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A reinvestigation of the reaction of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_{4-n}(CNR)_n]$ ($n = 1$ or 2) with strong alkylating agents

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Abstract

The reaction of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3(CNR)]$ with $R'OSO_2CF_3$ (R,R' = Me or Et) gives a mixture of *cis* and *trans*-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}CN(R')R\}]SO_3CF_3$. When $R = R' = Me$ the isomer ratio is variable, but the *cis* always predominates and is the only product when $R \neq R'$. The complexes $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNR)_2]$ react with $R'OSO_2CF_3$ and the more reactive alkyl halides R'X to give a mixture of *cis*-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNR)(\mu\text{-}CO)\{\nu\text{-}CN(R')R\}]X$ and *cis*-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2\{\mu\text{-}CN(R')R\}_2][X]_2$. In both series of cations the presence of μ-CN(R')R ligands give rise to isomers that differ in respect of orientation about the C=N bond. The cations are not fluxional and do not undergo *cis–trans* interconversion, bridge–terminal ligand exchange, or rotation about the μ-C = N(R')R double bond. The structure of the cations in the $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNMe)(\mu\text{-}CO)(\mu\text{-}CNMe_2)]BPh_4$ and $[Fe_2(\eta\text{-}C_5H_4Me)_2(CO)_2(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$ salts were confirmed as *cis* by X-ray diffraction studies. Their dimensions are similar to those previously found in *cis*-$[Fe_2(\eta\text{-}C_5H_4Me)_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CNMe_2)]I$, but with variations due to the differing acceptor and donor abilities of the various ligands. Infrared and NMR spectra of the complexes are reported and discussed.

Introduction

Previously it was reported that the reactions of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3(CNMe)]$, I, or $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNMe)_2]$, II, with RI and RBr give $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}CN(R)Me\}]^+$, $[III]^+$, and $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNMe)(\mu\text{-}CO)\{\mu\text{-}CN(R)Me\}]^+$, $[IV]^+$, salts. Spectroscopic data indicated that $[III]^+$ were *cis* isomers as was confirmed by an X-ray diffraction study of *cis*-$[Fe_2(\eta\text{-}C_5H_4Me)_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CNMe_2)]I$. $[IV]^+$ could also exist as *cis* and *trans*

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isomers, but the spectroscopic data could not distinguish between them, and crystals suitable for an X-ray diffraction study could not be obtained [1]. Similar studies were also carried out by others [2].

The reactions of I and II with more powerful alkylating agents such as $[Et_3O]BF_4$, $MeSO_3F$, $EtSO_3F$ or $[Ph_3C]BF_4$ did not give satisfactory results [1], but $MeOSO_2CF_3$ and $EtOSO_2CF_3$ have since become available. These cleanly and quickly alkylate I, II, their CNEt counterparts, and $[Fe_2(\eta\text{-}C_5H_4Me)_2(CO)_2(CNMe)_2]$. The *trans* isomer of $[III]^+$ has been obtained, and both isocyanide ligands of II have been alkylated. Furthermore, the molecular structures of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNMe)(\mu\text{-}CO)(\mu\text{-}CNMe_2)]BPh_4$ and $[Fe_2(\eta\text{-}C_5H_4Me)_2(CO)_2(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$ have been determined by X-ray crystallography and both cations shown to be *cis* isomers. ^1H and ^{13}C NMR spectra of the complexes have been obtained which are superior in quality to and more informative than those reported previously [1].

Experimental

Previously published methods were used to prepare $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3(CNMe)]$ [3], $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNMe)_2]$ [4] and their CNEt counterparts, and $[Fe_2(\eta\text{-}C_5H_4Me)_2(CO)_2(CNMe)_2]$. Other chemicals were purchased.

Unless otherwise stated reactions were carried out at room temperature under nitrogen in dried and deoxygenated solvents.

Infrared spectra were obtained on a Perkin Elmer 1710 or 1720 FTIR spectrometer. NMR spectra were obtained on a JEOL GNMX-270 using Me_4Si as an internal standard. Analyses were carried out by the Analytical Laboratory of University College, Dublin.

The reaction of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3(CNR)]$ with $R'OSO_2CF_3$ (R,R' = Me or Et)

$R'OSO_2CF_3$ was added to a solution of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3(CNMe)]$ (1–3 g; mole ratio 1.66 : 1) in benzene (50–100 cm^3). An immediate reaction took place to give a red powder, which was filtered off and recrystallized from acetonitrile-ether or methanol-ether mixtures to give $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}CN(R')Me\}]SO_3CF_3$ (yield 90%).

The method may be extended to reactions carried out in carbon disulphide, chloroform, or acetonitrile in refluxing solvents as well as at room temperature, and to $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3(CNEt)]$, which gives $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}CN(R')Et\}]SO_3CF_3$ (yield 90%).

A 90 : 10 mixture of *cis* and *trans* $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CNMe_2)]SO_3CF_3$ was chromatographed on alumina with chloroform-methanol mixtures as eluent and separated into orange-red *cis*-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CNMe_2)]SO_3CF_3$ and purple-red 60 : 40 mixture of *trans* and *cis*-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CNMe_2)]SO_3CF_3$. Some demethylation also took place to give $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3CNMe]$.

The reaction of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNR)_2]$ with $R'OSO_2CF_3$ (R,R' = Me or Et)

$MeOSO_2CF_3$ was added rapidly to a solution of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNMe)_2]$ (1.8 gm; mole ratio 3 : 1) in benzene (60 cm^3), and the mixture stirred for 2.5 h. The precipitated solid was filtered off and extracted with chloroform. The insoluble residue was analytically pure orange-red $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$ (yield 50%). It could be recrystallized from acetonitrile if required. The filtered extracts were evaporated to dryness at reduced pressure and the residue recrystallized from ethanol-ether mixtures to give $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNMe)(CNMe_2)]SO_3CF_3$ as a red powder (yield 45%).

$[Fe_2(\eta\text{-}C_5H_4Me)_2(CO)_2(CNMe)(CNMe_2)]SO_3CF_3$ (yield < 5%) and $[Fe_2(\eta\text{-}C_5H_4Me)_2(CO)_2(CNMe_2)_2][SO_3CF_3]_2$ (yield 80%) may be prepared similarly from $[Fe_2(\eta\text{-}C_5H_4Me)_2(CO)_2(CNMe)_2]$. Orange crystals of $[Fe_2(\eta\text{-}C_5H_4Me)_2(CO)_2(CNMe_2)_2][SO_3CF_3]_2$, suitable for an X-ray diffraction study, were grown from acetonitrile-ether mixtures (see below).

By the same procedure, $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNEt)_2]$ and $MeOSO_2CF_3$ or $EtOSO_2CF_3$ gave $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2\{CN(Me)Et\}_2][SO_3CF_3]_2$ (yield 20%) and $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNEt)\{CN(Me)Et\}]SO_3CF_3$ (yield 20%), or $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNEt)(CNEt_2)]SO_3CF_3$ and $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNEt_2)_2][SO_3CF_3]_2$. The last is very unstable and does not give consistent analyses.

