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The reaction of R,S and $R,R/S,S$-$[Fe_2\{\eta,\eta\text{-}C_5H_4CH(NMe_2)CH(NMe_2)C_5H_4\}(CO)_2(\mu\text{-}CO)_2]$ and $[Fe_2\{\eta,\eta\text{-}C_5H_4CH_2CH(NMe_2)C_5H_4\}(CO)_2(\mu\text{-}CO)_2]$ with alkylating agents. Preparation, structure and spectra of $[Fe_2\{\eta,\eta\text{-}C_5H_4CH(NMe_2)CH(NMe_3)C_5H_4\}(CO)_2(\mu\text{-}CO)_2]^+$ and $[Fe_2\{\eta,\eta\text{-}C_5H_4CH_2CH(NMe_3)C_5H_4\}(CO)_2(\mu\text{-}CO)_2]^+$ salts

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Abstract

The reagents MeI and $MeOSO_2CF_3$ methylate R,S-$[Fe_2\{\eta,\eta\text{-}C_5H_4CH(NMe_2)CH(NMe_2)C_5H_4\}(CO)_2(\mu\text{-}CO)_2]$, **1**, its $R,R/S,S$ isomer **2**, and $[Fe_2\{\eta,\eta\text{-}C_5H_4CH_2CH(NMe_2)C_5H_4\}(CO)_2(\mu\text{-}CO)_2]$, **3**, at one N atom only. Subsequent anion exchange gives salts of the R,S and $R,R/S,S$-$[Fe_2\{\eta,\eta\text{-}C_5H_4CH(NMe_2)CH(NMe_3)C_5H_4\}(CO)_2(\mu\text{-}CO)_2]^+$ and $[Fe_2\{\eta,\eta\text{-}C_5H_4CH_2CH(NMe_3)C_5H_4\}(CO)_2(\mu\text{-}CO)_2]^+$ cations, [**4**]X, [**5**]X and [**6**]X, respectively ($X^- = Cl^-$, Br^-, I^-, $[SO_3CF_3]^-$, $[PF_6]^-$ or $[BPh_4]^-$). The ^{1}H-NMR spectra of the cations show that rotation about the C–NMe_3 bond and rotation–inversion of NMe_2 groups can be slowed in [**4**]$^+$ and [**5**]$^+$ but not in [**6**]$^+$, but there is no evidence for partial rotation about the ring-linking C–C bond in any cation, as there is in free **1**. The chemical shifts of the Me_3NC–H and, to a lesser extent, the cyclopentadienyl hydrogen atoms only of all three cations are strongly dependent on the nature of the anion X^- and the solvent. This is attributed to strong interactions between the Me_3NC–H hydrogen atom and the solvent or anion, which decrease along the series $X^- = Cl^- > Br^- > I^- > [SO_3CF_3]^- > [PF_6]^- > [BPh_4]^-$. There is indirect evidence for $Me_2N\text{-} > CH(NMe_3)^+$ interactions in [**4**]$^+$ and [**5**]$^+$. Attempts to prepare the $X^- = F^-$ salts failed. Reactions of [**4**][SO_3CF_3] with [n-Bu_4N]F in tetrahydrofuran/acetonitrile gave [**4**][H_4F_5] whilst [**5**][SO_3CF_3] and [Et_4N]F · $2H_2O$ in dichloromethane gave [**5**][H_5F_6]. In acetonitrile [Et_4N]F · $2H_2O$ acts a source of $[OH]^-$ ions. It brings about Me_3N and H^+ elimination from [**4**][SO_3CF_3] to give an enamine $[Fe_2\{\eta,\eta\text{-}C_5H_4CHC(NMe_2)C_5H_4\}(CO)_2(\mu\text{-}CO)_2]$, a water-gas shift mediated Me_3N displacement by H^- from [**5**][SO_3CF_3] to give **3**, and converts [**6**][SO_3CF_3] to [**6**][OH]. X-ray diffraction has been used to determine the crystal and molecular structures of R,S-$[Fe_2\{\eta,\eta\text{-}C_5H_4CH(NMe_2)CH(NMe_3)C_5H_4\}(CO)_2(\mu\text{-}CO)_2]$I · 2MeCN and R,S-$[Fe_2\{\eta,\eta\text{-}C_5H_4CH(NMe_2)CH(NMe_3)C_5H_4\}(CO)_2(\mu\text{-}CO)_2][SO_3CF_3]$ · CH_2Cl_2. Despite the very different ^{1}H-NMR spectra of these salts in solution, both cations have structures based on that of **1** with methylation of the NMe_2 group that is transoid to a cyclopentadienyl ring rather than that which is transoid to a hydrogen atom. Bond lengths and bond angles are similar to those found in **1**, **2** and related species.

