

Preparation, spectra and structure of $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{L})(\text{CN})(\mu\text{-CO})\{\mu\text{-CN}(\text{R}')\text{R}\}]$, $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})(\text{CN})\{\mu\text{-CNMe}_2\}_2]^+$ and $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CN})_2\{\mu\text{-CNMe}_2\}_2]$ zwitterions ($\text{L} = \text{CO}$ or organoisocyanide) and their reactions with alkyl and protic electrophiles

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Abstract

The thermal, photolytic or chemical activation of $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-CNMe}_2)]\text{X}$ and *cis*- $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})(\text{CNMe})(\mu\text{-CO})(\mu\text{-CNMe}_2)]\text{X}$ and related salts ($\text{X}^- = \text{I}^-$ or $[\text{SO}_3\text{CF}_3]^-$) allows replacement of one *t*-CO ligand by $\text{L} = \text{CN}^-$, CNMe or $\text{CNC}_6\text{H}_3\text{Et}_{2,6}$ to give respectively $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})(\text{L})(\mu\text{-CO})(\mu\text{-CNMe}_2)]^+$ and $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{L})(\text{CNMe})(\mu\text{-CO})(\mu\text{-CNMe}_2)]^+$ derivatives. Similar reactions of *cis*- $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_2(\mu\text{-CNMe}_2)]\text{[SO}_3\text{CF}_3\text{]}_2$ allows the replacement of one or both *t*-CO groups in turn by $\text{L} = \text{CN}^-$, CNMe or $\text{CNC}_6\text{H}_{11}$ to give respectively $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})(\text{L})(\mu\text{-CNMe}_2)_2]^{2+}$ and $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{L})_2(\mu\text{-CNMe}_2)_2]^{2+}$ derivatives. Some of these substitution reactions take place with isomerism of the $\text{Fe}_2(\text{L})_2(\mu\text{-L})_2$ framework *cis* $\leftrightarrow$ *trans*, but the *cis* isomers always predominate no matter what the precursor. However, alkylation of the *t*-CN ligand by ROSO_2CF_3 , but not RI, proceeds without any such isomerism, which allows correlation of spectra with structure for a number of different types of compound. Protonation of the *t*-CN ligands of $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})(\text{CN})(\mu\text{-CNMe}_2)_2]^+$ and $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CN})_2(\mu\text{-CNMe}_2)_2]$ to give complexes containing *t*-CNH ligands may be effected by HOSO_2CF_3 , but this straight-forward approach does not work for $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})(\text{CNH})(\mu\text{-CO})(\mu\text{-CNMe}_2)]^+$ which is best prepared by the reaction of $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})(\text{CN})(\mu\text{-CO})(\mu\text{-CNMe}_2)]$ with $\text{EtOSO}_2\text{CF}_3$ in wet chloroform. The spectra of the various compounds are reported and discussed. There is no exchange between *cis* and *trans* isomers or bridging and terminal ligands, or rotation about the $\text{C}=\text{N}$ bonds of the $\mu\text{-C}=\text{NR}_2$ ligands in any of the complexes reported below 80°C .

Keywords: Alkylation; Iron; Substitution; Protonation; Isocyanide; Cyanide ion

1. Introduction

The $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_{4-n}(\text{CNMe})_n]$ derivatives where $n = 1\text{--}3$ [1] react with protic acids, alkyl halides and alkyl trifluoromethane sulphonates, RX , to give salts containing the $\mu\text{-CN}(\text{R})\text{Me}^+$ ligand [1c,1d,2,3]. Related $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_{4-n}(\text{CSR})_n]\text{X}_n$ salts ($n = 1$ or 2) which contain a $\mu\text{-CSR}^+$ group react with nucleophiles Nu either by CO replacement [4] or by attack at the $\mu\text{-C}$ atom to give complexes containing the $\mu\text{-C}(\text{Nu})\text{SR}$ carbene ligand [5]. More recently it was re-

ported [6] that various nucleophiles attack $[\text{M}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_2(\mu\text{-CO})\{\mu\text{-CN}(\text{CH}_2\text{Ph})\text{Me}\}]^+$ cations ($\text{M} = \text{Fe}$ or Ru) at $\mu\text{-CN}(\text{CH}_2\text{Ph})\text{Me}$, *t*-CO or $\eta\text{-C}_5\text{H}_5$ sites. Therefore, we have investigated the reactions of our $\mu\text{-CN}(\text{R}')\text{R}^+$ -containing salts with nucleophiles, and report here on those with organoisocyanides and KCN when R and R' are alkyl groups, normally Me, and on some of the subsequent reaction of the species thus obtained. In a reaction related to those described here, it has been reported that CN^- displaces Me_3P from $[(\eta\text{-C}_5\text{H}_5)\text{Co}(\text{PMe}_3)(\mu\text{-CO})(\mu\text{-CSMe})\text{Mn}(\text{CO})(\eta\text{-C}_5\text{H}_4\text{-Me})]\text{PF}_6$ to give $[(\eta\text{-C}_5\text{H}_5)\text{Co}(\text{CN})(\mu\text{-CO})(\mu\text{-CSMe})\text{Mn}(\text{CO})(\eta\text{-C}_5\text{H}_4\text{Me})]$ which may be alkylated to $[(\eta\text{-C}_5\text{H}_5)\text{Co}(\text{CNMe})(\mu\text{-CO})(\mu\text{-CSMe})\text{Mn}(\text{CO})(\eta\text{-C}_5\text{H}_4\text{-Me})]\text{PF}_6$ [7].

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2. Experimental details

Previously published methods were used to prepare CNR [8], $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_3(\text{CNR})]$, $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_2(\text{CNR})_2]$, and $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})(\text{CNMe})_3]$ [1], $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-CN(R')R})]\text{X}$ [2,3], $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})(\text{CNR})(\mu\text{-CO})(\mu\text{-CN(R')R})]\text{X}$ [2,3], and $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_2(\mu\text{-CNMe})_2][\text{SO}_3\text{CF}_3]_2$ [3]. Other chemicals were purchased.

Reactions were carried out under an atmosphere of nitrogen at room temperature in dried and deoxygenated solvents unless it is stated otherwise. They were monitored by infrared spectroscopy. Chromatography was carried out using Merck 1097 alumina, activity II/III.

2.1. The reaction of $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-CN(R')R})]\text{X}$ with KCN on heating

A solution of $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-CNMe})_2]\text{I}$ (1.2 g, 2 mmol) and KCN (0.143 g, 2.2 mmol) in ethanol (50 cm³) was refluxed for 2 h. Its colour changed from red to green. The mixture was filtered and the solvent removed at reduced pressure from the filtrate. The residue was shaken with a mixture of water (50 cm³) and chloroform (100 cm³). The chloroform layer was separated, dried over magnesium sulphate, and the solvent removed at reduced pressure. The residue was recrystallized from dichloromethane-hexane mixtures to give $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})(\text{CN})(\mu\text{-CO})(\mu\text{-CNMe})_2]$. The *cis* and *trans* isomers were sep-

