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The reaction of [Fe$_2$(η-C$_5$H$_5$)$_2$(CO)(CNMe)(μ-CO)(μ-CNMe$_2$)]$^+$ and related salts with trifluoromethanesulphonic acid, HOSO$_2$CF$_3$: structure of *cis*-[Fe$_2$(η-C$_5$H$_5$)$_2$(CO)$_2$(μ-CNMe) (μ-CNMe$_2$)] [BPh$_4$]

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Abstract

[Fe$_2$(η-C$_5$H$_5$)$_2$(L)(CNMe)(μ-CO)(μ-CNMe$_2$)][SO$_3$CF$_3$] where L = CO reacts with HOSO$_2$CF$_3$ in chloroform solution at room temperature (r.t.) to give [Fe$_2$(η-C$_5$H$_5$)$_2$(CO)$_2${μ-CN(H)Me}(μ-CNMe$_2$)][SO$_3$CF$_3$]$_2$ (reaction (i)). This salt readily and reversibly loses a proton to form [Fe$_2$(η-C$_5$H$_5$)$_2$(CO)$_2$(μ-CNMe)(μ-CNMe$_2$)][SO$_3$CF$_3$] (reaction (ii)) which, in solution, slowly reverts to [Fe$_2$(η-C$_5$H$_5$)$_2$(CO)(CNMe)(μ-CO)(μ-CNMe$_2$)][SO$_3$CF$_3$] under the influence of UV radiation (reaction (iii)) although it can be trapped by reaction with RX (R = H or alkyl; X$^-$ = I$^-$ or [SO$_3$CF$_3$]$^-$) to give [Fe$_2$(η-C$_5$H$_5$)$_2$(CO)$_2${μ-CN(R)Me}(μ-CNMe$_2$)][SO$_3$CF$_3$]$_2$ (reaction (iv)). In reactions closely related to (i) and (iii), [Fe$_2$(η-C$_5$H$_5$)$_2$(L)(CN)(μ-CO)(μ-CNMe$_2$)] (L = CO or CNMe) is converted by HOSO$_2$CF$_3$ to [Fe$_2$(η-C$_5$H$_5$)$_2$(L)(CO)(μ-CNH$_2$)(μ-CNMe$_2$)][SO$_3$CF$_3$]$_2$ (reaction (v)); this is reversed by deprotonation and no intermediates are observed (reaction (vi)). The scope and limitations of these reactions have been investigated. Replacement of L by isocyanides shows that the ease with which *t*-CNR is converted to μ-CN(H)R (reactions (i) and (v)) decreases along the series CNR = CN$^-$/CNH ≫ CNXy′(Xy′ = C$_6$H$_3$Et$_2$-2,6) > CNMe > CNEt which reflects the μ-seeking ability of the CNR ligands and not their basicity. Reaction (i) does not take place with *cis* constrained complexes where the two cyclopentadienyl ligands are linked by a –CH$_2$C(O)-group, in donor solvents such as acetonitrile, or with weaker acids such as CF$_3$CO$_2$H or CH$_3$CO$_2$H. Reaction (iii) does not take place when L = CNMe or CNEt, or when μ-CNMe is replaced by μ-CNXy′ even when L = CO. Reaction (vi) always takes place; however, if L = CNMe either it or the *t*-CO may end-up in the μ-site but the latter is preferred. During reactions (i), (iii), (v) and (vi), *cis*↔*trans* isomerism may accompany ligand migration, but the *cis* is always the predominant product. Spectroscopic data is presented, assigned and used to distinguish between these isomers. Most is straight-forward, but the IR spectrum of [Fe$_2$(η-C$_5$H$_5$)$_2$(CO)$_2$(μ-CNXy′)(μ-CNMe$_2$)][SO$_3$CF$_3$] is very unusual as in solution its ν(μ-C-NXy′) absorption band has a very high frequency, > 1900 cm^{-1}, and is very broad, ca. 200 cm^{-1}. The structure of *cis*-[Fe$_2$(η-C$_5$H$_5$)$_2$(CO)$_2$(μ-CNMe)(μ-CNMe$_2$)][BPh$_4$] has been determined by X-ray crystallography. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Isocyanide; Cyclopentadienyl; Iron; Carbonyl

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1. Introduction

The reaction of [Fe$_2$(η-C$_5$H$_5$)$_2$(CO)$_2$(CNMe)$_2$] with MeOSO$_2$CF$_3$ gives a mixture of [Fe$_2$(η-C$_5$H$_5$)$_2$(CO)(CNMe)(μ-CO)(μ-CNMe$_2$)][SO$_3$CF$_3$], [**7**][SO$_3$CF$_3$] and [Fe$_2$(η-C$_5$H$_5$)$_2$(CO)$_2$(μ-CNMe$_2$)$_2$][SO$_3$-CF$_3$]$_2$, [**14**]-[SO$_3$CF$_3$]$_2$ [1]. However, [**7**][SO$_3$CF$_3$] cannot be converted to [**14**][SO$_3$CF$_3$]$_2$ even by dissolution in neat MeOSO$_2$CF$_3$. Consequently, it was very surprising when, during a workup of one of these reaction mixtures, we obtained the previously unknown [Fe$_2$(η-

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$C_5H_5)_2(CO)_2\{\mu\text{-}CN(H)Me\}(\mu\text{-}CNMe_2)][SO_3CF_3]_2$, [**34**]-$[SO_3CF_3]_2$. It was ascertained that this was the product of the reaction of [**7**]$[SO_3CF_3]$ with $HOSO_2CF_3$, the presence of which was fortuitous. It arose because the reaction had been carried out in chloroform using an old sample of $MeOSO_2CF_3$ which had partially hydrolysed to $HOSO_2CF_3$. This did not hinder the methylation of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2\text{-}(CNMe)_2]$, but promoted the subsequent migration/protonation reaction.

A detailed study of this and related reactions has been carried out and is described herein. A preliminary report has appeared [2].

2. Experimental

The following compounds were prepared by methods described elsewhere: [**4**]$[SO_3CF_3]$ [1], [**5**], [**6**]$[SO_3CF_3]$, [**7**]$[SO_3CF_3]$, [**8**]$[SO_3CF_3]$, [**9**]**I**, [**10**], [**11**]$[SO_3CF_3]$ and [**12**]**I** [3]. Other chemicals were purchased.

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

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. These tables are restricted to complexes containing the μ-$CNMe_2^+$ ligand. Others were prepared and characterised fully, but are not directly relevant to the main arguments and are not included so as to keep the tables to a manageable size.

2.1. The reaction of $HOSO_2CF_3$ with [7][SO_3CF_3] and related compounds (reaction (i))

A solution of [**7**]$[SO_3CF_3]$ (2 mmol) and $HOSO_2CF_3$ (10 mmol) in dry chloroform (50 cm^3) was stirred at r.t. for 1 h. The solvent was removed at reduced pressure, and the residue dissolved in a minimum of an ethanol–ether mixture. Cooling this overnight gave a 2.5:1 mixture of orange *cis* and purple *trans*-[**34**]$[SO_3CF_3]_2$ in a total yield of 85%. The two isomers could be separated by fractional crystallization to give each in > 95% purity in this particular instance, but this was not always possible.

The same procedure was used for the reactions of $HOSO_3CF_3$ with analogues of [**7**]$[SO_3CF_3]$ in which CNMe had been replaced by $^{13}CNMe$, $C^{15}NMe$, CNEt ([**8**]$[SO_3CF_3]$), $CNBu^t$, $CNXy'$([**9**]**I**) ($Xy' = 2,6\text{-}Et_2C_6H_3$ throughout this paper) and CNH ([**6**]$[SO_3CF_3]$), and $CNMe_2^+$ by $CN(Me)Et^+$ and $CNEt_2^+$. Some cases a mixture of *cis* and *trans* isomers were formed but could not always be separated even though they could be identified by ^1H-NMR spectroscopy. In other instances the *cis* isomer was the sole product, e.g. *cis*-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2\{\mu\text{-}CN(H)Bu^t\}(\mu\text{-}CNMe_2)][SO_3CF_3]_2$ only was obtained from the reaction of $[Fe_2(\eta\text{-}C_5H_5)_2(CNBu^t)(CO)(\mu\text{-}CO)(\mu\text{-}CNMe_2)][SO_3CF_3]$.

The same procedure was also used in the reaction of $HOSO_2CF_3$ with $[Fe_2(\eta\text{-}C_5H_5)_2(CNBu^t)_2(\mu\text{-}CO)(\mu\text{-}CNMe_2)][SO_3CF_3]$. However, the product was recrystallised from acetonitrile solution to give the green acetonitrile derivative $[Fe_2(\eta\text{-}C_5H_5)_2(NCMe)(CNBu^t)\text{-}\{\mu\text{-}CN(H)Bu^t\}(\mu\text{-}CNMe_2)][SO_3CF_3]_2$ in 58% yield.

Table 1
Analyses of the various compounds described in the text

CNR/L[a]	$[X]^-$	Analyses[b]		
		%C	%H	%N
$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CNR)(\mu\text{-}CNMe_2)]X$				
CNMe/–	$[SO_3CF_3]^-$	39.6 (39.7)	3.3 (3.5)	5.3 (5.2)
CNMe/–	$[BPh_4]^-$	68.7 (68.9)	5.5 (5.5)	3.7 (3.9)
CNMe/–	$[Cl]^- \cdot 0.5H_2O$	46.6 (46.4)	4.6 (4 6)	6.4 (6 4)
CNMe/–	Br^-	43.1 (43.0)	4.1 (4.0)	5.8 (5.9)
CNMe/–	I^-	39.2 (39.1)	3.7 (3.6)	5.2 (5.4)
$^{13}CNMe$/–	$[SO_3CF_3]^-$	39.9 (39.8)	3.4 (3.5)	4.8 (5.1)
$C^{15}NMe$/–	$[SO_3CF_3]^-$	39.9 (39.6)	3.4 (3.5)	5.1 (5.3)
CNEt/–	$[SO_3CF_3]^-$	40.7 (40.9)	3.8 (3.8)	4.8 (5.0)
CNXy′/–	$[SO_3CF_3]^-$	49.1 (48.9)	4.5 (4.4)	4.2 (4.2)
CNXy′/–	$[BPh_4]^-$	71.8 (72.1)	5.8 (5.9)	3.3 (3.4)
$[Fe_2(\eta\text{-}C_5H_5)_2(L)(CNMe)(\mu\text{-}CNR)(\mu\text{-}CNMe_2)]X$				
CNMe/CO	$[SO_3CF_3]^-$	40.6 (40.9)	4.0 (4.0)	7.3 (7.5)
CNXy′/CO	$[BPh_4]^-$	72.4 (72.4)	6.0 (6.2)	4.7 (5.0)
CNMe/I^-		37.8 (37.5)	4.0 (4.1)	7.3 (7.5)
$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2\{\mu\text{-}CN(H)R\}(\mu\text{-}CNMe_2)]X_2$				
CNH/–	$[SO3CF_3]^- \cdot 0.5H_2O$	31.1 (31.0)	2.7 (2.9)	4.0 (4.0)
^{13}CNH/–	$[SO_3CF_3]^-$	32.2 (31.9)	2.6 (2.6)	3.9 (4.1)
$C^{15}NH$/–	$[SO_3CF_3]^-$	31.6 (31.7)	2.7 (2.6)	3.9 (4.3)
CNH[c]/–	$[SO_3CF_3]^-$	33.2 (32.9)	3.0 (2.9)	3.9 (4.0)
^{13}CNH[c]/–	$[SO_3CF_3]^-$	32.9 (33.0)	2.9 (2.9)	3.9 (4.0)
CNH[d]/–	$[SO_3CF_3]^-$	34.3 (33.9)	3.2 (3.1)	3.7 (4.0)
CNMe/–	$[SO_3CF_3]^-$	32.8 (32.9)	3.0 (2.9)	3.9 (4.0)
$^{13}CNMe$/–	$[SO_3CF_3]^-$	32.9 (33.0)	3.3 (2.9)	3.9 (4.0)
$C^{15}NMe$/–	$[SO_3CF_3]^- \cdot 0.75H_2O$	31.6 (31.6)	3.0 (3.2)	3.5 (4.0)
CNEt/–	$[SO_3CF_3]^-$	34.2 (33.9)	3.5 (3.1)	3.8 (4.0)
$CNBu^t$/–	$[SO_3CF_3]^- \cdot 0.25CHCl_3$	33.2 (33.9)	3.3 (3.3)	3.4 (3.5)
CNXy′/–	$[SO_3CF_3]^-$	41.5 (41.4)	3.9 (3.7)	3.2 (3.5)
$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2\{\mu\text{-}CN(Me)R\}(\mu\text{-}CNMe_2)]X_2$				
CNEt/–	$[SO_3CF_3]^- \cdot 0.5CHCl_3$	31.7 (31.4)	3.0 (3.0)	3.4 (3.3)

[a] $Xy' = 2,6\text{-}(Et)_2C_6H_3$.
[b] Found (calculated).
[c] μ-$CNMe_2$ replaced by μ-CN(Et)Me.
[d] μ-$CNMe_2$ replaced by μ-$CNEt_2$.

