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The reactions of *cis*-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$ and related compounds with nucleophiles

Kevin Boss, M. Gary Cox, Conor Dowling, Anthony R. Manning *

Department of Chemistry, University College Dublin, Belfield, Dublin 4, Ireland

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Abstract

The terminal CO ligands in the *cis*-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CNMe_2)_2]^{2+}$ cation are both labile and susceptible to nucleophilic attack at carbon depending on the nucleophile and the reaction conditions. The CO substitution is effected by nucleophiles L such as organonitriles, acetone or tertiary phosphines to give $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(L)(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$ and $[Fe_2(\eta\text{-}C_5H_5)_2(L)_2(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$ salts. Coordinated acetone is replaced by organonitriles and these in turn are displaced by phosphines. These reactions may be brought about thermally or more reliably by photolysis. The consequences of varying the UV lamp power and the nature of the phosphine are reported. Similar reactions take place with *cis*-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2\{\mu\text{-}CN(H)Me\}(\mu\text{-}CNMe_2)][SO_3CF_3]_2$ and *cis*-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CNH_2)(\mu\text{-}CNMe_2)][SO_3CF_3]_2$ salts, but phosphines deprotonate the μ-CNH_2 ligand and lead to decomposition. Harder nucleophiles Nu^- such as OH^-, OR^- (from NaCN–ROH) or NHR^- (from RNH_2) deprotonate the μ-CN(H)Me and μ-CNH_2 ligands but do not de-methylate the μ-$CNMe_2$ ligand to any great extent. Instead they attack one terminal CO ligand of *cis*-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$ to give *cis*-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)\{C(O)Nu\}(\mu\text{-}CNMe_2)_2][SO_3CF_3]$ with no evidence for attack elsewhere in the molecule. When $RNH_2=C_6H_{11}NH_2$, the reaction work-up may be modified so that $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNC_6H_{11})(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$ and $[Fe_2(\eta\text{-}C_5H_5)_2(CNC_6H_{11})_2(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$ are the products. They result from the dehydration of the first-formed carbamoyl complexes; a reaction which does not take place with the more volatile ^{i}PrNH$_2$. The mechanism of the reactions and the spectra of the products are discussed. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Iron; μ-Dimethylaminocarbyne; Substitution; Nucleophiles

1. Introduction

The relatively high *v*(CO) stretching frequencies of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CNEt_2)][SO_3CF_3]$, [**1**]-$[SO_3CF_3]$, and $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CNMe_2)_2]$-$[SO_3CF_3]_2$, [**3**]$[SO_3CF_3]_2$ [1,2], suggest that (a) their Fe–CO bonds should be relatively weak and the CO ligands susceptible to replacement, and (b) the CO should be electrophilic and susceptible to nucleophilic attack at carbon. During work which has been reported previously, we have found (a) to be the case. For example, both [**1**]$[SO_3CF_3]$ and [**3**]$[SO_3CF_3]_2$ undergo thermal and photochemical CO substitution with organoisocyanides and CN^- [3]. More interestingly, attempts to grow crystals of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CNMe_2)][SO_3CF_3]$ from acetonitrile solution resulted in its slow conversion to $[Fe_2(\eta\text{-}C_5H_5)_2$-$(CO)(NCMe)(\mu\text{-}CO)(\mu\text{-}CNMe_2)][SO_3CF_3]$ after 3 months at −10°C [4], and $[Fe_2(\eta\text{-}C_5H_5)_2(CO)$-$(CNBu^t)\{\mu\text{-}CN(H)Bu^t\}(\mu\text{-}CNMe_2)][SO_3CF_3]_2$ could not be isolated from its solutions in acetonitrile as it immediately converted to the isolable $[Fe_2(\eta\text{-}C_5H_5)_2$-$(CNBu^t)(NCMe)\{\mu\text{-}CN(H)Bu^t\}(\mu\text{-}CNMe_2)][SO_3CF_3]_2$ [5]. These observations led to an investigation into the CO substitution reactions of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2$-$(\mu\text{-}CO)(\mu\text{-}CNEt_2)][SO_3CF_3]$, $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$, and their various counterparts, with organonitriles and phosphines. Also included in this report are studies of the reactions of the nitrile-substituted species in which the nitriles are replaced by other ligands such as phosphines. These take place under mild conditions and allow the preparation of otherwise inaccessible compounds.

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* Corresponding author. Tel.: +353-1-7062311; fax: +353-1-7062127.

E-mail address: anthony.manning@ucd.ie (A.R. Manning).

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To investigate the electrophilicity of the CO ligands, (b) above, we have looked at the reactions of **[3]**$^{2+}$ with harder nucleophiles Nu$^-$ such as OH$^-$, OR$^-$, NR$_2^-$, H$^-$ and Me$^-$. Instead of CO replacement we observe only attack at the C atom of a terminal CO ligand converting it to a t-C(O)Nu$^-$ ligand. There is no evidence for attack at the μ-C atom of the μ-CNMe$_2^+$ ligand or any other site in the cation under the conditions used for these reactions. These results differ from those reported by Busetto et al. who found that [Fe$_2$(η-C$_5$H$_5$)$_2$(CO)$_2$(μ-CO)(μ-CNMe$_2$)]$^+$ and [Fe$_2$(η-C$_5$H$_5$)$_2$-(CO)(CNCH$_2$Ph)(μ-CO){μ-CN(Me)CH$_2$Ph}]$^+$ underwent nucleophilic attack at various sites [6].

2. Experimental

All reactions were carried out at room temperature in dried and deoxygenated solvents under an atmosphere of nitrogen unless it is stated otherwise. They were monitored by IR spectroscopy where appropriate. The photolytic reactions were carried out using a Philips HPR 125 W UV lamp (125 W) or an Applied Photophysics UV reactor with a HPR 400 W lamp (400 W).

Elemental analyses (Table 1) were determined by the Microanalytical Laboratory at University College Dublin. IR spectra (Table 1) were run on a Perkin–Elmer 1720 or a Mattson Galaxy FTIR 3000 spectrometer, and NMR spectra (Tables 2–4) on a JEOL JNM-GX 270 spectrometer.

Literature methods were used to prepare *cis*-[Fe$_2$(η-C$_5$H$_5$)$_2$(CO)$_2$(μ-CO)(μ-CNEt$_2$)][SO$_3$CF$_3$] [2], *cis*-[Fe$_2$(η-C$_5$H$_5$)$_2$(CO)(CNMe)(μ-CO){μ-CN(Et)Me}]I [1,3], *cis*-[Fe$_2$(η - C$_5$H$_5$)$_2$(CO)(CNEt)(μ - CO){μ - CN(Et)Me}]-[SO$_3$CF$_3$] [1,3], *cis*-[Fe$_2$(η-C$_5$H$_5$)$_2$(CO)$_2$(μ-CNMe$_2$)$_2$]-[SO$_3$CF$_3$]$_2$ [2], *cis*-[Fe$_2$(η-C$_5$H$_5$)$_2$(CO)$_2${μ-CN(H)Me}(μ-CNMe$_2$)][SO$_3$CF$_3$]$_2$ and *cis*-[Fe$_2$(η-C$_5$H$_5$)$_2$(CO)$_2$(μ-CNH$_2$)(μ-CNMe$_2$)][SO$_3$CF$_3$]$_2$ [5]. Other chemicals were purchased.

2.1. Reaction of *cis-[Fe$_2$(η-C$_5$H$_5$)$_2$(CO)(CNMe)(μ-CO)-{μ-CN(Et)Me}]$^+$ salts with PR$_3$ (R = Me or Et) in the presence of Me$_3$NO·2H$_2$O*

Me$_3$NO·2H$_2$O (0.4 g, 3 mmol) was added to a solution of *cis*-[Fe$_2$(η-C$_5$H$_5$)$_2$(CO)(CNMe)(μ-CO){μ-CN-(Et)Me}]I (0.45 g, 1 mmol) and PEt$_3$ (0.36 g, 3 mmol) in acetonitrile (50 cm^3). The mixture was stirred for 3 h, and the solvent removed at reduced pressure. The residue was taken up in chloroform. The solution was dried over magnesium sulfate, filtered and the solvent removed at reduced pressure. This residue was recrystallised from ethanol–ether mixtures to give brown crystals of [Fe$_2$(η-C$_5$H$_5$)$_2$(CNMe)(PEt$_3$)(μ-CO){μ-CN(Et)Me}][I], **[7b]**I, in 80% yield. [Fe$_2$(η-C$_5$H$_5$)$_2$-(CNEt)(PMe$_3$)(μ-CO){μ-CN(Et)Me}][SO$_3$CF$_3$], **[7c]**-[SO$_3$CF$_3$], was prepared similarly from *cis*-[Fe$_2$-(η-C$_5$H$_5$)$_2$(CO)(CNEt)(μ-CO){μ-CN(Et)Me}][SO$_3$CF$_3$] (yield 85%).

2.2. Reaction of *cis-[Fe$_2$(η-C$_5$H$_5$)$_2$(CO)$_2$(μ-CO)-(μ-CNEt$_2$)][SO$_3$CF$_3$] with MeCN*

A solution of *cis*-[Fe$_2$(η-C$_5$H$_5$)$_2$(CO)$_2$(μ-CO)(μ-CNEt$_2$)][SO$_3$CF$_3$] (0.47 g, 1 mmol) in acetonitrile was irradiated (125 W). After 2 h the reaction was complete. The solution was filtered, and an excess of Na[BPh$_4$] added. The solvent was removed at reduced pressure, and the resultant oil recrystallised from ethanol to give deep-green crystals of [Fe$_2$(η-C$_5$H$_5$)$_2$(CO)(NCMe)(μ-CO)(μ-CNEt$_2$)][BPh$_4$], **[6]**[BPh$_4$], which were filtered off and dried (yield 80%).

2.3. *The reaction of cis-[Fe$_2$(η-C$_5$H$_5$)$_2$(CO)$_2$(μ-CNMe$_2$)$_2$][SO$_3$CF$_3$]$_2$ and related salts with RCN (R = Me, Et, Ph)*

A solution of *cis*-[Fe$_2$(η-C$_5$H$_5$)$_2$(CO)$_2$(μ-CNMe$_2$)$_2$]-[SO$_3$CF$_3$]$_2$ (0.94 g, 1.5 mmol) in RCN (50 cm^3) was irradiated (125 W) for ca. 2 min. It turned green, was filtered, ether added, and cooled to −20°C overnight to give green crystals of [Fe$_2$(η-C$_5$H$_5$)$_2$(CO)(NCR)(μ-CNMe$_2$)$_2$][SO$_3$CF$_3$]$_2$, **[10a–c]**[SO$_3$CF$_3$]$_2$ {R = (**a**) Me, (**b**) Et, and (**c**) Ph}, in 85% yield. If the irradiation is carried out in acetonitrile with a 400 W lamp for 2 h, the same procedure gives yellow [Fe$_2$(η-C$_5$H$_5$)$_2$(NCMe)$_2$(μ-CNMe$_2$)$_2$][SO$_3$CF$_3$]$_2$, **[11]**[SO$_3$CF$_3$]$_2$, in 90% yield.

Similar procedures were used to convert *cis*-[Fe$_2$(η-C$_5$H$_5$)$_2$(CO)$_2${μ-CN(H)Me}(μ-CNMe$_2$)][SO$_3$CF$_3$]$_2$ to green [Fe$_2$(η-C$_5$H$_5$)$_2$(CO)(NCR){μ-CN(H)Me}(μ-CN-Me$_2$)][SO$_3$CF$_3$]$_2$, **[13a–c]**[SO$_3$CF$_3$]$_2$ {R = (**a**) Me, (**b**) Et, and (**c**) Ph} in 80% yields and yellow [Fe$_2$(η-C$_5$H$_5$)$_2$(NCMe)$_2${μ - CN(H)Me}(μ - CNMe$_2$)][SO$_3$CF$_3$]$_2$, **[14]**[SO$_3$CF$_3$]$_2$, (80% yield). They were also used to convert *cis*-[Fe$_2$(η-C$_5$H$_5$)$_2$(CO)$_2$(μ-CNH$_2$)(μ-CNMe$_2$)]-[SO$_3$CF$_3$]$_2$ to [Fe$_2$(η-C$_5$H$_5$)$_2$(CO)(NCPh)(μ-CNH$_2$)(μ-CNMe$_2$)][SO$_3$CF$_3$]$_2$, **[15]**[SO$_3$CF$_3$]$_2$, in 80% yield, and yellow [Fe$_2$(η-C$_5$H$_5$)$_2$(NCMe)$_2$(μ-CNH$_2$)(μ-CNMe$_2$)]-[SO$_3$CF$_3$]$_2$ which was isolated as [Fe$_2$(η-C$_5$H$_5$)$_2$-(NCMe)$_2$(μ-CNH$_2$)(μ-CNMe$_2$)][BPh$_4$]$_2$, **[16]**[BPh$_4$]$_2$ (yield 90%).

2.4. *The reaction of cis-[Fe$_2$(η-C$_5$H$_5$)$_2$(CO)$_2$-(μ-CNMe$_2$)$_2$][SO$_3$CF$_3$]$_2$ with acetone*

A solution of *cis*-[Fe$_2$(η-C$_5$H$_5$)$_2$(CO)$_2$(μ-CNMe$_2$)$_2$]-[SO$_3$CF$_3$]$_2$ (0.94 g, 1.5 mmol) in acetone (50 cm^3) was irradiated (125 W) for ca. 2 min. It was filtered, ether added, and cooled to −20°C overnight to give brown crystals of [Fe$_2$(η-C$_5$H$_5$)$_2$(CO)(Me$_2$C=O)(μ-CNMe$_2$)$_2$]-[SO$_3$CF$_3$]$_2$, **[12]**[SO$_3$CF$_3$]$_2$, in 85% yield.