Keywords: Iron; Carbonyls; Cyclopentadienyl; Crystal structure; Fluxionality; Hydrogen bonding

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1. Introduction

The complexes R,S- and $R,R/S,S$-$[Fe_2\{\eta,\eta\text{-}C_5H_4CH(NMe_2)CH(NMe_2)C_5H_4\}(CO)_2(\mu\text{-}CO)_2]$, **1** and **2** respectively, are products of the reaction of 6-dimethylaminofulvene with $[Fe(CO)_5]$ at 140°C [1]. The complex $[Fe_2\{\eta,\eta\text{-}C_5H_4CH_2CH(NMe_2)C_5H_4\}(CO)_2(\mu\text{-}CO)_2]$, **3**, may be obtained from either of them [1]. We describe below the reactions of all three with methylating agents that convert one of their NMe_2 groups into an $NMe_3{}^+$ group, and the spectra and structures of the $[Fe_2\{\eta,\eta\text{-}C_5H_4CH(Z)CH(NMe_3)C_5H_4\}(CO)_2(\mu\text{-}CO)_2][X]$ salts thus obtained (Z = NMe_2 or H).

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Table 1
Melting points and analyses of some of the $[Fe_2\{\eta,\eta\text{-}C_5H_4CH(Z)CH(NMe_3)C_5H_4\}(CO)_2(\mu\text{-}CO)_2]X$ salts described in the text (Z = NMe_2 or H)

Salt	M.p. (°C) [a]	Analyses [b]			
		%C	%H	%N	%Halogen
[**4**]Cl · $2H_2O$ [c]	189–191	45.9 (45.6)	4.9 (5.1)	4.9 (5.1)	6.9 (6.4)
[**4**]Br [c]	dec. 150	44.8 (45.0)	4.7 (4.5)	4.8 (5.0)	14.3 (14.2)
[**4**]I · 2MeCN	110–111	43.4 (43.5)	4.4 (4.5)	7.7 (8.1)	18.0 (18.4)
[**4**(CD_3)]I · 2MeCN	119–120	42.7 (42.3)	4.5 (4.3)	7.6 (7.9)	18.3 (17.9)
[**4**]CF_3SO_3	132–134	41.8 (41.9)	4.0 (4.0)	4.4 (4.4)	9.1 (9.0)
[**4**]PF_6 · $2H_2O$ [c]	110–113	37.8 (38.1)	4.5 (4.2)	4.5 (4.2)	17.9 (17.2)
[**4**]F_5H_4 [c]	dec. 110	43.8 (43.4)	5.1 (5.0)	4.2 (4.8)	17.1 (16.4)
[**5**]I	157–159	41.1 (41.5)	4.2 (4.1)	4.0 (4.1)	20.6 (20.9)
[**5**(CD_3)]I	169–170	41.6 (41.3)	3.8 (3.6)	4.6 (4.6)	20.4 (20.8)
[**5**]CF_3SO_3	186–188	41.8 (41.9)	4.1 (4.0)	4.4 (4.4)	9.3 (9.0)
[**5**]F_6H_5 [c]	dec. 120	42.2 (42.0)	5.8 (5.0)	4.4 (4.7)	18.9 (18.7)
[**6**]Cl · H_2O [c]	dec. 213	45.9 (46.4)	4.3 (4.5)	2.7 (2.8)	7.5 (7.2)
[**6**]Br · $2H_2O$ [c]	dec. 210	41.3 (41.1)	4.0 (4.3)	2.4 (2.5)	14.9 (14.4)
[**6**]I	dec. 197	40.0 (40.3)	3.7 (3.5)	2.2 (2.4)	
[**6**]CF_3SO_3 · H_2O	dec. 202	39.4 (39.7)	3.3 (3.8)	2.3 (2.3)	5.8 (5.3)
[**6**]PF_6 [c]	dec. 198	39.1 (39.1)	3.4 (3.4)	2.4 (2.4)	
[**6**]BPh_4 · H_2O [c]	dec. 203	67.1 (66.6)	5.4 (5.2)	1.8 (1.7)	
[**6**]OH · CH_2Cl_2	dec. 213	45.1 (44.5)	4.2 (4.3)	2.6 (2.6)	$\%F = 0$

[a] Determined in sealed tubes. dec. = decomposition.
[b] Found (calculated).
[c] Prepared by anion exchange.

2. Experimental section

Complexes **1**, **2**, and **3** were prepared as described elsewhere [1]. Other chemicals were purchased and used as received. Solvents were dried and deoxygenated by refluxing over calcium hydride under nitrogen and distilled prior to use. Unless otherwise stated, all reactions were carried out at room temperature in dried and deoxygenated solvents under nitrogen.

Preparation of [**4**]X, [**5**]X and [**6**]X Salts: solutions of **1**, **2** or **3** (1 g) were stirred with an excess of (a) $MeOSO_2CF_3$ (1 cm^3) in benzene (70 cm^3) for 1 h, (b) MeI (2 cm^3) in acetonitrile (20 cm^3) for 2 h, (c) CD_3I (2 cm^3) in acetonitrile (20 cm^3) for 24 h, or (d) Me_2SO_4 (1 cm^3), NH_4PF_6 (0.2 g) and 18-Crown-6 for 24 h. The products (Table 1) separated out from the reaction mixtures (benzene solution) or after removal of the solvent (acetonitrile solution). They were filtered off, washed with benzene and pentane, and recrystallized from dichloromethane–pentane mixtures if required.