Table 2
IR spectra of the complexes described in the text in the 1580–2200 cm^{-1} and ν(N–H) regions

Compound[a] CNR/L	Absorption bands[b]				
[Fe$_2$(η-C$_5$H$_5$)$_2$(CO)$_2$(μ-CNR)(μ-CNMe$_2$)][SO$_3$CF$_3$]					
CNMe/– (*cis*)	2013(10)	1981(3.0)	1786(1.8)	1600(2.2)	
CNMe/– (*trans*)		1985(10)	1806(1.5)	1588(1.8)	
^{13}CNMe/– (*cis*)	2012(10)	1980(2.3)	1752(1.6)	1598(1.8)	
C^{15}NMe/– (*cis*)	2013(10)	1981(2.4)	1760(1.8)	1599(2.0)	
C^{15}NMe/– (*trans*)		1985(10)	1790(2.0)	1587(1.9)	
CNEt/– (*cis*)	2012(10)	1980(2.3)	1795(1.7)	1598(2.2)	
CNXy′/– (*cis*)[c]	2017(10)	1984(1.6)	1864(1.4, br)	1582(2.9)	
CNXy′/– (*cis*)[c,d]	1996(10)	1961(4.6)	1777(4.1)	1584(4.7)	
[Fe$_2$(η-C$_5$H$_5$)$_2$(L)(CNMe)(μ-CNR)(μ-CNMe$_2$)][SO$_3$CF$_3$]					
CNMe/CO	2176(9.0)	1979(10)	1763(5.9)	1584(5.2)	
CNXy′/CO[c,d]	2178(6.4)	1962(10)	1789(6.7)	1578(7.2)	
CNMe/I$^-$[e]	2151(8.3)		1765(10)	1564(4.2) 1539(4.2)	
CNMe/Br$^-$[e]	2153(5.6)		1767(10)	1570(5.7) 1534(3.8)	
CNMe/Cl$^-$[e]	2156(9.6)		1769(10)	1574(4.6) 1547(5.0)	
[Fe$_2$(η-C$_5$H$_5$)$_2$(CO)(L){μ-CN(H)R}(μ-CNMe$_2$)][SO$_3$CF$_3$]$_2$					
CNH/CO (*cis*)[d]	2058(10)	2030(5.0)		1614(3.4)	3110(2.2) 3021(1.8)
CNH/CO (*trans*)[d]		2023(10)		1611(5.9)	3117(2.4) 2951(2.8)
^{13}CNH/CO (*cis*)[d]	2057(10)	2030(5.3)		1616(3.2) 1597(2.6)	3110(2.3) 3009(1.9)
^{13}CNH/CO (*trans*)[d]		2022(10)		1611(5.1)	3117(2.7) 2916(2.9)
C^{15}NH/CO (*cis*)[d]	2056(10)	2030(5.1)		1615(3.4)	3115(3.3) 3007(2.7)
CNH/CO (*cis*)[d,f]	2055(10)	2027(6.9)		1601(4.9)	3111(3.0) 3008(2.4)
CNH/CO (*trans*)[d,f]		2022(10)		1625(3.0) 1598(5.4)	3115(2.9) 2916(3.1)
^{13}CNH/CO (*cis*)[d,f]	2054(10)	2027(6.9)		1599(4.4)	3115(2.7) 3015(2.2)
CNH/CO (*cis*)[d,g]	2059(10)	2029(6.8)		1627(2.7) 1588(5.4)	
CNH/CO (*trans*)[d,g]		2027(10)		1631(2.3) 1588(4.7)	3114(3.1) 2995(2.5)
CNH/CNMe[d]	2215(5.5)	2010(10)		1600(5.3)	3122(5.9)
CNMe/CO (*cis*)[d]	2048(10)	2023(6.6)		1620(6.5)	
CNMe/CO (*cis*)[h]	2051(8.2)	2014(10) 1981(2.4)	1796(1.6)	1616(3.1) 1599(2.1)	
CNMe/CO (*trans*)[d]		2028(10)		1615(6.8)	
^{13}CNMe/CO (*cis*)[d]	2048(10)	2023(6.1)		1625(2.5) 1603(5.0)	
C^{15}Nme/CO (*cis*)[d]	2048(10)	2023(6.9)		1625(2.6) 1604(5.9)	
C^{15}Nme/CO (*trans*)[d]		2027(10)		1625(2.6) 1602(3.9)	
CNEt/CO (*cis*)[d]	2054(10)	2027(5.2)		1610(5.1)	
CNBu^t/(*cis*)[d]	2046(10)	2023(6.4)		1614(3.6)	
CNXy′/CO (*cis*)[d]	2040(10)	2022(7.1)		1625(2.9) 1594(1 5)	
CNXy′/CO (*cis*)[i]	2049(5.3)	2014(10) 1981(2.4)	1794(2.1)	1616(3.1) 1597(2.3)	
[Fe$_2$(η-C$_5$H$_5$)$_2$(CO)$_2${μ-CN(Me)R}(μ-CNMe$_2$)][SO3CF$_3$]$_2$					
CNEt/CO (*cis*)[d]	2054(10)	2029(6.1)		1601(6.9)	

[a] Isomer in parentheses where known. Xy′, 2,6-(Et)$_2$C$_6$H$_3$.

[b] Peak positions with relative peak heights in parentheses. Absorption bands due to ν(CNR) (2150–2180 cm^{-1}), ν(CO) (1960–2060 cm^{-1}), ν(μ-CNR) (1750–1870 cm^{-1}), ν(μ-C=NR$_2$)(1530–1635 cm^{-1}), and ν(N–H) (2910–3120 cm^{-1}) vibrations. Spectra run in dichloromethane solution unless it is stated otherwise.

[c] [BPh$_4$]$^-$ salt.

[d] Spectra run on solid samples (KBr disc).

[e] Not a salt. It does not contain [SO$_3$CF$_3$]$^-$ anion.

[f] μ-CNMe$_2$ ligand replaced by μ-CN(Et)Me.

[g] μ-CNMe$_2$ ligand replaced by μ-CNEt$_2$.

[h] Spectra run in methanol solution.

[i] Spectra run in ethanol solution.

Table 3
^{1}H-NMR spectra of the compounds described in the text

CNR; L; isomer; solvent[a]	Resonances[b]			
	C_5H_5	μ-$CNMe_2$	μ-CNR	*t*-CNR or NH
$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CNR)(\mu\text{-}CNMe_2)][SO_3CF_3]$				
CNMe; –; *cis*; A	5.25(10)	4.22(6)	3.22(3)	
CNMe; –; *trans*; A	5.09(10)	4.36(6)	3.88(3)	
^{13}CNMe; –; *cis*; B	5.48(10)	4.28(6)	3.78(3,d, $J = 7.0$)	
^{13}CNMe; –; *trans*; B	5.32(10)	4.40(6)	3.97(3,d, $J = 7.0$)	
C^{15}NMe; –; *cis*; B	5.48(10)	4.29(6)	3.78(3,d, $J = 1.4$)	
C^{15}NMe; –; *trans*; B	5.31(10)	4.41(6)	3.96(3,d, $J = 1.40$)	
CNEt;–;*cis*;A	5.26(10)	4.21(6)	3.95(2,q), 1.42(3,t, $J = 7.3$)	
CNXy′;–; *cis*; C[c]	5.20(10)	4.12(6)	2.77(4,q), 1.27(6,t, $J = 7.5$)	
CNXy′;–; *trans*; C[c]	5.03(10)	4.38(6)	2.90(4,q), 1.39(6,t, $J = 7.5$)	
$[Fe_2(\eta\text{-}C_5H_5)_2(L)(CNMe)(\mu\text{-}CNR)(\mu\text{-}CNMe_2)][SO_3CF_3]$				
CNMe; CO; –; C	4.92(5)	4.03(3)	3.67(3)	2.99(3)
	5.07(5)	4.08(3)		
^{13}CNMe; CO; –;C	4.92(5)	4.03(3)	3.67(3,d, $J = 7.15$)	2.99(3)
	5.07(5)	4.08(3)		
CNXy′; CO; –; C[c]	4.92(5)	4.07(3)	2.77(4,q)	3.04(3)
	4.99(5)	4.12(3)	1.27(6, t, $J = 7.5$)	
			7.21(m)	
CNMe; CNMe; –; C	4.78(10)	4.06(6)	3.67(3)	
^{13}CNMe; CNMe/ –; C	4.78(10)	4.06(6)	3.67(3,d, $J = 7.15$)	
CNMe; I^-; –; C[d]	4.62(5)	4.23(3)		2.94(3)
	4.70(5)	4.53(3)		
$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(L)\{\mu\text{-}CN(H)R\}(\mu\text{-}CNMe_2)][SO_3CF_3]_2$				
CNH; CO; *cis*; C	5.61(10)	4.11(6)		12.05(2,br)
CNH; CO; *trans*; C	5.54(10)	4.23(6)		12.05(2,br)
CNH; CO; *cis*; B e	5.98(10)	4.42(6)		
CNH; CO; *trans*; B e	5.89(10)	4.54(6)		
CNH; CO; *cis*; C[e,f]	5.62(5)	4.08(3)		12.07(2,br)
	5.65(5)	4.44(2, m)		
		1.59(3,t, $J = 7.3$)		
CNH; CO; *trans*; C[e,f]	5.53(5)	4.22(3)		12.07(2,br)
	5.55(5)	4.62(2,m)		
		1.64(3,t, $J = 7.3$)		
CNH; CO; *cis*; C[g]	5.62(10)	4.47(4,m)		12.1(2,br)
		1.56(6,t, $J = 7.3$)		
CNH; CO; *trans*; C[g]	5.52(10)	4.64(4,m)		12.1(2,br)
		1.59(6,t, $J = 7.3$)		
CNH; CNMe; *cis*; C	5.27(5)	4.20(3)	3.10(3)	11.6(1,br)
	5.38(5)	4.24(3)		11.9(1,br)
CNH; CNMe; *trans*; C	5.32(5)	4.07(3)	3.08(3)	11.6(1,br)
	5.43(5)	4.11(3)		11.9(1,br)
CNMe; CO; *cis*; C	5.65(10)	4.12(6)	3.89(3)	12.3(1,br)
CNMe; CO; *cis*; C[h]	5.59(5)	4.11(6)	3.88(3,d, $J = 5.1$)	11.7(1,br)
	5.64(5)			
CNMe; CO; *trans*; C	5.57(10)	4.24(6)	4.06(3)	12.3(1,br)
CNMe; CO; *cis*; D	5.49(10)	4.19(6)	3.83(3)	
CNMe; CO; *trans*; D	5.21(10)	4.27(6)	3.93(3)	
CNMe; CO; *cis*; B	6.01(10)	4.41(6)	4.11(3)	
CNMe; CO; *trans*; B	5.88(10)	4.54(6)	4.26(3)	
^{13}CNMe; CO; *cis*; C	5.64(10)	4.12(6)	3.89(3,d, $J_{CH} = 5.3$)	12.3(1,br)
^{13}CNMe; CO; *cis*; C[h]	5.64(5)	4.11(6)	3.88(3,t, $J_{CH} = 5.1$, $J_{HH} = 5.1$)	11.68(1,br)
	5.59(5)			
^{13}CNMe; CO; *trans*; C	5.57(10)	4.24(6)	4.05(3,d, $J = 5.3$)	12.3(1,br)
C^{15}NMe; CO; *cis*; C	5.66(10)	4.12(6)	3.89(3,d, $J = 1.5$)	12.3(1,br)
C^{15}NMe; CO; *cis*; C[h]	5.64(5)	4.11(6)	3.88(3,dd, $J_{NH} = 1.84$, $J_{HH} = 4.9$)	11.68(1,br,d, $J_{NH} = 91.7$)
	5.59(5)			
C^{15}NMe; CO; *trans*; B	5.88(10)	4.54(6)	4.26(3,d, $J = 1.5$)	
CNEt; CO; *cis*; C	5.64(10)	4.11(6)	4.39(2,m,br)	12.3(1,br)
			1.53(3,t, $J = 7.3$)	

Table 3 (Continued)

CNR; L; isomer; solvent^a	Resonances^b			
	C_5H_5	μ-$CNMe_2$	μ-CNR	*t*-CNR or NH
CNEt; CO; *cis*; C^h	5.60(5) 5.63(5)	4.11(6)	4.39(1,m,br) 1.53(3,t, *J* = 7.3)	11.65(1,br)
CNEt; CO; *trans*; C	5.69(10)	4.07(6)	4.07(2,m,br) 1.59(3,t, *J* = 7.3)	12.3(1,br)
CNBu^t; CO; *cis*; A	5.66(10)	4.11(6)	1.70(9)	
CNBu^t; CO; *cis*; A^h	5.62(5) 5.66(5)	4.10(3) 4.11(3)	1.70(9)	
CNXy′; CO; *cis*; C^{c,h}	5.23(5) 5.74(5)	4.13(3) 4.15(3)	2.28(2,m) 2.95(2,m) 1.10(3,t, *J* = 7.51) 7.5(3,m)	11.70(1,br)
$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2\{\mu\text{-}CN(Me)R\}(\mu\text{-}CNMe_2)][SO_3CF_3]_2$				
CNEt; CO; *cis*; C	5.69(5) 5.70(5)	4.10(3) 4.11(3) 4.07(3) 4.45(2,m) 1.56(3,t, *J* = 7.3)		

[a] Isomer when known; solvent, A, $CDCl_3$; B. $(CD_3)_2CO$; C, CD_3CN; and D, CD_3OD.·Xy′, 2,6-$(Et)_2C_6H_3$.