Table 1
Analyses and IR spectra of the compounds described in the text

Number	Compound	Analyses [a]			IR Spectra [b]		
		%C	%H	%N	$\nu(CO)/\nu(CN)$	$\nu(CO_\mu)/\nu(CN_\mu)$	$\nu(\mu\text{-}CNR_2)$
6	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(NCMe)(\mu\text{-}CO)(\mu\text{-}CNEt_2)][BPh_4]$	69.7 (69.5)	5.4 (5.9)	3.6 (3.8)	1979 (10)	1814 (7.4)	1557 (4.0)
7a	$[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)(PPh_3)(\mu\text{-}CO)(\mu\text{-}CNMe_2)][SO_3CF_3]$	53.7 (54.0)	4.4 (4.4)	3.5 (3.6)	2168 (6.4) [c]	1767 (10)	1551 (3.9)
7b	$[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)(PEt_3)(\mu\text{-}CO)\{\mu\text{-}CN(Et)Me\}][I]$	44.0 (44.1)	6.0 (5.8)	4.1 (4.5)	2139 (7.3) [c]	1748 (10)	1549 (5.0)
7c	$[Fe_2(\eta\text{-}C_5H_5)_2(CNEt)(PMe_3)(\mu\text{-}CO)\{\mu\text{-}CN(Et)Me\}][SO_3CF_3]$	42.5 (42.6)	5.2 (5.2)	4.4 (4.5)	2135 (8.1) [c]	1763 (10)	1551 (5.2)
8a	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(PMe_3)(\mu\text{-}CNMe)(\mu\text{-}CNMe_2)][SO_3CF_3]$	40.7 (40.5)	4.8 (4.7)	4.5 (4.7)	1965 (10)	1729 (6.1) [c]	1577 (5.2)
8b	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(PEt_3)(\mu\text{-}CNMe)(\mu\text{-}CNMe_2)][SO_3CF_3]$	43.8 (43.5)	5.5 (5.4)	4.4 (4.4)	1968 (10)	1731 (3.2) [c]	1563 (4.8)
8c	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(PPh_2Me)(\mu\text{-}CNMe)(\mu\text{-}CNMe_2)][SO_3CF_3]$	50.0 (50.3)	4.5 (4.5)	3.8 (3.9)	1968 (10)	1771 (5.4) [c]	1558 (4.4)
9	$[Fe_2(\eta\text{-}C_5H_5)_2(PMe_3)_2(\mu\text{-}CNMe)(\mu\text{-}CNMe_2)][SO_3CF_3]\cdot H_2O$	40.7 (40.9)	4.3 (4.20	4.0 (4.3)		1705 (10) [c]	1541 (9.3)
10a	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(NCMe)(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2\cdot H_2O$	33.8 (34.1)	3.4 (3.7)	5.7 (5.7)	2035 (10)		1606 (8.8)
10b	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(NCEt)(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$	35.6 (35.9)	3.6 (3.7)	5.6 (5.7)	2032 (10)		1605 (9.6)
10c	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(NCPh)(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$	39.8 (39.9)	3.4 (3.5)	5.2 (5.4)	2034 (10)		1602 (7.6)
11	$[Fe_2(\eta\text{-}C_5H_5)_2(NCMe)_2(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$	36.0 (36.0)	3.8 (3.8)	3.6 (3.7)			1591 (10)
12	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(Me_2C{=}O)(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$	34.6 (34.9)	3.8 (4.0)	3.6 (3.7)	2021 (10)		1606 (9.6)
13a	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(NCMe)\{\mu\text{-}CN(H)Me\}(\mu\text{-}CNMe_2)][SO_3CF_3]_2$	34.2 (34.0)	3.4 (3.3)	6.3 (5.9)	2022 (10)		1605 (10)
13b	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(NCEt)\{\mu\text{-}CN(H)Me\}(\mu\text{-}CNMe_2)][SO_3CF_3]_2$	34.7 (35.0)	3.5 (3.5)	5.5 (5.8)	2022 (10)		1604 (10)
13c	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(NCPh)\{\mu\text{-}CN(H)Me\}(\mu\text{-}CNMe_2)][SO_3CF_3]_2$	39.4 (39.0)	3.3 (3.3)	5.2 (5.5)	2027 (10)		1606 (5.8)
14	$[Fe_2(\eta\text{-}C_5H_5)_2(NCMe)_2\{\mu\text{-}CN(H)Me\}(\mu\text{-}CNMe_2)][SO_3CF_3]_2$	34.9 (35.0)	3.6 (3.6)	7.5 (7.8)			1591 (10)
15	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(NCPh)(\mu\text{-}CNH_2)(\mu\text{-}CNMe_2)][SO_3CF_3]_2$	37.9 (38.2)	3.0 (3.1)	5.5 (5.6)	2020 (10)		1613 (5.0)
16	$[Fe_2(\eta\text{-}C_5H_5)_2(NCMe)_2(\mu\text{-}CNH_2)(\mu\text{-}CNMe_2)][BPh_4]_2$	75.4 (75.7)	6.0 (6.1)	5.2 (5.4)			1612 (7.9), 1589 (10)
17a	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(PMe_3)(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$	35.0 (34.9)	4.2 (4.1)	3.8 (3.7)	2012 (10)		1591 (8.1)
17b	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(PEt_3)(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$	37.7 (37.6)	4.7 (4.6)	3.5 (3.5)	2008 (7.6), 1991 (10)		1586 (9.8)
17c	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(PPh_2Me)(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2\cdot H_2O$	42.6 (42.8)	3.9 (4.1)	3.1 (3.1)	2006 (10)		1580 (7.5)
17d	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(PPh_3)(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2\cdot 3H_2O$	44.8 (44.6)	4.3 (4.3)	2.6 (2.8)	2019 (10)		1592 (7.8)
17e	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(\eta^1\text{-}DPPM)(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2\cdot H_2O$	48.5 (48.8)	4.3 (4.3)	2.4 (2.6)	2012 (10)		1580 (9.7)
17f	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(\eta^1\text{-}DPPE)(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2\cdot H_2O$	49.2 (49.3)	4.4 (4.4)	2.5 (2.6)	2002 (9.2)		1583 (10)
18a	$[Fe_2(\eta\text{-}C_5H_5)_2(PMe_3)_2(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$	35.5 (35.8)	5.0 (5.0)	3.4 (3.5)			1562 (10)
18b	$[Fe_2(\eta\text{-}C_5H_5)_2(\eta^2\text{-}DPPM)(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2\cdot 2H_2O$	48.1 (48.1)	4.2 (4.5)	2.6 (2.6)			1553 (10)
18c	$[Fe_2(\eta\text{-}C_5H_5)_2(\eta^2\text{-}DPPE)(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2\cdot H_2O$	49.3 (49.4)	4.5 (4.5)	2.4 (2.6)			1552 (10)
18d	$[Fe_2(\eta\text{-}C_5H_5)_2(\eta^2\text{-}DPPE)(\mu\text{-}CNMe_2)_2][BPh_4]_2$	77.3 (77.6)	6.0 (6.1)	2.3 (2.0)			1551 (10)
19a	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(PMe_3)\{\mu\text{-}CN(H)Me\}(\mu\text{-}CNMe_2)][SO_3CF_3]_2$	34.1 (34.0)	4.2 (3.9)	3.5 (3.8)	2004 (10)		1588 (8.7)

Table 1 (*Continued*)

Number	Compound	Analyses[a]			IR Spectra[b]		
		%C	%H	%N	$\nu(CO)/\nu(CN)$	$\nu(CO_{\mu})/\nu(CN_{\mu})$	$\nu(\mu\text{-}CNR_2)$
19b	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(PEt_3)\{\mu\text{-}CN(H)Me\}(\mu\text{-}CNMe_2)][SO_3CF_3]_2$	36.3 (36.7)	5.5 (5.2)	3.3 (3.3)	2005 (10)		1584 (9.6)
19c	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(PPh_2Me)\{\mu\text{-}CN(H)Me\}(\mu\text{-}CNMe_2)][SO_3CF_3]_2 \cdot 0.5Me_2C{=}O$	43.8 (43.6)	4.0 (4.0)	3.1 (3.1)	2012 (10)		1584 (7.7)
20	$Fe_2(\eta\text{-}C_5H_5)_2(PMe_3)_2\{\mu\text{-}CN(H)Me\}(\mu\text{-}CNMe_2)][SO_3CF_3]_2 \cdot 2H_2O$	33.7 (33.9)	3.6 (3.70	3.4 (3.4)			1562 (10)
21	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNCy)(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$	37.6 (37.8)	4.0 (4.4)	5.4 (5.2)	2173 (9.3), 2031 (10)		1589 (10)
22	$[Fe_2(\eta\text{-}C_5H_5)_2(CNCy)_2(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$	43.7 (43.2)	5.3 (5.1)	6.3 (6.4)	2175 (10)		1591 (7.7)
23a	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)\{C(O)OH\}(\mu\text{-}CNMe_2)_2][SO_3CF_3]$	40.3 (39.7)	4.4 (4.4)	4.6 (4.6)	2000 (10), 1601 (sh)[d]		1579 (6.5)
23b	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)\{C(O)OMe\}(\mu\text{-}CNMe_2)_2][SO_3CF_3]$	41.0 (40.7)	4.2 (4.3)	4.5 (4.8)	2009 (10), 1996 (4.3), 1613 (sh)[d]		1587 (9.6)
23c	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)\{C(O)OEt\}\ (\mu\text{-}CNMe_2)_2][SO_3CF_3] \cdot H_2O$	41.0 (40.5)	4.4 (4.4)	4.5 (4.5)	2008 (10), 1994 (3.7), 1614 (sh)[d]		1589 (10)
23d	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)\{C(O)O^iPr\}(\mu\text{-}CNMe_2)_2][SO_3CF_3] \cdot H_2O$	41.7 (41.5)	4.6 (4.6)	4.4 (4.4)	2008 (10), 1996 (5.2), 1618 (sh)[d]		1589 (8.70)
24a	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)\{C(O)NH_2\}(\mu\text{-}CNMe_2)_2][SO_3CF_3] \cdot MeCN$				2004 (10)		1610 (8.1)
24b	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)\{C(O)N(H)^iPr\}(\mu\text{-}CNMe_2)_2][SO_3CF_3] \cdot 2H_2O$	42.8 (43.2)	5.0 (5.4)	6.5 (6.3)	1998 (10), 1536 (3.1)[d]		1581 (5.9)
24c	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)\{C(O)N(H)Cy\}(\mu\text{-}CNMe_2)_2][SO_3CF_3] \cdot H_2O$	44.9 (44.8)	5.4 (5.5)	6.5 (6.3)	1982 (10), 1544 (4.9)[d]		1577 (9.2)
24d	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)\{C(O)NC_5H_{10}\}(\mu\text{-}CNMe_2)_2][SO_3CF_3]$				2006 (10)		1572 (3.3)
25a	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)\{C(O)H\}(\mu\text{-}CNMe_2)_2][SO_3CF_3]$				2005 (10)		1614 (6.1)
25b	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)\{C(O)Me\}(\mu\text{-}CNMe_2)_2][SO_3CF_3]$				2003 (10)		1618 (6.5)

[a] Found (Calc.).

[b] IR spectra (1500–2200 cm^{-1}) measured in KBr discs. Peak positions (cm^{-1}) with relative peak heights in parentheses. $\nu(t\text{-}CNR) = 2135\text{–}2168\ cm^{-1}$, $\nu(t\text{-}CO) = 1965\text{–}2035\ cm^{-1}$, $\nu(\mu\text{-}CO) = 1748\text{–}1814\ cm^{-1}$, $\nu(\mu\text{-}CNR) = 1705\text{–}1729\ cm^{-1}$, $\nu(\mu\text{-}CNR_2) = 1541\text{–}1613\ cm^{-1}$, and $\nu\{C{=}O(Nu)\} = 1544\text{–}1618\ cm^{-1}$.

[c] $\nu(C\text{–}NR)$ modes.

[d] $\nu\{C{=}O(Nu)\}$ modes.