Solutions of [**4**][SO_3CF_3], [**5**][SO_3CF_3] or [**6**][SO_3CF_3] (0.5 g) and a fivefold molar excess of [n-Bu_4N]Cl, [n-Bu_4N]Br, [n-Bu_4N]I, or [Et_4N][PF_6] in acetonitrile (30 cm^3) were stirred for 2 h. The solvents were then removed under reduced pressure and the residues recrystallized from dichloromethane (yields 70%).

2.1. The Reaction of [4][SO_3CF_3], [5][SO_3CF_3] and [6][SO_3CF_3] with [R_4N]F

A solution of [n-Bu_4N]F (1 M) in tetrahydrofuran (2 cm^3) was added to one of [**4**][SO_3CF_3] (0.6 g) in acetonitrile (25 cm^3). After 10 min the solvent was removed under reduced pressure and the residue chromatographed (alumina/methanol) to give [**4**][H_4F_5] as the principal product (75% yield) and some $[Fe_2\{\eta,\eta\text{-}C_5H_4CH_2C(O)C_5H_4\}(CO)_2(\mu\text{-}CO)_2]$ (yield 10%).

Table 2
The infrared spectra of the $[Fe_2\{\eta,\eta\text{-}C_5H_4CH(Z)CH(NMe_3)C_5H_4\}(CO)_2(\mu\text{-}CO)_2]X$ salts between 1750 and 2050 cm^{-1} (Z = H or NMe_2)

Compound	Absorption bands [a]			
1	1767 (5.0)	1798 (1.0)	1958 (1.8)	2000 (10)
2	1768 (4.8)	1812 (1.0)	1962 (2.0)	2001 (10)
3	1768 (4.5)		1960 (1.7)	2002 (10)
[**4**]Cl·$2H_2O$	1777 (5.0)	1817 (1.0)	1971 (1.8)	2010 (10)
[**4**]Br	1779 (4.7)	1818 (0.5)	1971 (1.6)	2009 (10)
[**4**]I·2MeCN	1778 (5.0)	1815 (1.4)	1971 (2.0)	2010 (10)
[**4**(CD_3)]I·2MeCN	1778 (5.0)	1815 (0.9)	1972 (2.0)	2010 (10)
[**4**]CF_3SO_3	1780 (4.5)	1821 (1.0)	1974 (1.6)	2012 (10)
[**4**]PF_6·$2H_2O$	1780 (4.5)	1820 (1.0)	1973 (1.5)	2012 (10)
[**4**]F_5H_4 [b]	1773 (8.7)	1803 (3.8)	1965 (5)	2005 (10)
[**5**]I	1781 (4.1)	1822 (1.0)	1973 (1.6)	2016 (10)
[**5**(CD_3)]I	1779 (5.0)	1817 (1.0)	1972 (1.8)	2011 (10)
[**5**]CF_3SO_3	1783 (4.2)	1827 (1.0)	1974 (1.6)	2012 (10)
[**5**]F_6H_5 [c]	1794 (5.8)		1966 (1.8)	2005 (10)
[**6**]Cl [c]	1784 (7)		1959 (1.7)	2000 (10)
[**6**]Br [c]	1780 (5.5)	1820 (0.5)	1967 (1.8)	2006 (10)
[**6**]I [c]	1784 (6.9)		1959 (1.7)	2001 (10)
[**6**]CF_3SO_3	1780 (5)	1810 (0.5)	1975 (1.5)	2013 (10)
[**6**]PF_6	1781 (5)	1812 (0.5)	1973 (1.6)	2012 (10)
[**6**]BPh_4 [c]	1784 (6.8)		1959 (1.7)	2001 (10)
[**6**]OH	1774 (5.7)		1961 (2.1)	2004 (10)

[a] Peak positions (cm^{-1}) with relative peak heights in parentheses. Spectra measured in chloroform solution. Due to ν(CO) vibrations. See text.
[b] Dichloromethane solution.
[c] Acetonitrile solution.

These were recrystallized from dichloromethane-hexane.

The salts [**5**][SO_3CF_3] (0.5 g) and [Et_4N]F · $2H_2O$ (0.7 g) in dichloromethane (100 cm^3) gave, after 10 min, [**5**][H_5F_6] as the only product, which was isolated and purified as above.

