The Reactions of Acids and Alkyl Iodides with $[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)_4]$ and Related Complexes

A. R. Manning * **and Paul Murray**
Department of Chemistry, University College, Belfield, Dublin 4, Ireland

The very high nucleophilicity and basicity of the N atoms of the μ-CNR ligands in $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNMe)_3]$ and $[Fe_2(\eta\text{-}C_5H_5)_2(CNR)_4]$ [R = Me (black isomer) or Et] is illustrated by their ability to react with R'I (R' = Me, Et, or Pr^n) to give in turn $[Fe_2(\eta\text{-}C_5H_5)_2L(CNR)(\mu\text{-}CNR)\{\mu\text{-}CN(R)R'\}]I$ and $[Fe_2(\eta\text{-}C_5H_5)_2L(CNR)\{\mu\text{-}CN(R)R'\}_2]I_2$ (L = CO or CNR). The strong acid $HPF_6\cdot Et_2O$ gives $[Fe_2(\eta\text{-}C_5H_5)_2(CNR)_2\{\mu\text{-}CN(R)H\}_2][PF_6]_2$ which with $[Fe_2(\eta\text{-}C_5H_5)_2(CNR)_4]$ forms $[Fe_2(\eta\text{-}C_5H_5)_2(CNR)_2(\mu\text{-}CNR)\{\mu\text{-}CN(R)H\}][PF_6]$. These all contain N–R' or N–H bonds. Weak acids such as $PhCO_2H$ or $MeCO_2H$ (= HA) form only $[Fe_2(\eta\text{-}C_5H_5)_2(CNR)_2(\mu\text{-}CNR)\{\mu\text{-}CN(R)H\}][A]$ complexes, but somewhat stronger acids (HA = $CH_{3-n}Cl_nCO_2H$ where n = 1—3) form both these and $[Fe_2(\eta\text{-}C_5H_5)_2(CNR)_2\{\mu\text{-}CN(R)H\}_2][A]_2$ derivatives. For these salts there is strong spectroscopic evidence for hydrogen bonding of the type $NH \cdots A^-$. Although the residual basicity of the μ-CNMe ligand in $[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)_2(\mu\text{-}CNMe)(\mu\text{-}CNMe_2)]I$ is illustrated by its reaction with HPF_6 to give $[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)_2\{\mu\text{-}CN(Me)H\}(\mu\text{-}CNMe_2)]I[PF_6]\cdot H_2O$, the reaction of $[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)_2(\mu\text{-}CNMe)\{\mu\text{-}CN(Me)H\}][PF_6]$ with MeI results in dimer cleavage to a salt of the $[Fe(\eta\text{-}C_5H_5)(CNMe)_3]^+$ cation. The brown form of $[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)_4]$, which is a mixture of the black isomer and another, reacts with MeI to give a mixture of $[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)_2(\mu\text{-}CNMe)(\mu\text{-}CNMe_2)]I$ and $[Fe(\eta\text{-}C_5H_5)(CNMe)_2I]$, whilst with CCl_3CO_2H it gives a mixture of $[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)_2(\mu\text{-}CNMe)\{\mu\text{-}CN(Me)H\}][CCl_3CO_2]$ and an unidentified $[Fe(\eta\text{-}C_5H_5)(CNMe)_2X]$ species. The i.r. and ^1H n.m.r. spectra of the various products are reported and discussed.

The nitrogen atoms of the μ-CNR ligands of $[Fe_2(\eta\text{-dienyl})_2(CO)_{4-n}(CNR)_n]$ complexes (dienyl = C_5H_5, MeC_5H_4, or C_9H_7; n = 1 or 2; R = alkyl or aryl) are very susceptible to attack by electrophiles.[1] They may be protonated,[1,2] alkylated,[3] or acylated[4] to give derivatives containing the $\mu\text{-}CN(R)R'^+$ or iminium ligand [R' = H, R, C(O)R, or C(O)Ph]. Other $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_{4-n}(CNR)_n]$ (R = Me or Et) complexes where n = 3 or 4 have now been found to undergo similar reactions with protic acids and alkyl halides. The results of these investigations are reported here.

Experimental

Previously reported methods were used to prepare $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNMe)_3]$[5] and $[Fe_2(\eta\text{-}C_5H_5)_2(CNR)_4]$ (R = Me or Et).[6] Other chemicals were obtained from the usual commercial sources and generally used as received.

All reactions were carried out in purified solvents under an atmosphere of nitrogen at room temperature and in the dark using the black isomer of $[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)_4]$ unless it is stated otherwise.

Infrared spectra were run on Perkin-Elmer 283B or 337 spectrometers with the latter being equipped with a Hitachi Perkin-Elmer readout recorder. They were calibrated using polystyrene or DCl and water vapour. Proton n.m.r. spectra were measured on a Perkin-Elmer R12B spectrometer in $CDCl_3$ solutions using $SiMe_4$ as an internal standard.

Elemental analyses were carried out in the Analytical Laboratory of University College, Dublin.

Preparation of $[Fe_2(\eta\text{-}C_5H_5)_2(CNR)_3\{CN(R)H\}][A]$ (R = Me *or* Et; A^- = $PhCO_2^-$, $MeCO_2^-$, *or* $CCl_3CO_2^-$).—A solution of the weak acid HA in diethyl ether (20 cm^3) was added to one of $[Fe_2(\eta\text{-}C_5H_5)_2(CNR)_4]$ (0.3 g) in the same solvent (20 cm^3), using a reactant molar ratio of 1:1. The products precipitated as dark brown powders when R = Me and oils when R = Et. The powders were filtered off, washed with cold ether, and dried. The oils were isolated by removing the solvent at reduced pressure. In all cases the yields of $[Fe_2(\eta\text{-}C_5H_5)_2(CNR)_3\{CN(R)H\}][A]$ were quantitative.