[b] Chemical shifts δ measured as ppm downfield from Me_4Si as an internal standard with relative integrations in parentheses. Resonances are singlets unless it is stated otherwise (d = doublet, dd = double doublet, t = triplet, m = multiplet, br = broad) with coupling constants *J* in Hz. N*H* resonances are those at ca. 12 ppm.

[c] Anion is $[BPh_4]$.

[d] This does not contain an anion. I^- is coordinated.

[e] μ-$^{13}CNH_2$ and μ-$C^{15}NH_2$ complexes have identical spectra.

[f] μ-$CNMe_2$ replaced by μ-CN(Me)Et.

[g] μ-$CNMe_2$ replaced by μ-$CNEt_2$.

[h] $HOSO_2CF_3$ added to NMR tube.

$[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)(CNE^t)(\mu\text{-}CO)(\mu\text{-}CNMe_2)][SO_3CF_3]$, [**11**][$SO_3CF_3$], gave two products which were identified by spectroscopy as $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNMe)\{\mu\text{-}CN(H)Et\}(\mu\text{-}CNMe_2)][SO_3CF_3]_2$, [**36**][$SO_3CF_3$]$_2$, and $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNEt)\{\mu\text{-}CN(H)Me\}(\mu\text{-}CNMe_2)][SO_3CF_3]_2$, [**37**][$SO_3CF_3$]$_2$, in the ratio of 40:60, These could not be separated by fractional crystallization and when they were eluted down an alumina column with acetone they gave a 40:60 mixture of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNMe)(\mu\text{-}CNEt)(\mu\text{-}CNMe_2)][SO_3CF_3]$, [**27**][$SO_3CF_3$], and $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNEt)(\mu\text{-}CNMe)(\mu\text{-}CNMe_2)][SO_3CF_3]$, [**28**][$SO_3CF_3$], which could be identified by spectroscopy but not separated. A similar work-up of the product from the reaction of $[Fe_2(\eta\text{-}C_5H_5)_2(CNxy')(CNMe)(\mu\text{-}CO)(\mu\text{-}CNMe_2)][SO_3CF_3]$, [**12**][$SO_3CF_3$], with $HOSO_2CF_3$ followed by anion exchange with Na[BPh_4] in dichloromethane solution and recrystallization from ethanol–ether mixtures gave $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNMe)(\mu\text{-}CNXy')(\mu\text{-}CNMe_2)][BPh_4]$, [**29**][$BPh_4$], in 90% yield. The ^{1}H-NMR spectrum of this showed that it contained traces (< 5%) of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNXy')(\mu\text{-}CNMe)(\mu\text{-}CNMe_2)][BPh_4]$.

In a related reaction, the addition of $HOSO_2CF_3$ to a solution of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CNMe_2)][SO_3CF_3]$ [**4**][SO_3CF_3], precipitated a deep red oil, but all attempts to identify this failed as it reverted instantaneously to [**4**][SO_3CF_3] on work-up.

The reaction does not take place if (a) chloroform is replaced by a more donating solvent such as acetonitrile, (b) if neat $HOSO_2CF_3$ is replaced by weaker acids such as neat CF_3CO_2H or CH_3CO_2H, 48% aqueous HBF_4 or 60% aqueous HPF_6 (strong mineral acids such as H_2SO_4, HNO_3 or $HClO_4$ were not investigated), or (c) if the two cyclopentadienyl rings in [**7**][SO_3CF_3] are linked by a –$CH_2C(O)$– bridge which constrains the molecule to a *cis* configuration.

2.2. Deprotonation of [34][SO_3CF_3]$_2$ and related salts (reaction (ii))

A solution of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2\{\mu\text{-}CN(H)Me\}(\mu\text{-}CNMe_2)][SO_3CF_3]_2$, [**34**][$SO_3CF_3$]$_2$, in acetone was passed down a chromatography column packed with basic alumina (Merck 1097 activity II-III). Removal of the solvent at reduced pressure and recrystallization of the residue from ethanol–ether mixtures gave $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\eta\text{-}CNMe)(\mu\text{-}CNMe_2)][SO_3CF_3]$, [**23**][$SO_3CF_3$] in > 90% yields.

This general procedure was extended to the preparation of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CNXy')(\mu\text{-}CNMe_2)][SO_3CF_3]$, [**25**][$SO_3CF_3$], $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CNEt)$-

$(\mu\text{-CNMe}_2)][SO_3CF_3]$, **[24]**$[SO_3CF_3]$, $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNMe)(\mu\text{-CNXy}')(\mu\text{-CNMe}_2)][SO_3CF_3]$, **[29]**$[SO_3CF_3]$ (see above), and an inseparable mixture of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNMe)(\mu\text{-CNEt})(\mu\text{-CNMe}_2)][SO_3CF_3]$ **[27]**$[SO_3CF_3]$, and $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNEt)(\mu\text{-CNMe})(\mu\text{-CNMe}_2)][SO_3CF_3]$, **[28]**$[SO_3CF_3]$ (see above).

In some instances anion exchange was effected by the addition of $KX(X^- = Cl^-$, Br^- or I^-; 5 mmol) to a solution of, for example, *cis*-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-CNMe})(\mu\text{-CNMe}_2)][SO_3CF_3]$ **[23]**$[SO_3CF_3]$ (1 mmol) in methanol (50 cm^3). After 10 min the solvent was removed from the mixture at reduced pressure, and the residue extracted into dichloromethane. This solution was dried over magnesium sulphate, and then evaporated to dryness. Recrystallization of the residue from ethanol–ether mixtures gave the various *cis*-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-CNMe})(\mu\text{-CNMe}_2)]X$ salts in 90% yields.

2.3. Bridging to terminal migration of CNMe ligand of ***[23]****$[SO_3CF_3]$ and related compounds (reaction (iii))*

A stirred solution of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-CNMe*})(\mu\text{-CNMe}_2)]X$, **[23]**X, (0.37 mmol) in dichloromethane (50 cm^3) was irradiated with a Philips HPR 125 W lamp, and the reaction monitored using IR spectroscopy. When it was complete, the solvent was removed from the mixture at reduced pressure and the product recrystallized from ethanol–ether mixtures. There was no reaction in the dark, a slow reaction in daylight (ca. 1 day), and a very slow reaction (weeks) in the solid state in daylight.

After 20 min irradiation *cis*-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-CNMe*})(\mu\text{-CNMe}_2)]X$, **[23]**X, ($X^- = [SO_3CF_3]^-$ or $[BPh_4]^-$; CNMe* = ^{12}CNMe or ^{13}CNMe) gave *cis*-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNMe)(\mu\text{-CO})(\mu\text{-CNMe}_2)]X$, **[7]**X, in 90% yields. In contrast, *trans*-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-CNMe})(\mu\text{-CNMe}_2)]X$ gave a 60:40 mixture of *cis* and *trans*-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNMe*)(\mu\text{-CO})(\mu\text{-CNMe}_2)]X$ in 85% total yield.

If the irradiation of *cis*-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-CNMe})(\mu\text{-CNMe}_2)][SO_3CF_3]$ (CNMe* = ^{12}CNMe or ^{13}CNMe) is carried out in the presence of CNMe (18.0 mmol), a mixture of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNMe)(\mu\text{-CNMe})(\mu\text{-CNMe}_2)][SO_3CF_3]$, **[13]**$[SO_3CF_3]$, and $[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)_2(\mu\text{-CNMe})(\mu\text{-CNMe}_2)][SO_3CF_3]$, **[30]**$[SO_3CF_3]$, were obtained. They were separated by chromatography (total yield = 90%). Irradiation for 45 min gave $[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)_2(\mu\text{-CNMe*})(\mu\text{-CNMe}_2)][SO_3CF_3]$ as the major product (yield 90%) but it contained traces (< 5%) of $[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)(CNMe*)(\mu\text{-CNMe})(\mu\text{-CNMe}_2)][SO_3CF_3]$. When CNMe* = ^{13}CNMe the reactions were carried out on 1/10 scale and the products identified by spectroscopy only.

There was no reaction on the photolysis of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNMe)(\mu\text{-CNMe})(\mu\text{-CNMe}_2)][SO_3CF_3]$, **[13]**$[SO_3CF_3]$, in the absence of CNMe even after 2 h. Continued photolysis in the presence of CNMe (18 mmol) gave $[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)_2(\mu\text{-CNMe})(\mu\text{-CNMe}_2)][SO_3CF_3]$, **[30]**$[SO_3CF_3]$.

Table 4
^{13}C-NMR spectra of the compounds described in the text

CNR; L; isomer; solvent[a]	Resonances[b]						
	C_5H_5	μ-CN*Me*$_2$	μ-CN*R*/μ-CN(H)*R*	*t*-*C*NR	*t*-*C*O	μ-*C*NR/μ-*C*N(H)R	μ-*C*NMe$_2$
$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-CNR})(\mu\text{-CNMe}_2)][SO_3CF_3]$							
CNMe; –; *cis*; A	88.9	53.9	44.3		208.9	226.7	318.8
^{13}CNMe; –; *cis*; B	89.9	54.4	44.7 (d, *J* = 5.1)		210.6	226.1	320.1
C^{15}NMe; –; *cis*; C	89.9	54.4	44.8(br)		210.6	225.7 (d, *J* = 10.2)	319.9
$[Fe_2(\eta\text{-}C_5H_5)_2(L)(CNMe)(\mu\text{-CNR})(\mu\text{-CNMe}_2)][SO_3CF_3]$							
CNMe; CO; –; C	87.9 88.4	53.2 53.6	45.1	31.1	212.6	238.0	325.6
$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(L)\{\mu\text{-CN(H)R}\}(\mu\text{-CNMe}_2)][SO_3CF_3]_2$							
CNH; CO; *cis*; C	93.6	55.8			205.1	318.8	309.0
^{13}CNH; CO; *cis*; C	93.5	55.8			205.4 (d, *J* = 6.9)	319.0	309.3
CNH; CNMe; *cis*; C	93.2	54.5		31.1	206.9	327.6	319.8
	93.8	54.6					
CNMe; CO; *cis*; B	93.4	55.5	45.4		206.1		309.5
CNMe; CO; *trans*; B	98.5	55.5	46.1		205.1		315.0
^{13}CNMe; CO; *cis*; C	93.1	55.7	45.8(br)		205.6 (d, *J* = 6.8)		309.5
C^{15}NMe; CO; *cis*; C	93.2	55.7	45.8 (d, *J* = 7.2)		205.4	309.3 (d, *J* = 6.8)	309.1

[a] Isomer when known; solvent A, $CDCl_3$; B, $(CD_3)_2CO$; C, CD_3CN; and D, CD_3OD.

[b] Chemical shifts δ measured as ppm downfield from Me_4Si as an internal standard. Resonances are singlets unless it is stated otherwise (d = doublet, br = broad) with coupling constants *J* in Hz.

Irradiation of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-CNMe})(\mu\text{-CNMe}_2)]X$ ($X^- = I^-$) gave an unisolable product which on further photolysis was largely converted to isolable $[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)(I)(\mu\text{-CO})(\mu\text{-CNMe}_2)]$, [**31**], after 3 h (brown crystals; yield 60%). Similar behaviour was observed when $X^- = Cl^-$ or Br^-, but the reaction times were longer, 4.5 and 6 h. respectively, and the final products too unstable to be isolated. If the irradiation of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-CNMe})(\mu\text{-CNMe}_2)]I$ is carried out in the presence of CNMe (18 mmol), the sole detectable product contained the $[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)_2(\mu\text{-CNMe})(\mu\text{-CNMe}_2)]^+$ cation, but it was not isolated.

Neither $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-CNXy}')(\mu\text{-CNMe}_2)]I$, [**25**]**I**, nor $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNMe)(\mu\text{-CNXy})(\mu\text{-CNMe}_2)][SO_3CF_3]$, [**29**][$SO_3CF_3$], were affected even after extended irradiation (>6 h), and these salts could be isolated in yields of >90% from their reaction mixtures.