The reaction of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNMe)_2]$ *with R'X (R'X = MeI,* $PhCH_2Br$ *or* CH_2CHCH_2I*)*

$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNMe)_2]$ (1 g) was dissolved in R'X (10 cm^3). After *ca.* 1 h, benzene (30 cm^3) or benzene-hexane (1 : 1, 60 cm^3) was added to the mixture, and the precipitate filtered off. It was a mixture of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CNMe)\{\mu\text{-}CN(R')Me\}]X$ and $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2\{\mu\text{-}CN(R')Me\}_2]X_2$ salts. No attempt was made to isolate the former as they are best prepared as described elsewhere [1]. The latter were separated and purified by repeated crystallizations from chloroform, ether or their mixtures. Their yields in the original product mix were *ca.* 12% (R'X = MeI), 20% ($PhCH_2Br$) and 30% (CH_2CHCH_2I), but the first of these was very unstable and consistent analyses could not be obtained.

The preparation of cis-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNMe)(\mu\text{-}CO)(\mu\text{-}CNMe_2)]BPh_4$

A solution of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNMe)(\mu\text{-}CO)(\mu\text{-}CNMe_2)]SO_3CF_3$ and $NaBPh_4$ (mole ratio 1 : 3) in acetonitrile was stirred for 3 h before the solvent was removed under reduced pressure. The residue was extracted with dichloromethane, and the extracts filtered and evaporated to dryness at reduced pressure. The residue was dissolved in acetonitrile-ether mixtures and allowed to stand at −15°C. Ruby crystals of *cis*-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNMe)(\mu\text{-}CNMe_2)]BPh_4$ precipitated and were used for the crystal structure determination (see below).

The crystal and molecular structures of cis-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNMe)(\mu\text{-}CO)(\mu\text{-}CNMe_2)]BPh_4$ *and* $[Fe_2(\eta\text{-}C_5H_4Me)_2(CO)_2(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$

The crystal data are summarised in Table 1. The structures were solved by direct methods, SHELX86 [5], and refined by full matrix least squares using SHELX76 [6]. Data were corrected for Lorentz and polarisation effects but not for absorption. One of the cyclopentadienyl rings of *cis*-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNMe)(\mu\text{-}CO)(\mu\text{-}CNMe_2)]BPh_4$, C(8)–C(12), was disordered over two sites in the ratio of 0.75 to 0.25. The carbon atoms of the other cyclopentadienyl ring, C(13)–C(17), were not disordered but had large thermal parameters and hydrogen atoms were not attached to them. Other hydrogen atoms were included in calculated positions

Table 1

Crystal data for (a) *cis*-[$Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNMe)(\mu\text{-}CO)(\mu\text{-}CNMe_2)$]$BPh_4$ and (b) *cis*-[$Fe_2(\eta\text{-}C_5H_4Me)_2(CO)_2(\mu\text{-}CNMe_2)_2$][$SO_3CF_3$]$_2$

Crystal Data	(a)	(b)
Crystal size (mm)	0.38×0.35×0.25	0.40×0.35×0.33
Formula	$C_{41}H_{39}BFe_2N_2O_2$	$C_{22}H_{26}F_6Fe_2N_2O_8S_2$
M (a.m.u.)	602.581	736.260
Space group	Triclinic	Monoclinic
	$P\bar{1}$	$P2_1/n$ No. 14
a (Å)	9.370(1)	10.400(5)
b (Å)	13.682(1)	8.033(2)
c (Å)	14.830(1)	35.11(1)
α°	103.54(1)	90
β°	90.46(1)	93.62(2)
γ°	109.47(1)	90
U (Å^3)	1734.97	2927(2)
Z	2	4
D_c (g cm^{-3})	1.15	1.67
μ cm^{-1}	8.18	11.36
F (000)	744	1496
Radiation	Mo-K_α	Mo-K_α
Graphite monochromator	$\lambda = 0.7093$ Å	$\lambda = 0.7093$ Å
Diffractometer	Enraf-Nonius CAD4F	Enraf-Nonius CAD4F
Orienting reflections, range	25, $13 < \theta < 20$°	25, $13 < \theta < 20$°
Temperature (°C)	22	22
Scan method	$\omega - 2\theta$	$\omega - 2\theta$
Data collection range	$2 < 2\theta < 60$°	$2 < 2\theta < 48$°
No. of unique data	7867	4084
Total $I > 3\sigma I$	4089	3246
No. of parameters fitted	307	379
R, R_w	5.60%, 6.51%	6.24%, 6.86%
Quality-of-fit indicator	3.6	0.85
Largest Shift/esd, final cycle	< 0.001	< 0.001
Largest positive peak (e/Å^3)	0.31	0.56
Largest negative peak (e/Å^3)	−0.16	−0.26

$R = [\Sigma \| F_o | - | F_c \|]/\Sigma | F_o |$. $R_w = [[\Sigma(| F_o | - | F_c |)^2]/[\Sigma(| F_o |)^2]^{1/2}$; $w = 1/[(\sigma F_o)^2 - 0.0011 \cdot F_o^2]$. Quality-of-fit $= [\Sigma w(| F_o | - | F_c |)/N_{obs-} N_{parameters})]^{1/2}$

with fixed thermal parameters (0.075). The non-hydrogen atoms of the cations except those of the disordered cyclopentadienyl ring were refined anisotropically. The atomic scattering factors for non-hydrogen atoms and hydrogen atoms and the anomalous dispersion correction factors were taken from the literature [7,8,9]. All calculations were performed on a VAX 8700 computer. The ORTEP program was used to obtain the drawings [10].

The structure of the cations and atom labelling schemes are shown in Figs. 1 and 2. Heavy atom coordinates are given in Tables 2 and 3, and selected bond lengths and angles in Tables 4 and 5. Complete lists of bond lengths and angles, tables of hydrogen atom coordinates, anisotropic thermal parameters for non-hydrogen atoms and isotropic thermal parameters (for *cis*-[$Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNMe)(\mu\text{-}CO)(\mu\text{-}CNMe_2)$]$BPh_4$ only) have been deposited with the

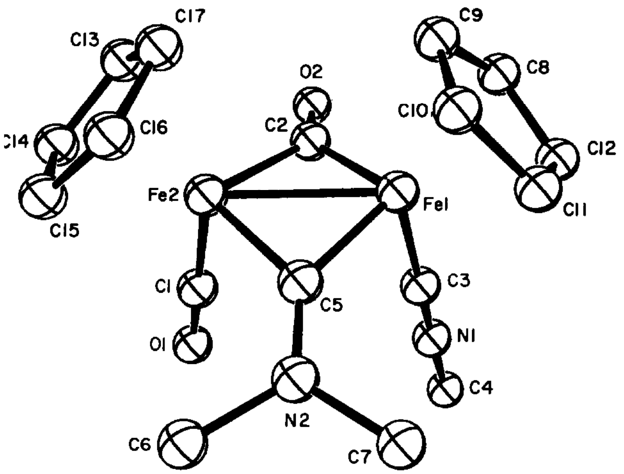

Fig. 1. Structure and atom labelling of the *cis*-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNMe)(\mu\text{-}CO)(\mu\text{-}CNMe_2)]^+$ cation.