Preparation of $[Fe_2(\eta\text{-}C_5H_5)_2(CNR)_2\{CN(R)H\}_2][A]_2$ (R = Me *or* Et; A^- = $CH_2ClCO_2^-$, $CHCl_2CO_2^-$, *or* $CCl_3CO_2^-$).—To a stirred solution of $[Fe_2(\eta\text{-}C_5H_5)_2(CNR)_4]$ (0.3 g) in diethyl ether (20 cm^3) was added one of the weak acid HA (molar ratio 1:2) in the same solvent (20 cm^3). The products precipitated as light green solids which were filtered off, washed with cold ether, and dried. The yields of the $[Fe_2(\eta\text{-}C_5H_5)_2(CNR)_2\{CN(R)H\}_2][A]_2$ salts were quantitative. Benzoic acid does not give this reaction.

Preparation of $[Fe_2(\eta\text{-}C_5H_5)_2(CNR)_2\{CN(R)H\}_2][PF_6]_2$ (R = Me *or* Et).—The complex $[Fe_2(\eta\text{-}C_5H_5)_2(CNR)_4]$ (0.3 g) was dissolved in diethyl ether (30 cm^3) and $HPF_6\cdot Et_2O$ (0.3 g) was added to this stirred solution. A green oil precipitated immediately. The supernatant was decanted off. The addition of chloroform (10 cm^3) to the oil gave a green powder that was filtered off, washed with cold chloroform and ether in turn, and dried. The yields of $[Fe_2(\eta\text{-}C_5H_5)_2(CNR)_2\{CN(R)H\}_2][PF_6]_2$ were quantitative.

Preparation of $[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)_3\{CN(Me)H\}][PF_6]$.—Equimolar amounts of $[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)_4]$ (0.3 g) and $[Fe_2(\eta\text{-}C_5H_5)(CNMe)_2\{CN(Me)H\}_2][PF_6]_2$ were stirred together in diethyl ether (30 cm^3). After 2 h the brown precipitate was filtered off, washed with cold ether, and dried. The yield of $[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)_3\{CN(Me)H\}][PF_6]$ was low.

Table 1. Decomposition temperatures, analyses, and conductivity data for $[Fe_2(\eta\text{-}C_5H_5)_2L(CNR)(\mu\text{-}CNR)\{\mu\text{-}CN(R)R'\}]I$ and $[Fe_2(\eta\text{-}C_5H_5)_2L(CNR)\{\mu\text{-}CN(R)R'\}_2]I_2$ salts (L = CO or RNC)

Complex	R	R′	Decomp. pt. (°C)	Analyses[a] (%)				Λ[b]/ohm^{-1} cm^2 mol^{-1}
				C	H	N	I	
(**1**) $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNMe)_2\{\mu\text{-}CN(Me)R'\}]I$	Me	Me	189	39.9 (40.4)	4.1 (4.1)	7.6 (7.8)	—	70
	Me	Et	202	41.1 (41.5)	4.2 (4.4)	7.8 (7.6)	23.5 (23.1)	74
(**2**) $[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)_3\{\mu\text{-}CN(Me)R'\}]I$	Me	Me	156	40.6 (41.6)	4.7 (4.7)	9.4 (10.2)	23.2 (23.2)	41
(**3**) $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNMe)\{\mu\text{-}CN(Me)R'\}_2]I_2$	Me	Me	320	33.0 (33.7)	4.1 (3.7)	6.6 (6.2)	—	135
(**4**) $[Fe_2(\eta\text{-}C_5H_5)_2(CNR)_2\{\mu\text{-}CN(Me)R'\}_2]I_2$	Me	Me	315	34.3 (34.8)	4.3 (4.1)	8.3 (8.1)	36.8 (36.8)	130
	Me	Et	315	36.0 (36.8)	4.7 (4.5)	8.3 (7.8)	—	—
	Me	Pr^n	*ca.* 20[c]	40.1 (38.6)	4.8 (4.8)	—	—	105
	Me	H,Me[d]	—	32.1 (32.1)	3.9 (3.6)	7.9 (7.9)	17.3 (17.8)	—
	Et	Me	284	38.8 (38.6)	4.0 (4.8)	7.3 (7.5)	—	—
	Et	Et	275	40.1 (40.3)	5.2 (5.2)	7.3 (7.2)	33.0 (32.8)	—

[a] Calculated values in parentheses. [b] For *ca.* 10^{-3} mol dm^{-3} solutions in nitromethane. [c] Decomposes at approximately room temperature within 1 h. [d] $[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)_2\{\mu\text{-}CN(Me)H\}\{\mu\text{-}CN(Me)Me\}]I[PF_6]\cdot H_2O$; F = 16.0 (16.0%).

Reaction of $[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)_4]$ (*Isomer Mixture*) *with* CCl_3CO_2H.—To a stirred solution of brown $[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)_4]$ (0.3 g) in benzene (30 cm^3) was added one of CCl_3CO_2H (reactant molar ratio 1:1) in the same solvent (10 cm^3). A brown powder precipitated. On the basis of its i.r. spectrum it was identified as a mixture of $[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)_3\{CN(Me)H\}][CCl_3CO_2]$ and a $[Fe(\eta\text{-}C_5H_5)(CNMe)_2X]$ species. They could not be separated.

Reaction of $[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)_{4-n}\{CN(Me)H\}_n][PF_6]_n$ (*n* = 1 *or* 2) *with Water*.—The salt $[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)_3\{CN(Me)H\}][PF_6]$ (0.3 g) was dissolved in water (10 cm^3) and the solution stirred for 20 min. It was then filtered and the solvent removed at reduced pressure to give a yellow powder, which was shown to be $[Fe(\eta\text{-}C_5H_5)(CNMe)_3][PF_6]$ by analysis and i.r. spectroscopy [ν(CN) 2 178vs and 2 218m, ν(P–F) 840 cm^{-1} in CsBr disc].

When a solution of $[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)_2\{CN(Me)H\}_2][PF_6]_2$ (0.3 g) was dissolved in water (10 cm^3) and stirred for 24 h no reaction occurred.

Reaction of $[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)_3\{CN(Me)H\}][PF_6]$ *with* MeI.—A solution of $[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)_3\{CN(Me)H\}][PF_6]$ (0.55 g) and MeI (0.06 cm^3, molar ratio 1:1) in diethyl ether (30 cm^3) was stirred. The yellow solid which precipitated was a salt of the $[Fe(\eta\text{-}C_5H_5)(CNMe)_3]^+$ cation, as shown by i.r. spectroscopy.