Table 2
^1H-NMR spectra of the complexes described in the text

	Compounds	Resonances [a]			
		η-C_5H_5	μ-$CNMe_2$	μ-CNMe, μ-CNH_2, μ-CN(H)Me	t-CNMe, t-NCR, PR_3, t-C(O)OR, t-C(O)NHR
6	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(NCMe)(\mu\text{-}CO)(\mu\text{-}CNEt_2)][BPh_4]$ [b]	5.17(5), 4.97(5)	5.22(1, m), 5.19(1, m, $J_{AB} = 15.41$), 1.77(3, t, $J_{HH} = 7.41$), 4.71(4, m, $J_{AB} = 14.47$), 1.59(3, t, $J_{HH} = 7.35$)		1.99(3), 6.78–7.33(20, b, m)
7a	$[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)(PPh_3)(\mu\text{-}CO)(\mu\text{-}CNMe_2)][SO_3CF_3]$	4.81(5), 4.45(5, d, $J_{PH} = 1.28$)	4.33(3, d, $J_{PH} = 1.10$), 4.12(3)		2.42(3), 7.40(m, 9), 7.21(m, 6)
7b	$[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)(PEt_3)(\mu\text{-}CO)\{\mu\text{-}CN(Et)Me\}][I]$ (isomer A) [e]	4.78(5), 4.68(5, d, $J_{PH} = 1.28$)	4.13(3), 4.51(m, 1), 4.72(m, 1), 1.58(3, t, $J_{HH} = 7.33$)		3.03(3), 1.85(6, m, $J_{PH} = 7.74$), 0.96 (9, m, $J_{PH} = 14.86$), $J_{HH} = 7.43$)
7b	$[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)(PEt_3)(\mu\text{-}CO)\{\mu\text{-}CN(Et)Me\}][I]$ (isomer B) [e]	4.78(5), 4.66(5, d, $J_{PH} = 1.28$)	4.12(3, d, $J_{PH} = 0.60$), obs, 1.72(3, $J_{HH} = 7.33$)		3.08(3) obs
7c	$[Fe_2(\eta\text{-}C_5H_5)_2(CNEt)(PMe_3)(\mu\text{-}CO)\{\mu\text{-}CN(Et)Me\}][SO_3CF_3]$ (isomer A) [e]	4.79(5), 4.65(5, d, $J_{PH} = 1.65$)	4.08(3), 4.61(1, m), 4.18(1, m), 1.67(3, t, $J_{HH} = 7.33$)		3.37(2, dq), 1.12(3, t, $J_{HH} = 7.24$), 0.94 (9, d, $J_{PH} = 9.52$)
7c	$[Fe_2(\eta\text{-}C_5H_5)_2(CNEt)(PMe_3)(\mu\text{-}CO)\{\mu\text{-}CN(Et)Me\}][SO_3CF_3]$ (isomer B) [e]	4.78(5), 4.67(5, d, $J_{PH} = 1.65$)	4.06(3), CH_2 obs, 1.55(3, t, $J_{HH} = 7.33$)		CH_2 obs, 1.11(3, t, $J_{HH} = 7.24$), 0.95 (9, d, $J_{PH} = 9.53$)
8a	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(PMe_3)(\mu\text{-}CNMe)(\mu\text{-}CNMe_2)][SO_3CF_3]$	5.12(5), 4.74(5, d, $J_{PH} = 1.47$)	4.07(3), 4.01(3, d, $J_{PH} = 1.10$)	3.64(3, d, $J_{PH} = 1.65$)	0.88(9, d, $J_{PH} = 9.71$)
8b	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(PEt_3)(\mu\text{-}CNMe)(\mu\text{-}CNMe_2)][SO_3CF_3]$ [b]	5.34(5), 4.96(5, d, $J_{PH} = 1.28$)	4.33(3), 4.22(3, d, $J_{PH} = 0.91$)	3.77(3, d, $J_{PH} = 1.65$)	1.51(6, m $J_{PH} = 7.69$), 0.95(dt, $J_{PH} = 14.29$, $J_{HH} = 7.31$)
8c	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(PPh_2Me)(\mu\text{-}CNMe)(\mu\text{-}CNMe_2)][SO_3CF_3]$	5.10(5), 4.79(5, d, $J_{PH} = 1.47$)	3.99(3, d, $J_{PH} = 1.10$), 3.87(3)	3.65(3, d, $J_{PH} = 1.46$)	1.40(3, d, $J_{PH} = 8.80$), 7.44(10, b, m)
9	$[Fe_2(\eta\text{-}C_5H_5)_2(PMe_3)_2(\mu\text{-}CNMe)(\mu\text{-}CNMe_2)][SO_3CF_3]\cdot H_2O$ (isomer A) [f]	5.07(d, 10, $J_{PH} = 1.69$)	4.13(6)	3.62(3)	1.06(18, d, $J_{PH} = 9.28$)
9	$[Fe_2(\eta\text{-}C_5H_5)_2(PMe_3)_2(\mu\text{-}CNMe)(\mu\text{-}CNMe_2)][SO_3CF_3]\cdot H_2O$ (isomer B) [f]	5.08(10, d, $J_{PH} = 1.46$)	4.20(6)	3.72(3)	1.14(18, d, $J_{PH} = 9.16$)
10a	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(NCMe)(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2\cdot H_2O$ [c]	5.59(5), 5.42(5)	4.51(6), 4.28(6)		2.04(3)
10b	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(NCEt)(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$	5.76(5), 5.57(5)	4.70(6), 4.42(6)		2.44(2, q, $J_{HH} = 7.32$), 0.95(3, t)
10c	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(NCPh)(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$ [b]	5.85(5), 5.75(5)	4.76(6), 4.46(6)		7.62(5, b, m)
11	$[Fe_2(\eta\text{-}C_5H_5)_2(NCMe)_2(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$ [b]	5.24(10)	4.69(12)		2.05(6)
12	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(Me_2C{=}O)(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$ [b]	5.70(5), 5.52(5)	4.86(6), 4.49(6)		3.09(6, b)
13a	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(NCMe)\{\mu\text{-}CN(H)Me\}(\mu\text{-}CNMe_2)][SO_3CF_3]_2$ [b]	5.75(5), 5.55(5)	4.69(3), 4.41(3)	4.16(3, b)	2.04(3)
13b	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(NCEt)\{\mu\text{-}CN(H)Me\}(\mu\text{-}CNMe_2)][SO_3CF_3]_2$	5.38(5), 5.23(5)	4.42(3), 4.17(3)	4.04(3, b)	2.36(2, q, $J_{HH} = 7.51$), 1.21(3, t)

Table 2 (*Continued*)

	Compounds	Resonances [a]			
		$\eta\text{-}C_5H_5$	$\mu\text{-}CNMe_2$	$\mu\text{-}CNMe$, $\mu\text{-}CNH_2$, $\mu\text{-}CN(H)Me$	t-CNMe, t-NCR, PR_3, t-C(O)OR, t-C(O)NHR
13c	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(NCPh)\{\mu\text{-}CN(H)Me\}(\mu\text{-}CNMe_2)]$-$[SO_3CF_3]_2$ [b]	5.79(5), 5.67(5)	4.78(3), 4.46(3)	4.28(3, b)	7.61(5, b, m)
14	$[Fe_2(\eta\text{-}C_5H_5)_2(NCMe)_2\{\mu\text{-}CN(H)Me\}(\mu\text{-}CNMe_2)][SO_3CF_3]_2$	5.42(5), 5.15(5)	4.72(6)	4.41(3)	2.00(6)
15	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(NCPh)(\mu\text{-}CNH_2)(\mu\text{-}CNMe_2)][SO_3CF_3]_2$	5.41(5), 5.33(5)	4.48(3), 4.20(3)	12.33(1, b) 11.6(1, b)	7.66(5, b, m)
16	$[Fe_2(\eta\text{-}C_5H_5)_2(NCMe)_2(\mu\text{-}CNH_2)(\mu\text{-}CNMe_2)][BPh_4]_2$ [b]	5.13(10)	4.69(6)		1.92(6)
17a	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(PMe_3)(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$	5.50(5), 5.28(5, d, $J_{PH} = 1.65$)	4.13(6, d, $J_{PH} = 0.66$) 4.10 (6, d, $J_{PH} = 1.46$)		1.05(9, d, $J_{PH} = 10.1$)
17b	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(PEt_3)(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$[b]	5.89(5), 5.68(5, d, $J_{PH} = 1.28$)	4.49(6), 4.38(6, d, $J_{PH} = 1.1$)		1.66(6, m, $J_{HH} = 7.51$, $J_{PH} = 7.71$), 1.05 (9, d, t, $J_{PH} = 14.84$)
17c	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(PPh_2Me)(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2\cdot H_2O$[b]	5.88(5), 5.66(5, d, $J_{PH} = 1.28$)	4.33(6, d, $J_{PH} = 1.28$), 4.11(6)		1.72(9, d, $J_{PH} = 8.98$), 7.64(10, m)
17d	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(PPh_3)(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2\cdot 3H_2O$	5.61(5, d, $J_{PH} = 0.92$), 5.46(5)	3.99(6, d, $J_{PH} = 1.1$), 3.88(6)		7.34(15, m)
17e	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(\eta^1\text{-}DPPM)(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2\cdot H_2O$	5.46(5), 5.39(5, d, $J_{PH} = 1.29$)	4.03(6, d, $J_{PH} = 1.29$), 3.92(6)		3.55(2, m), 7.25(20, b, m)
17f	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(\eta^1\text{-}DPPE)(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2\cdot H_2O$	5.47(5), 5.14(5, d, $J_{PH} = 1.28$)	3.95(6, d, $J_{PH} = 1.46$), 3.69(6, d, $J_{PH} = 0.55$)		3.53(4, b, m), 7.55(10, b, m), 7.14(10, b, m)
18a	$[Fe_2(\eta\text{-}C_5H_5)_2(PMe_3)_2(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$ (isomer A)[g]	5.08(10, d, $J_{PH} = 1.46$)	4.20(12)		1.04(18, d, $J_{PH} = 9.28$)
18a	$[Fe_2(\eta\text{-}C_5H_5)_2(PMe_3)_2(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$ (isomer B)[g]	5.07(10, d, $J_{PH} = 1.69$)	4.13(12)		1.06(18, d, $J_{PH} = 9.28$)
18b	$[Fe_2(\eta\text{-}C_5H_5)_2(\eta^2\text{-}DPPM)(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2\cdot 2H_2O$	5.73(10)	3.68(12)		3.52(2, m), 7.66(20, b, m)
18c	$[Fe_2(\eta\text{-}C_5H_5)_2(\eta^2\text{-}DPPE)(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2\cdot H_2O$	5.62(10, d, $J_{PH} = 0.92$)	3.66(12)		3.53(4, b, m), 7.63(20, b, m)
19a	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(PMe_3)\{\mu\text{-}CN(H)Me\}(\mu\text{-}CNMe_2)]$-$[SO_3CF_3]_2$[d]	5.47(5), 5.24(5, d, $J_{PH} = 1.84$)	4.10(3), 4.07(3, d, $J_{PH} = 1.10$)	3.82(3, dd, $J_{PH} = 1.10$, $J_{HH} = 4.77$)	1.09(9, d, $J_{PH} = 10.25$)
19b	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(PEt_3)\{\mu\text{-}CN(H)Me\}(\mu\text{-}CNMe_2)]$-$[SO_3CF_3]_2$[d]	5.50(5), 5.23(5, d, $J_{PH} = 1.10$)	4.15(3), 4.06(3, d, $J_{PH} = 1.10$)	3.86(3, dd, $J_{HH} = 4.67$, $J_{PH} = 0.73$)	1.46(6, m, $J_{HH} = 7.69$, $J_{PH} = 13.19$), 0.93 (9, m,. $J_{HH} = 7.69$, $J_{PH} = 15.02$)
19c	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(PPh_2Me)\{\mu\text{-}CN(H)Me\}(\mu\text{-}CNMe_2)]$-$[SO_3CF_3]_2\cdot 0.5Me_2CO$[d]	5.46(5), 5.31(5, d, $J_{PH} = 1.47$)	4.21(3), 4.07(3, d, $J_{PH} = 1.28$)	3.66(3, dd, $J_{HH} = 4.77$, $J_{PH} = 1.29$)	1.60(3, d, $J_{PH} = 9.16$), 7.49(6, b, m), 7.26 (4, b, m)

Table 2 (*Continued*)

	Compounds	Resonances [a]			
		$\eta\text{-}C_5H_5$	$\mu\text{-}CNMe_2$	μ-CNMe, $\mu\text{-}CNH_2$, μ-CN(H)Me	t-CNMe, t-NCR, PR_3, t-C(O)OR, t-C(O)NHR
20	$Fe_2(\eta\text{-}C_5H_5)_2(PMe_3)_2\{\mu\text{-}CN(H)Me\}(\mu\text{-}CNMe_2)][SO_3CF_3]_2\cdot 2H_2O$ (isomer A)[h]	5.06(5)	4.17(6)	3.98(3)	1.04(18, d, $J_{PH} = 9.16$)
20	$Fe_2(\eta\text{-}C_5H_5)_2(PMe_3)_2\{\mu\text{-}CN(H)Me\}(\mu\text{-}CNMe_2)][SO_3CF_3]_2\cdot 2H_2O$ (isomer B)[h]	4.93(5)	4.10(6)	3.86(3)	1.16(18, d, $J_{PH} = 9.15$)
21	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNCy)(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$ (*trans* isomer)	5.41(5), 5.27(5)	4.39(6), 4.17(6)		3.78 (1, m), 1.09–1.82(10, m)
	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNCy)(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$ (*cis* isomer)	5.52(5), 5.40(5)	4.11(6), 4.06(6)		3.78 (1, m), 1.09–1.82(10, m)
22	$[Fe_2(\eta\text{-}C_5H_5)_2(CNCy)_2(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$	5.38(10)	4.16(12)		3.57(2, m), 1.23–1.77(20, m)
23a	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)\{C(O)OH\}(\mu\text{-}CNMe_2)_2][SO_3CF_3]$[b]	5.25(5), 5.15(5)	4.06(6), 4.00(6)		12.73(1, br)
23b	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)\{C(O)OMe\}(\mu\text{-}CNMe_2)_2][SO_3CF_3]$	5.18(5), 5.08(5)	4.02(6), 3.92(6)		0.92(3)
23c	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)\{C(O)OEt\}\ (\mu\text{-}CNMe_2)_2][SO_3CF_3]\cdot H_2O$	5.20(5), 5.06(5)	4.00(6), 3.92(6)		3.46(2, q, $J_{HH} = 7.33$), 0.87(3, t)
23d	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)\{C(O)O^iPr\}(\mu\text{-}CNMe_2)_2][SO_3CF_3]\cdot H_2O$	5.23(5), 5.04(5)	4.01(6), 3.88(6)		3.94(1, sp, $J_{HH} = 6.4$), 0.94(6, d)
24b	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)\{C(O)N(H)^iPr\}(\mu\text{-}CNMe_2)_2][SO_3CF_3]\cdot 2H_2O$[b]	5.42(5), 5.20(5)	4.14(6), 4.05(6)		3.63(1, m, $J_{HH} = 6.55$), 0.82(6, d)
24c	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)\{C(O)N(H)Cy\}(\mu\text{-}CNMe_2)_2][SO_3CF_3]\cdot H_2O$[b]	5.43(5), 5.21(5)	4.15(6), 4.06(6)		3.28(1, m), 0.97–1.56(10, m)

[a] Chemical shifts (δ) measured in ppm downfield from Me_4Si as an internal standard in CD_3CN solution unless it is stated otherwise. In parentheses are (integration, multiplicity, coupling constants in Hz). All resonances are singlets unless it is stated otherwise; d = doublet, t = triplet, q = quartet, m = multiplet, br = broad.

[b] Spectra run in $(CD_3)_2CO$ solution.

[c] Spectra run in CD_3OD solution.

[d] Spectra run in acidified CD_3CN solution.

[e] α/β isomers, A:B = ca. 52:48 in both cases.

[f] Isomer ratio A:B = ca. 50:50.

[g] Isomer ratio A;B = 90:10.

[h] Isomer ratio A:B = ca. 50:50.