Table 1
Analyses of compounds described in the text

R(R')/R'' ^a	Analyses ^b			<i>cis</i> : <i>trans</i> ratio ^c
	%C	%H	%N	
$[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})(\text{CN})(\mu\text{-CO})(\mu\text{-CN(R')R})]$				
Me(Me)	49.9 (50.5)	4.3 (4.2)	7.2 (7.4)	75:25
Me(Me) ^d	49.1 (50.5)	4.2 (4.2)	7.0 (7.3)	75:25
Me(Me) ^e	50.3 (50.4)	4.3 (4.2)	7.3 (7.6)	75:25
Me(Et)	52.3 (51.8)	4.6 (4.6)	6.5 (7.1)	> 99: < 1
Me(Et) ^d + H ₂ O	49.8 (49.6)	4.5 (4.8)	6.7 (6.8)	86:14
Me(Et) ^e + H ₂ O	50.0 (49.6)	4.5 (4.8)	7.7 (7.0)	85:15
Et(Et)	52.1 (52.9)	4.8 (4.9)	6.7 (6.8)	> 99: < 1
$[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})(\text{CNR'')}(\mu\text{-CO})(\mu\text{-CN(R')R})][\text{SO}_3\text{CF}_3]$				
Me(Me)/H	38.5 (38.5)	3.5 (3.2)	5.0 (5.0)	
Me(Me)/Me	40.0 (39.7)	3.6 (3.5)	5.1 (5.1)	
Me(Me)/Me ^d	38.9 (39.7)	3.5 (3.5)	4.8 (5.1)	
Me(Me)/Me ^e	39.4 (39.6)	3.6 (3.5)	5.3 (5.3)	
Me(Me)/Et	40.8 (40.9)	3.8 (3.8)	5.0 (5.0)	
Me(Et)/Me	40.6 (40.9)	3.8 (3.8)	4.8 (5.0)	
Me(Et)/Me ^d	40.8 (40.9)	3.8 (3.8)	4.8 (5.0)	
Et(Et)/Me	41.6 (42.0)	4.0 (4.0)	4.7 (4.9)	
Me(Me)/Ar ^f	47.6 (47.8)	4.5 (4.6)	4.2 (4.5)	
$[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CNMe})(\text{CN})(\mu\text{-CO})(\mu\text{-CN(R')R})]$				
Me(Me) + 1/2H ₂ O	50.6 (50.8)	4.9 (5.0)	10.1 (10.5)	90:10
$[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CNMe})(\text{CNR'')}(\mu\text{-CO})(\mu\text{-CN(R')R})][\text{SO}_3\text{CF}_3]$				
Me(Me)/Me	40.5 (40.9)	4.0 (4.0)	7.2 (7.5)	
Me(Me)/Et	41.7 (42.0)	3.9 (4.2)	7.4 (7.4)	
Me(Me)/Ar ^g	49.6 (49.6)	5.3 (5.2)	6.0 (6.1)	
$[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CNMe})(\text{CO})(\mu\text{-CNMe})(\mu\text{-CN(R')R})][\text{SO}_3\text{CF}_3]$				
Me(Me)	40.6 (40.9)	4.0 (4.0)	7.3 (7.5)	
$[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})(\text{CN})(\mu\text{-CN(R')R})_2][\text{SO}_3\text{CF}_3]$				
Me(Me) + H ₂ O	40.0 (39.7)	4.1 (4.2)	7.3 (7.3)	100:0
$[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CN})_2(\mu\text{-CN(R')R})_2]$				
Me(Me) + H ₂ O	50.7 (50.9)	5.7 (5.7)	13.1 (13.2)	75:25
$[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})(\text{CNR'')})(\mu\text{-CN(R')R})_2][\text{SO}_3\text{CF}_3]_2$				
Me(Me)/H + 3H ₂ O	31.5 (31.5)	3.8 (3.8)	5.4 (5.5)	
Me(Me)/Me	36.0 (36.0)	3.5 (3.4)	5.6 (5.7)	
Me(Me)/C ₆ H ₁₁	37.8 (38.1)	4.2 (4.0)	5.4 (5.2)	100:0
$[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CNR'')}_2(\mu\text{-CN(R')R})_2][\text{SO}_3\text{CF}_3]_2$				
Me(Me)/H + 4H ₂ O	30.7 (30.9)	4.3 (4.1)	7.3 (7.2)	
Me(Me)/Me	36.0 (36.0)	3.8 (3.8)	7.7 (7.6)	100:0
Me(Me)/C ₆ H ₁₁	43.7 (44.2)	5.3 (5.1)	6.3 (6.4)	100:0

^a Ar = 2,6-Et₂C₆H₃. ^b Found (calculated). ^c From CO substitution reactions. ^d Contains ¹³CN or ¹³CNMe ligands. ^e Contains C¹⁵N or C¹⁵NMe ligands. ^f Counteranion is I⁻. ^g Counteranion is I⁻ · 2H₂O.

arated by further recrystallization, which gave the less soluble *cis* isomer as brown crystals (99% purity). Subsequent chromatography of the resultant mother liquors (alumina-dichloromethane) allowed isolation of the more soluble *trans* isomer as green crystals (90% purity).

Many $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})(\text{CN})(\mu\text{-CO})\{\mu\text{-CN(R')-R}\}]$ were prepared in 80–90% yield, but only those with

$\text{CN(R')R} = \text{CNMe}_2$, CN(Et)Me or CNEt_2 and their $^{13}\text{CN}/^{15}\text{N}$ counterparts are listed in Tables 1–4.

2.2. The reaction of $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-CNMe}_2)]\text{X}$ with ArNC ($\text{Ar} = 2,6\text{-Et}_2\text{C}_6\text{H}_3$) or MeNC

A solution of $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-CNMe}_2)]\text{I}$ (1.2 g, 2 mmol) and ArNC (0.7 cm³, 4

Table 2
Infrared spectra of compounds described in the text

R(R')/R''	Absorption bands ^a			
	$\nu(\text{C}=\text{N})$	$\nu(\mu\text{-CO})$	$\nu(\text{CO})$	$\nu(\text{C}=\text{N})$ ^b
$[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})(\text{CN})(\mu\text{-CO})\{\mu\text{-CN(R')R}\}]$				
<i>cis</i> -Me(Me)	1578 (2.8)	1806 (6.2)	1990 (10)	2090 (3.8)
<i>trans</i> -Me(Me)	1569 (5.1)	1807 (9.1)	1966 (10)	2089 (7.3)
Me(Me) ^c	1576 (3.8)	1807 (9.5)	1989 (10)	2044 (5.9)
<i>cis</i> -Me(Me) ^d	1579 (3.1)	1806 (6.4)	1990 (10)	2060 (4.3)
<i>trans</i> -Me(Me) ^d	1568 (3.1)	1806 (6.7)	1964 (10)	2056 (2.7)
Me(Et)	1554 (5.1)	1806 (7.8)	1990 (10)	2089 (5.8)
Me(Et) ^c	1554 (5.6)	1806 (8.7)	1989 (10)	2044 (6.8)
<i>cis</i> -Me(Et) ^d	1554 (3.4)	1806 (6.4)	1990 (10)	2060 (4.2)
<i>cis</i> -Et(Et)	1539 (4.1)	1805 (7.8)	1989 (10)	2090 (4.6)
$[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})(\text{CNR''})(\mu\text{-CO})\{\mu\text{-CN(R')R}\}][\text{SO}_3\text{CF}_3]$				
<i>cis</i> -Me(Me)/H	1590 (5.6)	1785 (9.9)	1974 (10)	2102 (6.9)
<i>cis</i> -Me(Me)/Me	1591 (5.2)	1809 (7.4)	1985 (10)	2174 (8.5)
<i>trans</i> -Me(Me)/Me	1585 (5.9)	1811 (7.1)	1983 (10)	2190 (6.4)
Me(Me)/Me ^c	1592 (4.5)	1809 (6.3)	1985 (10)	2135 (8.3)
<i>cis</i> -Me(Me)/Me ^d	1592 (4.1)	1809 (6.4)	1985 (10)	2136 (8.6)
<i>cis</i> -Me(Me)/Et ^{c,f}	1587 (3.8)	1817 (7.2)	1986 (10)	2067 (7.0)
Me(Et)/Me	1577 (4.6)	1809 (6.8)	1985 (10)	2173 (7.8)
Me(Et)/Me ^c	1576 (3.3)	1810 (5.9)	1984 (10)	2135 (6.3)
Et(Et)/Me ^c	1561 (4.6)	1819 (8.8)	1987 (9.4)	2181 (10)
Me(Me)/Ar ^{g,h}	1598 (3.2)	1816 (7.1)	1976 (10)	2112 (7.3)
$[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CNMe})(\text{CN})(\mu\text{-CO})\{\mu\text{-CN(R')R}\}_2]$				
Me(Me) ^c	1577 (2.8), 1547 (4.2)	1773 (10)		2079 (4.6), 2158 (9.0)
$[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CNMe})(\text{CNR''})(\mu\text{-CO})\{\mu\text{-CN(R')R}\}_2][\text{SO}_3\text{CF}_3]$				
Me(Me)/Me ^c	1577 (2.6)	1795 (5.4)		2177 (10)
Me(Me)/Et ^g	1578 (3.5)	1796 (6.5)		2170 (10)
Me(Me)/Ar ^{g,h}	1581 (6.1)	1781 (10)		2093 (9.5), 2163 (8.9)
$[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CNMe})(\text{CO})(\mu\text{-CNMe})\{\mu\text{-CN(R')R}\}_2][\text{SO}_3\text{CF}_3]$				
Me(Me) ^c	1584 (5.2)	1763 (5.9) ⁱ	1979 (10)	2176 (9.0)
$[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})(\text{CN})(\mu\text{-CN(R')R})_2][\text{SO}_3\text{CF}_3]$				
Me(Me) ^c	1593 (9.0)		2017 (10)	2104 (3.3)
$[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CN})_2\{\mu\text{-CN(R')R}\}_2]$				
Me(Me)	1576 (10)			2093 (7.6)
$[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})(\text{CNR'})\{\mu\text{-CN(R')R}\}_2][\text{SO}_3\text{CF}_3]_2$				
Me(Me)/H ^g	1599 (8.6)		2035 (10)	2139 (5.4)
Me(Me)/Me ^g	1607 (9.7)		2021 (10)	2207 (9.5)
Me(Me)/C ₆ H ₁₁ ^g	1599 (10)		2031 (7.4)	2172 (6.3)
$[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CNR''})_2\{\mu\text{-CN(R')R}\}_2][\text{SO}_3\text{CF}_3]_2$				
Me(Me)/H ^g	1588 (10)			2116 (9.6)
Me(Me)/Me ^g	1593 (7.8)			2205 (10)
Me(Me)/C ₆ H ₁₁ ^g	1593 (8.3)			2176 (10)
	1610 (sh)			2165 (sh)

^a Peak positions (cm⁻¹) with relative peak heights in parentheses. Run in chloroform solution unless it is stated otherwise. ^b Absorption bands caused by the $\nu(\text{CN})$ vibrations of the CN or CNMe ligands as required by the formulae. Those caused by the CN ligand are sharp. ^c Contains ^{13}CN or ^{15}N CNMe ligands. ^d Contains C¹⁵N or C¹⁵NMe ligands. ^e Spectra run in CH₂Cl₂ solution. ^f Anion is I⁻. ^g Spectra run in KBr disc. ^h Anion is I⁻. ⁱ $\nu(\mu\text{-CNMe})$.