Preparation of $[Fe_2(\eta\text{-}C_5H_5)_2(CNR)_2L\{CN(R)R'\}]I$ (R = Me *or* Et; R′ = Me, Et, *or* Pr^n; L = CO *or* CNR).—A solution of $[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)_4]$ (0.4 g) and R′I (molar ratio 1:3) in tetrahydrofuran (30 cm^3) was stirred until its colour changed from red to brown. This required less than 10 min with MeI or EtI, but over 20 h with Pr^{n}I. This reaction mixture was filtered and the solvent removed at reduced pressure. Only $[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)_3(CNMe_2)]I$ was a solid which could be purified by recrystallization from chloroform–hexane mixtures (yield 70%). The other products were oils for which good elemental analyses could not be obtained although they showed the correct C:H:N:I ratios.

A similar procedure was used for the reactions of $[Fe_2(\eta\text{-}C_5H_5)_2(CNEt)_4]$ but all the $[Fe_2(\eta\text{-}C_5H_5)_2(CNEt)_3\{CN(Et)R'\}]I$ complexes were brown oils which could not be purified.

A similar procedure was used for the reaction of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNMe)_3]$ with R′I. Here a reactant molar ratio of 1:10 was necessary for MeI and EtI with reaction times of 1 h. The $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNMe)_2\{CN(Me)R'\}]I$ salts precipitated as brown solids which were recrystallized from dichloromethane–pentane mixtures in yields of 70%.

Preparation of $[Fe_2(\eta\text{-}C_5H_5)_2(CNR)L\{CN(R)R'\}_2]I_2$ (R = Me *or* Et; R′ = Me, Et, *or* Pr^n; L = CO *or* CNR).—A solution of $[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)_4]$ (0.4 g) and R′I (molar ratio 1:30) in tetrahydrofuran (30 cm^3) was stirred. The precipitated solids were filtered off and recrystallized from methanol–diethyl ether mixtures to give green $[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)_2\{CN(Me)R'\}_2]I_2$ salts in 70% yield. The reactions required *ca.* 30 min for MeI and EtI but 90 h for Pr^{n}I before they were complete.

The same procedure was used to prepare $[Fe_2(\eta\text{-}C_5H_5)_2(CNEt)_2\{CN(Et)R'\}_2]I_2$ from $[Fe_2(\eta\text{-}C_5H_5)_2(CNEt)_4]$, and $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNMe)(CNMe_2)_2]I_2$ from $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNMe)_3]$. This last reaction required 4 h for completion, and the yield of the product was 55%.

Reaction of $[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)_4]$ (*Isomer Mixture*) *with* MeI.—A solution of MeI (0.05 cm^3) in tetrahydrofuran (10 cm^3) was added dropwise to a stirred solution of brown $[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)_4]$ (0.4 g, molar ratio 1:1) in tetrahydrofuran (30 cm^3) over a period of 30 min. The reaction mixture was filtered and the solvent removed at reduced pressure to give a dark brown powder, identified as a mixture of $[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)_3(CNMe_2)]I$ and $[Fe(\eta\text{-}C_5H_5)(CNMe)_2I]$ by i.r. and ^1H n.m.r. spectroscopy.

Reaction of $[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)_3(CNMe_2)]I$ *with* $HPF_6\cdot Et_2O$.—To a suspension of $[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)_3(CNMe_2)]I$ (0.3 g) in diethyl ether (30 cm^3) was added a slight excess of $HPF_6\cdot Et_2O$ (molar ratio 1:1). The reaction mixture was stirred until the brown solid was replaced by green $[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)_2\{CN(Me)H\}(CNMe_2)]I[PF_6]\cdot H_2O$. This was filtered off, washed with ether, and dried.

The analytical data, i.r. and ^1H n.m.r. spectra of the products are given in Tables 1 and 2, 3 and 4, and 5 respectively.

Results and Discussion

Spectroscopic evidence strongly suggests that $[Fe_2(\eta\text{-}C_5H_5)_2(CNR)_4]$ (R = Me or Et) and $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNMe)_3]$ have molecular structures similar to those of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ and $[Fe_2(\eta\text{-}C_5H_5)_2(CNPh)_4]$ with approximately planar $Fe_2(\mu\text{-}CNR)_2$ or $Fe_2(\mu\text{-}CNMe)(\mu\text{-}CO)$ moieties.[5–8]

Table 2. Analytical data for $[Fe_2(\eta\text{-}C_5H_5)_2(CNR)_3\{\mu\text{-}CN(R)H\}][A]$ and $[Fe_2(\eta\text{-}C_5H_5)_2(CNR)_2\{\mu\text{-}CN(R)H\}_2][A]_2$ salts

			Analyses[a] (%)			
Complex	R	$[A]^-$	C	H	N	X[b]
$[Fe_2(\eta\text{-}C_5H_5)_2(CNR)_3\{\mu\text{-}CN(R)H\}][A]$	Me	$[CCl_3CO_2]^-\cdot H_2O$	41.0 (40.8)	3.6 (4.2)	9.6 (9.5)	17.7 (18.1)
	Me	$[PhCO_2]^-\cdot H_2O$	53.1 (52.7)	5.3 (5.5)	9.7 (10.2)	—
	Me	$[MeCO_2]^-\cdot 5H_2O$	43.0 (43.2)	5.8 (6.5)	10.3 (10.1)	—
	Et	$[CCl_3CO_2]^-\cdot 2H_2O$	43.4 (43.5)	5.5 (5.3)	9.1 (8.5)	—
	Et	$[PhCO_2]^-$	60.2 (59.6)	6.0 (6.2)	9.6 (9.6)	—
$[Fe_2(\eta\text{-}C_5H_5)_2(CNR)_2\{\mu\text{-}CN(R)H\}_2][A]_2$	Me	$[PF_6]^-$	30.4 (30.9)	3.5 (3.5)	7.0 (8.0)	31.1 (32.5)
	Me	$[CCl_3CO_2]^-\cdot H_2O$	34.2 (34.3)	3.7 (3.6)	7.3 (7.3)	26.9 (27.7)
	Me	$[CH_2ClCO_2]^-\cdot 1.5H_2O$	40.6 (40.6)	5.4 (5.2)	8.8 (8.6)	6.6 (6.0)
	Et	$[PF_6]^-\cdot 0.5H_2O$	34.2 (34.2)	4.6 (4.4)	7.3 (7.3)	—
	Et	$[CCl_3CO_2]^-\cdot 0.5H_2O$	38.6 (38.7)	4.1 (4.2)	7.3 (6.9)	25.3 (26.4)
	Et	$[CHCl_2CO_2]^-\cdot 1.5H_2O$	40.6 (40.3)	4.2 (5.1)	7.2 (7.2)	20.7 (19.7)