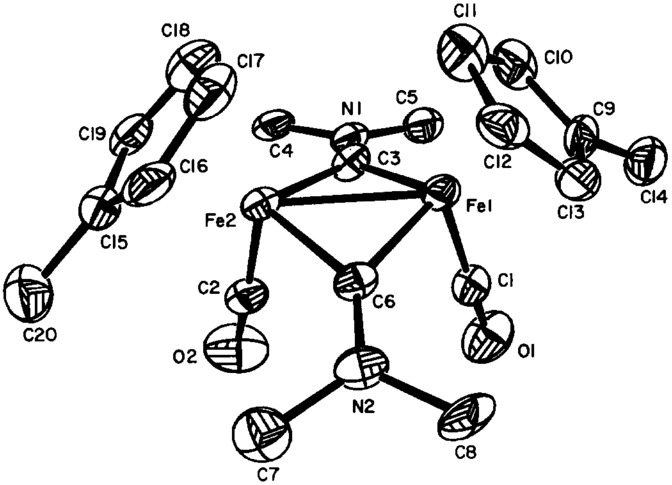

Fig. 2. Structure and atom labelling of the *cis*-$[Fe_2(\eta\text{-}C_5H_4Me)_2(CO)_2(\mu\text{-}CNMe_2)_2]^{2+}$ cation.

Cambridge Crystallographic Data Centre. Lists of observed and calculated structure factors are available from the authors.

Results and discussion

The compounds prepared in this study are all solids. Most are reasonably air-stable both in the solid state and in solution. They are listed in Table 6 together with their melting points and analyses. Their infrared spectra (1550–2200 cm^{-1}) are summarised in Table 7 and their ^1H NMR spectra in Table 8.

The ^1H NMR spectrum of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CNMe_2)]SO_3CF_3$, $[IIIa]SO_3CF_3$, prepared *in situ* shows that two species are present which do not

Table 2

Fractional atomic coordinates for *cis*-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNMe)(\mu\text{-}CO)(\mu\text{-}CMe_2)]BPh_4$

Atom	*x*	*y*	*z*
Fe(1)	0.39308(8)	0.64661(5)	0.71849(5)
Fe(2)	0.20548(9)	0.69066(6)	0.62776(5)
N(1)	0.1890(5)	0.4397(4)	0.7504(3)
N(2)	0.1819(5)	0.7323(3)	0.8307(3)
O(1)	−0.0687(5)	0.5137(4)	0.6301(3)
O(2)	0.3250(5)	0.5299(3)	0.5228(2)
C(1)	0.0401(7)	0.5826(5)	0.6276(4)
C(2)	0.3163(6)	0.5904(4)	0.5904(4)
C(3)	0.2690(6)	0.5200(4)	0.7387(3)
C(4)	0.0957(7)	0.3359(4)	0.7578(4)
C(5)	0.2438(6)	0.7040(4)	0.7552(3)
C(6)	0.0520(8)	0.7711(5)	0.8307(5)
C(7)	0.2311(8)	0.7222(5)	0.9215(4)
C(8)	0.6071(10)	0.6333(12)	0.6868(9)
C(9)	0.6066(10)	0.7363(12)	0.6842(9)
C(10)	0.5802(10)	0.7876(12)	0.7742(9)
C(11)	0.5644(10)	0.7163(12)	0.8324(9)
C(12)	0.5810(10)	0.6210(12)	0.7783(9)
C(13)	0.2600(8)	0.7394(5)	0.5025(4)
C(14)	0.1075(8)	0.7298(5)	0.5191(4)
C(15)	0.1099(8)	0.8025(5)	0.6055(4)
C(16)	0.2640(8)	0.8571(5)	0.6422(4)
C(17)	0.3567(8)	0.8181(5)	0.5785(4)
C(108)	0.6188(28)	0.6898(34)	0.6693(12)
C(109)	0.5943(28)	0.7794(34)	0.7286(12)
C(110)	0.5607(28)	0.7560(34)	0.8160(12)
C(111)	0.5646(28)	0.6519(34)	0.8107(12)
C(112)	0.6005(28)	0.6111(34)	0.7200(12)
B(1)	0.5159(6)	0.2113(4)	0.7928(4)
C(18)	0.6270(5)	0.1459(4)	0.7494(3)
C(19)	0.6178(6)	0.0937(4)	0.6558(3)
C(20)	0.7143(7)	0.0381(5)	0.6194(4)
C(21)	0.8230(7)	0.0326(5)	0.6778(4)
C(22)	0.8397(7)	0.0820(4)	0.7706(4)
C(23)	0.7439(6)	0.1383(4)	0.8056(4)
C(24)	0.4136(5)	0.2206(3)	0.7067(3)
C(25)	0.4535(6)	0.3072(4)	0.6662(3)
C(26)	0.3729(7)	0.3102(5)	0.5886(4)
C(27)	0.2470(7)	0.2240(5)	0.5492(4)
C(28)	0.2005(7)	0.1374(5)	0.5849(4)
C(29)	0.2821(6)	0.1358(4)	0.6635(3)
C(30)	0.4012(5)	0.1502(3)	0.8619(3)
C(31)	0.4215(6)	0.0714(4)	0.8993(3)
C(32)	0.3271(7)	0.0289(5)	0.9637(4)
C(33)	0.2102(7)	0.0605(5)	0.9902(4)
C(34)	0.1825(7)	0.1372(4)	0.9538(4)
C(35)	0.2764(6)	0.1802(4)	0.8917(3)
C(36)	0.6235(5)	0.3320(4)	0.8534(3)
C(37)	0.5919(6)	0.3857(4)	0.9390(3)
C(38)	0.6884(7)	0.4872(5)	0.9877(4)
C(39)	0.8165(7)	0.5390(5)	0.9531(4)
C(40)	0.8507(8)	0.4900(5)	0.8673(4)
C(41)	0.7557(6)	0.3892(4)	0.8199(4)

Table 3

Fractional atomic coordinates for *cis*-$[Fe_2(\eta\text{-}C_5H_4Me)_2(CO)_2(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$

Atom	*x*	*y*	*z*
Fe(1)	0.44527(7)	0.56435(9)	0.15750(2)
Fe(2)	0.28542(7)	0.52742(9)	0.10192(2)
N(2)	0.1727(4)	0.5401(5)	0.1781(1)
N(1)	0.5446(4)	0.3839(6)	0.0914(1)
O(1)	0.4620(5)	0.2355(6)	0.1920(1)
O(2)	0.2254(5)	0.1736(5)	0.1037(2)
C(1)	0.4539(5)	0.3648(7)	0.1792(2)
C(2)	0.2489(5)	0.3126(8)	0.1038(2)
C(3)	0.4608(5)	0.4653(6)	0.1095(1)
C(4)	0.5190(6)	0.3221(8)	0.0514(2)
C(5)	0.6722(6)	0.3448(9)	0.1088(2)
C(6)	0.2649(5)	0.5441(5)	0.1547(1)
C(7)	0.0361(5)	0.5221(8)	0.1655(2)
C(8)	0.1964(6)	0.5550(7)	0.2193(2)
C(9)	0.6114(5)	0.4424(8)	0.1920(2)
C(10)	0.6182(6)	0.7057(8)	0.1549(2)
C(11)	0.5110(7)	0.8059(7)	0.1459(2)
C(12)	0.4358(5)	0.8103(7)	0.1779(2)
C(13)	0.4958(5)	0.7090(7)	0.2056(2)
C(14)	0.7110(7)	0.5412(11)	0.2140(2)
C(15)	0.1257(5)	0.5662(7)	0.0618(2)
C(16)	0.1367(6)	0.7015(7)	0.0867(2)
C(17)	0.2564(7)	0.7785(7)	0.0846(2)
C(18)	0.3242(6)	0.6894(8)	0.0567(2)
C(19)	0.2436(6)	0.5584(7)	0.0433(2)
C(20)	0.0133(6)	0.4550(10)	0.0542(2)
S(1)	0.71067(14)	0.80492(20)	0.05252(5)
S(2)	1.06203(15)	0.00976(17)	0.19253(4)
F(1)	0.9055(7)	0.8537(8)	0.0120(2)
F(2)	0.7431(11)	1.0044(14)	−0.0030(3)
F(3)	0.8583(10)	1.0548(10)	0.0441(3)
F(4)	0.8518(6)	−0.0768(8)	0.1554(2)
F(5)	0.9323(4)	0.1464(6)	0.1350(1)
F(6)	0.8381(4)	0.1518(8)	0.1860(2)
O(3)	0.6599(7)	0.6847(8)	0.0268(2)
O(4)	0.6226(6)	0.9168(7)	0.0678(2)
O(5)	0.7997(5)	0.7320(8)	0.0802(2)
O(6)	1.1139(5)	0.1673(6)	0.2025(1)
O(7)	1.0207(5)	−0.0865(6)	0.2242(1)
O(8)	1.1315(5)	−0.0835(6)	0.1658(1)
C(21)	0.8137(10)	0.9350(10)	0.0257(3)
C(22)	0.9142(6)	0.0559(9)	0.1655(2)