Table 3

¹H NMR spectra of compounds described in the text ^a

R(R')R''	Resonances		
	C ₅ H ₅	R(R')	Others
[Fe ₂ (η-C ₅ H ₅) ₂ (CO)(CN)(μ-CO){μ-CN(R')R}]			
<i>cis</i> -Me(Me)	4.77, 4.81	Me 4.11 4.26	
<i>trans</i> -Me(Me)	4.71, 4.84	Me 4.22 4.34	
<i>cis</i> -Me(Me) ^b	4.78, 4.81	Me 4.11 4.26	
<i>trans</i> -Me(Me) ^b	4.71 4.85	Me 4.22 4.34	
<i>cis</i> -Me(Me) ^c	4.77, 4.81	Me 4.11, 4.26	
<i>trans</i> -Me(Me) ^c	4.71, 4.85	Me 4.22, 4.34	
<i>cis</i> -Me(Et) (α) ^d	4.77, 4.80	Me 4.20	
		Et 4.35–4.65 (m), 1.59 (t, <i>J</i> = 7.3)	
<i>cis</i> -Me(Et) (β) ^d	4.76, 4.81	Me 4.04	
		Et 4.35–4.65 (m), 1.68 (t, <i>J</i> = 7.3)	
<i>trans</i> -Me(Et) ^e	4.68, 4.69	Me 4.17 4.30	
	4.82, 4.83	Et 4.35–4.65 (m), 1.63 (t, <i>J</i> = 7.3), 1.70 (t, <i>J</i> = 7.2)	
<i>cis</i> -Me(Et) (α) ^b	4.77, 4.80	Me 4.19	
		Et 4.33–4.65 (m), 1.59 (t, <i>J</i> = 7.3)	
<i>cis</i> -Me(Et) (β) ^b	4.75, 4.81	Me 4.04	
		Et 4.33–4.65 (m), 1.68 (t, <i>J</i> = 7.3)	
<i>trans</i> -Me(Et) ^e	4.68, 4.69	Me 4.16 4.30	
	4.82, 4.83	Et 4.33–4.65 (m), 1.63 (t, <i>J</i> = 7.3), 1.70 (t, <i>J</i> = 7.2)	
<i>cis</i> -Me(Et) (α) ^{c,d}	4.77, 4.80	Me 4.20	
		Et 4.3–4.6 (m), 1.60 (t, <i>J</i> = 7.3)	
<i>cis</i> -Me(Et) (β) ^{c,d}	4.76, 4.81	Me 4.05	
		Et 4.3–4.6 (m), 1.69 (t, <i>J</i> = 7.2)	
[Fe ₂ (η-C ₅ H ₅) ₂ (CO)(CNR'')(μ-CO){μ-CN(R')R}][SO ₃ CF ₃]			
<i>cis</i> -Me(Me)/Me	5.03, 5.10	Me 4.23, 4.30	<i>t</i> -CNMe 3.10
<i>trans</i> -Me(Me)/Me	4.81, 4.99	Me 4.31, 4.40	<i>t</i> -CNMe 3.25
<i>cis</i> -Me(Me)/Me ^b	5.03, 5.10	Me 4.23, 4.29	<i>t</i> -CNMe 3.10 (d) ^f
<i>trans</i> -Me(Me)/Me ^b	4.81, 4.99	Me 4.31, 4.41	<i>t</i> -CNMe 3.25 (d) ^f
<i>cis</i> -Me(Et)/Me (α) ^d	5.05, 5.06	Me 4.20	<i>t</i> -CNMe 3.09
		Et 4.2–4.7 (m), 1.56 (t, <i>J</i> = 7.3)	
<i>cis</i> -Me(Et)/Me (β) ^d	5.01, 5.09	Me 4.13	<i>t</i> -CNMe 3.10
		Et 4.2–4.7 (m), 1.59 (t, <i>J</i> = 7.3)	
<i>trans</i> -Me(Et)/Me ^e	4.79, 4.81	Me 4.24, 4.35	<i>t</i> -CNMe 3.25, 3.26
	4.96, 4.97	Et 4.2–4.7 (m), 1.63 (t, <i>J</i> = 7.3), 1.71 (t, <i>J</i> = 7.1)	
<i>cis</i> -Me(Et)/Me (α) ^{c,d}	5.05, 5.06	Me 4.20	<i>t</i> -CNMe 3.09 (d) ^f
		Et 4.2–4.7 (m), 1.56 (t, <i>J</i> = 7.3)	
<i>cis</i> -Me(Et)/Me (β) ^{c,d}	5.01, 5.09	Me 4.13	<i>t</i> -CNMe 3.10 (d) ^f
		Et 4.2–4.7 (m), 1.59 (t, <i>J</i> = 7.3)	
<i>trans</i> -Me(Et)/Me ^{b,c}	4.76, 4.78	Me 4.24, 4.35	<i>t</i> -CNMe 3.25 (d) ^f
	4.96, 4.97	Et 4.2–4.7 (m), 1.63 (t, <i>J</i> = 7.3) 1.71 (t, <i>J</i> = 7.1)	3.26 (d) ^f
<i>cis</i> -Me(Me)/Ar ^{g,h}	5.26, 5.30	Me 4.35, 4.46	<i>t</i> -CNAr 2.51 (q, 4), 1.18 (t, 6, <i>J</i> = 7.5), 7.37 (m, 3)
[Fe ₂ (η-C ₅ H ₅) ₂ (CNMe)(CN)(μ-CO){μ-CN(R')R}]			
<i>cis</i> -Me(Me)	4.57, 4.61	Me 4.11, 4.19	<i>t</i> -CNMe 2.89
<i>trans</i> -Me(Me)	4.47, 4.56	Me 4.25, 4.32	<i>t</i> -CNMe 2.96
[Fe ₂ (η-C ₅ H ₅) ₂ (CNMe)(CNR'')(μ-CO){μ-CN(R')R}][SO ₃ CF ₃]			
<i>cis</i> -Me(Me)/Me	4.73	Me 4.22	<i>t</i> -CNMe 3.17
<i>cis</i> -Me(Me)/Et	4.79	Me 4.12	<i>t</i> -CNMe 3.02
			<i>t</i> -CNEt 3.28 (q, 2), 1.08 (t, 3, <i>J</i> = 7.2)
Me(Me)/Ar ^{h,i}	4.96, 4.87	Me 4.17, 4.25	<i>t</i> -CNMe 3.04
			<i>t</i> -CNAr 2.77 (q, 4), 1.27 (t, 6, <i>J</i> = 7.5) 7.21 (m, 3)
[Fe ₂ (η-C ₅ H ₅) ₂ (CO)(CNMe)(μ-CNMe){μ-CN(R')R}][SO ₃ CF ₃]			
Me(Me)	5.07, 4.92	Me 4.03, 4.08	<i>t</i> -CNMe 2.99
			μ-CNMe 3.67
[Fe ₂ (η-C ₅ H ₅) ₂ (CO)(CN){μ-CN(R')R ₂ }[SO ₃ CF ₃]			
Me(Me) ^j	5.16, 5.32	Me 4.00, 4.15	

Table 3 (continued)

R(R')R''	Resonances		
	C ₅ H ₅	R(R')	Others
[Fe ₂ (η-C ₅ H ₅) ₂ (CN) ₂ {μ-CN(R')R ₂ }]			
Me(Me) ^j	4.79	Me 4.07	
[Fe ₂ (η-C ₅ H ₅) ₂ (CO)(CNR''){μ-CN(R')R ₂ }][SO ₃ CF ₃] ₂			
Me(Me)/H ^j	5.36, 5.47	Me 4.04, 4.10	
Me(Me)/Me ^j	5.38, 5.50	Me 4.06, 4.10	<i>t</i> -CNMe 3.11
Me(Me)/C ₆ H ₁₁ ^j	5.40, 5.52	Me 4.06, 4.11	<i>t</i> -CNC ₆ H ₁₁ 3.56 (1, m), 1.2–1.8 (10, m)
[Fe ₂ (η-C ₅ H ₅) ₂ (CNR'') ₂ {μ-CN(R')R ₂ }][SO ₃ CF ₃] ₂			
Me(Me)/H ^j	4.93	Me 3.93	
Me(Me) ^j	5.18	Me 4.05	<i>t</i> -CNMe 3.09
Me(Me)/C ₆ H ₁₁ ^j	5.21	Me 4.05	<i>t</i> -C ₆ H ₁₁ 3.56 (1, m), 1.2–1.8 (10, m)

^a Run in CDCl₃ solution unless stated otherwise with chemical shifts quoted as ppm downfield from Me₄Si as an internal standard. All resonances are singlets unless it is stated otherwise; d = doublet, t = triplet, q = quartet, and m = multiplet. Coupling constants *J* are quoted in Hz. ^b Contains ¹³CN or ¹³CNMe ligands. ^c Contains C¹⁵N or C¹⁵NMe ligands. ^d For α and β forms see text. ^e All *trans* isomers also exist as mixtures of α and β forms in ca. equal amounts. See text. ^f In all cases the ¹³CNC¹H coupling constant is 3.7 Hz. ^g Counter anion is I[−].