Table 3
^{1}H-NMR spectra of [$Fe_2\{\eta,\eta$-$C_5H_4CH(Z)CH(NMe_3)C_5H_4\}(CO)_2$ (μ-$CO)_2$]X salts (Z = NMe_2 or H)

Compound	Solvent	T(K)	Resonances [a,b] CH–CH_n [c,d]
1	CS_2/CD_2Cl_2	298	3.01 3.01
2	CS_2/CD_2Cl_2	298	2.81 2.81
3	$CDCl_3$	293	3.04 2.36 2.03
[**4**]Cl	CD_2Cl_2	293	5.99 4.54
	CD_3CN	293	5.01 4.52
[**4**]Br	CD_2Cl_2	293	5.80 4.52
	CD_3CN	293	5.19 4.54
[**4**]I	CD_2Cl_2	293	5.52 4.50
	CD_2Cl_2	183	4.53 [b]
	CD_3CN	334	4.24 4.52
	CD_3CN	293	4.26 4.53
+[n-Bu_4N]I	CD_3CN	293	4.94 4.54
[**4**(CD_3)]I	CD_2Cl_2	293	5.47 4.50
	CD_2Cl_2	176	5.31 4.53
	CD_3CN	338	4.25 4.52
	CD_3CN	293	4.27 4.52
[**4**]CF_3SO_3	CH_2Cl_2	293	4.43 4.48
	CH_2Cl_2	182	4.37 4.47
	$CDCl_3$	293	4.49 4.49
+0.54 [n-Bu_4N]Br	$CDCl_3$	293	4.46 4.49
+0.97 [n-Bu_4N]Br	$CDCl_3$	293	5.39 4.50
+1.75 [n-Bu_4N]Br	$CDCl_3$	293	5.44 4.50
+ > 5.1 [n-Bu_4N]Br	$CDCl_3$	293	5.52 4.49
	CD_3CN	293	3.86 4.52
+[n-Bu_4N]I	CD_3CN	293	4.95 4.54
[**4**]PF_6	CD_3CN	293	3.85 4.52
	CD_3CN	359	3.85 4.51
[**4**]F_5H_4	CD_3OD	293	4.20 4.63
[**5**]I	$CDCl_3$	293	5.95 3.37
	CD_3CN	293	4.90 3.58
	CD_3CN	333	4.84 3.58
[**5**(CD_3)]I	CD_2Cl_2	293	5.90 3.39
	CD_2Cl_2	213	5.82 3.39
[**5**]CF_3SO_3	CD_2Cl_2	293	4.67 3.36
	CD_2Cl_2	192	4.62 3.35
	CD_3CN	293	4.13 3.56
+2.4 [n-Bu_4N]I	CD_3CN	293	5.09 3.60
+16 [n-Bu_4N]I	CD_3CN	293	5.44 3.67
[**5**]PF_6	CD_3CN	293	4.13 3.55
[**5**]F_6H_5	CD_3OD	293	4.36 3.71
[**6**]Cl	CD_3CN	293	4.75 2.83 2.34
[**6**]Br	CD_3CN	293	4.51 2.82 2.35
[**6**]Br	CD_3OD	293	4.20 3.01 2.45
[**6**]I	CD_3CN	293	4.32 2.85 2.36
+1 [Me_4N]PF_6	CD_3CN	293	4.08 2.83 2.34
+3 [Me_4N]PF_6	CD_3CN	293	3.91 2.87 2.33
+1 [6]CF_3SO_3	CD_3CN	293	4.20 2.84 2.36
+2 [6]CF_3SO_3	CD_3CN	293	4.15 2.84 2.36
[**6**]CF_3SO_3 [d]	CD_3CN	293	3.90 2.81 2.32
[**6**]CF_3SO_3	CD_3OD	293	4.10 2.95 2.44
[**6**]PF_6	CD_3CN	293	3.91 2.82 2.33
[**6**]PF_6	$(CD_3)_2CO$	293	4.45 3.21 2.70
[**6**]PF_6	$(CD_3)_2CO$	223	4.49 3.15 2.71
[**6**]BPh_4	CD_3CN	293	3.85 2.77 2.29
[**6**]OH	CD_3OH	293	4.11 [b] 2.44

Notes to Table 3:

[a] Chemical shifts given in ppm downfield from Me_4Si as an internal standard.

[b] Indicates a resonance hidden by the solvent or added salt.

[c] These resonances of [**4**]X and [**5**]X are doublets with integrations of unity unless it is stated otherwise. The chemical shift of the Me_3NC–H proton is given first, that of the Me_2NC–H proton is given second. The coupling constants lie in the range 6.1–6.5 Hz for [**4**]X, and 11.7–12.0 Hz for [**5**]X.

[d] These resonances of [**6**]X are double doublets with integrations of unity given in the order H_A, H_B, H_C with coupling constants J_{AB} = 2.4–2.5 Hz, J_{AC} = 12.6–12.7 Hz and J_{BC} = 14.6–15.2 Hz. The resonances due to H_B are often partially obscured by those due to the NMe_3 protons. The labelling of these protons is illustrated in Fig. 3.

The reaction between [**4**][SO_3CF_3] (0.5 g) and [Et_4N]F · $2H_2O$ (0.7 g) in acetonitrile (100 cm^3) was complete within a few minutes. Me_3N was evolved and identified by its distinctive smell. After 3 h the solvent was removed under reduced pressure and residue recrystallized from benzene to give the enamine [$Fe_2\{\eta,\eta$-$C_5H_4CHC(NMe_2)C_5H_4\}(CO)_2(\mu$-$CO)_2$] (yield 60%).