Table 3
^{13}C-NMR spectra of the complexes described in the text

	Compound	Resonances[a]			
		η-C_5H_5	μ-$CNMe_2$	μ-CO, μ-CNMe, μ-CN(H)Me	t-CO, t-CNMe, t-NCMe, PR_3, t-C(O)OR, t-C(O)NHR
8a	$[Fe_2(\eta-C_5H_5)_2(CO)(PMe_3)-(\mu-CNMe)(\mu-CNMe_2)][SO_3CF_3]$	88.69, 88.14	327.13(d, $J_{PC} =$ 20.45), 54.13, 52.93	238.97(d, $J_{PC} =$ 23.87), 45.50	217.51, 17.78(d, $J_{PC} = 30.70$)
10a	$[Fe_2(\eta-C_5H_5)_2(CO)(NCMe)-(\mu-CNMe_2)_2][BPh_4]$	91.78, 90.47	318.02, 54.34, 53.76		207.83, ---, 4.94
10c	$[Fe_2(\eta-C_5H_5)_2(CO)(NCPh)-(\mu-CNMe_2)_2][SO_3CF_3]_2$[b]	92.33, 91.25	318.06, 54.61, 53.73		208.70, 110.93, 130.28–135.52
11	$[Fe_2(\eta-C_5H_5)_2(NCMe)_2-(\mu-CNMe_2)_2][SO_3CF_3]_2$	88.72	329.42, 52.55		133.94, 4.07
13a	$[Fe_2(\eta-C_5H_5)_2(CO)(NCMe)-\{\mu-CN(H)Me\}(\mu-CNMe_2)]-[SO_3CF_3]_2$[b]	91.78, 90.51(b)	319.07, 54.33, 53.71(b)	319.07, 44.19	208.38, 134.04, 4.04
13c	$[Fe_2(\eta-C_5H_5)_2(CO)(NCPh)-\{\mu-CN(H)Me\}(\mu-CNMe_2)]-[SO_3CF_3]_2$[b]	91.81, 90.76(b)	318.71, 54.04, 53.69(b)	318.71, 44.23	---, 144.21, 130.01–135.21
17a	$[Fe_2(\eta-C_5H_5)_2(CO)(PMe_3)-(\mu-CNMe_2)_2][SO_3CF_3]_2$	92.86, 91.08	316.57(d, $J_{PC} =$ 20.45), 55.77, 54.66		212.34, 19.23($J_{PC} = 130.71$)
17c	$[Fe_2(\eta-C_5H_5)_2(CO)(PPh_2Me)-(\mu-CNMe_2)_2][SO_3CF_3]_2\cdot H_2O$	93.61, 91.23	317.27(d, $J_{PC} =$ 17.11), 56.57, 53.91		211.79, 17.19(d, $J_{PC} = 30.73$), 135.21–130.43
17e	$[Fe_2(\eta-C_5H_5)_2(CO)(\eta^1-DPPM)-(\mu-CNMe_2)_2][SO_3CF_3]_2\cdot H_2O$	93.79, 90.47	3117.92(d, $J_{PC} =$ 17.03), 56.72, 54.16		209.91, 32.01(t, $J_{PC} = 35.80$), 129.62–138.51
17f	$[Fe_2(\eta-C_5H_5)_2(CO)(\eta^1-DPPE)-(\mu-CNMe_2)_2][SO_3CF_3]_2\cdot H_2O$	93.16, 91.17	318.11(d, $J_{PC} =$ 18.75), 56.39, 54.16		211.49, 22.81(t, $J_{PC} = 30.69$), 128.72–138.43
18a	$[Fe_2(\eta-C_5H_5)_2(PMe_3)_{2.}(\mu-CNMe_2)_2][SO_3CF_3]_2$ (isomer A)	91.25	328.34(t, $J_{PC} = 16.21$), 54.66		20.53(d, $J_{PC} = 30.72$)
18a	$[Fe_2(\eta-C_5H_5)_2(PMe_3)_2-(\mu-CNMe_2)_2]-[SO_3CF_3]_2$ (isomer B)	90.70	----, 54.11		21.51(d, $J_{PC} = 30.72$)
18b	$[Fe_2(\eta-C_5H_5)_2(\eta^2-DPPM)-(\mu-CNMe_2)_2][SO_3CF_3]_2\cdot 2H_2O$[b]	90.72	324.75(t, $J_{PC} = 17.10$), 54.49		19.27(t, $J_{PC} = 30.67$), 130.18–136.90
18c	$[Fe_2(\eta-C_5H_5)_2(\eta^2-DPPE)-(\mu-CNMe_2)_2][SO_3CF_3]_2\cdot H_2O$	90.77	322.77(t, $J_{PC} = 17.10$), 55.14		18.33(t, $J_{PC} = 32.42$), 130.50–137.45
19a	$[Fe_2(\eta-C_5H_5)_2(CO)(PMe_3)-\{\mu-CN(H)Me\}(\mu-CNMe_2)]-[SO_3CF_3]_2$[b]	92.43, 91.78	319.31(d, $J_{PC} = 18.75$), 55.41, 53.91	315.42(d, $J_{PC} = 22.17$), 45.25	212.89, 18.45(d, $J_{PC} = 32.34$)
19b	$[Fe_2(\eta-C_5H_5)_2(CO)(PEt_3)-\{\mu-CN(H)Me\}(\mu-CNMe_2)]-[SO_3CF_3]_2$[c]	92.23, 90.47	---, 55.59, 53.66	---, 45.32	212.25, 19.93(d, $J_{PC} = 27.31$), 8.41(d, $J_{PC} = 6.83$)
21	$[Fe_2(\eta-C_5H_5)_2(CO)(CNCy)-(\mu-CNMe_2)_2][SO_3CF_3]_2$ (*trans* isomer)	89.7, 89.3	317.9, 56.5, 52.6		206.1, 132.4
	$[Fe_2(\eta-C_5H_5)_2(CO)(CNCy)-(\mu-CNMe_2)_2][SO_3CF_3]_2$ (*cis* isomer)	89.6, 88.1	324.3, 52.6, 49.5		207.4, 133.1
22	$[Fe_2(\eta-C_5H_5)_2(CNCy)_2-(\mu-CNMe_2)_2][SO_3CF_3]_2$	89.7	314.3, 52.6		142.7
23a	$[Fe_2(\eta-C_5H_5)_2(CO)\{C(O)OH\}-(\mu-CNMe_2)_2][SO_3CF_3]$	91.1, 90.2	316.3, 55.6, 54.7		203.6, 173.2
23b	$[Fe_2(\eta-C_5H_5)_2(CO)\{C(O)OMe\}-(\mu-CNMe_2)_2][SO_3CF_3]$	91.4, 90.6	317.4, 56.3, 55.3		206.3, 198.8
23c	$[Fe_2(\eta-C_5H_5)_2(CO)\{C(O)OEt\}(\mu-CNMe_2)_2][SO_3CF_3]\cdot H_2O$	92.3, 91.6	318.1, 55.7, 54.9		204.2, 187.1
23d	$[Fe_2(\eta-C_5H_5)_2(CO)\{C(O)O^iPr\}-(\mu-CNMe_2)_2][SO_3CF_3]\cdot H_2O$	92.7, 92.1	318.7, 56.1, 55.8		205.3, 183.7
24b	$[Fe_2(\eta-C_5H_5)_2(CO)\{C(O)N-(H)^iPr\}(\mu-CNMe_2)_2][SO_3CF_3]\cdot 2H_2O$	90.9, 90.6	318.2, 52.8, 52.3		207.5, 172.1
24c	$[Fe_2(\eta-C_5H_5)_2(CO)\{C(O)N-(H)Cy\}(\mu-CNMe_2)_2][SO_3CF_3]\cdot H_2O$	91.4, 90.7	319.1, 54.8, 54.2		208.9, 169.1

[a] Chemical shifts (δ) measured in ppm downfield from Me_4Si as an internal standard in CD_3CN solution unless it is stated otherwise. In parentheses are (multiplicity, coupling constants in Hz). All resonances are singlets unless it is stated otherwise; d = doublet, t = triplet. --- indicates an anticipated resonance which was too weak to be detected or obscured.

[b] Spectra run in $(CD_3)_2CO$ solution.

[c] Spectrum run in acidified CD_3CN solution.

Table 4
^{31}P-NMR spectra of some of the complexes described in the text.

	Compound	Resonances[a]			
		$\delta_{coord}/\delta_{chelate}$	δ_{free}	Δ_1	Δ_2
17a	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(PMe_3)(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$	23.5			
17c	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(PPh_2Me)(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2\cdot H_2O$[b]	34.69			
17e	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(\eta^1\text{-}DPPM)(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2\cdot H_2O$	46.78(d, $J_{PP}=51.90$)	−25.00(d)	70.38	
17f	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(\eta^1\text{-}DPPE)(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2\cdot H_2O$	47.58(d, $J_{PP}=30.5$)	−11.75(d)	60.08	
18a	$[Fe_2(\eta\text{-}C_5H_5)_2(PMe_3)_2(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$[b]	18.78			
18b	$[Fe_2(\eta\text{-}C_5H_5)_2(\eta^2\text{-}DPPM)(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2\cdot 2H_2O$	72.2(b)			+25.44
18c	$[Fe_2(\eta\text{-}C_5H_5)_2(\eta^2\text{-}DPPE)(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2\cdot H_2O$	45.71			−1.87

[a] Chemical shifts (δ) measured in ppm downfield from 85% phosphoric acid in D_2O as an external standard in CD_3CN solution unless it is stated otherwise. In parentheses are (multiplicity, coupling constants in Hz). All resonances are singlets unless it is stated otherwise; d = doublet, t = triplet, b = broad. $\Delta_1=\delta_{coord}-\delta_{free}$. $\Delta_2=\delta_{chelate}-\delta_{coord}$.

[b] Spectra run in $(CD_3)_2CO$ solution.

Dissolution of [**12**]$[SO_3CF_3]_2$ in acetonitrile resulted in an instantaneous colour change from brown to green and the quantitative formation of [**13a**]$[SO_3CF_3]_2$.

2.5. The reaction of cis-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$ *and related salts with phosphines and diphosphines*

A solution of *cis*-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$ (0.94 g, 1.5 mmol) and Ph_3P (0.43 g, 1.65 mmol) in acetone (50 cm^3) was irradiated (125 W) for 1 h. The mixture was filtered, the solvent removed at reduced pressure, and the residue dissolved in the minimum of ethanol. On cooling, green crystals were deposited. They were filtered off, dried, and identified as $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(PPh_3)(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2\cdot 3H_2O$, [**17d**]$[SO_3CF_3]_2\cdot 3H_2O$ (yield 50%). If Ph_3P is replaced by $Ph_2P(CH_2)_nPPh_2$ {$n=1$ (DPPM), and 2 (DPPE)}, irradiation for 1 h and product crystallisation from propanol–ethanol mixtures gave green crystals of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)\{\eta^1\text{-}Ph_2P(CH_2)_nPPh_2\}(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2\cdot H_2O$, [**17e–f**]$[SO_3CF_3]_2\cdot H_2O$ {$n=$ (**e**) 1, and (**f**) 2}, (yield 65%). When the irradiation was continued for 2 h, yellow $[Fe_2(\eta\text{-}C_5H_5)_2\{\eta^2\text{-}Ph_2PCH_2PPh_2\}(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2\cdot 2H_2O$, [**18b**]$[SO_3CF_3]_2\cdot 2H_2O$, and $[Fe_2(\eta\text{-}C_5H_5)_2\{\eta^2\text{-}Ph_2P(CH_2)_2PPh_2\}(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2\cdot H_2O$, [**18c**]$[SO_3CF_3]_2\cdot H_2O$, were formed and isolated in 60% yields. The last was converted to $[Fe_2(\eta\text{-}C_5H_5)_2\{\eta^2\text{-}Ph_2P(CH_2)_2PPh_2\}(\mu\text{-}CNMe_2)_2][BPh_4]_2$ as in Section 2.2 above.

2.6. The reaction of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(NCR)(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$ *and related salts with phosphines and diphosphines*

$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(NCPh)(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$, [**10c**]$[SO_3CF_3]_2$, (1.05 g, 1.5 mmol) was dissolved in acetone (50 cm^3) and PMe_3 (0.39 g, 4.5 mmol) added. After stirring the reaction mixture for 1 h, it was filtered, ether added to it, and cooled to −20°C overnight. The deposited green crystals were filtered off and dried. They were identified as $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(PMe_3)(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$, [**17a**]$[SO_3CF_3]_2$ (yield 90%). Similar reactions of [**10c**]$[SO_3CF_3]_2$ with PEt_3 and PPh_2Me only took place on UV irradiation (125 W) to give green $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(PR_3)(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$, [**17b–c**]$[SO_3CF_3]_2$ {$PR_3=$ (**b**) PEt_3, and (**c**) PPh_2Me} (yields 90%).

$[Fe_2(\eta\text{-}C_5H_5)_2(NCMe)_2(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$, [**11**]$[SO_3CF_3]_2$, (0.98 g, 1.5 mmol) reacted with PMe_3 (0.78 g, 9 mmol) on stirring in the dark to give yellow $[Fe_2(\eta\text{-}C_5H_5)_2(PMe_3)_2(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$, [**18**]$[SO_3CF_3]_2$, in a yield of 95% after work-up as above.

If [**10c**]$[SO_3CF_3]_2$ or [**11**]$[SO_3CF_3]_2$ are replaced by $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(NCPh)\{\mu\text{-}CN(H)Me\}(\mu\text{-}CNMe_2)][SO_3CF_3]_2$,[**13c**]$[SO_3CF_3]_2$, or $[Fe_2(\eta\text{-}C_5H_5)_2(NCMe)_2\{\mu\text{-}CN(H)Me\}(\mu\text{-}CNMe_2)][SO_3CF_3]_2$, [**14**]$[SO_3CF_3]_2$, in the above reactions, the same procedures allow the isolation of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(PR_3)\{\mu\text{-}CN(H)Me\}(\mu\text{-}CNMe_2)][SO_3CF_3]_2$, [**19a**,**b**]$[SO_3CF_3]_2$ {$PR_3=$ (**a**) PMe_3, and (**b**) PEt_3}, $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(PPh_2Me)\{\mu\text{-}CN(H)Me\}(\mu\text{-}CNMe_2)][SO_3CF_3]_2\cdot 0.5Me_2C{=}O$, [**19c**]$[SO_3CF_3]_2\cdot 0.5Me_2C{=}O$, and $[Fe_2(\eta\text{-}C_5H_5)_2(PMe_3)_2\{\mu\text{-}CN(H)Me\}(\mu CNMe_2)][SO_3CF_3]_2\cdot 2H_2O$, [**20**]$[SO_3CF_3]_2\cdot 2H_2O$. [**13c**]$[SO_3CF_3]_2$ fails to react with PPh_3 or $Ph_2P(CH_2)_nPPh_2$ ($n=1$ or 2).

$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(NCPh)(\mu\text{-}CNH_2)(\mu\text{-}CNMe_2)][SO_3CF_3]_2$, [**15**]$[SO_3CF_3]_2$, and $[Fe_2(\eta\text{-}C_5H_5)_2(NCMe)_2(\mu\text{-}CNH_2)(\mu\text{-}CNMe_2)][BPh_4]_2$, [**16**]$[BPh_4]_2$, decompose on treatment with PMe_3, PPh_2Me and $Ph_2P(CH_2)_2PPh_2$.

2.7. The reaction of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(NCPh)(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$ *with KCN*

$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(NCPh)(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$, [**10c**]$[SO_3CF_3]_2$, (1.05 g, 1.5 mmol) was dissolved in methanol (50 cm^3) and KCN (1 g, 3 mmol) added.