2.4. The reaction of [23][SO_3CF_3] and related compounds with protic and alkyl electrophiles (reaction (iv))

A solution of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-CNMe})(\mu\text{-CNMe}_2)][SO_3CF_3]$, [**23**][$SO_3CF_3$], (1 mmol) and MeI (50 mmol) in dry chloroform was stirred overnight. Orange crystals of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-CNMe}_2)_2][I][SO_3CF_3]$ [**14**][I][SO_3CF_3], precipitated. They were filtered off, washed with cold chloroform–ether mixtures and dried (yield 40%).

If MeI is replaced by $ROSO_2CF_3$($R = H$, Me or Et) the reaction is complete within 3 h. giving orange crystals of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2\{\mu\text{-CN(R)Me}\}(\mu\text{-CNMe}_2)][SO_3CF_3]_2$ in 90% yield. By a judicious choice of substrate and reagents it is possible to prepare a wide range of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2\{\mu\text{-CN(R)R}'\}\{\mu\text{-CN(R}'')\text{-R}'''\}][SO_3CF_3]_2$ salts but not all would crystallize.

2.5. The reaction of $HOSO_2CF_3$ with [5] and related compounds (reaction (v))

A solution of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CN^*)\mu\text{-CO})(\mu\text{-CNMe}_2)]$, [**5**], (2 mmol; $CN^* = {}^{12}C^{14}N$, ${}^{13}C^{14}N$ or ${}^{12}C^{15}N$) and $HOSO_2CF_3$ (3 mmol) in chloroform (50 cm^3) was stirred at r.t. for 1 h. The solvent was removed at reduced pressure, and the residue recrystallized from an ethanol–ether mixture to give solid $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-CNH}_2)(\mu\text{-CNMe}_2)][SO_3CF_3]_2$, [**32**][$SO_3CF_3$]$_2$, in 85% yield. This could be separated by fractional crystallization into orange crystals of the *cis* isomer as the major product, and the dark purple crystals of the less abundant *trans* isomer.

The same procedure may be used to prepare other $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-CNH}_2)\{\mu\text{-CN(R}')R)][SO_3CF_3]_2$ salts where (R′)R = (Me)Et or Et_2.

Under the same conditions, $[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)(CN)(\mu\text{-CO})(\mu\text{-CNMe}_2)]$, [**10**], gives green crystals of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNMe)(\mu\text{-CNH}_2)(\mu\text{-CNMe}_2)][SO_3CF_3]_2$, [**33**][$SO_3CF_3$]$_2$, in 50% yield. Spectroscopy showed that this was a 10:1 mixture of two isomers which could not be separated.

2.6. Deprotonation of [32][SO_3CF_3]$_2$ and [33][SO_3CF_3]$_2$ (reaction (vi))

When a solution of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-CNH}_2^*)(\mu\text{-CNMe}_2)][SO_3CF_3]_2$, [**32**][$SO_3CF_3$]$_2$, in acetone is chro-

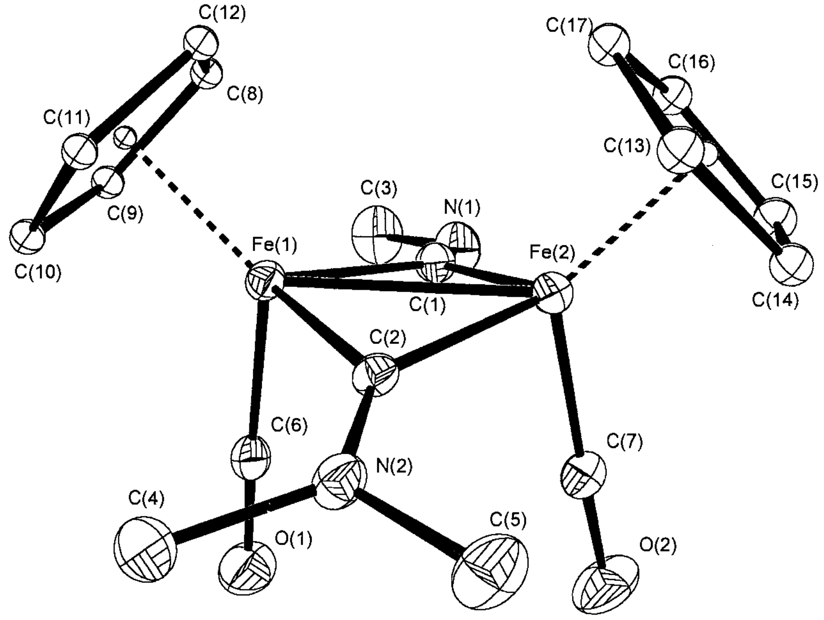


Fig. 1. Structure and atom labelling for the $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-CNMe})(\mu\text{-CNMe}_2)]^+$ cation, [**23**]$^+$.

Table 5
Crystal data and structure refinement for *cis*-[Fe_2(η-C_5H_5)$_2$(CO)$_2$(μ-CNMe)(μ-$CNMe_2$)][BPh_4]

Empirical formula	$C_{41}H_{39}BFe_2N_2O_2$
Formula weight	714.25
Temperature (K)	293(2)
Wavelength (Å)	0.70930
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	
a (Å)	13.8960(10)
b (Å)	17.853(4)
c (Å)	14.116(3)
β (°)	94.06(2)
V (Å^3)	3493.2(11)
Z	4
$D_{\text{calc.}}$ (g cm^{-3})	1.358
Absorption coefficient (mm^{-1})	0.869
F(000)	1488
Crystal size (mm)	0.40 × 0.35 × 0.25
Theta range for data collection (°)	2.13–27.91
Index ranges	$-8 \leq h \leq 15$, $0 \leq k \leq 19$, $-16 \leq l \leq 16$
Reflections collected	7988
Independent reflections	7611 [$R_{\text{int}} = 0.0126$]
Reflections observed ($>2\sigma$)	4442
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	7611/0/263
Goodness-of-fit on F^2	1.112
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0593$ [a]$wR_2 = 0.1703$
R indices (all data)	$R_1 = 0.1082$ [a]$wR_2 = 0.1866$
Largest difference peak and hole (e Å^{-3})	0.785 and −0.498

[a] R indices; $R_1 = [\Sigma||F_o| - |F_c||]/\Sigma|F_o|$ (based on F), $wR_2 = [[\Sigma w(|F_o^2 - F_c^2|)^2]/[\Sigma w(F_o^2)^2]]^{1/2}$ (based on F^2). $W = 1/[(\sigma F_o)^2 + (0.1*P)^2]$. Goodness-of-fit $= [\Sigma w(F_o^2 - F_c^2)^2/(\text{Nobs–Nparameters})]^{1/2}$.

matographed on alumina it is deprotonated and reverts immediately to [Fe_2(η-C_5H_5)$_2$(CO)(CN*)(μ-CO)(μ-CN-Me_2)], **[5]**, in quantitative yield.

Under the same conditions [Fe_2(η-C_5H_5)$_2$-(CO)-(CNMe)(μ-CNH_2)(μ-$CNMe_2$)][SO_3CF_3]$_2$, **[33]**[SO_3CF_3]$_2$, gives a 70:30 mixture of [Fe_2(η-C_5H_5)$_2$-(CNMe)(CN)(μ-CO)(μ-$CNMe_2$)], **[10]**, and [Fe_2(η-C_5H_5)$_2$(CO)(CN)(μ-CNMe)(μ-$CNMe_2$)], **[26]**.

2.7. The structure of cis-[$Fe_2(\eta$-$C_5H_5)_2(CO)_2(\mu$-$CNMe)(\mu$-$CNMe_2)$][BPh_4]

A crystal grown from acetonitrile solution was subject to a X-ray diffraction study. Crystal data is given in Table 5. The structure was solved by direct methods, SHELX-86 [4], and refined by full matrix least squares using SHELXL-93 [5]. SHELX operations were rendered paperless using ORTEX [6] which was also used to obtain the drawings. Data were corrected for Lorentz and polarisation effects but not for absorption. Hydrogen atoms were included in calculated positions with thermal parameters 30% larger than the atom to which

Table 6
Atomic coordinates (×10^4) and equivalent isotropic displacement parameters for *cis*-[Fe2(η-C_5H_5)$_2$(CO)$_2$(μ-CNMe)(μ-$CNMe_2$)][BPh_4]

Atom	x	y	z	U_{eq} [a]
Fe(1)	3202(1)	1303(1)	8491(1)	34(1)
Fe(2)	3129(1)	185(1)	7383(1)	37(1)
N(1)	1421(3)	360(2)	8494(3)	57(1)
N(2)	5097(2)	753(2)	7969(3)	41(1)
O(1)	3796(3)	477(2)	10195(2)	80(1)
O(2)	3576(3)	−1011(2)	8726(3)	85(1)
C(1)	2200(3)	540(2)	8248(3)	40(1)
C(2)	4164(3)	758(2)	7926(3)	34(1)
C(3)	810(4)	682(3)	9185(4)	76(2)
C(4)	5682(3)	1269(3)	8580(4)	58(1)
C(5)	5662(3)	217(3)	7446(4)	61(1)
C(6)	3546(3)	819(2)	9537(3)	43(1)
C(7)	3413(3)	−533(2)	8205(3)	47(1)
C(8)	2111(2)	2101(3)	8111(5)	45(2)
C(9)	2479(5)	2208(3)	9066(4)	47(2)
C(10)	3477(4)	2378(3)	9060(3)	47(2)
C(11)	3726(3)	2377(3)	8101(4)	42(2)
C(12)	2882(5)	2206(3)	7515(2)	42(2)
C(13)	3509(3)	316(4)	5969(4)	63(2)
C(14)	3369(5)	−452(3)	6181(4)	59(2)
C(15)	2396(6)	−546(3)	6407(4)	70(2)
C(16)	1936(3)	164(4)	6335(4)	61(2)
C(17)	2624(5)	697(2)	6065(4)	57(2)
C(108)	2133(6)	2170(6)	8581(11)	32(3)
C(109)	2917(12)	2318(7)	9255(5)	48(4)
C(110)	3760(6)	2411(7)	8755(12)	47(4)
C(111)	3497(10)	2321(8)	7771(9)	57(5)
C(112)	2492(11)	2172(7)	7663(7)	45(4)
C(113)	3683(5)	−166(7)	6069(8)	33(3)
C(114)	2912(10)	−640(4)	6295(8)	33(3)
C(115)	2073(6)	−191(7)	6341(8)	46(3)
C(116)	2326(8)	561(6)	6144(8)	28(3)
C(117)	3322(9)	576(5)	5976(9)	52(4)
B(1)	1668(3)	1161(2)	2868(3)	31(1)
C(18)	2776(3)	1457(2)	2793(3)	32(1)
C(19)	3448(3)	1527(2)	3577(3)	42(1)
C(20)	4401(3)	1722(3)	3495(3)	51(1)
C(21)	4741(3)	1851(3)	2616(3)	51(1)
C(22)	4111(3)	1766(3)	1820(3)	47(1)
C(23)	3156(3)	1578(2)	1919(3)	40(1)
C(24)	909(3)	1545(2)	2057(3)	32(1)
C(25)	1044(3)	2255(2)	1669(3)	43(1)
C(26)	363(4)	2578(3)	1016(3)	57(1)
C(27)	−472(4)	2202(3)	731(4)	58(1)
C(28)	−628(3)	1508(3)	1112(3)	49(1)
C(29)	40(3)	1193(2)	1772(3)	40(1)
C(30)	1218(3)	1376(2)	3883(3)	32(1)
C(31)	1468(3)	2018(2)	4417(3)	41(1)
C(32)	1042(3)	2196(3)	5254(3)	46(1)
C(33)	341(3)	1738(3)	5585(3)	50(1)
C(34).	55(3)	1113(3)	5067(3)	47(1)
C(35)	486(3)	936(2)	4240(3)	40(1)
C(36)	1736(3)	247(2)	2716(3)	33(1)
C(37)	1944(3)	−244(2)	3475(3)	44(1)
C(38)	2001(4)	−1019(3)	3329(4)	57(1)
C(39)	1883(4)	−1308(3)	2436(4)	59(1)
C(40)	1733(3)	−845(3)	1682(4)	56(1)
C(41)	1652(3)	−81(3)	1815(3)	47(1)

[a] U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor.