^h Ar = 2,6-Et₂C₆H₃. ⁱ Counteranion is I[−] · 2H₂O. ^j Run in CD₃CN solution.

mmol) in *n*-butanol (100 cm³) was refluxed for 3 h. The mixture was cooled and allowed to stand overnight. After filtering, washing with ether and drying, red crystals of [Fe₂(η-C₅H₅)₂(CO)(CNAr)(μ-CO)(μ-CNMe₂)]I were isolated in 90% yield. A similar reaction took place with MeNC, and on photolysis of the reaction mixtures at room temperature. However, if the I[−] anion is replaced by [SO₃CF₃][−], decomposition took place and no products could be isolated.

2.3. The reaction of *cis*-[Fe₂(η-C₅H₅)₂(CO)(CNMe)(μ-CO)(μ-CNMe₂)]I[SO₃CF₃]₂ with KCN

A solution of *cis*-[Fe₂(η-C₅H₅)₂(CO)₂(μ-CO)(μ-CNMe₂)]I[SO₃CF₃]₂ (2.2 g, 4 mmol) and KCN (1.3 g, 20 mmol) in methanol (300 cm³) was refluxed for 4 h. A very slow reaction took place to give a mixture of [Fe₂(η-C₅H₅)₂(CO)(CN)(μ-CO)(μ-CNMe₂)] and [Fe₂(η-C₅H₅)₂(CNMe)(CN)(μ-CO)(μ-CNMe₂)] identified by IR spectroscopy, but the conversion was small and the experiment abandoned.

An identical reaction mixture was irradiated for 2 h with a Philips HPR 125 W UV lamp. The solvent was removed at reduced pressure, the residue dissolved in dichloromethane, dried over MgSO₄ and filtered. On evaporation of the solvent, brown hygroscopic crystals of [Fe₂(η-C₅H₅)₂(CNMe)(CN)(μ-CO)(μ-CNMe₂)] were isolated in 85% yield.

2.4. The reaction of *cis*-[Fe₂(η-C₅H₅)₂(CO)(CNMe)(μ-CO)(μ-CNMe₂)]I with ArNC (Ar = 2,6-Et₂C₆H₃)

A solution of [Fe₂(η-C₅H₅)₂(CO)(CNMe)(μ-CO)(μ-CNMe₂)]I (1.2 g, 2 mmol) and ArNC (0.7 g, 4 mmol) in *n*-butanol (100 cm³) was refluxed for 10 h. No reaction took place. Me₃NO (0.3 g, 4 mmol) was

added and the mixture stirred at room temperature for a further 3 h. The solvent was removed at reduced pressure, the residue dissolved in dichloromethane, dried over MgSO₄ and recrystallized from ethanol/ether to give red crystals of [Fe₂(η-C₅H₅)₂(CNMe)(CNAr)(μ-CO)(μ-CNMe₂)]I in 70% yield.

2.5. The reaction of *cis*-[Fe₂(η-C₅H₅)₂(CO)₂(μ-CNMe₂)]I[SO₃CF₃]₂ with KCN on heating

A solution of [Fe₂(η-C₅H₅)₂(CO)₂(μ-CNMe₂)]I[SO₃CF₃]₂ (0.71 g, 1 mmol) and KCN (0.065 g, 1 mmol) in ethanol (50 cm³) was refluxed for 1 h. Removal of the solvent followed by careful recrystallization from ethanol–ether mixtures gave dark-green crystals of [Fe₂(η-C₅H₅)₂(CO)(CN)(μ-CNMe₂)]I[SO₃CF₃]₂ · H₂O in 45% yield.

A similar reaction using 2 mmol (0.13 g) of KCN, a reaction time of 2 h, separation by chromatography (dichloromethane/alumina), and purification by recrystallization from dichloromethane–ether mixtures gave light-green crystals of [Fe₂(η-C₅H₅)₂(CN)₂(μ-CNMe₂)]I · H₂O in 15% yield.

2.6. The reaction of [Fe₂(η-C₅H₅)₂(CO)₂(μ-CNMe₂)]I[SO₃CF₃]₂ with CNC₆H₁₁ and CNMe

A solution of [Fe₂(η-C₅H₅)₂(CO)₂(μ-CNMe₂)]I[SO₃CF₃]₂ (0.71 g, 1 mmol) and CNC₆H₁₁ (0.11 g, 1 mmol) in ethanol (300 cm³) was irradiated for 1 h in an Applied Photophysics Photochemical Reactor with a 400 W mercury lamp. Removal of the solvent followed by careful recrystallization from ethanol–ether mixtures gave crystals of [Fe₂(η-C₅H₅)₂(CO)(CNC₆H₁₁)(μ-CNMe₂)]I[SO₃CF₃]₂ in 40% yield.

A repeat of the reaction using a large excess of CNC₆H₁₁ (1 g, 10 mmol) or CNMe (0.3 g, 10 mmol)

gave red crystals of $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CNC}_6\text{H}_{11})_2(\mu\text{-CNMe}_2)_2][\text{SO}_3\text{CF}_3]_2$ or $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CNMe})_2(\mu\text{-CNMe}_2)_2][\text{SO}_3\text{CF}_3]_2$ in 90% yields.

2.7. Reaction of $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})(\text{CN})(\mu\text{-CO})\{\mu\text{-CN}(\text{Me})\text{R}\}]$ and other complexes with $\text{MeOSO}_2\text{CF}_3$

$\text{MeOSO}_2\text{CF}_3$ (1 cm³) was added to a solution of $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})(\text{CN})(\mu\text{-CO})\{\mu\text{-CN}(\text{Me})\text{R}\}]$ (2 mmol., R = Me 0.76 g, or Et 0.79 g) in dichloromethane, and the mixture stirred for 1 h. The colour changed from green or brown to red. The solvent was removed at reduced pressure, and the residue recrystallized from ethanol–ether mixtures to give either *cis*- or *trans*- $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})(\text{CNMe})(\mu\text{-CO})\{\mu\text{-CN}(\text{Me})\text{R}\}][\text{SO}_3\text{CF}_3]$ or a mixture of the two in yields greater than 90%. Some of the related salts prepared in this way are listed in Table 1, together with their melting points and analyses.

The same experimental procedure was used to convert $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CNMe})(\text{CN})(\mu\text{-CO})(\mu\text{-CNMe}_2)]$ to $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CNMe})_2(\mu\text{-CO})(\mu\text{-CNMe}_2)]$ -

$[\text{SO}_3\text{CF}_3]$ or $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CNMe})(\text{CNEt})(\mu\text{-CO})(\mu\text{-CNMe}_2)][\text{SO}_3\text{CF}_3]$, $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})(\text{CN})(\mu\text{-CNMe}_2)_2][\text{SO}_3\text{CF}_3] \cdot \text{H}_2\text{O}$ to $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})(\text{CNMe})(\mu\text{-CNMe}_2)_2][\text{SO}_3\text{CF}_3]_2$, and $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CN})_2(\mu\text{-CNMe}_2)_2] \cdot \text{H}_2\text{O}$ to $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CNMe})_2(\mu\text{-CNMe}_2)_2][\text{SO}_3\text{CF}_3]_2$.

2.8. Reaction of $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})(\text{CNMe})_3]$ with $\text{MeOSO}_2\text{CF}_3$