[a] Calculated values in parentheses. [b] X = F or Cl.

Table 3. Infrared spectra of $[Fe_2(\eta\text{-}C_5H_5)_2(CNR)_2\{\mu\text{-}CN(R)R'\}]I$ and $[Fe_2(\eta\text{-}C_5H_5)_2L(CNR)\{\mu\text{-}CN(R)R'\}_2]I_2$ (L = CO or RNC) salts between 1 500 and 2 250 cm^{-1}

			Absorption bands[a] (cm^{-1})			
Complex	R	R′	$\nu[C{=}N(R)R']_\mu$	$\nu(CNR)_\mu$	$\nu(CO)_t$	$\nu(CNR)_t$
$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNMe)_3]$[b]				1 687s	1 921s	2 070s
$[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)_4]$				1 640 (10)	—	2 134 (10)
$[Fe_2(\eta\text{-}C_5H_5)_2(CNEt)_4]$				1 630 (10)	—	2 128 (10)
$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNMe)_2\{\mu\text{-}CN(Me)R'\}]I$	Me	Me	1 583 (6.7)	1 742 (5.4)	1 973 (10)	2 166 (9.8)
	Me	Et	1 574 (6.6)	1 754 (4.9)	1 955 (10)	2 164 (9.5)
$[Fe_2(\eta\text{-}C_5H_5)_2(CNR)_3\{\mu\text{-}CN(R)R'\}]I$	Me	Me	1 578 (2.6)	1 708 (2.8)	—	2 180 (10)
	Me	Me[b]	1 585m	1 703m,br	—	2 165s
	Me	Et	1 566 (2.7)	1 724 (3.4)	—	2 176 (10)
	Me	Pr^n	1 568 (1.7)	1 712 (2.7)	—	2 175 (10)
	Et	Me	1 560 (2.1)	1 723 (3.3)	—	2 162 (10)
	Et	Et	1 562 (3.5)	1 724 (3.3)	—	2 162 (10)
$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNMe)\{\mu\text{-}CN(Me)R'\}_2]I_2$	Me	Me[b]	1 608s	—	2 024s	2 202s
$[Fe_2(\eta\text{-}C_5H_5)_2(CNR)_2\{\mu\text{-}CN(R)R'\}_2]I_2$	Me	Me[b]	1 595s	—	—	2 198s
	Me	Et[b]	1 581s	—	—	2 200s
	Me	Pr^n[b]	1 575s	—	—	2 197s
	Et	Me[b]	1 576s	—	—	2 177s
	Et	Et[b]	1 561s	—	—	2 178s
	Me	H[b,c]	1 598s	—	—	2 206s

[a] Relative peak heights in parentheses in $CHCl_3$ solution unless otherwise stated. [b] In CsBr disc. [c] $[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)_2\{\mu\text{-}CN(Me)H\}\{\mu\text{-}CN(Me)Me\}]I[PF_6]\cdot H_2O$, $\nu(N\text{-}H)$ 3 310 cm^{-1}.

Two forms of $[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)_4]$ may be separated.[6] The first, black crystals, appears to be the pure *cis* isomer* whilst the second, a brown powder, is a mixture of *cis* and *trans* isomers which do not interconvert at room temperature. The complex $[Fe_2(\eta\text{-}C_5H_5)_2(CNEt)_4]$ is a brown oil that is either a single isomer or a rapidly interconverting mixture of *cis* and *trans* isomers at room temperature. The complex $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNMe)_3]$ exists in solution as a mixture of *cis* and *trans* isomers with bridging or terminal CO ligands.[7]

Reactions with Alkyl Iodides.—All three complexes react with alkyl iodides to give two series of salts in which one or both μ-CNR ligands are converted into $\mu\text{-}CN(R)R'^+$ with the formation of new N–C bonds. They are the monoalkylated $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNMe)_2\{CN(Me)R'\}]I$ (**1**; R′ = Me) and $[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)_3\{CN(Me)R'\}]I$ (**2**), and the dialkylated $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNMe)\{CN(Me)R'\}_2]I_2$ (**3**) and $[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)_2\{CN(Me)R'\}_2]I_2$ (**4**). Studies on related alkylation reactions of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_{4-n}(CNR)_n]$ have shown that the basicity of the N atom of the bridging isocyanide ligands increases as *n* increases from 1 to 2.[3] It is consistent with this that both bridging isocyanide ligands may be alkylated by MeI when *n* = 3 or 4 but not when *n* = 2.[3,†] Furthermore, the times taken for the reactions to go to completion decrease along the series *n* = 2 > 3 > 4 for monoalkylation and *n* = 3 > 4 for dialkylation. Also EtI will form a dialkylated product when *n* = 4 but not when *n* = 3. The conversion of the substrates into complexes (**1**) and (**2**) results in an increase in the frequency of the ν(CN) vibration of the remaining μ-CNR ligand. This indicates a decrease in the back bonding to that ligand and a decrease in the basicity of its N atom. Consequently it is not

---

* The evidence, though strong, is circumstantial and not unambiguous.[7]

† This may not be as definitive as it seems. The first products of these reactions are the monoalkylated species $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_{4-n}(CNR)_{n-1}\{CN(R)Me\}]^+$. These do not undergo bridge–terminal ligand exchange and contain μ-CNR ligands when *n* = 3 or 4, but not 2.