After stirring the reaction mixture for 1 h, it was filtered, and the solvent removed at reduced pressure. The residue was taken up in the minimum of dichloromethane, the solution dried with $MgSO_4$, and ethanol–ether mixtures added to it. The whole was cooled to −20°C overnight, and the deposited green crystals were filtered off and dried. They were identified as $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CN)(\mu\text{-}CNMe_2)_2][SO_3CF_3]$ (yield 50%). If this reaction is repeated in the presence of UV irradiation (400 W) $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CN)(\mu\text{-}CNMe_2)_2][SO_3CF_3]$ is formed first, but after 2 h the sole product is $[Fe_2(\eta\text{-}C_5H_5)_2(CN)_2(\mu\text{-}CNMe_2)_2]$ which was isolated by column chromatography (ethanol–alumina) and crystallised as green crystals in 90% yield. Both have been reported previously [3].

2.8. Deprotonation of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(PR_3)\{\mu\text{-}CN(H)Me\}(\mu\text{-}CNMe_2)][SO_3CF_3]_2$ and related salts

When solutions of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(PR_3)\{\mu\text{-}CN(H)Me\}(\mu\text{-}CNMe_2)][SO_3CF_3]_2$, [**19a**–**c**]$[SO_3CF_3]_2$ $\{PR_3 =$ (**a**) PMe_3, (**b**) PEt_3, and (**c**) $PPh_2Me\}$ or $[Fe_2(\eta\text{-}C_5H_5)_2(PMe_3)_2\{\mu\text{-}CN(H)Me\}(\mu\text{-}CNMe_2)][SO_3CF_3]_2$, [**20**]$[SO_3CF_3]_2$, in acetone are passed down a basic alumina column the cations are deprotonated. Removal of the solvent followed by recrystallisation of the residues from ethanol–ether mixtures allows the isolation in high yields (>90%) of green $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(PR_3)(\mu\text{-}CNMe)(\mu\text{-}CNMe_2)][SO_3CF_3]$, [**8a**–**c**]$[SO_3CF_3]$ $\{PR_3 =$ (**a**) PMe_3, (**b**) PEt_3, and (**c**) $PPh_2Me\}$, and $[Fe_2(\eta\text{-}C_5H_5)_2(PMe_3)_2(\mu\text{-}CNMe)(\mu\text{-}CNMe_2)][SO_3CF_3]$, [**9**]$[SO_3CF_3]$.

2.9. Deprotonation of cis-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNPh)\{\mu\text{-}CN(H)Me\}(\mu\text{-}CNMe_2)][SO_3CF_3]_2$

A solution of *cis*-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNPh)\{\mu\text{-}CN(H)Me\}(\mu\text{-}CNMe_2)][SO_3CF_3]_2$ (1.16 g, 1.5 mmol) in acetone was passed down a basic alumina column. The product was very unstable but if the eluent was collected in a flask containing a solution of PPh_3 (0.39 g, 1.5 mmol) in acetone and the mixture stirred for 10 min, a brown solid could be isolated by removal of the solvent at reduced pressure. Recrystallisation of the residue from ethanol–ether gave $[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)(PPh_3)(\mu\text{-}CO)(\mu\text{-}CNMe_2)][SO_3CF_3]$, [**7a**]$[SO_3CF_3]$, in 85% yield.

2.10. The reaction of cis-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$ with NaOH

A solution of *cis*-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$ (0.5 g, 0.71 mmol) and NaOH (0.06 g, 1.5 mmol) in MeOH (50 cm^3) was stirred for 3 h. It was filtered, an equal volume of ether added, and cooled to −20°C overnight. Green crystals of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)\{C(O)OH\}(\mu\text{-}CNMe_2)_2][SO_3CF_3]$, [**23a**]$[SO_3CF_3]$, were filtered off, washed with cold methanol and dried (yield 40%).

2.11. The reaction of cis-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$ with NaCN in ROH

A solution of *cis*-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$ (0.5 g, 0.71 mmol) and NaCN (0.09 g, 1.5 mmol) in ROH (50 cm^3) was stirred for 3 h. It was filtered, an equal volume of ether added, and cooled to −20°C overnight. Green crystals of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)\{C(O)OR\}(\mu\text{-}CNMe_2)_2][SO_3CF_3]$, [**23**]$[SO_3CF_3]$, were filtered off, washed with cold ROH and dried {R (yield) = (**b**) Me (65%), (**c**) Et (65%), and (**c**) ^{i}Pr (50%)}.

2.12. The reaction of cis-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$ with RNH_2

A solution of *cis*-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$ (0.5 g, 0.71 mmol) in liquid ammonia (50 cm^3) was stirred for 3 h. Removal of the solvent by evaporation gave a green solid which decomposed on work-up to give *cis*-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$ in nearly quantitative yield.

When ammonia is replaced by liquid primary amines, RHN_2, the same procedure gave a green solid which was filtered off, washed with pentane and recrystallised from acetonitrile–ether mixtures to give green crystals of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)\{C(O)N(H)R\}(\mu\text{-}CNMe_2)_2][SO_3CF_3]$, [**24**]$[SO_3CF_3]$, {R (yield) = (**b**) ^{i}Pr (75%), and (**c**) C_6H_{11} (80%)}.

If the above reaction mixtures are taken and the solvents removed at reduced pressure at ca. 50°C, the products were unchanged for *iso*-propylamine, but underwent further reaction for *cyclo*-hexylamine. Two new products were formed, separated by column chromatography (alumina–acetonitrile), isolated by removal of the solvent at reduced pressure, recrystallised from acetonitrile–ether mixtures, and identified as green $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNC_6H_{11})(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$ (yield 25%) and green $[Fe_2(\eta\text{-}C_5H_5)_2(CNC_6H_{11})_2(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$ (yield 30%) [3].

If *cis*-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$ is dissolved in piperidine, a purple solid is formed, but it decomposes on work-up with partial reformation of *cis*-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$.

2.13. The reaction of cis-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$ with $LiAlH_4$, $NaBH_4$ and MeLi

Although *cis*-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$ (0.5 g, 0.71 mmol) in tetrahydrofuran solution (50 cm^3) reacted with $LiAlH_4$, $NaBH_4$ or MeLi, the green products were unstable and decomposed very quickly although it was possible to obtain crude IR spectra for them (Table 1).

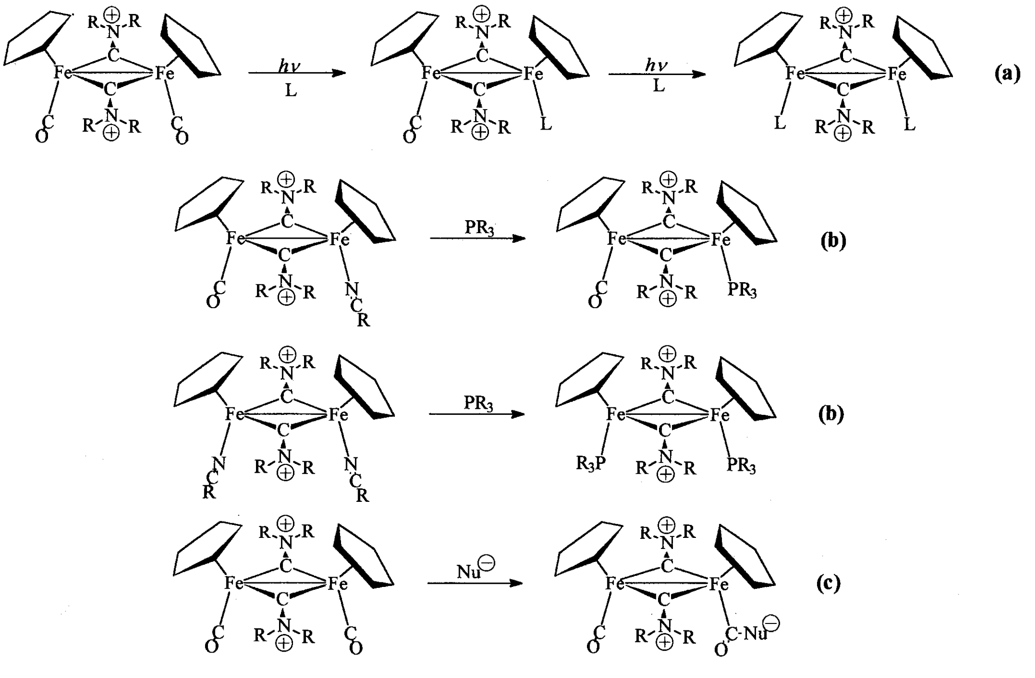
3. Results and discussion

The bulk of this work has been devoted to the study of three types of reactions which are illustrated in Scheme 1: (a) the photolytic CO-substitution reactions of $[\mathbf{3}][SO_3CF_3]_2$ and related salts with organonitriles, acetone and phosphines; (b) the replacement of the labile nitrile and acetone ligands in these products by other nucleophiles; and (c) the attack by hard nucleophiles on the CO ligands of $[\mathbf{3}][SO_3CF_3]_2$. (a) and (b) and reactions related to them are summarised in Scheme 2; (c) is summarised in Scheme 3. These are, in general, restricted to substrates with CNMe, $CNMe_2$, CN(H)Me and CNH_2 ligands, but some reactions have been carried out with compounds in which Me has been replaced by Et and follow the same course. This work is also restricted to *cis* precursors as the *trans* isomers of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CNEt_2)][SO_3CF_3]$, $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNMe)(\mu\text{-}CO)(\mu\text{-}CN(Et)Me)][SO_3CF_3]$, $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNEt)(\mu\text{-}CO)(\mu\text{-}CN(Et)Me)][SO_3CF_3]$, $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$, $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2\{\mu\text{-}CN(H)Me\}(\mu\text{-}CNMe_2)][SO_3CF_3]_2$ and $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CNH_2)(\mu\text{-}CNMe_2)][SO_3CF_3]_2$ can be prepared only in low yields if at all. Furthermore, although the CO ligands in these precursors are thermally labile, we found that in most instances more consistent results and faster reactions were realised for (a) and (b) using UV radiation from either 125 or 400 W lamps.

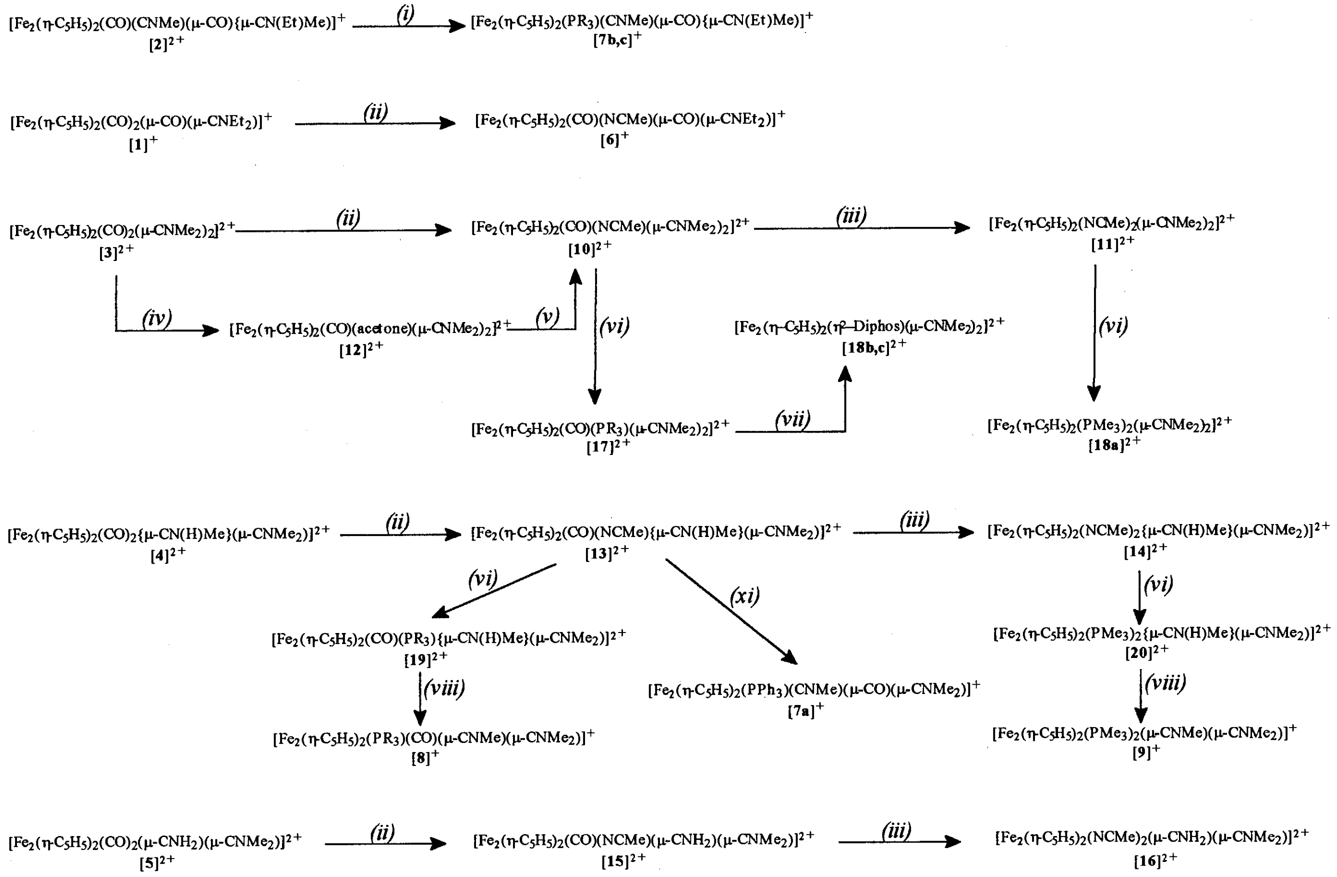
The compounds used in this work are listed in Table 5. They are salts which on heating do not melt below 200°C. They are soluble in polar organic solvents but not in non-polar ones. They are reasonably air-stable in the solid state and in solution except for $[\mathbf{9}][SO_3CF_3]_2$ and the acetone complex $[\mathbf{12}][SO_3CF_3]_2$ which decompose within days even at $-15°C$. Salts which contain the $\mu\text{-}CNH_2^+$ ligand readily take up water from the atmosphere and must be handled accordingly.