undergo interconversion at +50°C. The principal isomer has a *cis* geometry similar to that found for $[Fe_2(\eta\text{-}C_5H_4Me)_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CNMe_2)]I$ [1]. The minor species is probably its *trans* counterpart. Although a pure sample of it has not been isolated, the separation of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CNMe_2)]SO_3CF_3$ into the orange-red *cis* and a 40:60 mixture of this with the red-purple *trans* isomer has been achieved by careful chromatography. Complete separation of the two isomers was hampered by the low proportion of the *trans* species and

Table 4

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

Bond lengths			
Fe(1)–Fe(2)	2.512(1)	Fe(1)–C(2)	1.909(5)
Fe(1)–C(3)	1.830(6)	Fe(1)–C(5)	1.848(5)
Fe(1)–C(8)	2.120(7)	Fe(1)–C(9)	2.11(1)
Fe(1)–C(10)	2.11(1)	Fe(1)–C(11)	2.126(9)
Fe(1)–C(12)	2.13(1)	Fe(1)–C(108)	2.18(2)
Fe(1)–C(109)	2.11(3)	Fe(1)–C(110)	2.05(3)
Fe(1)–C(111)	2.07(3)	Fe(1)–C(112)	2.16(3)
Fe(2)–C(1)	1.749(7)	Fe(2)–C(2)	1.967(6)
Fe(2)–C(5)	1.876(5)	Fe(2)–C(13)	2.127(5)
Fe(2)–C(14)	2.105(60	Fe(2)–C(15)	2.097(5)
Fe(2)–C(16)	2.114(6)	Fe(2)–C(17)	2.132(6)
N(1)–C(3)	1.157(6)	N(1)–C(4)	1.429(7)
N(2)–C(5)	1.303(7)	N(2)–C(6)	1.481(7)
N(2)–C(7)	1.470(7)	O(1)–C(1)	1.142(7)
O(2)–C(2)	1.163(6)	C(8)–C(9)	1.420(1)
C(8)–C(12)	1.420(1)	C(9)–C(10)	1.420(1)
C(10)–C(11)	1.420(1)	C(11)–C(12)	1.420(1)
C(13)–C(14)	1.420(1)	C(13)–C(17)	1.420(1)
C(14)–C(15)	1.420(1)	C(15)–C(16)	1.420(1)
C(16)–C(17)	1.420(1)	C(108)–C(109)	1.420(1)
C(108)–C(112)	1.420(1)	C(109)–C(110)	1.420(1)
C(110)–C(111)	1.420(1)	C(111)–C(112)	1.420(1)
B(1)–C(18)	1.632(7)	B(1)–C(24)	1.643(7)
B(1)–C(30)	1.651(7)	B(1)–C(36)	1.653(7)
C(18)–C(19)	1.392(7)	C(18)–C(23)	1.417(7)
C(19)–C(20)	1.402(8)	C(20)–C(21)	1.363(8)
C(21)–C(22)	1.365(8)	C(22)–C(23)	1.398(8)
C(24)–C(25)	1.395(6)	C(24)–C(29)	1.400(6)
C(25)–C(26)	1.387(7)	C(26)–C(27)	1.365(8)
C(27)–C(28)	1.352(8)	C(28)–C(29)	1.397(7)
C(30)–C(31)	1.385(7)	C(30)–C(35)	1.405(7)
C(31)–C(32)	1.401(8)	C(32)–C(33)	1.336(8)
C(33)–C(34)	1.380(8)	C(34)–C(35)	1.375(7)
C(36)–C(37)	1.398(7)	C(36)–C(41)	1.393(7)
C(37)–C(38)	1.396(7)	C(38)–C(39)	1.349(8)
C(39)–C(40)	1.386(8)	C(40)–C(41)	1.381(8)
Bond angles			
C(2)–Fe(1)–Fe(2)	50.6(2)	C(3)–Fe(1)–Fe(2)	99.8(2)
C(3)–Fe(1)–C(2)	87.5(2)	C(5)–Fe(1)–Fe(2)	48.0(2)
C(5)–Fe(1)–C(2)	96.1(2)	C(5)–Fe(1)–C(3)	88.3(2)
C(8)–Fe(1)–Fe(2)	130.9(5)	C(8)–Fe(1)–C(2)	91.1(3)
C(8)–Fe(1)–C(3)	108.9(5)	C(8)–Fe(1)–C(5)	161.7(4)
C(9)–Fe(1)–Fe(2)	104.3(5)	C(9)–Fe(1)–C(2)	91.8(4)
C(9)–Fe(1)–C(3)	148.2(4)	C(9)–Fe(1)–C(5)	123.4(4)
Fe(1)–C(3)–N(1)	179.0(5)	C(3)–N(1)–C(4)	174.7(5)
Fe(2)–C(1)–O(1)	177.9(6)	C(5)–N(2)–C(6)	127.7(5)
Fe(1)–C(2)–Fe(2)	80.8(2)	C(5)–N(2)–C(7)	122.0(5)
Fe(1)–C(5)–Fe(2)	84.8(2)	C(6)–N(2)–C(7)	115.2(5)

competing demethylation. The *cis*:*trans* product ratio is a function of the solvent in which $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CNMe_2)]SO_3CF_3$ was prepared. It increases from 90:10 in boiling carbon disulphide to 94:6 in benzene and 100:0 in acetonitrile.

The reaction of I with MeI in benzene is much slower than that with $MeOSO_2CF_3$ but the ratio of *cis*:*trans* $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CNMe_2)]^+$ in the products is comparable. Both *cis*- and *trans*-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CNEt_2)]SO_3CF_3$ (ratio 88:12) are formed, but only the *cis* isomer could be detected for all $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}CN(R')R\}]X$ salts where $R \neq R'$.