Table 4. Infrared spectra of $[Fe_2(\eta\text{-}C_5H_5)_2(CNR)_3\{\mu\text{-}CN(R)H\}][A]$ and $[Fe_2(\eta\text{-}C_5H_5)_2(CNR)_2\{\mu\text{-}CN(R)H\}_2][A]_2$ salts between 1 500 and 2 250 cm^{-1}

			Absorption bands[a] (cm^{-1})				
Complex	R	$[A]^-$	$\nu[C{=}N(R)H]_\mu$	$\nu(CNR)_\mu$	$\nu(CNR)$	$\nu(NH)$	$\nu(CO_2)$ and others
$[Fe_2(\eta\text{-}C_5H_5)_2(CNR)_3\{\mu\text{-}CN(R)H\}][A]$	Me	$[PF_6]^-$	1 568m	1 729m	2 176vs	3 335w	835s,br[b]
	Me	$[CCl_3CO_2]^-$	1 589m	1 719m	2 166vs	—	1 683s
	Me[c]	$[CCl_3CO_2]^-$	1 582 (2.9)	1 703(sh) (3.2)	2 159 (10)	—	1 671 (4.7)
	Me	$[PhCO_2]^-$	1 570(sh)	1 696m	2 172vs	—	1 550vs, 1 595s[d]
	Me[c]	$[PhCO_2]^-$	1 550br (5.3)	1 705 (4.2)	2 168 (10)	—	1 550br (5.3),[e] 1 595 (6.2)[d]
	Me	$[MeCO_2]^-$	1 570s,br	1 700s	2 169vs	—	1 570br[e]
	Et[f]	$[CCl_3CO_2]^-$	1 568m	1 730m(sh)	2 141vs	—	1 681vs
	Et[f]	$[PhCO_2]^-$	1 550s,br	1 700s	2 164vs	—	1 550s,br,[e] 1 598m[d]
$[Fe_2(\eta\text{-}C_5H_5)_2(CNR)_2\{\mu\text{-}CN(R)H\}_2][A]_2$	Me	$[PF_6]^-$	1 593m	—	2 200(sh), 2 213vs	3 318w	830vs,br[b]
	Me	$[CCl_3CO_2]^-$	1 583m	—	2 164vs	—	1 670vs
	Me[c]	$[CCl_3CO_2]^-$	1 600 (3.8)	—	2 183 (10)	—	1 673 (5.8)
	Me	$[CHCl_2CO_2]^-$	1 592s	—	2 201vs	—	1 640s,br
	Me[c]	$[CHCl_2CO_2]^-$	1 594 (4.0)	—	2 195 (10)	—	1 635 (4.2)
	Me	$[CH_2ClCO_2]^-$	1 598s,br	—	2 192vs	—	1 598s,br[e]
	Me[c,g]	$[CH_2ClCO_2]^-$	1 598br (8.2)	1 694 (3.5)	2 167 (10)	—	1 598br (8.2)[e]
	Et	$[PF_6]^-$	1 580s	—	2 195vs	3 300w	840vs,br[b]
	Et	$[CCl_3CO_2]^-$	1 586m	—	2 176vs	—	1 683vs
	Et	$[CCl_3CO_2]^-$	1 586 (4.3)	—	2 172 (10)	—	1 664 (7.1)

[a] Relative peak heights in parentheses. Spectra obtained using KBr discs unless stated otherwise; m = medium, s = strong, and br = broad. [b] ν(PF). [c] In $CHCl_3$ solution. [d] ν(C–C) of phenyl ring. [e] $\nu(CO_2)$ of $[A]^-$ and ν[C=N(R)H] coincident. [f] Neat oil. [g] Dissociates in solution to $[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)_3\{\mu\text{-}CN(Me)H\}][CH_2ClCO_2]$, see text.

Table 5. Proton n.m.r. spectra of some complexes (**1**)—(**6**) described in the text[a]

Complex	$\eta\text{-}C_5H_5$	R in μ-CN(R)R′	μ-CNR	t-CNR	NH
$[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)_4]$	4.67 (10)	—	3.77 (6)	2.91 (6)	—
$[Fe_2(\eta\text{-}C_5H_5)_2(CNEt)_4]$	4.63 (10)	—	CH_2 4.06 (4)[b] CH_3 1.46 (6)[b]	CH_2 3.19 (4)[c] CH_3 1.10 (6)[c]	— —
$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNMe)(\mu\text{-}CNMe)(\mu\text{-}CNMe_2)]I$	5.15 (5), 5.04 (5)	4.31 (3), 4.22 (3)	3.71 (3)	3.12 (3)	—
$[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)_2(\mu\text{-}CNMe)(\mu\text{-}CNMe_2)]I$	4.76 (10)	4.32 (6)	3.70 (3)	3.28 (3)	—
$[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)_2\{\mu\text{-}CN(Me)H\}_2][CCl_3CO_2]_2$	5.14 (10)	3.99 (3)	—	3.28 (6)	3.52 (2)
$[Fe_2(\eta\text{-}C_5H_5)_2(CNEt)_2\{\mu\text{-}CN(Et)H\}_2][CCl_3CO_2]_2$	5.19 (10)	CH_2 4.35 (4)[d] CH_3 1.62 (6)[d]	—	CH_2 3.49 (4)[e] CH_3 1.20 (6)[e]	3.77 (2)

[a] In $CDCl_3$ solution. Resonances in δ downfield from $SiMe_4$ as an internal standard. Integrations in parentheses. [b] J = 7.0 Hz. [c] J = 7.1 Hz. [d] J = 7.1 Hz. [e] J = 7.3 Hz.

surprising that monoalkylation is more rapid than dialkylation. Finally the order of reactivity MeI > EtI > Pr^{n}I is as expected.

