosions have previously been reported on distillation of isonitriles.[2] During phosgene addition, exit gases were passed through sodium hydroxide solution and monitored for phosgene using filter paper soaked in an alcoholic solution containing 10% of a mixture of equal parts of *p*-dimethylaminobenzaldehyde and colourless diphenylamine.

$[\{Fe_2(cp)_2(CO)_3\}_2\{CN(CH_2)_6NC\}]$ (2d).—1,6-Di-isocyanohexane (0.68 g) was added to a solution of $[Fe_2(cp)_2(CO)_4]$ (3.54 g) in benzene (80 cm^3) and stirred overnight at room temperature. Solvent was removed and the residue was chromatographed on grade IV alumina using CH_2Cl_2 as eluant. After elution of starting material, a second purple band gave the product (2d) as purple crystals after recrystallization from CH_2Cl_2–light petroleum (b.p. 40—60 °C) (1.5 g, 36%). Complexes (2a)—(2c) were prepared similarly.

$[\{Fe_2(cp)_2(CO)_3\}_2\{CN(H)(CH_2)_6(H)NC\}][PF_6]_2$ (3b) —Complex (2d) (400 mg) was suspended in OEt_2 and enough CH_2Cl_2 added to cause dissolution. Hexafluorophosphoric acid (75% aqueous) was added dropwise until precipitation ceased. The brick red precipitate was collected and purified by reprecipitation using CH_2Cl_2–light petroleum to yield (3b) (480 mg, 85%). Complex (3a) was prepared in the same way.

$[\{Fe(cp)(CO)I\}_2\{CN(CH_2)_6NC\}]$ (4b).—Iodine (500 mg) was added to a solution of (2d) (500 mg) in chloroform (15 cm^3) and refluxed for 30 min. The excess of iodine was removed by extraction with sodium thiosulphate solution and the solvent was also removed. The residue was chromatographed on alumina grade IV. Elution with CH_2Cl_2 yielded first a brown band of $[Fe(cp)(CO)_2I]$ (300 mg, 42%) and secondly a black-green band of the product (4b) (230 mg, 19%) which was recrystallized from CH_2Cl_2–light petroleum. Complex (4a) was similarly prepared.

$[\{Fe(CO)_4\}_2\{CN(CH_2)_6NC\}]$ (5b).—1,6-Di-isocyanohexane (1d) (136 mg) was added to an excess of $[Fe_2(CO)_9]$ (1.0 g) in diethyl ether (50 cm^3) and the mixture was refluxed for 30 min. The solvent was removed and the residue was chromatographed on alumina grade IV. A light yellow band was eluted with CH_2Cl_2–light petroleum (1 : 1). The solvent was removed at 0 °C under reduced pressure (0.1 mmHg) to yield (5b) as a light yellow solid (400 mg, 85%). Complex (5a) was prepared in a similar manner. The same products are obtained on reaction of (1a) or (1d) with $[Fe_3(CO)_{12}]$ in refluxing benzene.

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* Throughout this paper: 1 mmHg = 13.6 × 9.8 Pa.