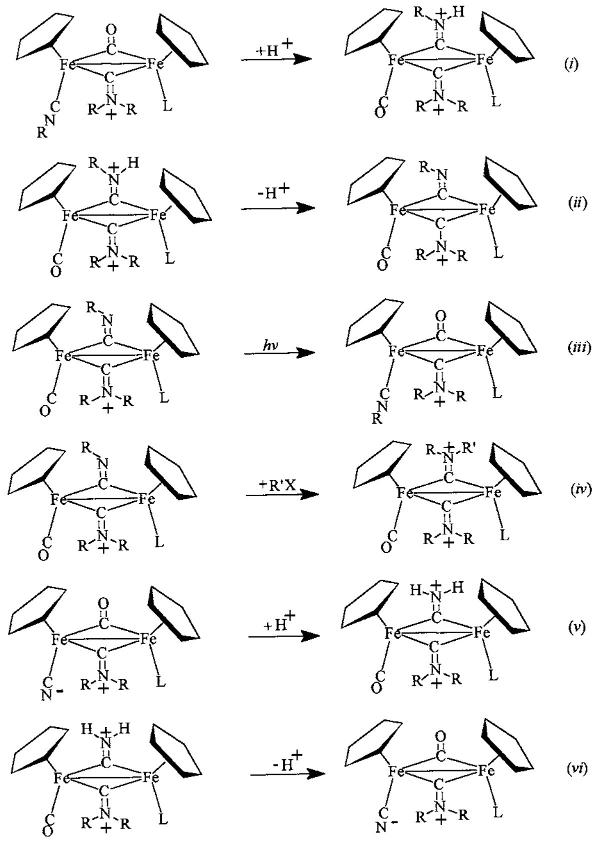
they were attached. The cyclopentadienyl rings were disordered over two positions. The remaining non-hydrogen atoms in the metal coordination sphere were refined anisotropically. All calculations were performed on a Silicon Graphics R4000 computer. The structure of the cation together with the atom labelling is illustrated in Fig. 1. Atom coordinates are given in Table 6 and selected bond lengths and bond angles are listed in Table 7.

3. Results and discussion

The six general reactions studied in the course of this course of this work are (i) those of $[Fe_2(\eta\text{-}C_5H_5)_2(L)(CNR)(\mu\text{-}CO)(\mu\text{-}CNMe_2)]^+$ salts with $HOSO_2CF_3$ to give $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(L)\{\mu\text{-}CN(H)Me\}(\mu\text{-}CNMe_2)]^{2+}$, (ii) their subsequent deprotonation to give $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(L)(\mu\text{-}CNR)(\mu\text{-}CNMe_2)]^+$ which may revert (iii) to $[Fe_2(\eta\text{-}C_5H_5)_2(L)(CNR)(\mu\text{-}CO)(\mu\text{-}CNMe_2)_2]^+$ or are trapped (iv) by protonation or alkylation with R′X to give $(\eta\text{-}C_5H_5)_2(CO)(L)\{\mu\text{-}CN(R')Me\}(\mu\text{-}CNMe_2)]^{2+}$. In these reaction CNMe can be replaced by other organoisocyanides, and the Me groups in the $\mu\text{-}CNMe_2^+$ by ethyl groups. A special case of this overall scheme is (v) the reaction of $[Fe_2(\eta\text{-}C_5H_5)_2(L)(CN)(\mu\text{-}CO)(\mu\text{-}CNMe_2)]$ and $[Fe_2(\eta\text{-}C_5H_5)_2(L)(CNH)(\mu\text{-}CO)(\mu\text{-}CNMe_2)]^+$ salts with $HOSO_2CF_3$ to give $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(L)(\mu\text{-}CNH_2)(\mu\text{-}CNMe_2)]^{2+}$ salts, and (vi) their instantaneous reversion to $[Fe_2(\eta\text{-}C_5H_5)_2(L)(CN)(\mu\text{-}CO)(\mu\text{-}CNMe_2)]^+$ on deprotonation. These are shown in Scheme 1 where *cis* isomers only are illustrated, but the scheme also applies to *trans* isomers (see Section 3.6). L is a two-electron donor ligand, usually CO but it may be anorgano-isocyanide.

The individual reactions carried out in the course of this work are summarised in Schemes 2 and 3 which are based on compounds containing the $\mu\text{-}CNMe_2^+$ ligand, but many of the reactions have also been carried out using compounds containing $\mu\text{-}CN(Me)Et^+$ or $\mu\text{-}CNEt_2^+$ instead. These are listed in Tables 1–4 where appropriate. The numbering of the various compounds continues on from that given in Ref. [3], but some are common to both papers. Compounds [**5**]$^+$–[**12**]$^+$ and [**31**] are of the type $[Fe_2(\eta\text{-}C_5H_5)_2(L)(L')(\mu\text{-}CO)(\mu\text{-}CNMe_2)]^+$, [**23**]$^+$–[**30**]$^+$ are of the type $[Fe_2(\eta\text{-}C_5H_5)_2(L)(L')(\mu\text{-}CNR)(\mu\text{-}CNMe_2)]^+$ and [**32**]$^{2+}$–[**41**]$^{2+}$ are of the type $[Fe_2(\eta\text{-}C_5H_5)_2(L)(L')\{\mu\text{-}CN(R')R\}(\mu\text{-}CNMe_2)]^{2+}$ (R = H, alkyl or aryl; L, L′ = CO or CNR).

The various complexes are air-stable crystalline solids, but some are deliquescent especially those containing the $\mu\text{-}CNH_2^+$ ligand. All are soluble in polar organic solvents.



Scheme 1.

Table 7
Selected bond lengths and angles for *cis*-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CNMe)(\mu\text{-}CNMe_2)][BPh_4]$

Bond length (Å)			
Fe(l)–Fe(2)	2.532(1)		
Fe(1)–C(6)	1.748(4)	Fe(2)–C(7)	1.754(5)
Fe(1)–C(1)	1.960(4)	Fe(2)–C(1)	1.945(4)
Fe(1)–C(2)	1.876(4)	Fe(2)–C(2)	1.884(4)
C(6)–O(1)	1.145(5)	C(7)–O(2)	1.139(5)
C(1)–N(1)	1.204(5)	C(2)–N(2)	1.293(5)
N(1)–C(3)	1.457(7)	N(2)–C(4)	1.468(6)
		N(2)–C(5)	1.470(6)
Bond angles (°)			
Fe(2)–Fe(1)–C(6)	97.4(2)	Fe(1)–Fe(2)–C(7)	99.9(2)
C(1)–Fe(1)–C(2)	94.9(2)	C(1)–Fe(2)–C(2)	95.1(2)
Fe(1)–C(1)–Fe(2)	80.9(2)	Fe(1)–C(2)–Fe(2)	84.7(2)
Fe(1)–C(1)–N(1)	141.0(4)	Fe(2)–C(1)–N(1)	138.1(5)
Fe(1)–C(2)–N(2)	136.6(3)	Fe(2)–C(2)–N(2)	138.5(3)
C(1)–N(1)–C(3)	131.8(5)	C(2)–N(2)–C(4)	122.4(4)
		C(2)–N(2)–C(5)	123.4(4)

3.1. Acid-promoted RNC- and CN-migration (reactions (i) and (v))

The addition of neat trifluoromethanesulphonic acid to a solution of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNMe)(\mu\text{-}CO)(\mu\text{-}CNMe_2)][SO_3CF_3]$, [**7**][$SO_3CF_3$], in chloroform results in the formation of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2\{\mu\text{-}CN(H)Me\}$-

(μ-$CNMe_2$)][CF_3SO_3]$_2$, [**34**][CF_3SO_3]$_2$, salts in near quantitative yields as determined by NMR spectroscopy. The product is a 2.5:1 mixture of the orange *cis* isomer and the purple *trans* isomer which can be separated by fractional crystallization.

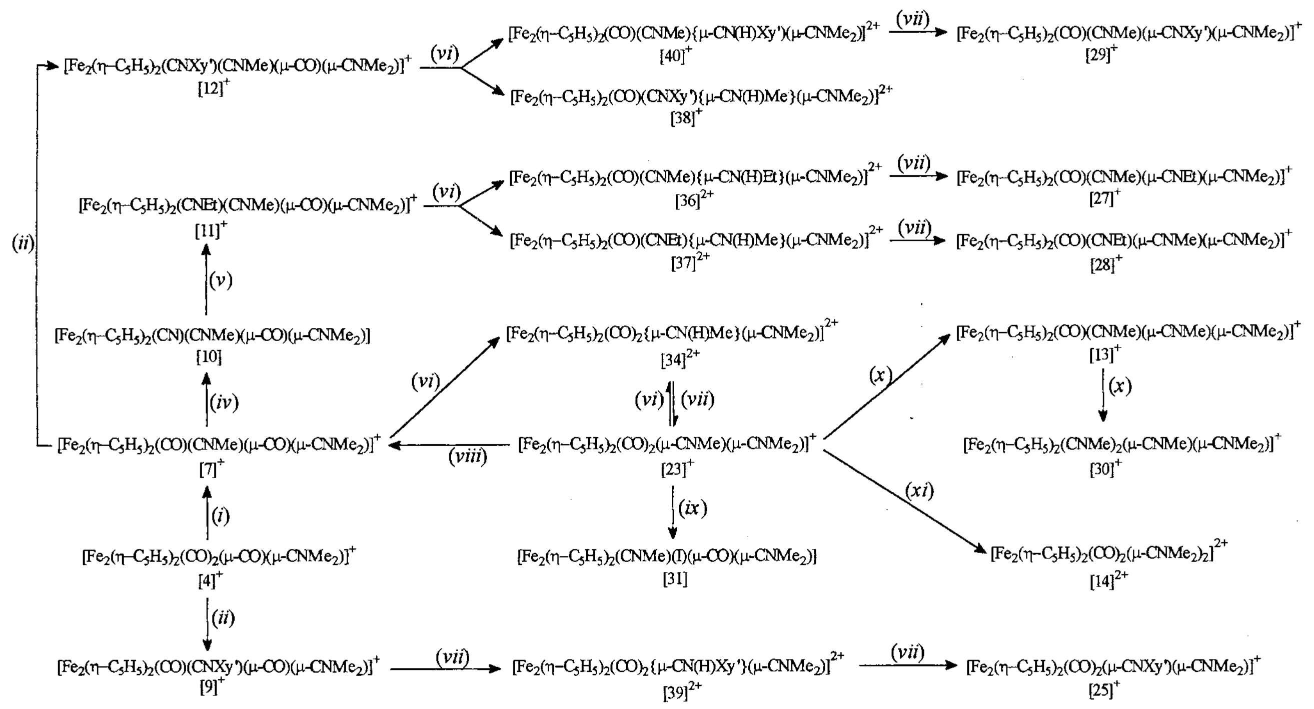
The reaction also takes place with analogues of [**7**]$^+$ in which the μ-$CNMe_2$ ligand is replaced by μ-CN(Et)Me or μ-$CNEt_2$, and *t*-CNMe is replaced by *t*-^{13}CNMe, *t*-C^{15}NMe, *t*-CNEt, CNBu^t or *t*-CNXy$'$ (Xy$'$ = 2,6-$Et_2C_6H_3$). However, it is not completely general. It does not take place if the two cyclopentadienyl rings of [**7**]$^+$ are linked by a –$CH_2C(O)$– bridge. It takes place in polar, non-donor solvents such as chloroform or dichloromethane but not in donor solvents such as acetonitrile. It is brought about only by the very strong acid $HOSO_2CF_3$, and weaker acids such as neat CF_3CO_2H, neat CH_3CO_2H, 40% aqueous HBF_4 or 60% aqueous HPF_6 are not effective.

A similar reaction takes place with the complexes [Fe_2(η-C_5H_5)$_2$(CNR)(CNR$'$)(μ-CO)(μ-$CNMe_2$)][SO_3CF_3] which have two terminal isonitrile ligands. Unfortunately, in no case could the anticipated initial products be isolated although they were formed and could be identified by spectroscopy. Where R = R$'$ a single product would be expected, [Fe_2(η-C_5H_5)$_2$(CO)(CNR){μ-CN(H)R}(μ-$CNMe_2$)][SO_3CF_3]$_2$ but in the only reaction of this type attempted, where R = Bu^t, the *t*-CO ligand was very labile and readily replaced by a solvent molecule when the product was recrystallized. Eventually the green acetonitrile derivative [Fe_2(η-C_5H_5)$_2$(NCMe)(CNBu^t){μ-CN(H)-Bu^t}(μ-$CNMe_2$)][SO_3CF_3]$_2$ was precipitated from acetonitrile solution.

When the precursors contain two different *t*-CNR ligands, they do not show an equal propensity to migrate. Thus protonation of [**11**]$^+$ gives a mixture of [**36**]$^+$, as a consequence of EtNC migration, and [**37**]$^+$, resulting from MeNC migration, in the ratio of 40:60. On the other hand, with [**12**]$^+$ MeNC migration gives [**38**]$^+$ as the minor product of protonation (< 5% detected by ^{1}H-NMR spectroscopy) and the major (> 95%) product, [**40**]$^+$, arises from Xy$'$NC migration.