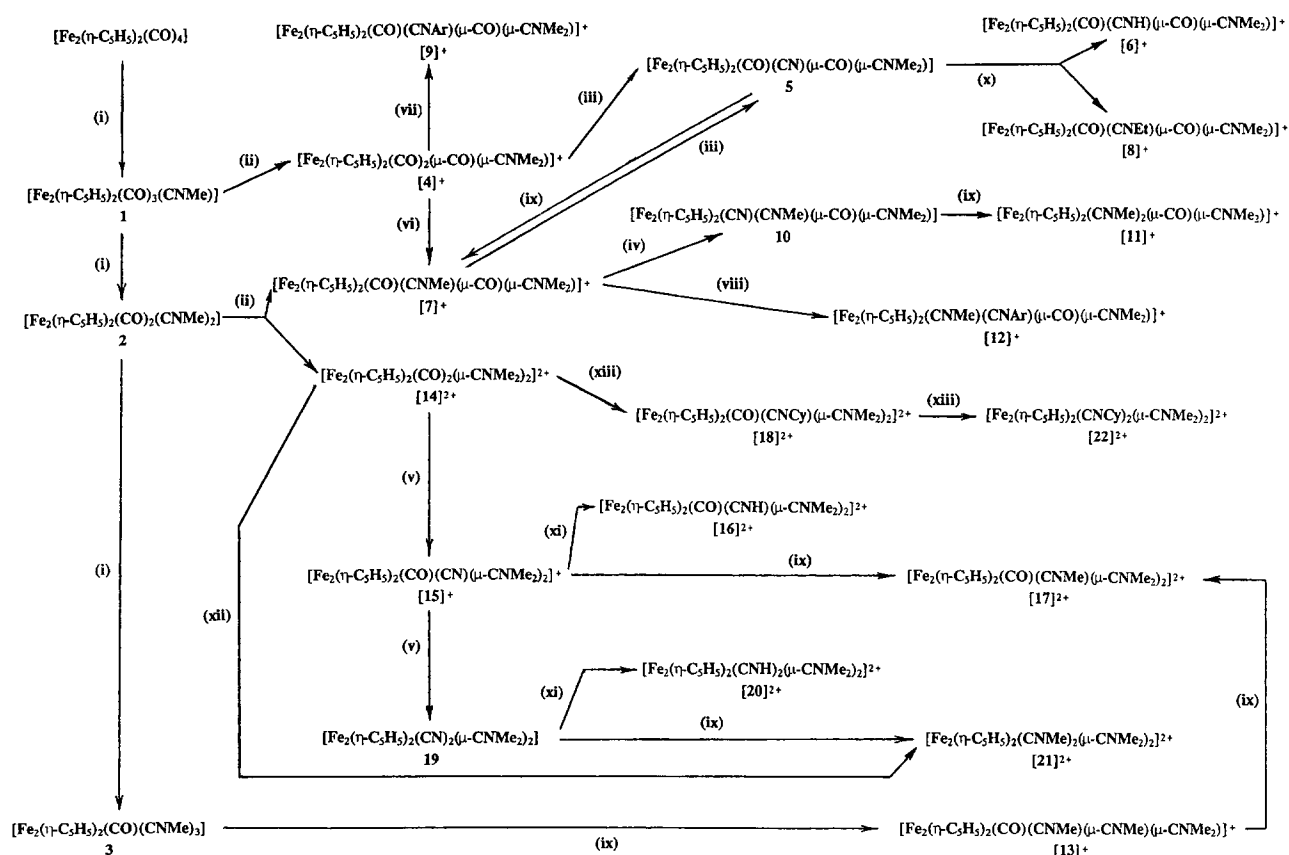
A solution of $\text{MeOSO}_2\text{CF}_3$ (0.33 g, 2 mmol) in benzene (50 cm³) was added dropwise to one of $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})(\text{CNMe})_3]$ (0.76 g, 2 mmol) in benzene (100 cm³) over a period of 3 h. The precipitate was filtered off and washed with benzene–ether mixtures to give red crystals of $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})(\text{CNMe})(\mu\text{-CNMe})(\mu\text{-CNMe}_2)][\text{SO}_3\text{CF}_3]$ in 90% yield. A similar reaction carried out with the rapid addition of $\text{MeOSO}_2\text{CF}_3$ (1 g, 6 mmol) as a single aliquot to the benzene solution of $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})(\text{CNMe})_3]$ gave red crystals of $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})(\text{CNMe})(\mu\text{-CNMe}_2)_2][\text{SO}_3\text{CF}_3]_2$ in 90% yield.

Table 4

¹³C NMR spectra of some of the complexes described in the text ^a

R(R')/R''	Resonances					
	$\mu\text{-C}\equiv\text{N}$	$\mu\text{-CO}$	<i>t</i> -CO	<i>t</i> -CN	C ₅ H ₅	Others
$[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})(\text{CN})(\mu\text{-CO})\{\mu\text{-CN}(\text{R}')\text{R}\}]$						
<i>cis</i> -Me(Me)	330.6	261.7	210.7	139.9	86.4, 87.0	52.0, 52.5
<i>trans</i> -Me(Me)	337.0	261.1	212.2	140.9	88.9, 89.8	51.8, 52.2
<i>cis</i> -Me(Et) ^b	329.2,	261.8,	210.7,	139.8,	86.3, 86.5	48.5, 48.9, 61.1,
	329.3	262.2	211.1	140.2	86.9, 87.0	61.3, 13.8, 14.2
<i>trans</i> -Me(Et) ^b				140.9,	88.9, 89.0,	
				141.0	89.9, 90.0	
$[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})(\text{CNR}'')(\mu\text{-CO})\{\mu\text{-CN}(\text{R}')\text{R}\}][\text{SO}_3\text{CF}_3]$						
<i>cis</i> -Me(Me)/Me	332.4	262.1	210.2	154.0 (br)	88.1, 88.5	53.3, 53.6, 30.7
<i>cis</i> -Me(Me)/Me ^c	322.7	262.2	210.3	154.5 (br)	88.1, 88.5	53.4, 53.6
	(d, <i>J</i> = 8.5)	(d, <i>J</i> = 6.8)				30.9 (d, <i>J</i> = 23.9)
<i>cis</i> -Me(Me)/Me ^d	322.9	262.1	210.2	154.0	88.1, 88.5	53.3, 53.5
				(d, <i>J</i> = 30.7)		30.7 (d, <i>J</i> = 13.6)
<i>cis</i> -Me(Me)/Et	323.8	263.1	211.7	153.1	88.9, 88.5	53.6, 54.1
						41.1, 15.4
$[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CNR}'')(\text{CN})(\mu\text{-CO})\{\mu\text{-CN}(\text{R}')\text{R}\}]$						
<i>cis</i> -Me(Me)/Me	336.5	275.4		143.9 (CN)	85.3, 86.1	51.7, 52.0
				162.7 (CNR)		30.7
$[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})(\text{CNR}'')(\mu\text{-CNMe})(\mu\text{-CN}(\text{R}')\text{R})][\text{SO}_3\text{CF}_3]$						
Me(Me)/Me	325.6	238.0	212.6		87.9, 88.4	53.2, 53.6
		($\mu\text{-CNMe}$)				45.2 (μ), 31.0 (t)
$[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})(\text{CN})(\mu\text{-CN}(\text{R}')\text{R})_2][\text{SO}_3\text{CF}_3]$						
Me(Me)	316.1		209.7	131.6	90.3, 90.5	53.3, 53.6
$[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CN})_2\{\mu\text{-CN}(\text{R}')\text{R}\}_2]$						
Me(Me)	325.1		139.1		86.4	51.6
$[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})(\text{CNR}'')(\mu\text{-CN}(\text{R}')\text{R})_2][\text{SO}_3\text{CF}_3]_2$						
Me(Me)/Me	314.0		207.7	151.2	91.1, 91.1	54.2, 54.4, 31.9
$[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CNR}'')_2\{\mu\text{-CN}(\text{R}')\text{R}\}_2][\text{SO}_3\text{CF}_3]_2$						
Me(Me)/Me	318.7				89.8	

^a Run in CDCl₃ solution with chemical shifts quoted as ppm downfield from Me₄Si as an internal standard. All resonances are singlets. Unless it is stated otherwise. Coupling constants *J* in Hz. ^b Contains α and forms (see text). ^c Contains ¹³CNMe ligands. ^d Contains C¹⁵NMe ligands.



Scheme 1. (i) Δ , CNMe; (ii) RI or ROSO_2CF_3 ; (iii) Δ , KCN; (iv) $h\nu$, KCN; (v) Δ or $h\nu$, KCN; (vi) Δ or $h\nu$, CNMe; (vii) Δ or $h\nu$, CNAr (Ar = 2,6-Et₂C₆H₃); (viii) Me₃NO, CNAr; (ix) MeOSO₂CF₃; (x) EtOSO₂CF₃ in wet CHCl₃; (xi) HOSO₂CF₃; (xii) $h\nu$, CNMe; (xiii) $h\nu$, CNCy (Cy = cyclo-C₆H₁₁).

2.9. Protonation of $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})(\text{CN})(\mu\text{-CO})(\mu\text{-CNMe}_2)]$ and other complexes

$\text{CF}_3\text{CO}_2\text{H}$ (0.5 cm³) or gaseous HCl was added to a solution of *cis*- $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})(\text{CN})(\mu\text{-CO})(\mu\text{-CNMe}_2)]$ (0.76 g, 2 mmol) in chloroform. Spectroscopic data suggested that $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})(\text{CNH})(\mu\text{-CO})(\mu\text{-CNMe}_2)]^+$ salts were formed, but they proved difficult to isolate and purify. HOSO₂CF₃ gave other products which will be discussed in a later publication. The desired complex was obtained if EtOSO₂CF₃ (0.57 g, 3 mmol) was added to a solution of *cis*- $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})(\text{CN})(\mu\text{-CO})(\mu\text{-CNMe}_2)]$ in incompletely dried chloroform (50 cm³). After 1 h, the filtered solution was cooled to -20°C for a further 5 h. Brown microcrystals of *cis*- $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})(\text{CNH})(\mu\text{-CO})(\mu\text{-CNMe}_2)]\text{[SO}_3\text{CF}_3]$ were filtered off and dried in a desiccator (yield 40%). Removal of the solvent from the filtrate and recrystallization of the residue from ethanol/ether gave red microcrystals of *cis*- $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})(\text{CNEt})(\mu\text{-CO})(\mu\text{-CNMe}_2)]\text{[SO}_3\text{CF}_3]$ in 50% yield.

HOSO₂CF₃ (0.9 g, 6 mmols) was added to a solution of $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})(\text{CN})(\mu\text{-CNMe}_2)_2]\text{[SO}_3\text{CF}_3] \cdot \text{H}_2\text{O}$ (0.57 g, 1 mmol) in dichloromethane (50 cm³).