$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNMe)(\mu\text{-}CO)\{\mu\text{-}CN(R)Me\}]^+$, $[IV]^+$, salts are the only products formed in the reaction of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNMe)_2]$ with alkyl halides or $R'OSO_2CF_3$ (R' = Me or Et) in only slight excess. The rapid addition of a large excess of $R'OSO_2CF_3$ (R' = Me or Et) to a solution of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNR)_2]$, R = Me (IIa) or Et (IIb), or the dissolution of IIa in the more reactive alkyl halides R'X (R'X = MeI, CH_2CHCH_2I or $PhCH_2Br$) give two products *cis*-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNR)(\mu\text{-}CO)\{\mu\text{-}CN(R')R\}]X$, [IV]X, and *cis*-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2\{\mu\text{-}CN(R')R\}_2]X_2$, $[V]X_2$, but not their *trans* counterparts. Analogues of $[V]X_2$ where $R' = H$ have been obtained previously as the sole products from the reactions of II with an excess of strong protic acids [11]. As the monoalkylated cations $[IV]^+$ are not fluxional and do not undergo terminal-bridge CO/CNMe site exchange, they do not react with $R'OSO_2CF_3$ to give $[V]^{2+}$ salts at room temperature. Consequently, $[IV]^+$ must have been formed from *cis*-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNR)(\mu\text{-}CO)(\mu\text{-}CNR)]$, and $[V]^{2+}$ from *cis*-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CNR)_2]$. This implies that the reaction of R'X with *cis*-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNR)(\mu\text{-}CO)(\mu\text{-}CNR)]$ is faster than with the other isomers of (II) but is still sufficiently slow that the equilibrium between these isomers [3,4] can be maintained throughout the alkylation. On the other hand, the rate of reaction of R'X in very large excess with II must be much faster than the rate of interconversion of their isomers so that mono- and bis-alkylated derivatives are formed. It is straightforward to account for the greater reactivity of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNR)(\mu\text{-}CO)(\mu\text{-}CNR)]$ than of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CNR)_2]$ in terms of (a) a terminal CO ligand being a poorer σ-donor/better π-acceptor than a μ-CO ligand, (b) a terminal CNR ligand being a better σ-donor/poorer π-acceptor than a μ-CNR ligand, (c) steric inhibition of the formation of the $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CNR)_2]$ precursor, or (d) a combination of all three. (a) and (b) result in greater back-donation into the μ-CNR ligand of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNR)(\mu\text{-}CO)(\mu\text{-}CNR)]$ than into the two μ-CNR ligands of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CNR_2]$, which makes the former more nucleophilic. However it is not easy to explain why, in both of these species and the $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CNR)]$ discussed above, the *cis* isomers react more rapidly than their *trans* counterparts, because infrared spectroscopy suggests that in all cases the *cis*:*trans* ratios in solutions of the substrates do not differ by as much as the *cis*:*trans* ratios in the alkylated products.

Infrared spectra

The most important absorption bands are those due to the stretching vibrations of μ-CNR_2 (*ca.* 1570–1630 cm^{-1}), μ-CO (*ca.* 1800–1840 cm^{-1}), terminal CO (*ca.* 1960–2050 cm^{-1}) and terminal CNR ligands (*ca.* 2160–2190 cm^{-1}) (Table 7). There are others due to both anions and cations which will not be discussed as they yield little structural information except to confirm the presence of the $[SO_3CF_3]^-$ where appropriate.

The relative intensities of the absorption bands due to the ν(CO) vibrations of the sole species present in solutions of $[V]X_2$ (see below) confirm that the cations

Table 5

Selected bond lengths (Å) and angles (°) for *cis*-$[Fe_2(\eta\text{-}C_5H_4Me)_2(CO)_2(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$

Bond lengths			
Fe(1)–Fe(2)	2.500(1)	Fe(1)–C(1)	1.774(6)
Fe(1)–C(3)	1.880(5)	Fe(1)–C(6)	1.879(5)
Fe(1)–C(9)	2.140(5)	Fe(1)–C(10)	2.134(6)
Fe(1)–C(11)	2.106(6)	Fe(1)–C(12)	2.106(5)
Fe(1)–C(13)	2.091(5)	Fe(2)–C(2)	1.769(6)
Fe(2)–C(3)	1.893(5)	Fe(2)–C(6)	1.883(5)
Fe(2)–C(15)	2.132(5)	Fe(2)–C(16)	2.128(5)
Fe(2)–C(17)	2.123(6)	Fe(2)–C(18)	2.112(6)
Fe(2)–C(19)	2.092(6)	N(2)–C(6)	1.301(6)
N(2)–C(7)	1.468(7)	N(2)–C(8)	1.459(8)
N(1)–C(3)	1.289(7)	N(1)–C(4)	1.497(7)
N(1)–C(5)	1.460(7)	O(1)–C(1)	1.134(7)
O(2)–C(2)	1.143(7)	C(9)–C(10)	1.402(9)
C(9)–C(13)	1.426(8)	C(9)–C(14)	1.494(9)
C(10)–C(11)	1.39(1)	C(11)–C(12)	1.410(9)
C(12)–C(13)	1.385(8)	C(15)–C(16)	1.395(8)
C(15)–C(19)	1.425(8)	C(15)–C(20)	1.482(9)
C(16)–C(17)	1.396(9)	C(17)–C(18)	1.435(9)
C(18)–C(19)	1.408(9)	S(1)–O(3)	1.402(6)
S(1)–O(4)	1.413(5)	S(1)–O(5)	1.426(6)
S(1)–C(21)	1.804(8)	S(2)–O(6)	1.411(5)
S(2)–O(7)	1.440(5)	S(2)–O(8)	1.432(4)
S(2)–C(22)	1.794(7)	F(1)–C(21)	1.28(1)
F(2)–C(21)	1.33(1)	F(3)–C(21)	1.23(1)
F(4)–C(22)	1.286(8)	F(5)–C(22)	1.317(8)
F(6)–C(22)	1.345(8)		
Bond angles			
C(1)–Fe(1)–Fe(2)	103.9(2)	C(3)–Fe(1)–Fe(2)	48.7(2)
C(3)–Fe(1)–C(1)	89.8(2)	C(6)–Fe(1)–FE(2)	48.4(2)
C(6)–Fe(1)–C(1)	88.1(2)	C(6)–Fe(1)–C(3)	93.3(2)
C(2)–Fe(2)–Fe(1)	102.8(2)	C(3)–Fe(2)–Fe(1)	48.3(2)
C(3)–Fe(2)–C(2)	86.8(2)	C(6)–Fe(2)–Fe(1)	48.3(1)
C(6)–Fe(2)–C(2)	89.8(2)	C(6)–Fe(2)–C(3)	92.8(2)
C(7)–N(2)–C(6)	123.4(5)	C(8)–N(2)–C(6)	122.6(5)
C(8)–N(2)–C(7)	114.0(5)	C(4)–N(1)–C(3)	123.0(5)
C(5)–N(1)–C(3)	121.9(5)	C(5)–N(1)–C(4)	115.1(4)
O(1)–C(1)–Fe(1)	177.6(5)	O(2)–C(2)–Fe(2)	177.8(5)
Fe(2)–C(3)–Fe(1)	83.0(2)	N(1)–C(3)–Fe(1)	139.1(4)
N(1)–C(3)–Fe(2)	137.8(4)	Fe(2)–C(6)–Fe(1)	83.3(2)
N(2)–C(6)–Fe(1)	137.9(4)	N(2)–C(6)–Fe(2)	138.8(4)
O(3)–S(1)–O(3)	117.1(4)	O(5)–S(1)–O(3)	111.0(4)
O(4)–S(1)–O(4)	114.3(4)	C(21)–S(1)–O(3)	106.0(4)
C(21)–S(1)–O(4)	104.5(4)	C(21)–S(1)–O(5)	102.3(5)
O(7)–S(2)–O(6)	114.7(3)	O(8)–S(2)–O(6)	115.6(3)
O(8)–S(2)–O(7)	114.4(3)	C(22)–S(2)–O(6)	104.3(3)
C(22)–S(2)–O(7)	103.3(3)	C(22)–S(2)–O(8)	102.3(3)
F(1)–C(21)–S(1)	112.6(6)	F(2)–C(21)–S(1)	108.7(8)
F(2)–C(21)–F(1)	108.6(9)	F(3)–C(21)–S(1)	113.3(7)
F(3)–C(21)–F(1)	109.0(1)	F(3)–C(21)–F(2)	104.0(1)
F(4)–C(22)–S(2)	112.1(5)	F(5)–C(22)–S(2)	112.4(5)
F(5)–C(22)–F(4)	109.2(7)	F(6)–C(22)–S(2)	110.5(5)
F(6)–C(22)–F(4)	108.6(7)	F(6)–C(22)–F(5)	103.7(6)