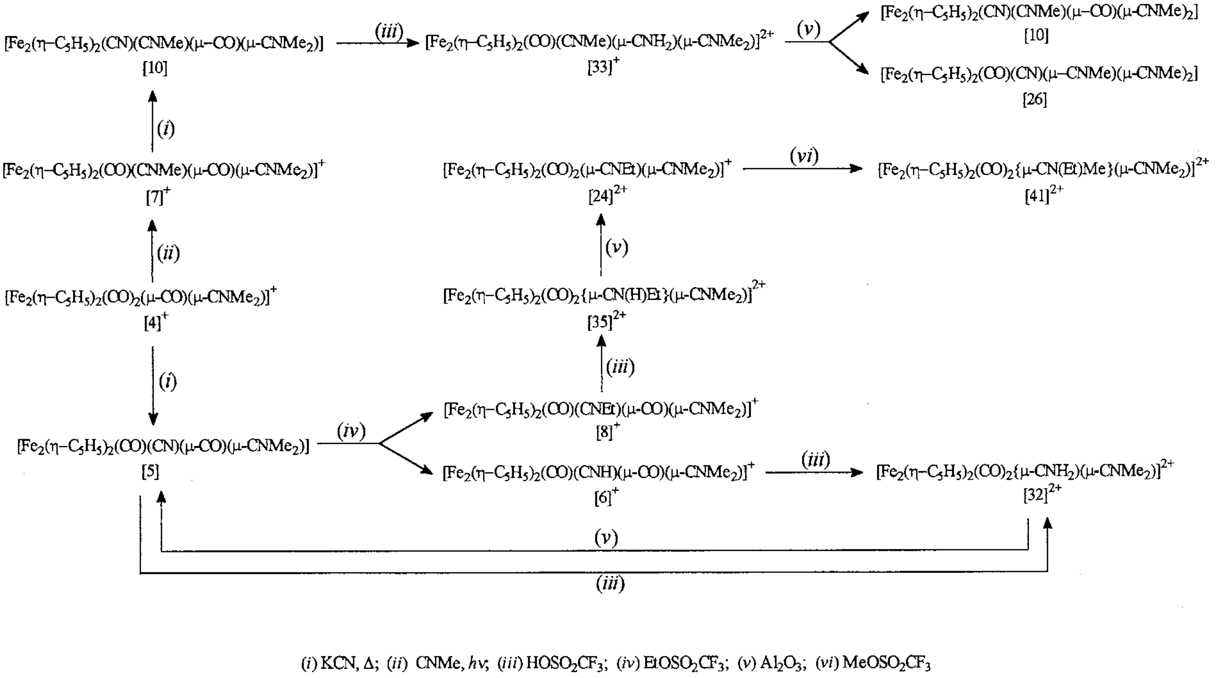
The addition of $HOSO_2CF_3$ to a chloroform solution of the cyano complex [**5**] results in the formation of [**32**]$^{2+}$, presumably via the HNC salt [**6**]$^+$ which also reacts with the acid to give [**32**]$^+$. Under the same conditions [**10**], which contains *t*-CNMe and *t*-CN$^-$, gives [**33**]$^{2+}$ as the sole product i.e. there is only CN$^-$ (or CNH) migration and no CNMe migration.

In a relevant experiment, a solution of [**4**][SO_3CF_3] in chloroform was treated with an excess of neat $HOSO_2CF_3$. The colour of the solution changed and a deep red oil precipitated. It was clear that something had happened, but all attempts to isolate the product gave only [**4**][SO_3CF_3].



(*i*) MeNC, hν; (*ii*) CNXy$'$, Δ; (*iii*) CNXy$'$, Me_3NO; (*iv*) KCN, Δ; (*v*) $EtOSO_2CF_3$; (*vi*) $HOSO_2CF_3$; (*vii*) Al_2O_3; (*viii*) hν ; (*ix*) hν of I$^-$ salt; (*x*) CNMe, hν ; (*xi*) $MeOSO_2CF_3$.

Scheme 2.



Scheme 3.

3.2. Deprotonation of complexes containing the CN(H)R$^+$ and CNH$_2^+$ ligands (reactions ii and vi)

$[\mathrm{Fe_2(\eta\text{-}C_5H_5)_2(CO)_2\{\mu\text{-}CN(H)Me\}(\mu\text{-}CNMe_2)][CF_3SO_3]_2}$, [**34**]$[\mathrm{SO_3CF_3}]_2$, dissolves unchanged in acetone or acetonitrile, but there is spectroscopic evidence for fast protonation–deprotonation processes (see below). In contrast in methanol its colour changes from green to red. Even though only [**34**]$[\mathrm{SO_3CF_3}]_2$ may be recovered from this solution, IR and ^{1}H-NMR spectroscopy (see below) show that the solution contains an equilibrium mixture of [**34**]$^{2+}$ and [**23**]$^+$ salts which are interconverting rapidly at r.t. The addition of a single drop of $\mathrm{HOSO_2CF_3}$ to the solution shifts the equilibrium so that only [**34**]$^{2+}$ could be detected.

The μ-CNXy′ ligand is much less basic than μ-CNMe so it is not surprising that [**39**]$^{2+}$ is dissociated to [**25**]$^+$ in acetonitrile and acetone as well as methanol. However, [**39**]$[\mathrm{SO_3CF_3}]_2$ can be isolated from these solutions whereas all attempts to isolate [**40**]$^{2+}$ salts failed. The green colour showed that they were formed but would not crystallize, and only the unprotonated [**29**]$^+$ could be isolated as its $[\mathrm{BPh_4}]^-$ salt.

The μ-CN(H)R$^+$ ligands in [**34**]$[\mathrm{SO_3CF_3}]_2$ and analogous salts $[\mathrm{Fe_2(\eta\text{-}C_5H_5)_2(CO)_2\{\mu\text{-}CN(H)Et\}(\mu\text{-}CNMe_2)][SO_3CF_3]_2}$, [**35**]$[\mathrm{SO_3CF_3}]_2$, $[\mathrm{Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNMe)\{\mu\text{-}CN(H)Et)(\mu\text{-}CNMe_2)][CF_3SO_3]_2}$, [**36**]$[\mathrm{SO_3CF_3}]_2$, $[\mathrm{Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNEt)\{\mu\text{-}CN(H)Me\}(\mu\text{-}CNMe_2)][SO_3CF_3]_2}$, [**37**]$[\mathrm{SO_3CF_3}]_2$, $[\mathrm{Fe_2(\eta\text{-}C_5H_5)_2(CO)_2\{\mu\text{-}CN(H)Xy'\}(\mu\text{-}CNMe_2)]\ [SO_3CF_3]_2}$, [**39**]$[\mathrm{SO_3CF_3}]_2$, and $[\mathrm{Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNMe)\{\mu\text{-}CN(H)Xy'\}(\mu\text{-}CNMe_2)][SO_3CF_3]_2}$, [**40**]$[\mathrm{SO_3CF_3}]_2$, are completely deprotonated by alumina to give the μ-CNR complexes [**23**]$[\mathrm{SO_3CF_3}]$ and its analogues, [**24**]$[\mathrm{SO_3CF_3}]$, [**27**]$[\mathrm{SO_3CF_3}]$, [**28**]$[\mathrm{SO_3CF_3}]$, [**25**]$[\mathrm{SO_3CF_3}]$, and [**29**]$[\mathrm{SO_3CF_3}]$ respectively. These reactions can be reversed by the addition of acids (see below).

If $[\mathrm{Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNMe)(\mu\text{-}CNH_2)(\mu\text{-}CNMe_2)][SO_3CF_3]_2}$, [**33**]$[\mathrm{SO_3CF_3}]_2$, is dissolved in dichloromethane, IR spectroscopy shows that a mixture of compound are present and that they contain *t*-CN, *t*-CNH, *t*-CNMe, *t*-CO, μ-CO, μ-CNMe, and μ-CNMe$_2^+$ ligands. They could not be separated as, when solutions of this compound in acetone are passed down an alumina column, a double deprotonation of the μ-CNH$_2^+$ ligand takes place and two products are obtained, [**26**] and [**10**] in the ratio 30:70. In the first of these it is the CNMe ligand which exchanges with μ-CN$^-$ or μ-CNH ligand formed on deprotonation, and in the second it is CO. Similarly [**32**]$[\mathrm{SO_3CF_3}]_2$ is deprotonated to [**5**]. In neither instance could we achieve a stepwise deprotonation of the CNH$_2^+$ ligand with the formation of complexes containing CNH or μ-CN ligands.

3.3. The protonation and alkylation of [23]$^+$ and related complexes (reaction (iv))

The reaction used to prepare the $[\mathrm{Fe_2(\eta\text{-}C_5H_5)_2(L)(CO)(\mu\text{-}CNMe)(\mu\text{-}CNMe_2)]^+}$ complexes, the deprotonation of $[\mathrm{Fe_2(\eta\text{-}C_5H_5)_2(L)(CO)\{\mu\text{-}CN(H)Me\}(\mu\text{-}CNMe_2)]^{2+}}$, may be reversed by their treatment with a strong acid. However, these μ-CNR ligands are relatively poor nucleophiles even when R = alkyl and very poor nucleophiles when it is aryl. This is because the strong electron-withdrawing effect of the μ-$CNMe_2^+$ ligand reduces back-bonding to the μ-CNR and hence its nucleophilicity. Consequently reprotonation requires a strong acid and alkylation requires strong electrophiles such as $MeOSO_2CF_3$; MeI is not effective.

This route to compounds such as $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$ allows the preparation of both their *cis* and *trans* isomers whereas only the former were obtained by alkylating $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNMe)_2]$. It also allows analogues of such salts to be prepared which contain various combination of alkyl groups in their two μ-CN(R′)R$^+$ ligands.

3.4. The migration of CNR from bridging to terminal sites (reaction (iii))

The [**25**]$^+$ and [**29**]$^+$ salts with their μ-CNXy′ ligands are indefinitely stable in both the solid state and in solution. In contrast, under the influence of light [**23**]$^+$ salts revert to [**7**]$^+$ salts in solution with *t*-CO/μ-CNMe exchange. The reaction is accelerated by UV radiation, but then the product depends on the counteranion, X$^-$. [**23**]X gives [**7**]X when X$^-$ = $[SO_3CF_3]^-$ or $[BPh_4]^-$, but when X$^-$ = Cl$^-$, Br$^-$ or I$^-$ the reaction proceeds via an unknown but detectable intermediate to $[Fe_2(\eta\text{-}C_5H_5)_2(X)(CNMe)(\mu\text{-}CO)(\mu\text{-}CNMe_2)]$. Although these complexes have similar IR spectra, only [**31**] where X = I was sufficiently stable to be isolated and characterised. The only IR absorption bands of the intermediates which are not obscured by the bands of their precursors or successors are at 1973 cm^{-1} (X = Cl), 1971 (X = Br) and 1969 cm^{-1} (X = I). These are probably due to their *ν*(CO) vibrations and as their frequencies depend on X, it suggests that the intermediates may be of the type $[Fe_2(\eta\text{-}C_5H_5)_2(X)(CO)(\mu\text{-}CNMe)(\mu\text{-}CNMe_2)]$ with coordinated X$^-$.

The photolysis of [**23**]$[SO_3CF_3]$ and its ^{13}CNMe counterpart were studied in detail. The *cis* isomers of both gave *cis*-[**7**]$[SO_3CF_3]$ or its labelled counterpart as the sole products in > 90% isolated yields, whereas *trans*-[**23**]$[SO_3CF_3]$ gave a mixture of *cis* and *trans*-[**7**]$[SO_3CF_3]$ in 60:40 ratio and 85% total yield. If the irradiation of the *cis* salts are carried out in the presence of an 18-fold excess of CNMe, [**13**]$[SO_3CF_3]$ and [**30**]$[SO_3CF_3]$ are formed in turn, again in > 90% yield. However, the labelled μ-^{13}CNMe ligand of [**23**]$[SO_3CF_3]$ is retained almost exclusively (> 98%) in the bridging site in both of these compounds and μ-CNMe/*t*-CO interchange does not take place. Pure [**13**]$[SO_3CF_3]$ is unaffected by irradiation but in the presence of CNMe it undergoes CO substitution to give [**30**]$[SO_3CF_3]$. Furthermore irradiation of [**23**]I in the presence of excess CNMe results in complete substitution of CO by CNMe to give [**13**]I without ligand migration or coordination of I$^-$.

3.5. Infrared spectra

The various compounds show strong absorption bands in the 1550–2200 cm^{-1} region which can be assigned to the CN or CO stretching vibrations of μ-CNR_2^+, μ-CNR, μ-CO, *t*-CO, *t*-CNR and *t*-CN$^-$ ligands (Table 2). This has been discussed elsewhere [1,3], except for the those due to the μ-CNR ligands (see below). The spectra also show characteristic absorption bands which confirm the presence of the $[SO_3CF_3]^-$ ions when appropriate, and other weaker bands which yield no important structural information.

Where *cis* and *trans* isomers are formed they usually have different spectra in this region. However, it is only where the complexes contain the $Fe_2(t\text{-}CO)_2$ moiety that the number and relative intensities of the absorption bands due to the *ν*(*t*-CO) vibrations can be used to distinguish the *cis* and *trans* isomers unambiguously [7].