Most of the monoalkylated derivatives (**1**) and (**2**) are purple-brown oils which would not crystallize and could not be purified. However the two listed in Table 1 were well characterized solids and so the others included in Table 3 could be identified unambiguously by spectroscopic data. The dialkylated salts (**3**) and (**4**) are green solids. All of these complexes are quite air-stable and soluble to various extents in polar organic solvents. The conductivities of their solutions are consistent with (**1**) and (**2**) being 1:1 electrolytes and (**3**) and (**4**) 1:2 electrolytes (*cf.* Λ = 85 ohm^{-1} cm^2 mol^{-1} for $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNMe)(CNMe_2)]I$ as a 10^{-3} mol dm^{-3} solution in nitromethane, and Λ = 214 ohm^{-1} cm^2 mol^{-1} for $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2\{CN(Me)H\}_2][PF_6]_2$ as a 1.6 × 10^{-3} mol dm^{-3} solution in nitromethane).

It is proposed that the cations of (**1**)—(**4**) have the molecular structures shown in the Figure. They are derived from that found for *cis*-$[Fe_2(\eta\text{-}C_5H_4Me)_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CNMe_2)]I$.[3] In complexes (**1**) and (**2**) the two Fe atoms are bridged by an isocyanide and a positively charged iminium ligand in an approximately planar assembly, whilst in (**3**) and (**4**) there are two bridging iminium ligands. There are also two terminal ligands, CO and CNMe in (**1**) or (**3**), or two CNR in (**2**) and (**4**), as well as the two $\eta\text{-}C_5H_5$ ligands in all complexes. Although both *cis* and *trans* isomers of (**1**)—(**4**) are possible, the available data do not allow a definitive choice to be made (see below).

There are four strong absorption bands between *ca.* 1 550 and 2 200 cm^{-1} in the i.r. spectra of complexes (**1**), three in the spectra of (**2**) and (**3**), and two in the spectra of (**4**) (Table 3). Those at *ca.* 1 550—1 600 cm^{-1} are assigned to ν(C=N) vibrations of the $\mu\text{-}CN(R)R'^+$ ligand, those at 1 700—1 755 cm^{-1} to $\nu(C{\equiv}NR)_\mu$, $\nu(CO)_t$ are found at *ca.* 1 950—2 030 cm^{-1}, and $\nu(C{\equiv}NR)_t$ at *ca.* 2 160—2 210 cm^{-1}, with the subscript t indicating a terminal ligand. Monoalkylation of the neutral compounds to (**1**) or (**2**) causes a marked increase in the

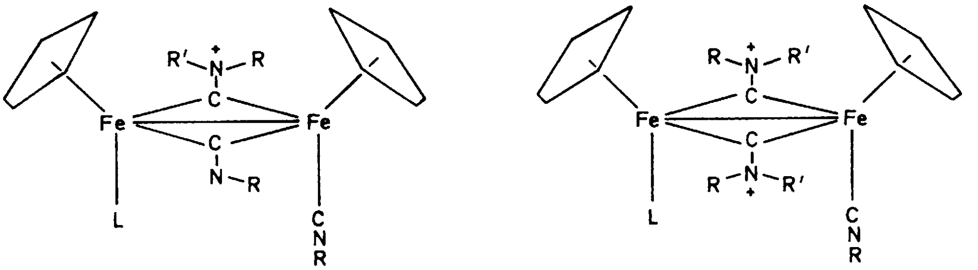

Figure. The structures of $[Fe_2(\eta\text{-}C_5H_5)_2L(CNR)(\mu\text{-}CNR)\{\mu\text{-}CN(R)R'\}]^+$ and $[Fe_2(\eta\text{-}C_5H_5)_2L(CNR)\{\mu\text{-}CN(R)R'\}_2]^{2+}$ cations (L = CO or CNR; R′ = H or alkyl). Only the *cis* isomers are shown

frequencies of the ν(CN) or ν(CO) vibrations of the unattacked ligands (Table 3). This is consistent with the very strong electron-withdrawing ability of the $\mu\text{-}CN(R)R'^+$ ligands which is much greater than those of μ-CNR. Dialkylation of complexes (**1**) and (**2**) to (**3**) and (**4**) results in further large increases in the frequencies of the terminal C≡O and C≡NR stretching vibrations whilst $\nu[C{=}N(R)R']_\mu$ also increase slightly possibly due to the competition of the two positively charged μ-iminium ligands for the available electron density. The variation of $\nu[C{=}N(R)R']_\mu$ with R and R′ is similar to that observed for ν(C=N) in complexes containing dithiocarbamate $S_2C{=}N(R)R'$ ligands where it was attributed to the consequences of coupling between ν(C=N) and ν(N–R) or ν(N–R′) vibrations.[9] The variation is most marked in the difference between the derivatives where R and R′ are Me and those where they are Et or higher homologues.

The low solubility of complexes (**3**) and (**4**) prevented us from obtaining their ^1H n.m.r. spectra. However those of (**1**) and (**2**), $[Fe_2(\eta\text{-}C_5H_5)_2L(CNMe)(\mu\text{-}CNMe)(\mu\text{-}CNMe_2)]I$ (L = CO or CNMe), which are summarized and assigned in Table 5, are consistent with the proposed structures. The cations are not fluxional and exist in solution as single isomers, but on the basis of the available data it is not possible to say whether they are *cis* or *trans*. The spectrum of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNMe)(\mu\text{-}CNMe)(\mu\text{-}CNMe_2)]I$ shows two equal-intensity cyclopentadienyl resonances at δ *ca.* 5 p.p.m., one attributable to $(\eta\text{-}C_5H_5)Fe(CO)$ and the other to $(\eta\text{-}C_5H_5)Fe(CNMe)$. This end-to-end difference causes the two methyl groups of the $\mu\text{-}CNMe_2$ ligand to give rise to separate signals, thus indicating that there is no rotation about the C=N bond. However, the methyl resonance attributable to the μ-CNMe ligand is a singlet which indicates that inversion at this N atom is fast.