Table 6

Melting points and analyses of salts described in the text

R′, R	m.p. (°C)	Analyses [a]		
		%C	%H	%N
$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}CN(R')R\}]SO_3CF_3$				
Me, Me	257–259	38.3 (38.4)	3.0 (3.0)	2.5 (2.6)
Et, Et + H_2O	219–222	39.9 (39.5)	3.5 (3.8)	2.3 (2.4)
Et, Me	223–226	39.4 (39.6)	3.3 (3.3)	2.6 (2.7)
$Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNR)(\mu\text{-}CO)\{\mu\text{-}CN(R')R\}]SO_3CF_3$				
Me, Me	151–156	39.4 (39.7)	3.6 (3.5)	5.0 (5.1)
Me, Me [b]		68.6 (68.9)	5.5 (5.5)	3.7 (3.9)
Me, Et		41.8 (42.0)	4.1 (4.0)	4.7 (4.9)
Et, Me	149–151	40.6 (40.9)	3.8 (3.8)	4.8 (5.0)
$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2\{\mu\text{-}CN(R')R\}_2][SO_3CF_3]_2$				
Me, Me + H_2O	dec. > 220	35.9 (35.9)	3.9 (3.6)	4.2 (4.4)
Me, Me + H_2O [c]	dec. > 220	34.9 (35.0)	3.5 (3.7)	3.7 (3.7)
Me, Et + H_2O	dec. > 220	35.0 (35.0)	3.8 (3.7)	3.7 (3.7)
$PhCH_2$, Me [d] + H_2O	dec. > 220	48.3 (48.7)	4.3 (4.3)	3.6 (3.8)
Allyl, Me [e] + H_2O	dec. > 220	36.3 (36.0)	3.6 (3.8)	3.6 (3.8)

[a] Found (calculated). [b] BPh_4^- as counteranion. [c] η-C_5H_4Me complex. [d] Br^- as counteranion. [e] I^- as counteranion.

Table 7

The infrared spectra of the salts described in the text between 1550 and 2200 cm^{-1} [a]

R′, R	Absorption bands and assignment				
	$\nu(\mu\text{-}C{=}N)$	$\nu(\mu\text{-}CO)$	$\nu(CO)$	$\nu(CO)$	$\nu(CN)$
$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}CN(R')R\}]SO_3CF_3$					
cis-Me, Me	1594 (w)	1817 (m)	1993 (w)	2027 (s)	
cis-Me, Me [b]	1602 (w)	1830 (m,br)	1991 (w)	2022 (s)	
trans-Me, Me [b]	1600 (w)	1842 (m)	1997 (s)		
Et, Me	1586 (w)	1833 (m)	1991 (m)	2017 (s)	
Et, Et	1596 (m)	1837 (m)	1985 (m)	2016 (s)	
cis-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNR)(\mu\text{-}CO)\{\mu\text{-}CN(R')R\}]SO_3CF_3$					
Me, Me	1586 (w)	1805 (m)		1987 (s)	2183 (m)
Me, Me [c]	1579 (w)	1816 (m)		1982 (s)	2186 (m)
Me, Et	1577 (w)	1810 (m)		1968 (s)	2169 (m)
cis-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2\{\mu\text{-}CN(R')R\}_2][SO_3CF_3]_2$					
Me, Me	1616 (m)		2027 (m)	2049 (s)	
Me, Me [d]	1611 (m), 1631 (w)		2016 (m)	2034 (s)	
Me, Et	1599 (m)		2027 (m)	2052 (s)	
$PhCH_2$, Me [e]	1593 (m)		2010 (m)	2033 (s)	
allyl, Me [f]	1549 (m), 1645 (w)		2012 (m)	2041 (s)	

[a] Spectra run as KBr pressed discs unless stated otherwise. Peak positions (cm^{-1}) with relative peak heights in parentheses. w = weak, m = medium, and s = strong. [b] Spectra run in chloroform solution. [c] BPh_4^- as counteranion. [d] η-C_5H_4Me complex. [e] Br^- as counteranion. [f] I^- as counteranion.

Table 8

The ^1H NMR spectra of the salts described in the text

Isomer, R′, R		Resonances [a]		
		C_5H_5	CN(R′)R	CNR
$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}CN(R')R\}]SO_3CF_3$				
cis, Me, Me		5.32	4.29	
trans, Me, Me		5.17	4.42	
cis, Et, Et		5.32	4.56 (m), 1.62 (t, $J = 7.3$)	
trans, Et, Et		5.10	[b]	
cis, Et, Me		5.34, 5.32	4.20; 4.65 (m), 1.56 (t, $J = 7.3$)	
cis-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNR)(\mu\text{-}CO)\{\mu\text{-}CN(R')R\}]SO_3CF_3$				
cis, Me, Me [c]		4.92, 4.82	3.95, 3.96	2.95
cis, Me, Me		5.10, 5.03	4.23, 4.30	3.10
cis, Me, Me [d]		5.18, 5.12	4.31, 4.39	3.14
cis, Me, Et	α [e]	5.09, 5.05	4.21; 4.60 (m), 1.53 (t, $J = 7.3$)	3.36 (m), 1.09 (t, $J = 7.1$)
	β [e]	5.11, 5.02	4.15; [b], 1.58 (t, $J = 7.2$)	3.48 (q), 1.21 t, $J = 6.6$)
cis Et, Me	α [e]	5.07, 5.04	[b], 1.52 (t, $J = 7.1$), 4.22	[b]
	β [e]	5.10, 5.02	4.66 (m), 1.58 (t, $J = 7.1$); 4.14	3.09
cis, Et, Et		5.08, 5.02	4.68 (m), 4.53 (m), 1.63 (t, $J = 7.2$), 1.54 (t, $J = 7.3$)	3.38 (q), 1.07 (t, $J = 7.3$)
cis, Et, Et [c]		4.69, 4.59	4.16 (m), 1.35 (br), 1.32 (br)	3.07 (br,m), 0.91 (t, $J = 6.4$)
cis-$\{Fe_2(\eta\text{-}C_5H_5)_2(CO)_2\{\mu\text{-}CN(R')R\}_2][SO_3CF_3]_2$				
cis, Me, Me		5.70	4.12	
cis, Me, Me [f]		5.76 (m), 5.11 (m)	4.11	
cis, Me, Et	*anti*	5.68	4.06; 4.43 (m) 1.59 (t, $J = 7.4$)	
	syn	5.70, 5.67	4.065; 4.43 (m) 1.59 (t, $J = 7.4$)	
cis, $PhCH_2$, Me [g]	*anti*	6.05	4.09; 5.89 (d), 5.79 (d) ($J_{AB} = 14.1$), 7.3–7.6 (m)	
	syn	6.07, 6.00	4.09; 5.91 (d), 5.80 (d) ($J_{AB} = 14.3$), 7.3–7.6 (m)	
cis, C_3H_5, Me [d]	*anti*	5.91	4.15; 6.23 (b,m), 5.66 (d, $J = 9.3$), 5.61, 5.06 (dq, $J = 13.2, 6.1$)	
	syn	5.93, 5.89	4.15; 6.23 (b,m), 5.66 (d, $J = 9.3$), 5.61, 5.06 (dq, $J = 13.2, 6.1$)	