Isotopic labelling of the CN, CNR and μ-CN(R′)R$^+$ ligands results in changes in the frequencies of their vibrations. This has been discussed elsewhere for all complexes except those with labelled μ-CNMe, μ-CN(H)Me$^+$ and μ-CNH_2^+ ligands. It is only for the first of these that ^{13}C or ^{15}N labelling results in decreases in *ν*(μ-CN) stretching frequencies which are close to those calculated on the basis of the reduced mass of the C–N simple harmonic oscillator. For example, the *ν*(μ-CNMe) of *cis*-[**23**]$[CF_3SO_3]$ decreases from 1786 to 1752 cm^{-1} (^{13}C) or 1760 cm^{-1} (^{15}N) (Table 2) compared with calculated values of 1749 cm^{-1} for ^{13}C–^{14}N and 1758 cm^{-1} for ^{12}C–^{15}N. For the μ-CN(H)Me$^+$ and μ-CNH_2^+ ligands, isotopic substitution results in frequency reductions which are much smaller than would be anticipated on the basis of this simple model. Similar behavior has been observed on isotopic substitution of *t*-CNMe in [**7**]$^+$ salts and has been attributed to the effect of the Me group on the reduced mass of the C–N oscillator [3].

The μ-CNMe and μ-CNEt ligands in [**13**]$^+$, [**23**]$^+$, [**24**]$^+$, [**26**]$^+$, [**27**]$^+$, [**28**]$^+$ and [**30**]$^+$ salts give rise to absorption bands between ca. 1780 and 1810 cm^{-1}. In general, these are rather broad and symmetrical in the solid state, but in solution are broad and unsymmetrical or with two clearly distinguishable components. The band shapes depend on the solvent. This is attributed to cation–anion or cation–solvent interactions similar to those invoked to account for the shape of the *ν*(μ-CO) absorption band of [**4**]$^+$ salts [8]. Their frequencies decrease as the *t*-CO ligands are replaced by *t*-CNR, and are not greatly dependent on the medium or the solvent. However, the same is not true for both *cis* and *trans*-[**25**]$[SO_3CF_3]$ where the *ν*(CN) band due to its μ-CNXy′ ligand is extremely broad in solution and lies at very high frequencies as compared with the solid state. This is illustrated in Fig. 2 for the *trans* isomer. This is unprecedented behaviour for which there is no

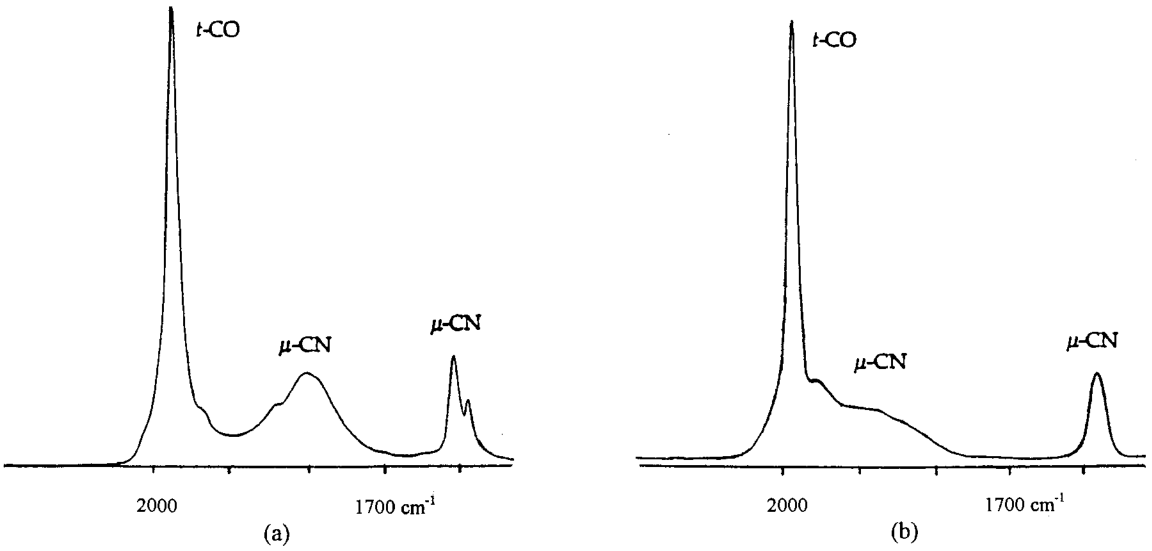


Fig. 2. The inhered spectrum of *trans*-[Fe_2(η-C_5H_5)$_2$(CO)$_2$(μ-CNMe)(μ-$CNMe_2$)][SO_3CF_3], [**25**][SO_3CF_3], in (a) the solid state (KBr) and (b) CH_2Cl_2 solution.

ready explanation especially as the frequencies of the other vibrations are almost unchanged.

There is a weak band in the IR spectrum of *cis*-[Fe_2(η-C_5H_5)$_2$(CO)$_2${μ-CN(H)Me}$_2$][SO_3CF_3]$_2$ at 3011 cm^{-1} (KBr disc) which is absent from the spectrum of *cis*-[Fe_2(η-C_5H_5)$_2$(CO)$_2$(μ-$CNMe_2$)$_2$][SO_3CF_3]$_2$. It is attributed to the ν(N–H) vibration of the μ-CN(H)Me ligands. Bands of similar frequency are observed in the spectra of all of the complexes containing this ligand and anion. The ν(N–H) vibrations of the μ-CNH_2^+ ligands of [Fe_2(η-C_5H_5)$_2$(CO)$_2$(μ-CNH_2)(μ-$CNMe_2$)]-[SO_3CF_3]$_2$ and related salts give rise to strong and broad absorption bands at ca. 2910–3120 cm^{-1} (KBr disc). The relatively low frequencies of these ν(NH) vibrations may be due to hydrogen bonding of the μ-CN(H)Me$^+$ or μ-CNH_2^+ ligands with the [SO_3CF_3]$^-$ anion. We were unable to identify absorption bands due to the δ(N–H) bending modes.

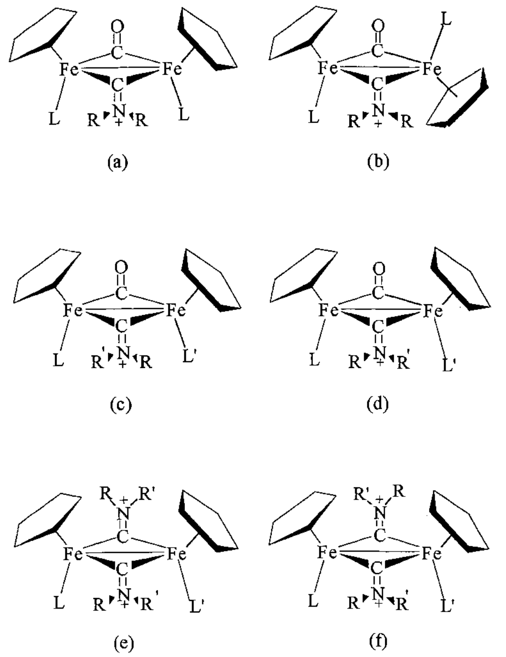
3.6. NMR spectra

The ^{1}H-NMR spectra of the complexes (Tables 3 and 4) are readily assigned by comparison with the spectra of related compounds. Those of *cis* and *trans* isomers are distinguishable as are those of the *syn* and *anti* forms of unsymmetrical complexes (see below). Those complexes containing μ-CN(H)R$^+$ and μ-CNH_2^+ ligands show broad resonances at ca. 12.3 δ due to the N-bound protons.

In general, complexes containing the μ-CN(R′)R$^+$ ligands do not undergo *cis–trans* isomer interchange or ligand site exchange and the same is true for the complexes described herein. However, the μ-CNR ligand in derivatives [**23**]$^+$–[**30**]$^+$ is bent at N (see the structure of [**23**][BPh_4] below), so they undergo rapid inversion at N which is fast even at low temperatures in both *cis* and *trans* isomers. Consequently in [**23**]$^+$ and related species the two Fe(η-C_5H_5) moieties and the two Me groups of the μ-$CNMe_2^+$ ligand are rendered equivalent on the NMR timescale so that only one signal due to each is observed in the NMR spectrum whereas two could have been expected for a static molecule. This rapid inversion at N also renders equivalent the two methylene protons of the μ-CNEt ligand of [**24**]$^+$, [Fe_2(η-C_5H_5)$_2$(CO)$_2$(μ-CNEt)(μ-$CNMe_2$)]$^+$.

Furthermore, for complexes containing the μ-CN(H)R$^+$ ligand, N–H$^+$ dissociation is facile, rapid and reversible. As the resultant μ-CNR ligand undergoes a fast inversion at N, the overall process deprotonation = inversion = protonation is fast on the NMR timescale at r.t. and results in a fast exchange of H and R groups of the μ-CN(H)R$^+$ ligands so that for [**34**]$^+$, for example, the NMR spectra is simpler than would have been expected and in such complexes it is not possible to distinguish between the two (η-C_5H_5)Fe sites or the Me groups of the μ-$CNMe_2^+$ ligands. If acid is added to the solution, the dissociation of H$^+$ is suppressed, the N–*H* resonance shifts noticeably, two (η-C_5H_5) signals are observed and the μ-CN(H)Me group gives rise to a doublet due to the N(H)CH_3 because of their coupling with the N(H) proton even though there is still a single μ-$CNMe_2$ resonance. Similar behaviour is observed in acetone solution, but the N–*H* resonance was not detected, perhaps due to H-bonding with the solvent.

IR spectroscopy has shown that in methanol-D_4 solution, *cis*-[**34**]$^{2+}$ partially dissociates and coexists in equilibrium with *cis*-[**23**]$^+$ (mole ratio = ca. 8:10). However the ^{1}H-NMR spectrum shows single signals due to C_5H_5, μ-$CNMe_2$, and μ-CN(H)Me ligands confi-



(a) (b)

(c) (d)

(e) (f)

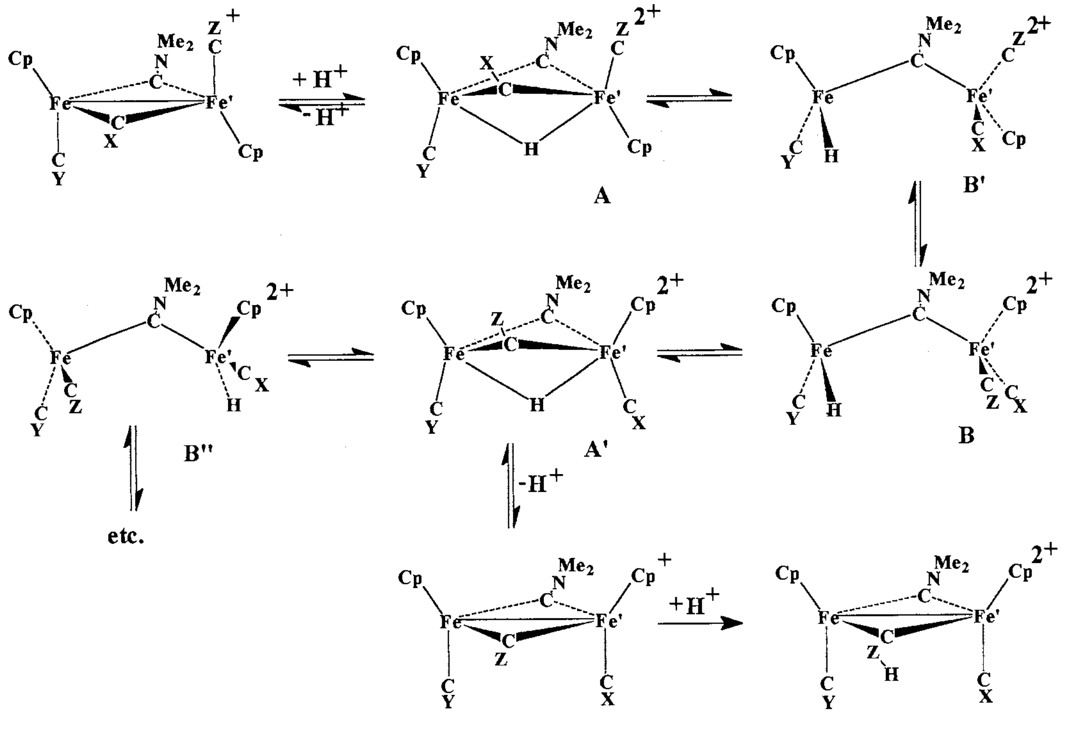
Fig. 3. (a) and (b) are *cis* and *trans* isomers; (c) and (d) are α and β isomers; and (e) and (f) are *syn* and *anti* isomers.

rming that interconversion of these two species is fast at r.t.