The reaction between [**5**][SO_3CF_3] (0.5 g) and [Et_4N]F · $2H_2O$ (0.7 g) in acetonitrile (100 cm^3) was complete only after 8 h; Me_3N was evolved. Chromatography (alumina/dichloromethane) followed by recrystallization from dichloromethane–hexane gave the mono-amine [$Fe_2\{\eta,\eta$-$C_5H_4CH_2CH(NMe_2)C_5H_4\}$ $(CO)_2(\mu$-$CO)_2$] in 20% yield. At 50°C the reaction time was reduced to ca. 0.5 h and if CO was bubbled through the reaction mixture the product yield was increased to 30%.

The salt [Et_4N]F · $2H_2O$ (0.7 g) was added to a solution of [**6**]SO_3CF_3] (0.6 g) in acetonitrile (80 cm^3). After 10 min, the mixture was chromatographed (alumina/methanol) and the isolated product was recrystallized from dichloromethane. [$Fe_2\{\eta,\eta$-C_5H_4 $CH_2CH(NMe_3)C_5H_4\}(CO)_2$-($\mu$-$CO)_2$][OH] · CH_2Cl_2 was the only product (yield 50%).

The salts prepared are summarised in Table 1 along with their yields, melting points, and analyses (from the Analytical Laboratory, University College, Dublin).

Infrared spectra were recorded on a Perkin Elmer 1710 or 1720 FTIR spectrometer, and NMR spectra on a Jeol GNM-X 270 NMR spectrometer. The more important data are summarised in Tables 2–4. Complete ^{1}H-NMR data are available from the authors.

2.2. *Structures of (a) R,S-[$Fe_2\{\eta,\eta$-$C_5H_4CH(NMe_2)$ $CH(NMe_3)\}(CO)_2(\mu$-$CO)_2$]I · 2MeCN and (b) R,S-[$Fe_2\{\eta,\eta$-$C_5H_4CH(NMe_2)CH(NMe_3)\}(CO)_2(\mu$-$CO)_2$]-[$SO_3CF_3$] · CH_2Cl_2*

The crystal data are summarised in Table 5. Unit cell dimensions were determined from diffractometer

Table 4
^{13}C-NMR spectra of the $[Fe_2\{\eta,\eta\text{-}C_5H_4CH(Z)CH(NMe_3)C_5H_4\}(CO)_2(\mu\text{-}CO)_2]X$ salts at 298 K. (Z = H or NMe_2)

Compound	Solvent	Resonances [a]						
		$N(CH_3)_2$ [b]	$N(CH_3)_3$	$CHNMe_2/CH_2$	$CHNMe_3$	Cyclopentadienyl [c]	CO	μ-CO
1	$CDCl_3$	45.2		65.4		79.52–100.81 (5)	210.3	271.9 273.7
2	$CDCl_3$	40.5		60.7		80.60–96.30 (5)	210.0	272.7
3	$CDCl_3$	40.87		60.72/29.14		80.65–98.70 (10)	209.59 209.63	272.27 272.50
[**4**]Br	CD_3CN	40.65(br) 46.54(br)	53.36	61.15	72.06	82.07–103.47 (10)	209.8(br)	267.5(br)
[**4**]I	CD_2Cl_2	40.68(s) 46.74(s)	53.19	60.76	71.46	81.52–102.67 (10)		
	$CDCl_3$	40.49(s) 46.63(s)	52.71	60.30	71.45	81.19–102.38 (10)		
	CD_3CN	[d]	53.59	61.04	73.17	82.20–101.91 (10)		
[**4**]SO_3CF_3	CD_2Cl_2	40.66(s) 46.19(br)	53.25	60.89	73.01	82.30–103.41 (10)	212.0(br)	
	CD_3CN	40.73(br) 46.44(br)	53.60	61.06	73.59	82.32–103.36 (9)		
[**4**]PF_6	CD_3CN	41.52(br) 46.54(br)	53.68	61.13	73.87	82.37–101.10 (9)		
[**5**]I	CD_3CN	39.39(s) 44.15(s)	53.49	62.87	68.67	81.73–98.75 (10)		
[**5**]SO_3CF_3	CD_2Cl_2	38.73(s) 44.64(s)	52.86	62.33	69.10	81.43–98.58 (9)		
	$(CD_3)_2CO$	39.09(s) 44.13(s)	53.64	62.79	69.93	81.60–96.92 (9)		
[**6**]Cl	CD_3OD		52.19	25.87	71.63	82.93–99.85 (10)	210.72 211.0	268.59 269.10
[**6**]Br	CD_3CN		52.34	25.95	70.12	82.82–99.66 (10)	210.98 211.25	268.30 269.10
[**6**]I	CD_3CN		52.44	26.01	70.31	82.79–99.49 (10)	210.90 211.15	268.15 269.47
[**6**]CF_3SO_3	CD_3CN		52.45	25.78	71.0	83.08–99.45 (10)	210.79 211.04	268.68 269.17
[**6**]PF_6	CD_3OD		52.13	25.82	71.78	82.96–99.81 (10)	210.70 211.02	268.61 268.97
[**6**]BPh_4	CD_3CN		52.44	25.76	71.05	83.13–99.43 (10)	210.74 211.02	268.85 269.14
[**6**]OH	CD_3OD		52.16	25.81	71.70	83.01–99.83 (10)	210.70 211.02	269.06 269.79

[a] ppm downfield from Me_4Si as an internal standard. All peaks are sharp singlets unless it is stated otherwise.