[a] Spectra run in $CDCl_3$ unless it is stated otherwise. Chemical shifts quoted as ppm downfield from Me_4Si. All resonances are singlets unless it is stated otherwise; m = multiplet, t = triplet, dq = double quartet and br = broad with coupling constants J given in Hz.. All integrations are as required by the formulae. [b] Resonance obscured by those due to major isomer. [c] BPh_4^- counteranion. CD_2Cl_2 solvent. [d] I^- counteranion. [e] α and β isomers. See text. [f] η-C_5H_4Me complex with Me resonance at 2.31 δ. [g] Br^- counteranion. CD_3OD solvent. *syn*:*anti* ratio = 45:55.

have the *cis*-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2\{\mu\text{-}CN(R')R\}_2]^{2+}$ structure (Fig. 2) with absorption bands at 2047 and 2022 cm^{-1} due respectively to their symmetric and antisymmetric ν(CO) vibrations and those at *ca.* 1600 and 1630 cm^{-1} due to the antisymmetric and symmetric ν(C=N) modes of a non-planar $Fe_2(\mu\text{-}CNR_2)_2$ moiety although it is only for *cis*-$[Fe_2(\eta\text{-}C_5H_4Me)_2(CO)_2(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$ that these last are clearly resolved. These spectra are similar to those of *cis*-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2\{\mu\text{-}CN(H)R\}_2]^{2+}$ salts [11]. The infrared spectra of $[III]^+$ and

$[IV]^+$ salts have been discussed and assigned in ref. 1. Those of the former are consistent with a *cis* cation which is shown by ^1H NMR spectroscopy to be the major or only species present. As anticipated, the spectrum of *trans*-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CNMe_2)]SO_3CF_3$ is similar but shows only a single $\nu(CO)$ absorption band at *ca.* 1997 cm^{-1} due to the antisymmetric mode. The spectra of $[IV]X$ are consistent with the $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNR)(\mu\text{-}CO)\{\mu\text{-}CN(R')R\}]^+$ structure for the cations but do not define whether they are *cis* or *trans*; this required an X-ray structure determination (see below).

NMR spectra

The ^1H NMR spectrum of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CNMe_2)]SO_3CF_3$ (Table 8) shows singlet resonances due to the cyclopentadienyl and μ-$CNMe_2$ protons of the *cis* isomer and another much weaker pair due to its *trans* isomer. Both sets of resonances are also present in the spectrum of $[Fe_2(\mu\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CNEt_2)]SO_3CF_3$ but only those due to the *cis* isomer are present in the spectra of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CN(Et)Me]SO_3CF_3$ and all other similar complexes with μ-CN(R)(R') ligands where $R \neq R'$. However, in such cases the two cyclopentadienyl ligands are not equivalent and give rise to two equal singlets.

$[IV]^+$ salts where $R = R' = Me$ exist as a single species in solution and it is assumed that their cation has the same structure as found for the $[BPh_4]^-$ salt in the solid state. Because of the difference between the CO and CNMe ligands there are two cyclopentadienyl and two NMe_2 singlets as well as the CNMe resonance. Similar comments apply when $R = R' = Et$, but the presence of the μ-CN(Me)Et ligand allows further isomerism (Fig. 3) and such cations shows two unequal sets of resonances due to α and β forms although it is not possible to assign them. The $\alpha : \beta$ ratio varies from sample to sample, and more markedly from cation to cation.

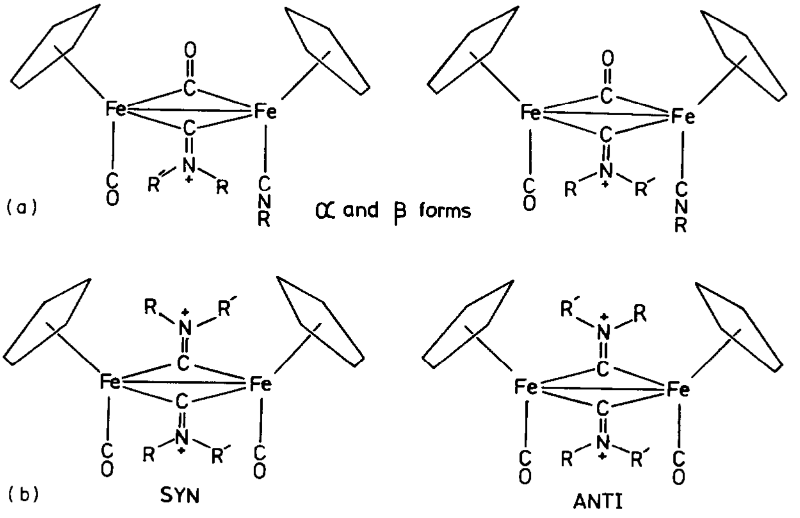

Fig. 3. (a) Isomers of the *cis*-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNR)(\mu\text{-}CO)\{\mu\text{-}CN(R')R\}]^+$ cation (α and β forms). (b) *syn* and *anti* isomers of the *cis*-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2\{\mu\text{-}CN(R')R\}_2]^{2+}$ cation.

Thus for $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNEt)(\mu\text{-}CO)\{\mu\text{-}CN(Me)Et\}]SO_3CF_3$ the α isomer predominates (92:8 in one sample and 79:21 in another) but for $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNMe)(\mu\text{-}CO)\{\mu\text{-}CN(Et)Me\}]SO_3CF_3$ the β isomer is the more important (12:88) even for reactions carried out in an NMR tube. These results imply that during the reaction of $R'OSO_2CF_3$ with $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNR)(\mu\text{-}CO)(\mu\text{-}CNR)]$ electrophilic attack on the μ-N atom occurs from one end of the molecule rather than the other. This may be because the *t*-CNR and *t*-CO ligands differently affect the approach of the electrophile. Alternatively it may be because one orientation of the non-linear μ-CNR ligand is favoured over the other in the substrate, perhaps due to steric interaction between μ-R and *t*-CNR groups. Either explanation is also consistent with the formation of *ca.* equal amounts of *syn* and *anti* isomers of *cis*-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2\{\mu\text{-}CN(Me)Et\}_2][SO_3CF_3]_2$ as here the two terminal ligands in the *cis*-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CNMe)\{\mu\text{-}CN(Me)Et\}]^+$ intermediate are identical (see below).