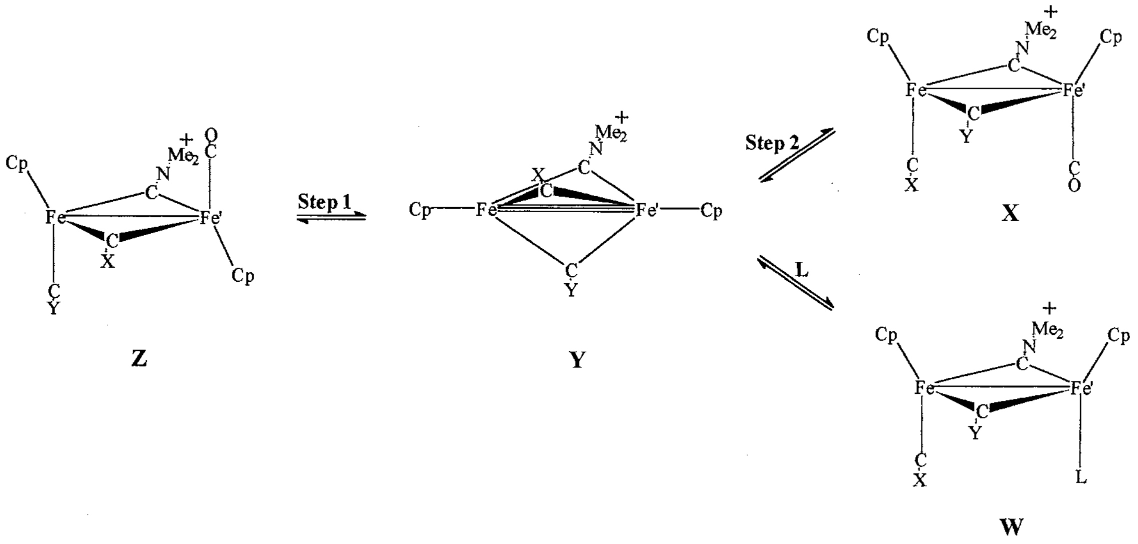
Similar behaviour and NMR spectra have also been observed for other complexes of the general type [Fe$_2$(η-C$_5$H$_5$)$_2$(CO)(L){μ-CN(H)R}(μ-CNMe$_2$)]$^{2+}$ where R = alkyl, but when R = Xy′ dissociation of H$^+$ is complete in all solvents except in the presence of excess acid which suppresses not only deprotonation = inversion = protonation but also the rotation of the Xy′ group about the N–Xy′ bond. As this rotation takes place in [Fe$_2$(η-C$_5$H$_5$)$_2$(CO)$_2$(μ-CNXy)(μ-CNMe$_2$)]$^+$, it does imply that rotation of Xy′ and inversion at N in [**25**]$^+$ are connected.

All spectra show the anticipated couplings of ^{1}H to ^{13}C or ^{15}N nuclei when suitably labelled CNR or CN(R′)R$^+$ ligands are used.

The ^{13}C-NMR spectra of the complexes in CD$_3$CN solution are as would be expected (Table 4). Single *C*$_5$H$_5$ and μ-CN(*C*H$_3$)$_2^+$ resonances show that there is fast inversion at N of the μ-CNR ligand of [**23**]$^+$ and its counterparts, and fast deprotonation = inversion = reprotonation of [**34**]$^{2+}$ and its counterparts. Comparison of the various spectra show that the chemical shifts of ligating ^{13}C atoms decreases along the ligand series CN$^-$ < *t*-CNMe < *t*-CO < μ-CNMe < μ-CO < μ-CN(H)Me$^+$ ~ μ-CNMe$_2^+$, although the actual values depend on the ligand combination. The spectra of complexes containing ^{13}C-labelled ligands exhibit some interesting coupling constants. Thus the μ-^{13}CNMe ligand does not couple to the *t*-CO or μ-CNMe$_2^+$ ligands in *cis*-[**23**]$^+$, but the *t*-^{13}CNMe ligand in *cis*-[**7**]$^+$ couples to both μ-CO and μ-CNMe$_2^+$ ligands. The μ-^{13}CN(H)R$^+$ ligands in [**34**]$^{2+}$ (R = Me) or [**32**]$^{2+}$ (R = H) couple to *t*-CO but not μ-CNMe$_2^+$ ligands.



Scheme 4.



Scheme 5.

3.7. Isomers

All of the complexes described have structures based on that of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CO)_2]$ [9] with a ca. planar $Fe_2(\mu\text{-}C)_2$ moiety. Consequently *cis* and *trans* isomers are possible (Fig. 3), but because of the presence of $\mu\text{-}CN(R')R^+$ ligands they do not interconvert and may often be separated by chromatography and fractional crystallization.

Reactions (ii) and (iv) involve only the periphery of ligands and so do not affect the $Fe_2(CO)_4$ part of the molecule or *cis–trans* isomer ratios. In contrast the reactions (i), (iii), (v) or (vi) involve migration of ligands between terminal and bridging sites so that *cis–trans* isomerisation can and does take place. However, the *cis* isomer is always the major product and may be the only product of these reactions no matter what the configuration of the starting complex.

The identification of *cis* and *trans* isomers has been discussed in detail elsewhere [1,3].

There are two other forms of isomerism exhibited by some of these complexes. The first are *syn* and *anti* isomers arising from the presence of a $Fe_2\{\mu\text{-}CN(H)R\}\{\mu\text{-}CN(R')R\}$ moiety and the second are the α and β isomers arising from the presence of both $\mu\text{-}CN(H)R^+$ ligands and an $Fe_2(t\text{-}L)(t\text{-}L')$ moiety within the same molecule (Fig. 3). Instances of both types of isomerism have been detected by NMR spectroscopy, but the isomers have never been separated.

3.8. Mechanism of reaction (i)

The facility with which the *t*-CNR ligand is converted to $\mu\text{-}CN(H)R^+$ increases along the series CNEt < CNMe < CNAr. This series reflects the increasing μ-seeking ability of these ligands in $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_{4-n}(CNR)n]$ complexes [10] and not their basicities when they occupy such sites. This suggests that the reactions proceed via protonated intermediates which are able to undergo ligand site exchange and that protonation of the CNR ligand takes place subsequently. Furthermore a reaction appears to take place when [**4**][SO_3CF_3], which does not possess a CNR ligand, is treated with $HOSO_2CF_3$ in chloroform solution. There is a colour change and an oil is precipitated, but it could not be identified.

There are two obvious sites of protonation in [**4**][SO_3CF_3], [**7**][SO_3CF_3] and related salts. The first is the $\mu\text{-}CN(R')R^+$ ligand which would be converted to $\mu\text{-}CN(H)(R')R^{2+}$. There is a precedent for this in the conversion of $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}S)(\mu_3\text{-}CNMe_2)]^+$ salts to $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}S)\{\mu_3\text{-}CN(H)Me_2\}]^{2+}$ [11]. However, as the $\mu\text{-}CN(R')R^+$ ligand inhibits ligand site exchange and *cis–trans* isomerism in [**7**]$^+$ and related species because of its μ-seeking abilities [1,3], it is probable that a $\mu\text{-}CN(H)(R')R^{2+}$ ligand in $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNMe)(\mu\text{-}CO)\{\mu\text{-}CN(H)Me_2\}]^{2+}$ would have a similar effect.

The second potential site of protonation is the Fe–Fe bond as has been observed in the reversible reaction of strong acids with $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ which give $[\{Fe(\eta\text{-}C_5H_5)_2(CO)_2\}_2H]^+$ salts [12]. This is more plausible, and a possible mechanism for reaction (i) based on it is illustrated in part in Scheme 4. The initially formed intermediate A could be in equilibrium with the species B or B′ with two fewer μ-ligands. It is possible to envisage a series of reactions involving bridge closing-and-opening and partial rotation about an Fe–CNMe$_2$ bond in B which would convert A to one of its isomers with a μ-CNR ligand. The possibility is then open for a sequence of reactions which would lead eventually to the protonation of this ligand and precipitation of the final product.

This proposed mechanism accounts for the observed characteristics of the reaction. A very strong acid would be required to protonate a cation, and donor solvents such as acetonitrile would reduce its efficacy in this respect. The preferred isomer of A would depend on the μ-seeking abilities of the CY and CZ ligands and not their basicities provided that the rates of interconversion between A and B and their various isomers/rotamers were fast as compared with the deprotonation of A. The *cis–trans* isomerism which is observed is easily rationalized as a single rotation through 60° about the Fe(1)–$CNMe_2$ bond in B which would interchange CO with CZ in B and hence in A would also result in *cis–trans* isomerism in A. Two such transformations would be required to bring about CO and CZ interchange without *cis–trans* isomerisation. Furthermore, this means that if the two cyclopentadienyl ligands are linked (in our case by a $CH_2C(O)$ moiety), the partial rotation in B/B′ cannot take place and no reaction would be expected.

3.9. Mechanism of reactions (ii) and (vi)

These are difficult to rationalize; (ii) is observed only when $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CNMe)(\mu\text{-}CNMe_2)][SO_3CF_3]$ converts to $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNMe)(\mu\text{-}CO)(\mu\text{-}CNMe_2)][SO_3CF_3]$. It does not take place (a) in the dark, so it appears to be photolytic rather than thermal, (b) if μ-CNMe is replaced by μ-CNAr, and (c) when one of the terminal CO ligands of [**23**] is replaced by CNMe, the use of labelled μ-CNMe* shows that there is no exchange of μ and *t* CNMe ligands. As the CNAr ligand has an inherently greater preference for μ as opposed to *t* coordination as compared with CNMe [10], (b) suggests that the reaction takes place via an intermediate which allows this isocyanide coordination preference to be exercised. If this is combined with (a), a possible intermediate Y is shown in Scheme 5. In step 1 of this scheme CO loss is more probable than CNR loss because the relatively electron-deficient nature of the precursor W favours the retention of the better σ-donor ligand in the intermediate Y. Re-attack of Y by CO would result in the reformation of Z (or its *trans* isomer), or of W (step 2) which is the product of CX–CY site exchange. As the various reactions (exemplified by steps 1 and 2 in Scheme 5) are reversible, the final products would be those in which the most suitable ligand would occupy the μ-site i.e. CNMe < CO < CNXy′ but the mechanism does not explain why such an intermediate is not formed from $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNMe)(\mu\text{-}CNMe)(\mu\text{-}CNMe_2)][SO_3CF_3]$.

In reaction (vi) it does not appear to be possible to remove one proton from the $\mu\text{-}CNH_2^+$ ligand of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(L)(\mu\text{-}CNH_2)(\mu\text{-}CNMe_2)][SO_3CF_3]_2$ (L = CO or CNMe) to give complexes containing the μ-CNH ligand. Every attempt to do so resulted in the removal of both protons and the migratory exchange of CN^- with either CO or CNMe in a fast reaction that takes place even in the dark. Similar behaviour has been observed in the deprotonation of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CNH_2)]X$ salts [13], and it is quite clear that the CN^- ion, though isoelectronic with CO, has a much reduced capacity to act as a two-electron donor, μ_2 ligand.

When the ‘bridging’ CN^- exchanges with a terminal ligand, it does so preferentially with CO rather than CNMe so that $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNMe)(\mu\text{-}CNH_2)(\mu\text{-}CNMe_2)][SO_3CF_3]_2$ giving $[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)(CN)(\mu\text{-}CO)(\mu\text{-}CNMe_2)]$ and $[Fe_2(CO)(CN)(\mu\text{-}CNMe)(\mu\text{-}CNMe_2)]$ in a ratio, 70:30. This is consistent with the relative μ-seeking abilities of CO and CNMe ligands in various $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_{4-n}(CNMe)_n)]$ complexes ($n = 1$ or 2) [10].

3.10. Structure of cis-[Fe$_2$(η-C$_5$H$_5$)$_2$(CO)$_2$(μ-CNMe)(μ-CNMe$_2$)][SO$_3$CF$_3$]

The structure and atom labelling of the cation is illustrated in Fig. 1, and selected bond lengths and angles are given in Table 7. The cation has a structure which is based on that of *cis*-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CO)_2]$ [9] and similar to that found previously in *cis*-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}CN(H)Me\}][BF_4]$ [8] and *cis*-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CNMe_2)]$**I** [14] but with the μ-CO ligand replaced by a μ-CNMe ligand which is bent at N. Bond lengths and angles are as would be expected. However, it should be noted that the μ-C=NMe_2 separation of 1.296(6) Å it is normal for a double bond but much longer than μ-C–NMe of 1.208(7) Å, indicating C–N triple bond character in the latter. This is consistent with the Fe–C bonds to the very strong acceptor ligand $\mu\text{-}CNMe_2^+$ (1.874, 1.884(5) Å) being significantly shorter than those to the poorer acceptor μ-CNMe (1.940, 1.955(6) Å). As would be expected, the dimensions of the μ-CNMe ligand in $[\mathbf{23}]^+$ differ from those of *t*-CNMe in its isomer $[\mathbf{7}]^+$ [3] with C–N of 1.208(7) Å vs. 1.157(6) Å and N–Me of 1.470(9) vs. 1.429(7) Å. The CO ligand undergoes similar variations in C–O bond length i.e. 1.163(6) Å for μ-CO in [**7**][BPh_4] and 1.142(7) Å for *t*-CO.

4. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 116144 for *cis*-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CNMe)(\mu\text{-}CNMe_2)][BPh_4]$. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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