After 10 min the solution was filtered, the solvent removed at reduced pressure, and the residue recrystallized from ethanol/ether to give hygroscopic red crystals of $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})(\text{CNH})(\mu\text{-CNMe}_2)_2]\text{[SO}_3\text{CF}_3]_2 \cdot 3\text{H}_2\text{O}$ (yield 80%). Using the

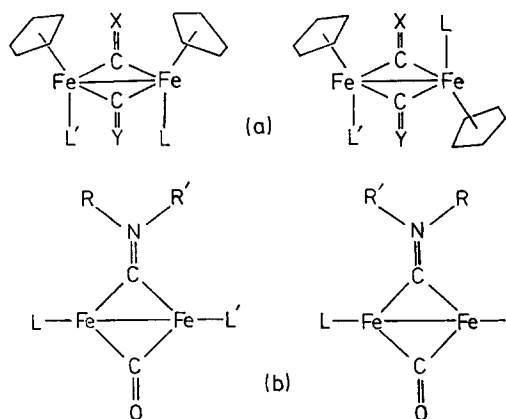


Fig. 1. (a) Structures of *cis*- and *trans*- $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{L})(\text{L}')\text{X}(\mu\text{-CX})(\mu\text{-CY})]$ complexes prepared during the course of this work where CX = CNMe_2^+ and CY = CO, or CX = CY = CNMe_2^+ , and L, L' = CO, CN⁻, CNH, CNMe, CNEt, CNC₆H₁₁ or C₆H₃Et₂, 2,6. (b) The α and β isomers when CX = $\text{CN}(\text{R}')\text{R}^+$ and CY = CO, and L $\neq$ L'. (C₅H₅ ligands have been omitted for the sake of clarity).

same procedure $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CN})_2(\mu\text{-CNMe}_2)_2] \cdot \text{H}_2\text{O}$ gave $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CNH})_2(\mu\text{-CNMe}_2)_2][\text{SO}_3\text{-CF}_3]_2 \cdot 4\text{H}_2\text{O}$ which was isolated as hygroscopic green crystals in 80% yield by the addition of pentane to the reaction mixture and cooling to -20°C overnight.

Elemental analyses (Table 1) were carried out by the Analytical Laboratory of University College, Dublin. IR spectra (Table 2) were run on Perkin Elmer 1710 and 1720 FTIR spectrometers, and NMR spectra (Tables 3 and 4) on a JEOL JNM-GX270 spectrometer.

3. Results and discussion

The compounds prepared during the course of this work are represented in Fig. 1. They are numbered systematically. 1–3 are the $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_{4-n}(\text{CNMe})_n]$ ($n = 1-3$) precursors, $[4]^+ - [12]^+$ have the general formulae $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{L})(\text{L}')(\mu\text{-CO})\{\mu\text{-CN}(\text{R}')\text{R}\}]^+$, $[13]^+$ is a $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{L})(\text{L}')(\mu\text{-CNR}'')\{\mu\text{-CN}(\text{R}')\text{R}\}]^+$ type of molecule, and $[14]^{2+} - [22]^{2+}$ have the formulae $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{L})(\text{L}')\{\mu\text{-CN}(\text{R}')\text{R}\}_2]^{2+}$. The order of ligand priority is $\text{L}, \text{L}' = \text{CO} > \text{CN}^- > \text{CNH} > \text{CNMe} > \text{CNEt} > \text{CNAr}$ ($\text{Ar} = 2,6\text{-Et}_2\text{C}_6\text{H}_3$). Most are air-stable solids, but those containing the CNH ligand are deliquescent and must be handled with care.

The reaction of $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_4]$ with CNMe (and other alkyl isocyanides) under suitable conditions gives in turn 1, 2 and 3, i.e. $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_{4-n}(\text{CNMe})_n]$, $n = 1 \rightarrow 2 \rightarrow 3$. 1 reacts with MeX ($\text{X} = \text{I}^-$ or CF_3SO_3^-) to give red *cis*- and purple *trans*- $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-CNMe}_2)]\text{X}$, $[4]\text{X}$; 2 gives a mixture of red *cis*- $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-CNMe}_2)]\text{X}$, $[7]\text{X}$, and orange *cis*- $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_2(\mu\text{-CNMe}_2)_2]\text{X}_2$, $[14]\text{X}_2$ salts; and 3 gives in turn $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})(\text{CNMe})(\mu\text{-CNMe})]\text{X}$, $[13]\text{X}$, and $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})(\text{CNMe})(\mu\text{-CNMe}_2)_2]\text{X}_2$, $[17]\text{X}_2$ salts. MeI may be replaced by other RI, and $\text{MeOSO}_2\text{CF}_3$ by $\text{EtOSO}_2\text{CF}_3$ to give analogues of $[4]\text{X}$, *cis*- $[7]\text{X}$ and *cis*- $[14]\text{X}_2$ (see Ref. [3]).

The subsequent reactions of the salts are summarised in Scheme 1. They may be divided into two classes: (a) CO substitution by CN^- , CNR and CNAr; (b) alkylation or protonation of *t*-CN to *t*-CNR ($\text{R} = \text{alkyl}$ or H).

3.1. Isomerism

All of the complexes have structures derived from that of $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_4]$ with a planar or near-planar $\text{Fe}_2(\mu\text{-C})_2$ moiety. Consequently they can exist as *cis* or *trans* isomers which do not interconvert because of the presence of the $\mu\text{-CN}(\text{R}')\text{R}^+$ ligand (see below and Ref. [3]). Reactions of class (b) involve only the periphery of ligands. Isomerism is not observed, and

is presumed not to occur as it is unreasonable to assume 100% isomerism. However, reactions of type (a) are often accompanied by partial isomerism, and in some cases the isomers have been separated by chromatography and fractional crystallization. Only when the isomers contain a $\text{Fe}_2(\text{-CO})_2$ moiety can they be distinguished by IR spectroscopy, i.e. for 4 and 14. However, the known structure and spectra of *cis*- $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})(\text{CNMe})(\mu\text{-CO})(\mu\text{-CNMe}_2)]\text{BPh}_4$ [3] allows the correlation of structure and spectra for all *cis*- and *trans*- $[7]^+$, $[6]^+$, $[8]^+$ and $[9]^+$ salts, and hence for all *cis*- and *trans*-5. In all cases where we are confident of the structures: (i) the ^1H NMR spectra of the isomers differ so that the mean chemical shifts, δ , of the cyclopentadienyl protons are *cis* > *trans* and of the NMe₂ protons are *trans* > *cis*; (ii) the *cis* isomer always predominates as the product of substitution reactions irrespective of the structure of the precursor. In all other instances where two products are obtained, conditions (i) and (ii) are both obeyed. Where only a single product is formed it has been assumed to be *cis*. On the basis of this last, $[15][\text{SO}_3\text{CF}_3]$ and 19 are *cis* isomers, as are $[16][\text{SO}_3\text{CF}_3]_2$, $[17][\text{SO}_3\text{CF}_3]_2$, $[18][\text{SO}_3\text{CF}_3]_2$, $[20][\text{SO}_3\text{CF}_3]_2$, $[21][\text{SO}_3\text{CF}_3]_2$ and $[22][\text{SO}_3\text{CF}_3]_2$; this is consistent with a previous suggestion that the spectroscopically identical cations in $[17]\text{I}_2$ and $[21]\text{I}_2$ prepared directly from $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})(\text{CNMe})_3]$ and $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CNMe})_4]$ respectively also have a *cis* conformation [9]. However, the evidence, though consistent, is circumstantial.

When $\text{R} \neq \text{R}'$, a second form of isomerism is possible for both *cis* and *trans*- $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{L})(\text{L}')(\mu\text{-L}')(\mu\text{-CN}(\text{R}')\text{R})]^+$ complexes. It has been observed previously in *cis*- $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})(\text{CNMe})(\mu\text{-CO})(\mu\text{-CN}(\text{Me})\text{Et})]^+$ [3]. As there is no rotation about the $\mu\text{-C}=\text{N}$ bond (see below) the two Fe atoms are now distinguishable, and either may be substituted by L or L' ligands to give α and β forms. This isomerism is detectable by NMR spectroscopy (see below), but attribution of the isomers was not possible and no attempt was made to separate them. The two isomers occur in varying ratios for the *cis* complexes, but in virtually equal ratios for the *trans*. This makes it impossible to assign the ^1H NMR spectra of the latter.

3.2. CO substitution by CN^- , CNR and CNAr ligands

The most extensively studied of the CO substitution reactions are those of KCN with $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-CNMe}_2)]\text{X}$, $[4]\text{X}$, and many related complexes containing different $\mu\text{-CN}(\text{R}')\text{R}$ ligands ($\text{R}, \text{R}' = \text{alkyl}$; $\text{X}^- = \text{I}^-$ or SO_3CF_3^-) in refluxing methanol or ethanol to give the zwitterions $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})(\text{CN})(\mu\text{-CO})(\mu\text{-CN}(\text{R}')\text{R})]$, 5 and its analogues. It should be noted that when $\text{R} = \text{R}' = \text{Me}$ these are stable isomers of 2. The reactions were extended to

$\eta\text{-C}_5\text{H}_4\text{Me}$ derivatives, and by using K^{13}CN and KC^{15}N . Reaction times (2–4 h) are a function of the $\mu\text{-CN(R')R}$ ligand and increase along the series $\text{R,R}' = \text{Me} < \text{CH}_2\text{Ph}$, allyl $< \text{Et}$. They are reduced by the addition of water or crown ethers in other solvents as well as alcohols. For example, $[\mathbf{4}][\text{SO}_3\text{CF}_3]$ does not react with KCN in refluxing dry acetonitrile even after 2 h, but it is completely converted to **5** after a further 2 h when water (ca. 2%) is added to the reaction mixture.