3.1. The CO replacement reactions

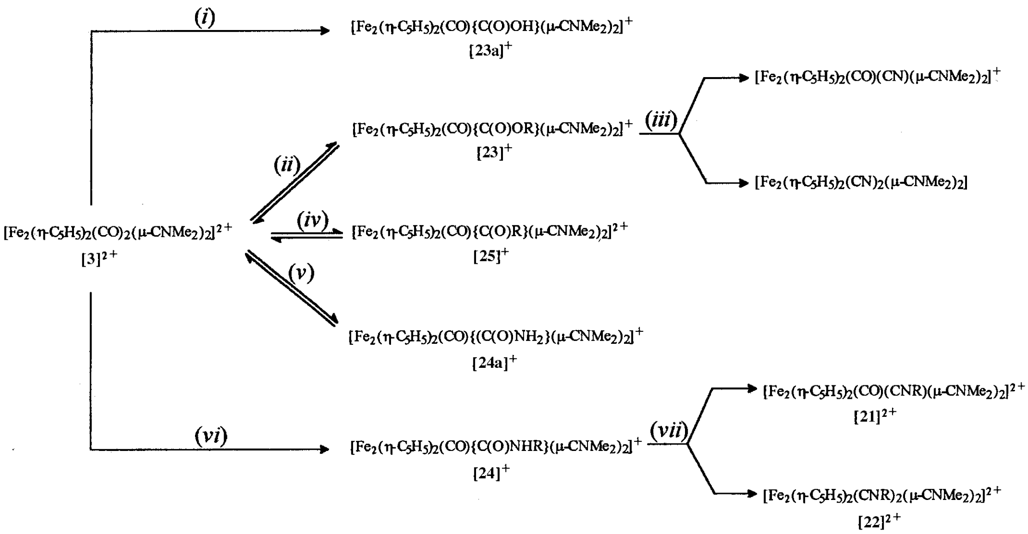
Photolysis of a solution of red *cis*-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CNEt_2)][SO_3CF_3]$, *cis*-$[\mathbf{1}][SO_3CF_3]$, in acetonitrile (125 W) converted it to green $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(NCMe)(\mu\text{-}CO)(\mu\text{-}CNEt_2)][SO_3CF_3]$, $[\mathbf{6}][SO_3CF_3]$. The reaction took 1 h, whereas the comparable photolyses of orange *cis*-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$, $[\mathbf{3}][SO_3CF_3]_2$, in organonitrile (RCN) solutions were complete within a few minutes to give green $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(NCR)(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$, $[\mathbf{10}][SO_3CF_3]_2$ {RCN = (**a**) MeCN, (**b**) EtCN, and (**c**) PhCN} with no further substitution. This can be effected by a more intense radiation source (400 W) which, in acetonitrile, gives yellow $[Fe_2(\eta\text{-}C_5H_5)_2(NCMe)_2(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$, $[\mathbf{11}][SO_3CF_3]_2$. Using the same reaction conditions orange *cis*-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2\{\mu\text{-}CN(H)Me\}(\mu\text{-}CNMe_2)][SO_3CF_3]_2$, $[\mathbf{4}][SO_3CF_3]_2$, gives green $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(NCR)\{\mu\text{-}CN(H)Me\}(\mu\text{-}CNMe_2)][SO_3CF_3]_2$, $[\mathbf{13}][SO_3CF_3]_2$ {RCN = (**a**) MeCN, (**b**) EtCN, and (**c**) PhCN}, and yellow $[Fe_2(\eta\text{-}C_5H_5)_2(NCMe)_2\{\mu\text{-}CN(H)Me\}(\mu\text{-}CNMe_2)][SO_3CF_3]_2$, $[\mathbf{14}][SO_3CF_3]_2$. Orange *cis*-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CNH_2)(\mu\text{-}CNMe_2)][SO_3CF_3]_2$, $[\mathbf{5}][SO_3\text{-}$



Scheme 1.



Scheme 2. (i) $Me_3NO{\cdot}2H_2O$, PEt_3; (ii) *hv* (125 W), RCN; (iii) *hv* (400 W), MeCN; (iv) *hv* (125 W), acetone; (v) MeCN; (vi) *hv* (125 W); (vii) *hv* (125 W); (viii) alumina; (ix) alumina, PPh_3; (ix) alumina, PPh_3.



Scheme 3. (i) NaOH, MeOH; (ii) NaCN, ROH, 25°C (R = Me, Et, or ^{i}Pr); (iii) NaCN, MeOH, reflux; (iv) LiMe (R = Me), $NaBH_4$ or $LiAlH_4$ (R = H), THF; (v) Liquid NH_3; (vi) Neat RNH_2 at 25°C (R = ^{i}Pr or C_6H_{11}); (vii) $C_6H_{11}NH_2$, Δ.

$CF_3]_2$, gives green $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(NCPh)(\mu\text{-}CNH_2)(\mu\text{-}CNMe_2)][SO_3CF_3]_2$, **[15]**$[SO_3CF_3]_2$, and yellow $[Fe_2(\eta\text{-}C_5H_5)_2(NCMe)_2(\mu\text{-}CNH_2)(\mu\text{-}CNMe_2)][SO_3CF_3]_2$ which is best isolated as $[Fe_2(\eta\text{-}C_5H_5)_2(NCMe)_2(\mu\text{-}CNH_2)(\mu\text{-}CNMe_2)][BPh_4]_2$, **[16]**$[BPh_4]_2$. The yields of all nitrile derivatives were high.

In a related reaction, photolysis of orange *cis*-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$, **[3]**$[SO_3CF_3]_2$, in acetone solution (125 W) was complete within a few minutes to give brown $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(Me_2C{=}O)(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$, [**12**]$[SO_3CF_3]_2$.

Table 5
The compounds used in this work and their numbering.

1	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CNEt_2)][SO_3CF_3]$
2	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNMe)(\mu\text{-}CO)\{\mu\text{-}CN(Et)Me\}][SO_3CF_3]$
3	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$
4	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2\{\mu\text{-}CN(H)Me\}(\mu\text{-}CNMe_2)][SO_3CF_3]_2$
5	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CNH_2)(\mu\text{-}CNMe_2)][SO_3CF_3]_2$
6	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(NCMe)(\mu\text{-}CO)(\mu\text{-}CNMe_2)][SO_3CF_3]$
7a	$[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)(PPh_3)(\mu\text{-}CO)(\mu\text{-}CNMe_2)][SO_3CF_3]$
7b	$[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)(PEt_3)(\mu\text{-}CO)\{\mu\text{-}CN(Et)Me)][I]$
7c	$[Fe_2(\eta\text{-}C_5H_5)_2(CNEt)(PMe_3)(\mu\text{-}CO)\{\mu\text{-}CN(Et)Me)][SO_3CF_3]$
8a	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(PMe_3)(\mu\text{-}CNMe)(\mu\text{-}CNMe_2)][SO_3CF_3]$
8b	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(PEt_3)(\mu\text{-}CNMe)(\mu\text{-}CNMe_2)][SO_3CF_3]$
8c	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(PPh_2Me)(\mu\text{-}CNMe)(\mu\text{-}CNMe_2)][SO_3CF_3]$
9	$[Fe_2(\eta\text{-}C_5H_5)_2(PMe_3)_2(\mu\text{-}CNMe)(\mu\text{-}CNMe_2)][SO_3CF_3]\cdot H_2O$
10a	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(NCMe)(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2\cdot H_2O$
10b	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(NCEt)(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$
10c	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(NCPh)(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$
11	$[Fe_2(\eta\text{-}C_5H_5)_2(NCMe)_2(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$
12	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(Me_2C{=}O)(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$
13a	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(NCMe)\{\mu\text{-}CN(H)Me\}(\mu\text{-}CNMe_2)][SO_3CF_3]_2$
13b	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(NCEt)\{\mu\text{-}CN(H)Me\}(\mu\text{-}CNMe_2)][SO_3CF_3]_2$
13c	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(NCPh)\{\mu\text{-}CN(H)Me\}(\mu\text{-}CNMe_2)][SO_3CF_3]_2$
14	$[Fe_2(\eta\text{-}C_5H_5)_2(NCMe)_2\{\mu\text{-}CN(H)Me\}(\mu\text{-}CNMe_2)][SO_3CF_3]_2$
15	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(NCPh)(\mu\text{-}CNH_2)(\mu\text{-}CNMe_2)][SO_3CF_3]_2$
16	$[Fe_2(\eta\text{-}C_5H_5)_2(NCMe)_2(\mu\text{-}CNH_2)(\mu\text{-}CNMe_2)][BPh_4]_2$
17a	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(PMe_3)(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$
17b	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(PEt_3)(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$
17c	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(PPh_2Me)(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2\cdot H_2O$
17d	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(PPh_3)(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2\cdot 3H_2O$
17e	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(\eta^1\text{-}DPPM)(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2\cdot H_2O$
17f	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(\eta^1\text{-}DPPE)(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2\cdot H_2O$
18a	$[Fe_2(\eta\text{-}C_5H_5)_2(PMe_3)_2(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$
18b	$[Fe_2(\eta\text{-}C_5H_5)_2(\eta^2\text{-}DPPM)(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2\cdot 2H_2O$
18c	$[Fe_2(\eta\text{-}C_5H_5)_2(\eta^2\text{-}DPPE)(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2\cdot H_2O$
18d	$[Fe_2(\eta\text{-}C_5H_5)_2(\eta^2\text{-}DPPE)(\mu\text{-}CNMe_2)_2]BPh_4]_2$
19a	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(PMe_3)\{\mu\text{-}CN(H)Me\}(\mu\text{-}CNMe_2)][SO_3CF_3]_2$
19b	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(PEt_3)\{\mu\text{-}CN(H)Me\}(\mu\text{-}CNMe_2)][SO_3CF_3]_2$
19c	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(PPh_2Me)\{\mu\text{-}CN(H)Me\}(\mu\text{-}CNMe_2)][SO_3CF_3]_2\cdot 0.5Me_2C{=}O$
20	$[Fe_2(\eta\text{-}C_5H_5)_2(PMe_3)_2\{\mu\text{-}CN(H)Me\}(\mu\text{-}CNMe_2)][SO_3CF_3]_2\cdot 2H_2O$
21	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNCy)(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$
22	$[Fe_2(\eta\text{-}C_5H_5)_2(CNCy)_2(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$
23a	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)\{C(O)OH\}(\mu\text{-}CNMe_2)_2][SO_3CF_3]$
23b	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)\{C(O)OMe\}(\mu\text{-}CNMe_2)_2][SO_3CF_3]$
23c	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)\{C(O)OEt\}(\mu\text{-}CNMe_2)_2][SO_3CF_3]\cdot H_2O$
23d	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)\{C(O)O^iPr\}(\mu\text{-}CNMe_2)_2][SO_3CF_3]\cdot H_2O$
24a	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)\{C(O)NH_2\}(\mu\text{-}CNMe_2)_2][SO_3CF_3]\cdot MeCN$
24b	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)\{C(O)N(H)^iPr\}(\mu\text{-}CNMe_2)_2][SO_3CF_3]\cdot 2H_2O$
24c	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)\{C(O)N(H)Cy\}(\mu\text{-}CNMe_2)_2][SO_3CF_3]\cdot H_2O$
24e	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)\{C(O)NC_5H_{10}\}(\mu\text{-}CNMe_2)_2][SO_3CF_3]$
25a	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)\{C(O)H\}(\mu\text{-}CNMe_2)_2][SO_3CF_3]$
25b	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)\{C(O)Me\}(\mu\text{-}CNMe_2)_2][SO_3CF_3]$

The photolysis (125 W) of an acetone solution of [**3**]$[SO_3CF_3]_2$ and PR_3 gave green $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(PR_3)(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$, [**17**]$[SO_3CF_3]_2$ $\{R_3P =$ (**d**) Ph_3P, (**e**) DPPM and (**f**) DPPE$\}$ in which only one of the P atoms in DPPM and DPPE are coordinated to Fe, but if either of these are subject to further irradiation (125 W) the second P atom also displaces CO to give, respectively yellow $[Fe_2(\eta\text{-}C_5H_5)_2(\eta^2\text{-}DPPM)(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$, [**18b**]$[SO_3CF_3]_2$, and $[Fe_2(\eta\text{-}C_5H_5)_2(\eta^2\text{-}DPPE)(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$, [**18c**]$[SO_3CF_3]_2$ in which the DPPM or DPPE ligand bridges the Fe–Fe bond.

The acetone ligand in [**12**]$[SO_3CF_3]_2$ is very labile and when this salt is dissolved in acetonitrile solution it is converted instantaneously to [**10a**]$[SO_3CF_3]_2$. The benzonitrile ligand in [**10c**]$[SO_3CF_3]_2$ (for example) is much less labile and continued photolysis (125 W) of this compound in acetonitrile brings about little conversion to [**10a**]$[SO_3CF_3]_2$.

However, the RCN ligands of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(NCR)(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$, [**10**]$[SO_3CF_3]_2$, $[Fe_2(\eta\text{-}C_5H_5)_2(NCMe)_2(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$, [**11**]$[SO_3CF_3]_2$, $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(NCR)\{\mu\text{-}CN(H)Me\}(\mu\text{-}CNMe_2)][SO_3CF_3]_2$, [**13**]$[SO_3CF_3]_2$, and $[Fe_2(\eta\text{-}C_5H_5)_2(NCMe)\{\mu\text{-}CN(H)Me\}(\mu\text{-}CNMe_2)][SO_3CF_3]_2$, [**14**]$[SO_3CF_3]_2$ are sufficiently labile that these may be utilised as synthetic intermediates in the preparation of certain other complexes. For example, with KCN, [**10c**]$[SO_3CF_3]_2$ and [**11**]$[SO_3CF_3]_2$, respectively give the previously reported $[Fe_2(\eta\text{-}C_5H_5)_2(CN)(CO)(\mu\text{-}CNMe_2)_2][SO_3CF_3]$ and $[Fe_2(\eta\text{-}C_5H_5)_2(CN)_2(\mu\text{-}CNMe_2)_2]$ which have been prepared by thermal reactions [3]. However, it is in their reactions with more basic phosphines that they are most useful as such phosphines tend to demethylate [**3**]$[SO_3CF_3]_2$ and deprotonate [**4**]$[SO_3CF_3]_2$.

All [**10**]$[SO_3CF_3]_2$, fail to react with Ph_3P, DPPM or DPPE, but Me_3P displaces PhCN from [**10c**]$[SO_3CF_3]_2$ in the dark, and Et_3P and Ph_2MeP do so on UV irradiation (125 W). They give green $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(PR_3)(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$, [**17**]$[SO_3CF_3]_2$, salts where $R_3P =$ (**a**) Me_3P, (**b**) Et_3P or (**c**) Ph_2MeP. As an extension to this reaction, Me_3P replaces both MeCN ligands in [**11**]$[SO_3CF_3]_2$ to give yellow $[Fe_2(\eta\text{-}C_5H_5)_2(PMe_3)_2(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$, [**18a**]$[SO_3CF_3]_2$. The yields of all these nitrile-replacement reactions are $> 90\%$.