[b] s = sharp, br = broad

[c] Number of resonances in parentheses.[d] Resonances not observed.

Table 5
Crystal data for the R,S-$[Fe_2\{\eta,\eta\text{-}C_5H_4CH(NMe_2)CH(NMe_3)C_5H_4\}(CO)_2(\mu\text{-}CO)_2]X$ salts (X^- = (a) $I^- \cdot 2CH_3CN$ and (b) $CF_3SO_3^- \cdot CH_2Cl_2$)

Crystal data	(a)	(b)
Crystal size (mm^3)	0.30 × 0.28 × 0.25	0.2 × 0.2 × 0.3
Formula	$C_{25}H_{31}Fe_2N_4O_4I$	$C_{23}H_{27}F_3Fe_2N_2O_7SCl_2$
M (a.m.u.)	690.1	715.1
Space group	Triclinic	Monoclinic
	$P\bar{1}$	$P21/n$
a (Å)	11.136(1)	9.171(2)
b (Å)	10.490(2)	10.240(2)
c (Å)	12.969(2)	30.837(5)
α (o)	79.54(1))	90
β (o)	73.91(1)	96.91(2)
γ (o)	74.81(2)	90
U (Å^3)	1395	2874.9
Z	2	4
D_c (g cm^{-3})		
μ cm^{-1}	1.64, 27.11	1.65, 12.51
F000	693.95	1455.93
Radiation	Mo Kα	Mo Kα
Graphite monochromator	λ = 0.71069 Å	λ = 0.71069 Å
Diffractometer	Enraf-Nonius CAD4F	Hilger and Watts Y290
Orienting reflections. range		
Temperature (°C)	25,13 < θ < 20°, 22	12,13 < θ < 20°, 22
Scan method	$\omega - 2\theta$	$\omega - 2\theta$
Data collection range	2 < 2θ < 25°	2 < 2θ < 22°
No. of unique data		
Total $I > 3\sigma I$	4504, 2570	1961, 1694
No. of parameters fitted	200	188
R [a], R_w [b]	5.60%, 5.40%	6.07%, 6.31%
Largest shift/esd, final cycle	< 0.001	< 0.002
Largest positive peak (e Å^3)	1.4	0.35
Largest negative peak (e Å^3)	2.28	−0.29

[a] $R = [\Sigma \| F_o| - |F_c\|]/[\Sigma |F_o|]$.

[b] $R_w = [[\Sigma(|F_o| - |F_c|)^2]/[\Sigma(|F_o|)^2]]^{1/2}$; $w = 1/[(\sigma F_o)^2 - 0.0011^* F_o^2]$.

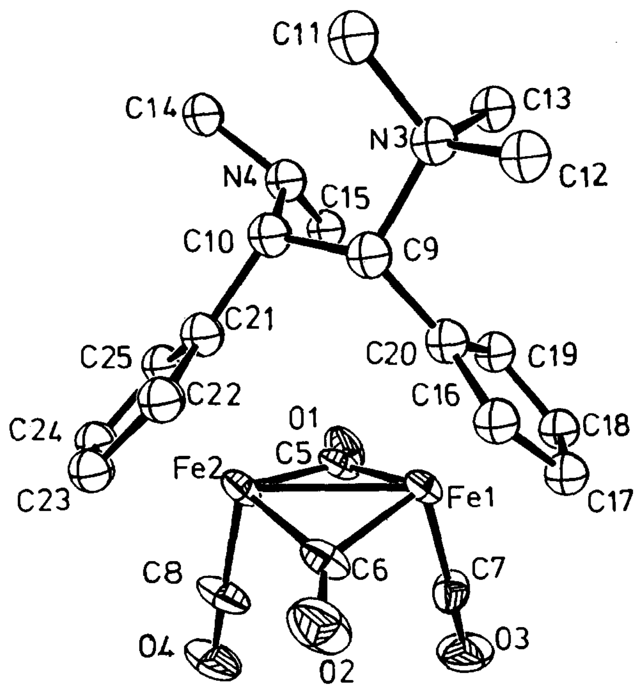

Fig. 1. The structure and atom labelling of the cation in $[Fe_2\{\eta,\eta\text{-}C_5H_4CH(NMe_2)CH(NMe_3)C_5H_4\}(CO)_2(\mu\text{-}CO)_2]I \cdot 2MeCN$.

data. The structure of (a) was solved by a combination of Patterson search and direct methods, SHELX86 [2], and that of (b) by direct methods, SHELX86 [2]. Both were refined by full matrix least squares using SHELX76 [3]. Data were corrected for Lorentz and polarisation effects but not for absorption. The crystal of (a) decomposed slowly during data collection. The final intensities observed for the intensity control reflexions were 50% of the starting values, and a simple linear correction was applied. Hydrogen atoms were included in calculated positions with fixed thermal parameters. Only the iodine atom, iron atoms and four carbonyl groups of (a), and the iron, chlorine and sulphur atoms of (b), 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 [4–6]. Calculations were performed on a VAX 8700 computer for (a) and a DEC 2060 for (b). The ORTEP program was used to obtain the drawings [7].