The reaction of a 14:1 mixture of *cis*- and *trans*- $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-CNMe}_2)][\text{SO}_3\text{CF}_3]$ with KCN gives a 4:1 mixture of *cis*- and *trans*- $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})(\text{CN})(\mu\text{-CO})(\mu\text{-CNMe}_2)]$, i.e. partial inversion of configuration has taken place at one iron atom on substitution. Pure samples of each isomer have been obtained, and have been identified by their subsequent alkylation to give the known $[\mathbf{7}]^+$ (see above). The *cis* is green and the *trans* brown. The latter are the more soluble in polar organic solvents, but neither are soluble in non-polar solvents. The *cis*:*trans* isomer ratio is variable, but the *cis* is always favoured.

The thermal reaction of $[\mathbf{7}]\text{X}$ with KCN or K^{13}CN was not investigated in detail. It is very slow and results largely in CNMe substitution to give **5** together with some $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CN})(\text{CNMe})(\mu\text{-CO})(\mu\text{-CNMe}_2)]$, **10**, the product of CO substitution. However, **10** is the major product of the photochemical reaction. It has been isolated as a brown hygroscopic solid, which is a mixture of major and minor isomers that we presume to be *cis* and *trans* respectively (see above).

The reaction between orange *cis*- $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_2(\mu\text{-CNMe}_2)_2][\text{SO}_3\text{CF}_3]_2$, $[\mathbf{14}][\text{SO}_3\text{CF}_3]_2$, and KCN in refluxing methanol results in substitution of each terminal CO group in turn giving dark-green $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})(\text{CN})(\mu\text{-CNMe}_2)_2][\text{SO}_3\text{CF}_3]$, $[\mathbf{15}][\text{SO}_3\text{CF}_3]$, and then a light-green dizwitterion $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CN})_2(\mu\text{-CNMe}_2)]$, **19**. A single isomer is isolated in both instances which we assume is *cis*, but their yields are comparatively low because of competing dealkylation reactions which convert one $\mu\text{-CNMe}_2^+$ ligand to $\mu\text{-CNMe}$.

$[\mathbf{4}]\text{I}$ undergoes thermal or photochemical CO substitution by CNMe or CNAr ($\text{Ar} = 2,6\text{-Et}_2\text{C}_6\text{H}_3$) to give $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})(\text{CNMe})(\mu\text{-CO})(\mu\text{-CNMe}_2)]\text{I}$, $[\mathbf{7}]\text{I}$, $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})(\text{CNAr})(\mu\text{-CO})(\mu\text{-CNMe}_2)]\text{I}$, $[\mathbf{9}]\text{I}$, or their analogues. The nature of the counteranion is important as $[\mathbf{4}][\text{SO}_3\text{CF}_3]$ does not give identifiable products under the same conditions. $[\mathbf{7}]\text{I}$ failed to react with CNAr in refluxing butanol, but on the addition of Me_3NO at room temperature it gave $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CNMe})(\text{CNAr})(\mu\text{-CO})(\mu\text{-CNMe}_2)]\text{I}$, $[\mathbf{12}]\text{I}$, in good yield. In contrast the CO ligands of $[\mathbf{14}][\text{SO}_3\text{CF}_3]_2$ are very labile, and its photolysis in the presence of $\text{CNC}_6\text{H}_{11}$ (CNCy) gives in turn single isomers of $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})(\text{CNCy})(\mu\text{-CNMe}_2)_2][\text{SO}_3\text{CF}_3]_2$, $[\mathbf{18}][\text{SO}_3\text{CF}_3]_2$, and then $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CNCy})_2(\mu\text{-CNMe}_2)_2][\text{SO}_3\text{CF}_3]_2$, $[\mathbf{22}][\text{SO}_3\text{CF}_3]_2$, while $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CNMe})_2(\mu\text{-CNMe}_2)_2][\text{SO}_3\text{CF}_3]_2$, $[\mathbf{21}][\text{SO}_3\text{CF}_3]_2$, was obtained when CNCy was replaced by CNMe.

3.3. Alkylation and protonation of *t*-CN ligands

Terminally coordinated CN^- ligands may be alkylated at N and converted to terminal (*t*) CNR ligands $[\mathbf{1d}]$. **5**, **10**, $[\mathbf{15}][\text{SO}_3\text{CF}_3]$ and **19** do not react with MeI at room temperature, but they do react with $\text{MeOSO}_2\text{CF}_3$ or $\text{EtOSO}_2\text{CF}_3$ to give respectively $[\mathbf{7}][\text{SO}_3\text{CF}_3]$ or $[\mathbf{8}][\text{SO}_3\text{CF}_3]$, red $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CNMe})_2(\mu\text{-CO})(\mu\text{-CNMe}_2)][\text{SO}_3\text{CF}_3]$, $[\mathbf{11}][\text{SO}_3\text{CF}_3]$, or its *t*-CNEt counterpart, red $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})(\text{CNMe})(\mu\text{-CNMe}_2)]\text{I}$, $[\mathbf{17}][\text{SO}_3\text{CF}_3]$, and green $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CNMe})_2(\mu\text{-CNMe}_2)_2][\text{SO}_3\text{CF}_3]_2$, $[\mathbf{21}][\text{SO}_3\text{CF}_3]_2$. The alkylation of ^{13}CN and C^{15}N -labelled **5** gives ^{13}CNR and C^{15}NR -labelled $[\mathbf{7}][\text{SO}_3\text{CF}_3]$. It should also be noted that this reaction allows the preparation of purple *trans*- $[\mathbf{7}][\text{SO}_3\text{CF}_3]$ whereas the direct reaction of **2** with MeX gives only the red *cis* salts $[\mathbf{3}]$.

The reaction of *cis*-**5** with either $\text{CF}_3\text{CO}_2\text{H}$ or gaseous HCl gives the $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})(\text{CNH})(\mu\text{-CO})(\mu\text{-CNMe}_2)]^+$ cation, but the salts could not be isolated, and HOSO_2CF_3 gave other products which will be described elsewhere. *Cis*- $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})(\text{CNH})(\mu\text{-CO})(\mu\text{-CNMe}_2)][\text{SO}_3\text{CF}_3]$, $[\mathbf{6}][\text{SO}_3\text{CF}_3]$, was finally obtained along with $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})(\text{CNEt})(\mu\text{-CO})(\mu\text{-CNMe}_2)][\text{SO}_3\text{CF}_3]$, $[\mathbf{8}][\text{SO}_3\text{CF}_3]$, from the reaction of **5** with $\text{EtOSO}_2\text{CF}_3$ in incompletely dried chloroform. The two were separated by fractional crystallization. Protonation of the cyanoligands in $[\mathbf{15}]^+$ and **19** with HOSO_2CF_3 gave respectively $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})(\text{CNH})(\mu\text{-CNMe}_2)_2][\text{SO}_3\text{CF}_3] \cdot 3\text{H}_2\text{O}$, $[\mathbf{16}][\text{SO}_3\text{CF}_3]_2 \cdot 3\text{H}_2\text{O}$, and $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CNH})_2(\mu\text{-CNMe}_2)_2][\text{SO}_3\text{CF}_3] \cdot 4\text{H}_2\text{O}$, $[\mathbf{20}][\text{SO}_3\text{CF}_3]_2 \cdot 4\text{H}_2\text{O}$ in good yields. On the basis of their spectra it is concluded that they have the same geometry as their MeNC counterparts $[\mathbf{17}][\text{SO}_3\text{CF}_3]_2$ and $[\mathbf{21}][\text{SO}_3\text{CF}_3]_2$.

3.4. Infrared spectra

The infrared spectra of the various complexes show many absorption bands. Where appropriate those caused by the vibrations of the $[\text{SO}_3\text{CF}_3]^-$ anions are readily identified, but otherwise the most important bands are caused by the CN- and CO-stretching vibrations of *t*-CN, *t*-CNR, *t*-CO, $\mu\text{-CO}$, $\mu\text{-CNR}$ and $\mu\text{-CN(R')R}$ ligands. These are listed and assigned in Table 2. When *cis* and *trans* isomers are formed and have been separated, their absorption bands differ (cf. Ref. [3]). Where these isomers have not been separated, composite absorption bands are observed which are often asymmetric and broad, but in all such cases the peak positions

quoted are those caused by the dominant *cis* isomers. There were no absorption bands in the spectra of **[6][SO₃CF₃]**, **[16][SO₃CF₃]₂ · 3H₂O** or **[20][SO₃CF₃]₂ · 4H₂O** which could be attributed to $\nu(\text{NH})$ vibrations.