Although the nitrile complexes $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(NCPh)(\mu\text{-}CNH_2)(\mu\text{-}CNMe_2)][SO_3CF_3]_2$, [**15**]$[SO_3CF_3]_2$, and $[Fe_2(\eta\text{-}C_5H_5)_2(NCMe)_2(\mu\text{-}CNH_2)(\mu\text{-}CNMe_2)][BPh_4]_2$, [**16**]$[BPh_4]_2$, decompose on treatment with various phosphines, $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(NCPh)\{\mu\text{-}CN(H)Me\}(\mu\text{-}CNMe_2)][SO_3CF_3]_2$, [**13**]$[SO_3CF_3]_2$, and $[Fe_2(\eta\text{-}C_5H_5)_2(NCMe)_2\{\mu\text{-}CN(H)Me\}(\mu\text{-}CNMe_2)][SO_3CF_3]_2$, [**14**]$[SO_3CF_3]_2$, react in exactly the same way as [**10**]$[SO_3CF_3]_2$ and [**11**]$[SO_3CF_3]_2$ to give $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(PR_3)\{\mu\text{-}CN(H)Me\}(\mu\text{-}CNMe_2)][SO_3CF_3]_2$,

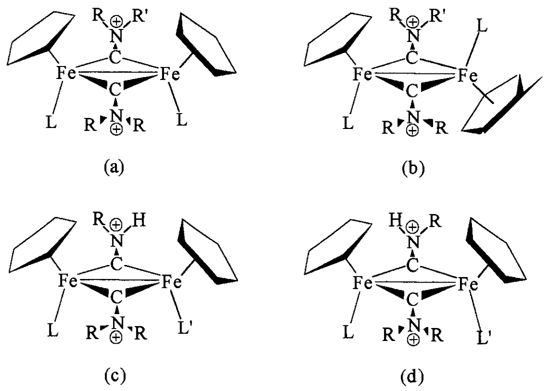


Fig. 1. (a) *cis* and *trans* isomers; (c) and (d) are α and β isomers.

$[\mathbf{19}][SO_3CF_3]_2$ {R_3P = (**a**) Me_3P, (**b**) Et_3P and (**c**) Ph_2MeP, but not Ph_3P, DPPM or DPPE}, and $[Fe_2(\eta\text{-}C_5H_5)_2(PMe_3)_2\{\mu\text{-}CN(H)Me\}(\mu\text{-}CNMe_2)][SO_3CF_3]_2$, $[\mathbf{20}][SO_3CF_3]_2$. Again the yields were high. The $\{\mu\text{-}CN(H)Me\}^+$ ligand in these phosphine complexes may be deprotonated by passing them down a basic alumina column and the following isolated: green $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(PR_3)(\mu\text{-}CNMe)(\mu\text{-}CNMe_2)][SO_3CF_3]$, $[\mathbf{8}][SO_3CF_3]$ {R_3P = (**a**) Me_3P, (**b**) Et_3P and (**c**) Ph_2MeP}, and yellow $[Fe_2(\eta\text{-}C_5H_5)_2(PMe_3)_2(\mu\text{-}CNMe)(\mu\text{-}CNMe_2)][SO_3CF_3]$, $[\mathbf{9}][SO_3CF_3]$. All are stable and do not undergo bridging-to-terminal MeNC migration on UV irradiation unlike $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CNMe)(\mu\text{-}CNMe_2)][SO_3CF_3]$ which does [5].

$[\mathbf{13c}][SO_3CF_3]_2$ does not react with Ph_3P, but if it is first deprotonated by eluting down a basic alumina column in acetone and Ph_3P added, it gives brown $[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)(PPh_3)(\mu\text{-}CO)(\mu\text{-}CNMe_2)][SO_3CF_3]$, $[\mathbf{7a}][SO_3CF_3]$. A similar complex, $[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)(PEt_3)(\mu\text{-}CO)\{\mu\text{-}CN(Et)Me\}][I]$, $[\mathbf{7b}]I$, is obtained when Me_3NO is used as a CO-labilising reagent (cf. Section 3.2) and added to an acetonitrile solution of $[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)(CO)(\mu\text{-}CO)\{\mu\text{-}CN(Et)Me\}][I]$ and Et_3P.

3.2. The CO attack reactions

The reactions of $[\mathbf{3}][SO_3CF_3]_2$ with NaCN in ROH gives the green carboxylate esters $[Fe_2(\eta\text{-}C_5H_5)_2(CO)\{C(O)OR\}(\mu\text{-}CNMe_2)_2][SO_3CF_3]$, $[\mathbf{23}][SO_3CF_3]$ {R = (**b**) Me, (**c**) Et, (**d**) ^{i}Pr}. The parent acid, $[Fe_2(\eta\text{-}C_5H_5)_2(CO)\{C(O)OH\}(\mu\text{-}CNMe_2)_2][SO_3CF_3]$, $[\mathbf{23a}][SO_3CF_3]$, is best prepared from $[\mathbf{3}][SO_3CF_3]_2$ using NaOH in methanol.

The reactions of $[\mathbf{3}][SO_3CF_3]_2$ with neat primary amines follows a course similar to the above with the formation of green carbamoyl complexes $[Fe_2(\eta\text{-}C_5H_5)_2(CO)\{C(O)NHR\}(\mu\text{-}CNMe_2)_2][SO_3CF_3]$, $[\mathbf{24}][SO_3CF_3]$ {R = (**b**) ^{i}Pr, and (**c**) C_6H_{11} (cyclohexyl)} which can be filtered from the reaction mixtures and be purified by recrystallisation from acetonitrile–ether mixtures. However, if the $[\mathbf{3}][SO_3CF_3]_2/C_6H_{11}NH_2$ reaction mixture was worked-up by removal of the solvent at reduced pressure and ca. 50°C, two further products were formed, $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNC_6H_{11})(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$, $[\mathbf{21}][SO_3CF_3]_2$, and $[Fe_2(\eta\text{-}C_5H_5)_2(CNC_6H_{11})_2(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$, $[\mathbf{22}][SO_3CF_3]_2$.

When $[\mathbf{3}][SO_3CF_3]_2$ is dissolved in liquid ammonia, the changes in colour and IR spectra are consistent with the formation of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)\{C(O)NH_2\}(\mu\text{-}CNMe_2)_2][SO_3CF_3]$, $[\mathbf{24a}][SO_3CF_3]$. However, removal of the ammonia leads to the reformation of $[\mathbf{3}][SO_3CF_3]$ in near quantitative yields.

Similarly the secondary amine piperidine also converts $[\mathbf{3}][SO_3CF_3]_2$ to a purple solid which appears to be $[Fe_2(\eta\text{-}C_5H_5)_2(CO)\{C(O)NC_5H_{10}\}(\mu\text{-}CNMe_2)_2][SO_3CF_3]$, $[\mathbf{24e}][SO_3CF_3]$, but it is unstable and decomposes with the partial reformation of $[\mathbf{3}][SO_3CF_3]_2$.

Both H^- (from $NaBH_4$ or $LiAlH_4$) and Me^- (from excess MeLi) form green adducts with $[\mathbf{3}][SO_3CF_3]_2$. We assume that they are, respectively, the formyl $[Fe_2(\eta\text{-}C_5H_5)_2(CO)\{C(O)H\}(\mu\text{-}CNMe_2)_2][SO_3CF_3]$, $[\mathbf{25a}][SO_3CF_3]$, and the acetyl $[Fe_2(\eta\text{-}C_5H_5)_2(CO)\{C(O)Me\}(\mu\text{-}CNMe_2)_2][SO_3CF_3]$, $[\mathbf{25b}][SO_3CF_3]$, but they were too unstable to be identified unambiguously. Only their IR spectra could be obtained and they were of poor quality.

3.3. Structures and isomerism

Spectroscopic evidence reported here, and structural evidence from a whole series of related compounds including *cis*-$[Fe_2(\eta\text{-}C_5H_4Me)_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CNMe_2)][SO_3CF_3]_2$ [1] and *cis*-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$ [2] suggest that the complexes described in this paper have structures based on that of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CO)_2]$ [7,8] with one or two μ-CNR_2^+ ligands so that *cis* and *trans* isomers are possible (Fig. 1) but cannot interconvert [2]. Most cations have been obtained as a single isomer. Although there is no unambiguous guide as to their geometries, except for $[\mathbf{1}]^+$–$[\mathbf{5}]^{2+}$ (cf. [3]), other work has shown that the *cis* isomers generally predominate over the *trans* and may even exclude them [3].

In the case of $[\mathbf{18a}][SO_3CF_3]_2$, $[Fe_2(\eta\text{-}C_5H_5)_2(PMe_3)_2(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$, NMR spectroscopy (see below) shows unambiguously that two species are present in solution as their ratio is 90:10, and the most rational interpretation of the data is that they are *cis* and *trans*-$[\mathbf{18a}]^{2+}$. For both $[\mathbf{20}][SO_3CF_3]_2$ and $[\mathbf{9}][SO_3CF_3]$, the NMR data is also best explained on the basis that *cis* and *trans* isomers are present in the ratio of ca. 1:1. The precursors of both of these, $[\mathbf{11}][SO_3CF_3]_2$, is a single species, so that the substitution $[\mathbf{11}]^{2+} \rightarrow [\mathbf{20}]^{2+}$ is accompanied by a change in the *cis*:*trans* isomer ratio. On the other hand the deprotonation $[\mathbf{20}]^{2+} \rightarrow [\mathbf{9}]^+$, is not. This last is consistent with observations that there is no change in the *cis*:*trans* isomer ratio on deprotonation of [**4**]$^{2+}$ and its derivatives [5].

The reactions of [**3**]$^{2+}$ with NH_3 and piperidine clearly take place without any change in the structure of the $Fe_2(\eta\text{-}C_5H_5)_2(\text{t-C})_2(\mu\text{-C})_2$ core of the cation. It is probable that this is the case for all of the CO-attack reactions described here so that all such products are *cis* isomers. On the other hand, the dehydration of the $C(O)NHC_6H_{11}$ ligand to CNC_6H_{11} does result in a change in configuration of the core of the molecule and hence in *cis–trans* isomerism. The identification of the *cis* and *trans* isomers on the basis of their ^{1}H-NMR spectra (Table 2) is based on criteria stated elsewhere [3].

Another form of isomerism is possible for the $[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)(PEt_3)(\mu\text{-CO})\{\mu\text{-CN(Et)Me}\}][I]$ and $[Fe_2(\eta\text{-}C_5H_5)_2(L)(L')\{\mu\text{-CN(H)Me}\}(\mu\text{-CNMe}_2)]^{2+}$ cations. These are the α and β forms [2] of both *cis* and *trans* isomers as is illustrated in Fig. 1. Again, we have not been able to assign the spectroscopic data more specifically.

Finally, it should be noted that in [**8**]$^+$ and [**9**]$^+$ the inversion at N of their μ-CNMe ligands is always fast on the NMR timescale (cf. [9] and references therein).

3.4. IR spectra

The IR data for the various compounds are summarised in Table 1 which give the frequencies and relative intensities of the absorption bands due to the *ν*(CN) and *ν*(CO) vibrations of the π-bonding ligands t-CO, t-CNMe, t-C(O)OR, t-C(O)NHR, μ-CO, μ-CNMe, μ-$CNMe_2$, μ-CN(H)Me and μ-CNH_2. There are many other bands in the spectra which yield no useful information except those due to the $[CF_3SO_3]^-$ ions which confirm its presence in the salts. The assignment of the absorption bands follows those made elsewhere for complexes such as [**1**]$^+$–[**5**]$^{2+}$ and related salts [1–3,5] where it was also observed that absorption bands due to the *ν*(C=NMe_2) and *ν*(C=N(H)Me)/*ν*(C=NH_2) cannot normally be resolved so that a broad irregular band is observed in the relevant region. Cations containing the μ-CNH_2 ligand always show quite intense absorption bands at ca. 3100 cm^{-1} which are due to *ν*(NH) stretching modes (cf. [5]).

When the CO is replaced by other ligands L in [**6**]$^+$–[**20**]$^{2+}$, the frequencies of the CO or CN stretching vibrations of the remaining π-acceptor CO, CNR or CNR_2 ligands decrease for L=NCR > Me_2C=O > PR_3. These frequencies imply an increasing electron-richness of the Fe_2 moiety along the above series which necessitates the increasing back-bonding to CO, CNR and CNR_2 ligands. They are a reflection of the combined σ-donor and π-acceptor abilities of L.

3.5. NMR spectra

The ^{1}H spectra (Table 2) are consistent with the proposed formulae. They are readily assigned by comparison with those of related complexes and the use of integration data. The resonances due to the NH protons are generally broad when they are observed, but they are absent from spectra run in acetone-d_6 perhaps due to hydrogen-bonding to the solvent. The chemical shifts of the various types of protons are unexceptional, but some coupling constants are worthy of note when P^{III} ligands are involved. In those complexes of the type $[Fe_2(\eta\text{-}C_5H_5)_2(L)(L')(\mu\text{-CX})(\mu\text{-CNMe}_2)]^+$ where the two terminal ligands are different, the two η-C_5H_5 ligands are distinguishable and the two Me groups of the μ-$CNMe_2$ ligand are inequivalent, and for both two resonances are observed. When one of the terminal ligands is a phosphine, ^{31}P–^{1}H coupling splits one of the η-C_5H_5 resonances but not the other (cf. [10]), and comparison of the observed ^{31}P–C_5H_5 coupling constants with those found in mononuclear complexes (ca. 1.4 Hz) implies C_5H_5–Fe–PR_3 coupling [11]. Furthermore, one of the Me resonances of the μ-$CNMe_2$ ligands is coupled to ^{31}P but the other is not, and there is no evidence as to which is which. In an extension of this phenomenon, the more important of the α and β isomers of [**7b**]I (see above and Fig. 1) shows ^{31}P coupling to the Et group of the μ-CN(Et)Me ligand (but not to Me) whilst in the minor isomer coupling is to Me but not Et. When CX = μ-CNMe in [**8**]$^+$ its Me resonance is a doublet due to ^{31}P–^{1}H coupling whilst there is fast inversion at N (see above).