Reaction with Acids.—The strong acid $HPF_6{\cdot}Et_2O$ reacts with $[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)_4]$ to give green $[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)_2\{CN(Me)H\}_2][PF_6]_2$ (**6**), but the monoprotonated species, brown $[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)_3\{CN(Me)H\}][PF_6]$ (**5**) has only been prepared by mixing equimolar amounts of (**6**) and $[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)_4]$. This reaction illustrates one important difference between alkylated and protonated derivatives; (**1**)—(**4**) are relatively inert to loss of R^+ but the H^+ in (**5**) and (**6**) are labile. These $[PF_6]^-$ salts are relatively air-stable.

The reactions of $[Fe_2(\eta\text{-}C_5H_5)_2(CNR)_4]$ (R = Me or Et) with acids HA such as $PhCO_2H$ or $MeCO_2H$ give only the monoprotonated species $[Fe_2(\eta\text{-}C_5H_5)_2(CNR)_3\{CN(R)H\}][A]$ (**3**) but CH_2ClCO_2H, $CHCl_2CO_2H$, and CCl_3CO_2H give both (**5**) and the diprotonated $[Fe_2(\eta\text{-}C_5H_5)_2(CNR)_2\{CN(R)H\}_2][A]_2$ (**6**) depending on the reactant molar ratio. The i.r. spectrum of $[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)_2\{\mu\text{-}CN(Me)H\}_2][CH_2ClCO_2]_2$ in the solid state is very similar to those of other salts (**6**), but in solution it is consistent with (**5**), being by far the most important species present (Table 4), which suggests that proton loss has occurred. The salts (**5**) where $[A]^-$ is a $[YCO_2]^-$ anion are brown powders when R = Me and oils when R = Et. They are all air-sensitive and thermally unstable. On standing they decompose to products which do not contain bridging ligands. Salts (**6**) are green solids or oils. Although they are somewhat air-sensitive, they are more easily handled than (**5**).

On the basis of the spectroscopic data discussed below it is proposed that the salts (**5**) and (**6**) have structures similar to those of (**2**) and (**4**), but with R′ = H (Figure) so that they respectively have one and two $\mu\text{-}CN(R)H^+$ ligands containing N–H bonds. These structures are based on that found for $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}CN(Me)H\}][BF_4]$.[2]

The i.r. spectra of salts (**5**) and (**6**) are consistent with the proposed structures. They are very similar to those of (**2**) and (**4**) in that they show absorption bands due to the C–N stretching vibrations of μ-[C=N(R)H], μ-CNR in (**5**) only, and terminal CNR ligands at *ca.* 1 570—1 600, 1 690—1 730, and 2 150—2 205 cm^{-1} respectively. Their frequencies and variation are much the same as for complexes (**2**) and (**4**) and much the same comments apply.

However, the i.r. spectra also contain absorption bands due to the anions $[A]^-$ and those due to ν(N–H) would also be expected. These last were only identified as sharp absorption bands when $[A]^- = [PF_6]^-$ at 3 335 cm^{-1} for (**5**) and 3 318 cm^{-1} for (**6**). When $[A]^-$ is the anion of a carboxylic acid, the ν(N–H) bonds are conspicuously absent from this region of the spectra and it is tentatively suggested that they are responsible for weak, broad bands at *ca.* 2 800 cm^{-1}. This may be because in such instances $[A]^-$ is a relatively strong base and there are $N{-}H\cdots O_2CY$ interactions. The absence of absorption bands at *ca.* 1 640 and 2 130 cm^{-1} shows that free $[Fe_2(\eta\text{-}C_5H_5)_2(CNR)_4]$ are not present in the solutions to any significant extent and that there are no equilibria between free and hydrogen-bonded molecules similar to those observed for $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_{4-n}(CNR)_n]$ (*n* = 0, 1, or 2) on dissolution in alcohols or phenols.[10] Also the close similarity between the i.r. spectra of (**2**)/(**4**) and (**5**)/(**6**) suggests that the N–H bonds are strong covalent bonds and not relatively weak hydrogen bonds.

Of the two anticipated absorption bands due to the ν(CO) vibrations of the carboxylate anions $[YCO_2]^-$,[11] only that attributable to the antisymmetric mode could be identified with confidence. Unfortunately, in salts with $[PhCO_2]^-$, $[MeCO_2]^-$, and $[CHCl_2CO_2]^-$ counter ions it is coincident with the absorption band due to ν(C=N) of the μ-iminium ligand, giving a broad, strong peak which could be identified by comparison of the band envelope with that found for the $\nu(C{=}NR_2)_\mu$ mode in the spectra of the $[PF_6]^-$ salts. In general these bands are sharper in the spectra of solid samples (KBr discs) than in the spectra of chloroform solutions where they are often very broad. Their frequencies indicate that essentially free carboxylate ions are present in all cases (*cf.* 1 680 cm^{-1} for $[C_5H_5NH][CCl_3CO_2]$[12] and 1 550 cm^{-1} for $[NH_4][MeCO_2]$[11]) which does not rule out the relatively weak $NH\cdots O_2CY$ hydrogen bonding discussed above.

The ^1H n.m.r. spectra of the salts (**5**) and (**6**) proved very difficult to obtain. Only those of $[Fe_2(\eta\text{-}C_5H_5)_2(CNR)_2\{\mu\text{-}CN(R)H\}_2][CCl_3CO_2]_2$ were reproducible. They are summarized and assigned in Table 5. They are consistent with the proposed structures. Apart from resonances due to cyclopentadienyl, terminal RNC, and μ-CN(R)H alkyl protons which are readily identified, the spectra each contain a small broad resonance at δ 3.5—3.7 which is attributed tentatively to the N–H protons.

Reactions of Brown $[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)_4]$.—The brown form of $[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)_4]$ is a mixture of *cis* and *trans* isomers, and its reactions with both CCl_3CO_2H and MeI follow two separate paths. It is reasonable to assume that the *cis* isomer reacts in the mixture in the same way as it does when it is pure as the black crystals and that it is responsible for $[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)_2(\mu\text{-}CNMe)\{\mu\text{-}CN(Me)R'\}][A]$ ($R'A$ = MeI or HO_2CCl_3) formed in the reactions. The *trans* isomer then gives the second products which are $[Fe_2(\eta\text{-}C_5H_5)(CNMe)_2X]$ derivatives identified by spectroscopic techniques.