On the basis of IR spectroscopy it was concluded that the $\mu\text{-CNMe}_2^+$ ligand is a more powerful π -acceptor than $\mu\text{-CO}$ (cf. $\nu(\text{CO})$ of **[Fe₂($\eta\text{-C}_5\text{H}_5$)₂(CO)₄]** at 1775, 1959, and 1998 cm⁻¹ [10] and those of *cis*-**[Fe₂($\eta\text{-C}_5\text{H}_5$)₂(CO)₂($\mu\text{-CO}$)($\mu\text{-CNMe}_2$)]** in Table 2) [2,3]). This is borne out in the present work. However, although the frequencies of the absorption bands caused by the $\nu(\text{CO})$ and $\nu(\text{CN})$ vibrations of the **[7]⁺** cations and **5** are almost independent of the $\mu\text{-C}=\text{N}(\text{R})\text{R}$ ligand, $\nu\{\mu\text{-C}=\text{N}(\text{R})\text{R}\}$ decreases along the series $\text{R}'\text{R}=\text{Me}_2 > (\text{Me})\text{Et} > \text{Et}_2$ (Table 2). Similar behaviour is also observed for **[4]⁺**, e.g. for both *cis*-**[Fe₂($\eta\text{-C}_5\text{H}_5$)₂(CO)₂($\mu\text{-CO}$)($\mu\text{-CNMe}_2$)]** and its $\mu\text{-CN}(\text{Me})\text{CD}_3$ counterpart $\nu(\text{CO})$ frequencies are 1839, 1991 and 2023 cm⁻¹, but $\nu(\mu\text{-C}=\text{NMe}_2)=1602$ cm⁻¹ and $\nu\{\mu\text{-CN}(\text{Me})\text{CD}_3\}=1589$ cm⁻¹ (CHCl₃ solution) [11]. It is probably because of a kinematic effect, indicating that the alkyl groups contribute to the reduced mass of the C=N vibrator (cf. Ref. [12]).

A comparison of the IR spectra of **[4]⁺** with those of **5** or **[7]⁺** implies that both CN⁻ and CNMe are better σ -donor/poorer π -acceptor ligands than CO. In both cases the frequencies of the $\nu(\text{CO})$, $\nu(\mu\text{-CO})$ and $\nu(\mu\text{-CNMe}_2)$ absorption bands decrease. However, the decreases are not the same for each type of vibration, and are different for the *cis* series compared to *trans*. Furthermore, alkylating the *t*-CN⁻ ligand in **5** results in an increase in the frequencies of all of these absorption bands except for the $\nu(\text{CO})$ band of the *cis* isomer which decreases by 5 cm⁻¹. The reasons for these variations are not clear. They may be artifacts arising from, for example, the anharmonicity or coupling of vibrations, but they may reflect differences in the bonding preferences of the *cis*- and *trans*-**Fe₂($\eta\text{-C}_5\text{H}_5$)₂($\mu\text{-CO}$)($\mu\text{-CNMe}_2$)** moieties.

On coordination of CN⁻, its $\nu(\text{CN})$ frequency increases slightly from ca. 2080 cm⁻¹ to ca. 2090–2104 cm⁻¹ in **5**, **10**, **[15]⁺** and **19**. Its C lone pair is C–N σ -antibonding [13] so that coordination without backbonding would result in a large increase in $\nu(\text{CN})$ (e.g. to 2170 cm⁻¹ in MeCN), which implies significant Fe to CN π -bonding in **5**, **10** and **19**, and less in **[15]⁺**. The very large increase in the $\nu(\text{CN})$ frequency on alkylation (Table 2) is a result of the C–N σ^* character of the N lone pair of a CN⁻ ligand (cf. the increase of the $\nu(\text{CN})$ frequency of MeCN when it acts as a ligand). The frequency of the $\nu(\text{CN})$ vibration of the *t*-CNMe ligand in **[7]⁺** is greater than that of the *t*-CNEt in **[8]⁺**. A similar effect is observed for all CNR and their complexes as $\nu(\text{C-NR})$ decrease along the series $\text{R}=\text{Me} > \text{Et} > \text{CHMe}_2 > \text{CMe}_3$ [1]. It appears to be caused by a kinematic effect similar to that discussed above for

the $\mu\text{-CNR}_2$ ligands (see also below and Ref. [12]). However, the *t*-CNH ligand is anomalous as its $\nu(\text{CN})$ stretching vibrations have frequencies that are ca. 80 cm⁻¹ lower than those of their *t*-CNMe counterparts. This may be a consequence of the greater effective mass of the H group because of hydrogen bonding to H₂O and other species, or perhaps there is greater backbonding into the C–N π^* orbitals. However, the magnitude of the effect is so great that neither explanation is convincing. It is possible that the CN–H bond is weak, and so the consequent reduction in the C–N σ^* contribution on its formation (see above) may be less than for organoisocyanides with their stronger CN–R bonds, and so the increase in the $\nu(\text{CN})$ frequency on protonation will also be less.

Comparison of the infrared spectra **5** and **[7]X** with those of their ¹³CN or C¹⁵N labelled counterparts (Table 2), show that the absorption bands caused by the $\nu(\text{CNMe})$ vibration of **[Fe₂($\eta\text{-C}_5\text{H}_5$)₂(CO)(CNMe*)($\mu\text{-CO}$)($\mu\text{-CNMe}_2$)]⁺ or the $\nu(\text{CN})$ vibration of **[Fe₂($\eta\text{-C}_5\text{H}_5$)₂(CO)(CN*)($\mu\text{-CO}$)($\mu\text{-CNMe}_2$)]** (the asterisk indicates a labelled ligand) have moved to lower frequencies whereas those caused by the $\nu(\text{CO})$, $\nu(\mu\text{-CO})$ and $\nu(\mu\text{-C}=\text{NMe}_2)$ modes are virtually unaffected. For **[Fe₂($\eta\text{-C}_5\text{H}_5$)₂(CO)(CN*)($\mu\text{-CO}$)($\mu\text{-CNMe}_2$)]** the frequency shifts are close to those expected on the basis of the reduced mass of ¹²C¹⁴N vs. ¹³C¹⁴N or ¹²C¹⁵N if it is assumed that the CN ligand acts as an isolated simple harmonic oscillator. This is not true for the CNMe ligand of *cis*-**[Fe₂($\eta\text{-C}_5\text{H}_5$)₂(CO)(CNMe*)($\mu\text{-CO}$)($\mu\text{-CNMe}_2$)]**[SO₃CF₃] where the observed shifts are less than would be expected on this simple basis. This is attributed to the effect of Me on the reduced mass of the CN oscillator, as discussed above.**

3.5. NMR spectra

In general, the ¹H NMR spectra of the various complexes (Table 3) are much as would be expected and may be assigned on the basis of *cis* and *trans* isomers and, where appropriate, α and β forms (see above). Those of *cis*- and *trans*-**5**, **[7]X** and related compounds differ sufficiently (Table 3) for the two isomers to be identified unequivocally by comparison with the spectrum of *cis*-**[Fe₂($\eta\text{-C}_5\text{H}_5$)₂(CO)(CNMe)($\mu\text{-CO}$)($\mu\text{-CNMe}_2$)]**[BPh₄] (see above). The proton resonance of the CNH ligand has been observed as broad singlet in the spectrum of **[6][SO₃CF₃]** at 3.33 δ . It was not detected for **[16][SO₃CF₃]₂** or **[20][SO₃CF₃]₂**.

The ¹³C NMR spectra (Table 4) of the *cis* and *trans* isomers of the complexes and, where appropriate, their α and β forms also differ. The ¹³C chemical shift of the $\mu\text{-CN}(\text{R})\text{R}$ ligands at ca. 330 ppm is downfield of

μ -CO at ca. 260 ppm, while the CO ligand (ca. 210 ppm) is downfield of CNMe (ca. 155 ppm) and CN (ca. 140 ppm).

The presence of 99% $^{13}\text{C}\text{N}$ or ^{13}CNR ligands in **5** and **[7]X** greatly enhances the intensities of their ^{13}C resonances, while the use of 99% C^{15}N and C^{15}NMe allows detection of the following ^{15}N resonances: *cis*- $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})(\text{C}^{15}\text{N})(\mu\text{-CO})(\mu\text{-CNMe}_2)]$ at 74.3 ppm, its *trans* isomer at 73.0, the α and β forms of *cis*- $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})(\text{C}^{15}\text{N})(\mu\text{-CO})(\mu\text{-CN}(\text{Me})\text{Et})]$ at 73.6 and 74.5, and *cis*- $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})(\text{C}^{15}\text{NMe})(\mu\text{-CO})(\mu\text{-CNMe}_2)]\text{[SO}_3\text{CF}_3]$ at 214.7. All were measured in CDCl_3 solution and chemical shifts are quoted as ppm downfield from CH_3NO_2 as an external standard. The $^{13}\text{C}\text{N}\text{C}^1\text{H}_3$ and $\text{C}^{15}\text{N}\text{C}^1\text{H}_3$ couplings are readily detected in the ^1H NMR spectra, both giving rise to doublets with coupling constants of 3.5 Hz.

The ^1H NMR spectra of all complexes are virtually independent of temperature. There is no evidence for *cis*–*trans* isomer exchange, μ –*t* ligand exchange or for rotation about the $\mu\text{-C}=\text{NR}_2$ bond.

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