Similar behaviour is observed in $[Fe_2(\eta\text{-}C_5H_5)_2(L)(L')(\mu\text{-CNMe}_2)_2]^{2+}$ species, i.e. two η-C_5H_5 and two $CNMe_2$ resonances, one of each split by ^{31}P coupling when L = PR_3. However, there is a single exception to this last as in [**17a**]$^{2+}$ both $CNMe_2$ resonances are coupled to $^{31}PMe_3$ but the two coupling constants differ. One is a normal 1.46 Hz whilst the other is much smaller at 0.55 Hz; perhaps in other instances the second coupling is too small to be resolved. There is one other peculiarity of these spectra in that when L = L′ = PR_3 in [**18a–c**]$^{2+}$ there are single η-C_5H_5 and $CNMe_2$ resonances, but whereas the latter are all singlets and any ^{1}H–^{31}P coupling cannot be resolved, the former are doublets for [**18a**]$^{2+}$ and [**18c**]$^{2+}$ but only a singlet for the $Ph_2PCH_2PPh_2$ cation [**18b**]$^{2+}$.

Replacement of one of the μ-$CNMe_2$ ligands in $[Fe_2(\eta\text{-}C_5H_5)_2(L)(L')(\mu\text{-CNMe}_2)_2]^{2+}$ by μ-CN(H)Me to give $[Fe_2(\eta\text{-}C_5H_5)_2(L)(L')\{\mu\text{-CN(H)Me}\}(\mu\text{-CNMe}_2)]^{2+}$ leads to relatively simple ^{1}H-NMR spectra. This implies that although α and β isomers are possible, either only one is present or they interchange rapidly on the NMR timescale by a loss of proton from μ-CN(H)Me, inversion of the μ-CNMe at N and reprotonation to give the inverted μ-CN(Me)H (Scheme 4). There is evidence for this proton loss process as the μ-CN(H)Me resonance is a doublet for $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(PR_3)\{\mu\text{-}CN(H)Me\}(\mu\text{-}CNMe_2)]^{2+}$, if a drop of CF_3SO_3H is added to their solutions in the NMR tube it changes to a double doublet due to the appearance of $CN(H)CH_3$ coupling as the exchange process is slowed. However, only one of the α/β forms appears to be present.

In most of the ^{13}C-NMR spectra, all of the anticipated resonances can be detected and assigned by reference to previously reported data. In some instances, decomposition and solubility problems prevents the detection of the weaker resonances.

In all $[Fe_2(\eta\text{-}C_5H_5)_2(L)(L')(\mu\text{-}CX)(\mu\text{-}CNMe_2)]^+$ complex cations where L = L′, single η-C_5H_5 and μ-$CNMe_2$ ^{13}C resonances are observed. When L and L′ are different, there are two of each, but no coupling to ^{31}P when L = R_3P. However, there is coupling to ^{31}P of the μ-*C*X and μ-*C*NMe$_2$ resonances, but not of the L′ resonances.

Similar effects are observed in the spectra of the $[Fe_2(\eta\text{-}C_5H_5)_2(L)(L')(\mu\text{-}CNMe_2)_2]^{2+}$ salts, and it should be noted that when L = L′ = R_3P, the μ-*C*NMe$_2$ resonance is a triplet. In the $[Fe_2(\eta\text{-}C_5H_5)_2(L)(L')\{\mu\text{-}CN(H)Me\}(\mu\text{-}CNMe_2)]^{2+}$, the μ-*C*N(H)Me and μ-*C*NMe$_2$ signals cannot always be distinguished (cf. [5]).

The ^{31}P-NMR spectra of particular interest are those of the cations which contain the $Ph_2PCH_2PPh_2$ (DPPM) and $Ph_2PCH_2CH_2PPh_2$ (DPPE) ligands. In $[\mathbf{17e}]^{2+}$ and $[\mathbf{17f}]^{2+}$ these coordinate through one P atom only so that they give rise to two coupled ^{31}P resonances. Those with chemical shifts further downfield (δ_{coord}) are assigned to the coordinated P atom as the up-field resonances have chemical shifts (δ_{free}) similar to those of the free ligands and are attributed to the pendant P atom. The difference in these chemical shifts is defined as $\Delta_1 = \delta_{coord} - \delta_{free}$ and they are similar for the two ligands. When both P atoms of DPPM and DPPE coordinate so that these ligands bridge the Fe–Fe bonds, a single resonance is observed having a chemical shift ($\delta_{chelate}$) which depends on the diphosphine. If $\Delta_2 = \delta_{chelate} - \delta_{coord}$, this is positive for DPPM which is part of a five-membered ring, and small but negative for DPPE which is part of a six-membered ring. Similar effects are observed for the mononuclear complexes $[Mn(\eta\text{-}C_6H_6)(CO)(\eta^2\text{-}L)][PF_6]$ where $L = Ph_2P(CH_2)_nPPh_2$ (n = 1, 2, 3) [12].

3.6. Reaction mechanisms

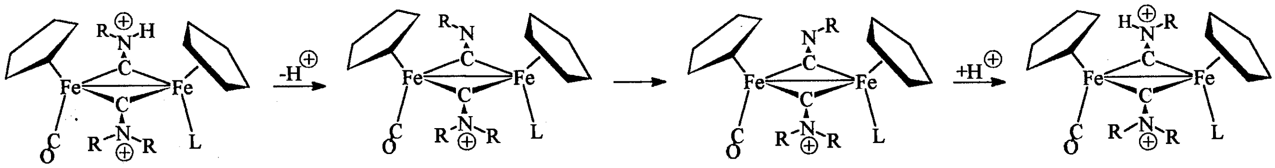
CO is replaced less readily in $[\mathbf{1}]^+$ than in $[\mathbf{3}]^{2+}$ or $[\mathbf{5}]^{2+}$ both in the dark and on irradiation. This may be attributed to the increasing positive charge of the cation which results in decreasing M → CO back-bonding and weaker M–C bonds. However, there does appear to be a steric effect as the CO ligand in $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNMe)(\mu\text{-}CNMe_2)_2]^{2+}$ is much less labile than that in $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNBu^t)\{\mu\text{-}CN(H)Bu^t\}(\mu\text{-}CNMe_2)]^{2+}$ [5].

The CO replacement reactions of $[\mathbf{3}][SO_3CF_3]_2$ in the dark are markedly dependent on the incoming nucleophile L. They take place with acetonitrile or the hard phosphine PMe_3 but not the softer PEt_3 or PPh_2Me. They may proceed by way of a simple CO-dissociation process followed by further reactions in which L competes with CO for the electron-deficient intermediate as shown in Scheme 5(a). However ligand dependency suggests that L may attack $[\mathbf{3}]^{2+}$ at the μ-$CNMe_2^+$ to give a 1:1 adduct containing the μ-$C(NMe_2)$ ← L ligand or at t-CO to give a t-C(O)L species, and it is this which converts to the CO-substituted product (Scheme 5(b) and (c). This would account for the facility with which $[\mathbf{3}]^{2+}$ reacts with PMe_3 but not PEt_3 or PPh_2Me. The photolytic reaction, on the other hand, probably proceeds by a simple CO dissociation {Scheme 5(a)}.

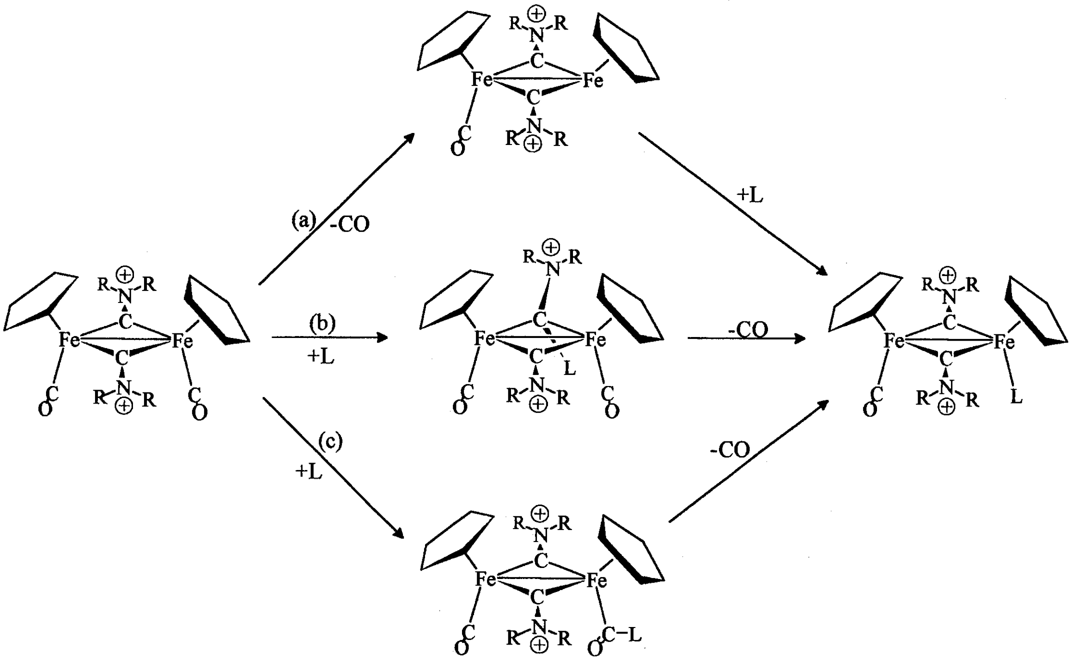
Similar considerations are applicable to the nitrile displacements from $[\mathbf{10}]^{2+}$ and $[\mathbf{13}]^{2+}$ salts as it is only effected in the dark by the very basic PMe_3. However, this basicity of the PMe_3 appears to be sufficient to deprotonate $[\mathbf{15}][SO_3CF_3]_2$ and $[\mathbf{16}][SO_3CF_3]_2$, and decomposition results.

The deprotonation of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(NCMe)\{\mu\text{-}CN(H)Me\}(\mu\text{-}CNMe_2)][SO_3CF_3]_2$ will give $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(NCMe)(\mu\text{-}CNMe)(\mu\text{-}CNMe_2)][SO_3CF_3]$. Some complexes of this type are unstable towards migration of CNMe from bridging to terminal and of CO migration from terminal to bridging coordination sites. It has been suggested [5] that this reaction may take place by loss of a t-ligand to give an intermediate such as $[(\eta\text{-}C_5H_5)Fe(\mu\text{-}CO)(\mu\text{-}CNMe)(\mu\text{-}CNMe_2)Fe(\eta\text{-}C_5H_5)]^+$. If the lost ligand is the labile NCMe as is shown in Scheme 6, its facile replacement by PPh_3 is well-accounted for by this suggestion.

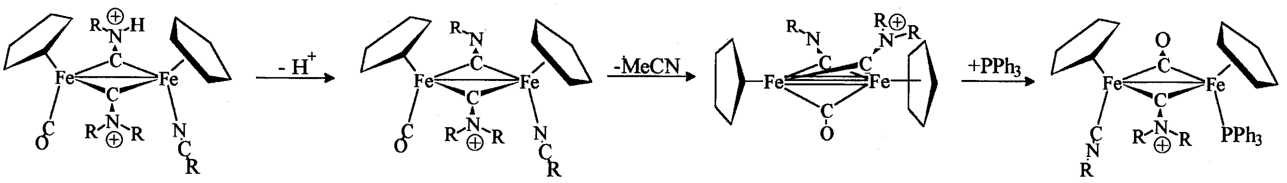
It has been shown that monocations such as $[\mathbf{2}]^+$ undergo nucleophilic attack at various sites in the



Scheme 4.



Scheme 5.



Scheme 6.

molecule, particularly the C atom of the μ-CNR_2^+ ligand. However, the Me_3NO-promoted CO substitution reactions of [**2a**][SO_3CF_3] with PEt_3 and [**2b**][SO_3CF_3] with PMe_3 probably take place by way of nucleophilic attack of Me_3NO on t-CO followed by β-elimination of CO_2. The ν(CO frequencies of $[\mathbf{2}]^+$ are rather low, but still within the range where such reactions are found [13]. Those of $[\mathbf{3}]^{2+}$ are much higher due to the presence of two powerful π-acceptor μ-$CNMe_2^+$ ligands which render its CO ligands particularly electrophilic. Consequently $[\mathbf{3}]^{2+}$ has a very strong preference for nucleophilic attack at t-CO rather than at other sites within the cation.

It is clear that many of the C-attack reactions of $[\mathbf{3}]^{2+}$ are reversible. This is directly observable when NH_3 and piperidine are the nucleophiles, but it is implied in the reactions with NaCN in ROH. At room temperature this gives a CO-attack product (see above) in refluxing MeOH, CN^- replaces CO [3].

It is surprising that RO^- are the effective nucleophiles in alcohol solutions of NaCN, but they probably arise from the equilibrium $ROH + CN^- = RO^- + HCN$, and must be more effective than CN^- for attack on $[\mathbf{3}]^{2+}$. Also it is probable that amines rather than RNH^- are the true nucleophiles in their reactions with $[\mathbf{3}]^{2+}$, but the initial product is deprotonated by excess amine {Eq. (1); $M_2 = Fe_2(\eta\text{-}C_5H_5)_2(CO)(\mu\text{-}CNMe_2)_2$}.

$$M_2(CO)^{2+} + 2RNH_2 = M_2\{C(O)NH_2R\}^{2+} + RNH_2 = M_2\{C(O)NHR\}^{+} + RNH_3^+ \quad (1)$$

The dehydration of the t-C(O)NHR ligand to t-CNR or CN^- when R = H (Eq. (2)) is a not uncommon reaction [14]. In the present example it takes place for R = *cyclo*-C_6H_{11} but not ^{i}Pr. This is probably a consequence of the differing volatilities of the two amines versus that of water. The overall reaction is an equilibrium (Eq. (3)). Therefore, if the amine is more volatile than water (as it is for $^i PrNH_2$) it is preferentially removed from the reaction mixture and the equilibrium moves to the left, but if water is the more volatile (as it is for *cyclo*-$C_6H_{11}NH_2$) it is preferentially removed, the equilibrium shifts to the right and the coordinated carbon monoxide is converted to coordinated *cyclo*-hexylisocyanide. The most rational explanation for the conversion of the remaining t-CO ligand in $[\mathbf{21}]^{2+}$ to isocyanide in $[\mathbf{22}]^{2+}$ is that it is also susceptible to nucleophilic attack by amine and subsequent dehydration {Eqs. (1) and (2); $M_2 = Fe_2(\eta\text{-}C_5H_5)_2(CNC_6H_{11})(\mu\text{-}CNMe_2)_2$}.

$$M_2\{C(O)NHR\}^+ + RNH_3^+ = M_2(CNR) + RNH_2 + H_2O \qquad (2)$$

$$M_2(CO) + RNH_2 = M_2(CNR)^{2+} + H_2O \qquad (3)$$

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