The *cis* isomer is the sole cation found in solutions of $[V][SO_3CF_3]_2$ ($R = R' = Me$) in acetonitrile. It gives rise to two singlet resonances due to cyclopentadienyl and μ-$CNMe_2$ ligands (Table 8). Similar comments are valid for the C_5H_4Me complex and when $R = R' = Et$. However as a consequence of the asymmetrical μ-CN(R′)Me ligand there are two possible isomers of $[V]^{2+}$ when R′ = Et, CH_2Ph or allyl (Fig. 3), and both are formed in *ca.* equal amounts (see above). The *syn* gives rise to two cyclopentadienyl resonances and the *anti* to one, but the resonances due to their μ-CN(R′)Me ligand are sometimes coincident (Table 8).

The ^1H NMR spectra of all $[III]^+$, $[IV]^+$ and $[V]^{2+}$ salts are independent of temperature. They indicate that there is no facile *cis–trans* interconversion in $[III]^+$ or CO–CNMe exchange in $[IV]^+$. This rigidity contrasts with the fluxionality of their precursors I and II. Perhaps the very high π-acceptor ability of the $CNR_2{}^+$ ligands and their very strong preference for bridging as against terminal coordination means that non-bridged intermediates are energetically not accessible. Furthermore there is no rotation about the C=N bond of the μ-CN(R′)R group in any cation. This is consistent with the shortness and high order of this bond (see below), and provides further confirmation that the ligand is best thought of as C=N(R′)R with a positively charged nitrogen atom rather than as μ_2-carbyne with a C–N(R′)R single bond.

The ^{13}C NMR spectrum of *cis*-$[Fe_2(\eta\text{-}C_5H_4Me)_2(CO)_2(\mu\text{-}CNMe_2)_2][SO_3CF_3]_2$ (CD_3CN solution) shows resonances at 112.1, 91.6, 91.7, and 12.45 ppm downfield from Me_4Si due to the C_5H_4Me ligand, at 205.4 ppm due to the *t*-CO ligands, and at 308.1 and 54.7 ppm due to the μ-$CNMe_2$ groups. The spectrum of *cis*-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CNMe_2)][SO_3CF_3]$ ($CDCl_3$ solution) shows resonances at 315.7 and 55.5 (μ-$CNMe_2$), 255.4 (μ-CO), 207.6 (*t*-CO) and 90.1 ppm (η-C_5H_5). Very weak resonances at 91.5 and 56.2 ppm are due the *trans* isomer. The spectrum of *cis*-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNMe)(\mu\text{-}CO)(\mu\text{-}CNMe_2)]I$ ($CDCl_3$ solution) shows resonances at 322.3, 54.5 and 54.4 (μ-$CNMe_2$), 262.2 (μ-CO), 210.3 (*t*-CO), 154.2 and 31.4 (*t*-CNMe) and 88.7 and 88.3 ppm (η-C_5H_5).

The ^{13}C chemical shifts of the μ-CN(R′)R ligands in $[III]^+$, $[IV]^+$ and $[V]^{2+}$ cations compare with *e.g.* those of *ca.* 317 ppm in $[Fe_2(CNEt)_6(\mu\text{-}CNEt)\{\mu\text{-}CN(R')Et\}_2]^{2+}$ salts [12] (R′ = Me, Et), and 312 ppm in $[W_2(\eta^2\text{-}S_2CNEt_2)_2(\mu\text{-}CNEt_2)(S_2CNEt_2)(\mu\text{-}S_2SnR_2)]$ {$R = CH(SiMe_3)_2$} [13].

The structures of cis-*[$Fe_2(\eta$-$C_5H_5)_2(CO)(CNMe)(\mu$-$CO)(\mu$-$CNMe_2)]BPh_4$ and* cis-*[$Fe_2(\eta$-$C_5H_5)_2(CO)_2(\mu$-$CNMe_2)_2][SO_3CF_3]_2$*. Both cations have structures (Figs. 1 and 2) similar to that of *cis*-[$Fe_2(\eta$-$C_5H_4Me)_2(CO)_2(\mu$-$CO)(\mu$-$CNMe_2)]^+$ with a *cis* geometry [1]. In the [$Fe(\eta$-$C_5H_5)_2(CO)(CNMe)(\mu$-$CO)(\mu$-$CNMe_2)]^+$ cation, bond lengths correlate with the bonding abilities of the various ligands. Thus, the Fe–C distances to the μ-$CNMe_2$ ligand (1.876, 1.830 Å) are much shorter than those to μ-CO (1.967, 1.909 Å), which is consistent with the stronger π-acceptor ability of μ-$CNMe_2{}^+$ as compared with μ-CO. Furthermore, a terminal CO group is stronger π-acceptor than a terminal CNMe, and so Fe(2)–CO (1.749 Å) is much shorter than Fe(1)–CNMe (1.830 Å) with a compensating secondary effect that π-bonding between the bridging ligands and Fe(1) is increased over their π-bonding to Fe(2). Consequently, Fe(1)–Cμ distances are slightly shorter than Fe(2)–Cμ.

As the two terminal ligands in the [$Fe_2(\eta$-$C_5H_4Me)_2(CO)_2(\mu$-$CNMe_2)_2]^{2+}$ cation are identical, all four Fe–C distances to the μ-C=NMe_2 ligands are comparable (1.879–1.893 Å). Their mean (1.886 Å) is somewhat longer than the 1.830 and 1.876 Å (mean 1.853 Å) found in *cis*-[$Fe_2(\eta$-$C_5H_5)_2(CO)(CNMe)(\mu$-$CO)(\mu$-$CNMe_2)]^+$, which may be attributed to the presence of two very powerful π-acceptor $CNMe_2$ ligands competing for the available back-bonding.

The coordination about N in the $CNMe_2$ ligands is planar with short C=N distances of 1.289–1.303 Å (*cf.* N–CH_3 = 1.459–1.497 Å), consistent with a multiple bond and the very high barrier to rotation about it. The bond is somewhat longer than that found in imines (1.28 Å) [14].

The $Fe_2(\mu$-$CNMe_2)$ and $Fe_2(\mu$-CO) moieties in both cations are planar. The dihedral angle between the two bridging moieties is 154.8° in *cis*-[$Fe_2(\eta$-$C_5H_5)_2(CO)(CNMe)(\mu$-$CO)(\mu$-$CNMe_2)]^+$ which is comparable with the 154° found in *cis*-[$Fe_2(\eta$-$C_5H_4Me)_2(CO)_2(\mu$-$CO)(\mu$-$CNMe_2)]^+$ [1]. In *cis*-[$Fe_2(\eta$-$C_5H_4Me)_2(CO)_2(\mu$-$CNMe_2)_2]^{2+}$ it is smaller at 149.5° and both are smaller than 161° in *cis*-[$Fe_2(\eta$-$C_5H_5)_2(CO)(CN{}^iPr)(\mu$-$CO)(\mu$-$CN{}^iPr)$ [4] and 164° in *cis*-[$Fe_2(\eta$-$C_5H_5)_2(CO)_2(\mu$-$CO)_2$] [15]. It appears that the dihedral angle between the two $Fe_2(\mu$-L) planes decreases as μ-CO or CNR ligands are replaced by μ-C=NMe_2.

Acknowledgments

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