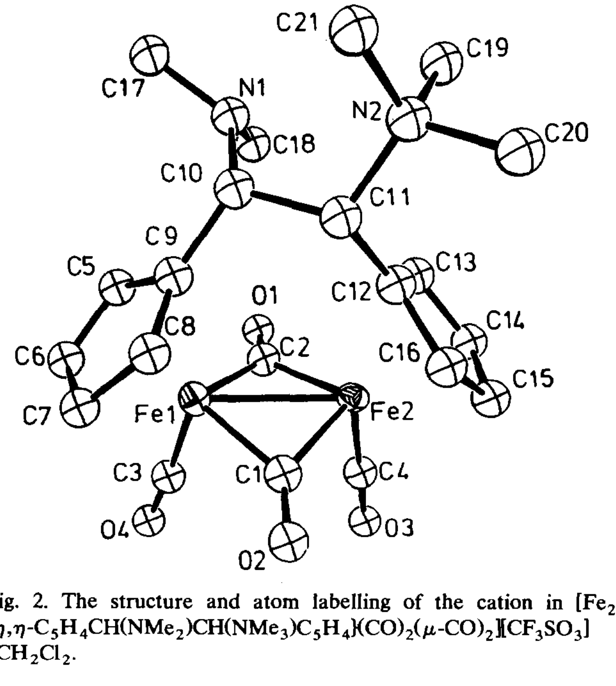

Fig. 2. The structure and atom labelling of the cation in $[Fe_2\{\eta,\eta\text{-}C_5H_4CH(NMe_2)CH(NMe_3)C_5H_4\}(CO)_2(\mu\text{-}CO)_2][CF_3SO_3] \cdot CH_2Cl_2$.

The structure of the cations and atom labelling schemes are shown in Figs. 1 and 2. Heavy atom coordinates are given in Tables 6 and 7, and selected bond lengths and angles in Tables 8 and 9. Tables of hydrogen atom coordinates and anisotropic thermal parameters for non-hydrogen atoms have been de-

Table 6
Fractional atomic coordinates for *R*,*S*-$[Fe_2\{\eta,\eta\text{-}C_5H_4CH(NMe_2)CH(NMe_3)C_5H_4\}(CO)_2(\mu\text{-}CO)_2]I \cdot 2CH_3CN$

Atom	*x*	*y*	*z*
I1	0.22660(8)	0.18967(9)	0.15391(7)
Fe1	0.0109(1)	0.2865(2)	−0.1637(1)
Fe2	0.0607(1)	0.2293(2)	−0.3515(1)
O1	0.0141(8)	0.5111(8)	−0.3328(6)
O2	0.1606(8)	0.0193(9)	−0.1979(7)
O3	0.2462(8)	0.3536(10)	−0.1590(8)
O4	0.3242(8)	0.2509(10)	−0.4353(8)
C5	0.0228(10)	0.3976(12)	−0.2995(9)
C6	0.1054(11)	0.1266(12)	−0.2254(9)
C7	0.1540(12)	0.3238(12)	−0.1580(9)
C8	0.2214(12)	0.2438(13)	−0.4036(11)
N1	0.6391(12)	0.3478(12)	0.1933(10)
N2	0.3624(12)	−0.0700(12)	0.4451(10)
N3	−0.4002(8)	0.2229(8)	−0.0906(7)
N4	−0.3426(9)	0.3928(9)	−0.3108(7)
C1	0.7143(14)	0.3194(13)	0.2389(11)
C2	0.8138(14)	0.2769(15)	0.2967(12)
C3	0.4203(14)	0.0028(14)	0.3941(11)
C4	0.4961(14)	0.0934(14)	0.3310(11)
C9	−0.2619(9)	0.2148(10)	−0.1667(8)
C10	−0.2643(10)	0.2620(10)	−0.2852(8)
C11	−0.4811(11)	0.1698(11)	−0.1390(9)
C12	−0.3893(11)	0.1365(11)	0.0136(8)
C13	−0.4684(11)	0.3612(11)	−0.0641(9)
C14	−0.4057(13)	0.3992(13)	−0.3981(10)
C15	−0.2983(12)	0.5116(12)	−0.3152(10)
C16	−0.1047(10)	0.1731(11)	−0.0445(8)
C17	−0.0541(12)	0.2454(12)	0.0037(10)
C18	−0.0976(12)	0.3778(13)	−0.0277(9)
C19	−0.1794(10)	0.3955(11)	−0.0962(8)
C20	−0.1826(10)	0.2616(10)	−0.1111(8)
C21	−0.1275(10)	0.2223(10)	−0.3616(8)
C22	−0.0497(10)	0.0920(11)	−0.3546(9)
C23	0.0567(11)	0.0899(12)	−0.4460(9)
C24	0.0420(11)	0.2170(11)	−0.5077(9)
C25	−0.0714(11)	0.3001(11)	−0.4538(9)