These results are consistent with others obtained in our laboratories. The $[Fe_2\{\eta^5{:}\eta^5\text{-}C_5H_4CH(NMe_2)CH(NMe_2)C_5H_4\}L_2(\mu\text{-}L)_2]$ complexes where L is CO or an organic isocyanide are constrained to a *cis* configuration. They are more resistant to attack by electrophiles or form more stable adducts resembling (**1**)—(**6**) than the $[Fe_2(\eta\text{-}C_5H_5)_2L_2(\mu\text{-}L)_2]$ derivatives which are either *trans* isomers or a rapidly interconverting mixture of *cis* and *trans* isomers.[13] In the present instance it is extremely unlikely that *trans*-$[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)_4]$ does not form *trans*-$[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)_2(\mu\text{-}CNMe)\{\mu\text{-}CN(Me)R'\}]^+$ adducts. Therefore it must be assumed that such adducts are very unstable towards subsequent reactions which result in breakdown of the dimer unit.

Some Reactions of Complexes (**1**)—(**6**).—The basicity of the μ-CNR ligand in complexes (**3**) is illustrated by their reactions with R′I to give (**4**), and that of $[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)_2(\mu\text{-}CNMe)(\mu\text{-}CNMe_2)]I$ with $HPF_6{\cdot}Et_2O$ to give $[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)_2\{\mu\text{-}CN(Me)H\}(\mu\text{-}CNMe_2)]I[PF_6]$. The i.r. spectrum of this compound is much as might be expected with absorption bands due to the C–N stretching vibrations of the terminal isocyanide and the two types of bridging C=N(R)R′ ligands. Attempts to make the same cation by reaction of $[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)_2(\mu\text{-}CNMe)\{\mu\text{-}CN(Me)H\}][PF_6]$ with MeI failed. Instead a $[Fe(\eta\text{-}C_5H_5)(CNMe)_3]^+$ salt was obtained. As will be discussed below, monoprotonated species such as (**5**) are very susceptible to breakdown to mononuclear species, and in this context MeI is a suitable reagent.

Although $[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)_2\{\mu\text{-}CN(Me)H\}_2][PF_6]_2$ is stable when dissolved in water, $[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)_2(\mu\text{-}CNMe)\{\mu\text{-}CN(Me)H\}][PF_6]$ decomposes to $[Fe(\eta\text{-}C_5H_5)(CNMe)_3][PF_6]$ which is readily identifiable. Other studies in our laboratories have shown that various $[Fe_2(\eta\text{-}C_5H_5)_2L_3\{\mu\text{-}CN(Me)H\}][A]$ salts are susceptible to attack by electrophiles whereas $[Fe_2(\eta\text{-}C_5H_5)_2L_2\{\mu\text{-}CN(Me)H\}_2][A]_2$ are not unless they are deprotonated first.[13] Similar behaviour is shown by the effect of amines on complexes (**3**) and (**4**). Dealkylation does not occur and $[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)_2(\mu\text{-}CNMe_2)_2]I_2$ may be recovered unchanged, but $[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)(\mu\text{-}CNMe)(\mu\text{-}CNMe_2)]I$ is converted into $[Fe(\eta\text{-}C_5H_5)(CNMe)_3]I$.

Comments on the Structures of Complexes (**3**)—(**6**).—The black form of $[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)_4]$ which has been used throughout this work is thought to be the *cis* isomer. It does not interconvert with the *trans* isomer and *cis–trans* mixtures of differing isomer ratios are known to be stable in solution. Thus it seems reasonable to assume that the complexes (**3**)—(**6**) derived from it are also *cis* isomers as illustrated in the Figure. As the i.r. and ^1H n.m.r. spectra of these complexes are only superficially dependent on R, it seems reasonable to assume that the adducts where CNMe has been replaced by CNEt are also *cis* isomers.

Conclusions

The complex *cis*-$[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)_4]$ reacts with electrophiles such as alkyl iodides and acids, R′A, to give two series of adducts, the moderately stable $[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)_2(\mu\text{-}CNMe)\{\mu\text{-}CN(Me)R'\}][A]$ and the very stable $[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)_2\{\mu\text{-}CN(Me)R'\}_2][A]_2$. These are probably *cis* isomers also. On the other hand, the similar adducts of *trans*-$[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)_4]$ are not stable and decompose rapidly to species containing only one iron atom.

References

1 P. M. Treichel, J. J. Benedict, R. W. Hess, and J. P. Stenson, *Chem. Commun.*, 1970, 1627.
2 S. Willis, A. R. Manning, and F. S. Stephens, *J. Chem. Soc., Dalton Trans.*, 1979, 23.
3 S. Willis, A. R. Manning, and F. S. Stephens, *J. Chem. Soc., Dalton Trans.*, 1980, 186.
4 S. Willis and A. R. Manning, *J. Chem. Soc., Dalton Trans.*, 1981, 322.
5 M. Ennis, R. Kumar, A. R. Manning, J. A. S. Howell, P. Mathur, A. J. Rowan, and F. S. Stephens, *J. Chem. Soc., Dalton Trans.*, 1981, 1251.
6 G. McNally, P. T. Murray, and A. R. Manning, *J. Organomet. Chem.*, 1983, **243**, C87.
7 A. R. Manning and P. T. Murray, unpublished work.
8 R. D. Adams and F. A. Cotton, *Inorg. Chem.*, 1974, **13**, 249.
9 D. A. Brown, W. K. Glass, and M. A. Burke, *Spectrochim. Acta, Part A*, 1976, **32**, 137.
10 S. Willis and A. R. Manning, *J. Chem. Res.*, 1978, (*S*)390, (*M*)4573.
11 R. M. S. Silverstein, G. C. Bassler, and T. C. Morrill, 'Spectrometric Identification of Organic Compounds,' 4th edn., Wiley, New York, 1981.
12 B. A. Dawa and J. A. Gowland, *Can. J. Chem.*, 1978, **56**, 2567.
13 A. R. Manning, unpublished work.

Received 5th November 1985; *Paper* 5/1942