Table 7
Fractional atomic coordinates for R,S-[$\mathrm{Fe_2\{\eta,\eta\text{-}C_5H_4CH(NMe_2)\text{-}CH(NMe_3)C_5H_4\}(CO)_2(\mu\text{-}CO)_2][SO_3CF_3]\cdot CH_2Cl_2}$

Atom	x	y	z
Fe1	0.1423(2)	0.3231(2)	0.0667(1)
Fe2	0.39358(19)	0.23191(16)	0.06376(5)
S1	0.4225(4)	0.1573(3)	0.2536(1)
Cl1	0.6312(6)	0.3659(6)	0.4020(2)
Cl2	0.6802(8)	0.4860(9)	0.3211(2)
F1	0.4331(10)	−0.0960(9)	0.2632(3)
F2	0.4520(12)	−0.0301(10)	0.1992(3)
F3	0.2442(14)	−0.0263(12)	0.2225(4)
O1	0.2898(10)	0.4105(9)	−0.0070(3)
O2	0.2047(10)	0.0812(10)	0.1140(3)
O3	0.3340(12)	0.0304(11)	−0.0017(4)
O4	−0.0461(12)	0.1740(12)	0.0032(4)
O5	0.3683(10)	0.2386(10)	0.2177(3)
O6	0.3443(13)	0.1641(12)	0.2908(4)
O7	−0.0762(14)	0.6592(12)	0.2373(4)
N1	0.3830(12)	0.6697(10)	0.1072(3)
N2	0.5944(11)	0.5150(9)	0.1709(3)
C1	0.2343(14)	0.1676(13)	0.0911(4)
C2	0.2772(14)	0.3500(13)	0.0256(4)
C3	0.0326(16)	0.2310(14)	0.0283(4)
C4	0.3596(15)	0.1158(14)	0.0253(4)
C5	0.0974(14)	0.5232(12)	0.0743(4)
C6	−0.0289(16)	0.4508(13)	0.0738(4)
C7	−0.0138(15)	0.3621(13)	0.1093(4)
C8	0.1269(14)	0.3858(12)	0.1320(4)
C9	0.1991(13)	0.4837(11)	0.1099(4)
C10	0.3392(12)	0.5516(11)	0.1292(4)
C11	0.4647(13)	0.4502(11)	0.1438(4)
C12	0.5155(12)	0.3514(11)	0.1124(3)
C13	0.5748(13)	0.3658(11)	0.0722(4)
C14	0.6202(13)	0.2423(12)	0.0599(4)
C15	0.5923(14)	0.1523(13)	0.0925(4)
C16	0.5288(13)	0.2175(12)	0.1252(4)
C17	0.3024(16)	0.7867(14)	0.1158(5)
C18	0.4101(16)	0.6622(14)	0.0613(4)
C19	0.6947(15)	0.5892(13)	0.1452(4)
C20	0.6876(15)	0.4098(13)	0.1959(4)
C21	0.5485(16)	0.6053(14)	0.2057(4)
C22	0.1139(18)	0.4961(15)	0.2660(5)
C23	0.5535(22)	0.4067(18)	0.3495(5)

posited at the Cambridge Crystallographic Data Centre.

3. Results and discussion

Both R,S- and $R,R/S,S$-[$\mathrm{Fe_2\{\eta,\eta\text{-}C_5H_4CH(NMe_2)CH(NMe_2)C_5H_4\}(CO)_2(\mu\text{-}CO)_2}$], **1** and **2** respectively, react with methylating agents MeX in benzene or acetonitrile with retention of configuration at the ring-linking carbon atoms to give respectively R,S' and $R,R'/S,S'$-[$\mathrm{Fe_2\{\eta,\eta\text{-}C_5H_4CH(NMe_2)CH(NMe_3)C_5H_4\}(CO)_2(\mu\text{-}CO)_2}$]X salts, [**4**]X and [**5**]X. Even use of a large excess of $\mathrm{MeOSO_2CF_3}$ does not bring about methylation of the second $\mathrm{NMe_2}$ group. The methylation rates decrease in the order $\mathrm{X = CF_3SO_3 > I \gg}$

Table 8
Selected bond lengths and bond angles for R,S-[$\mathrm{Fe_2\{\eta,\eta\text{-}C_5H_4CH(NMe_2)CH(NMe_3)C_5H_4\}(CO)_2(\mu\text{-}CO)_2]I\cdot 2CH_3CN}$

Bond lengths (Å)			
Fe1–Fe2	2.492(2)	Fe1–C5	1.919(12)
Fe1–C6	1.912(12)	Fe1–C7	1.761(13)
Fe2–C6	1.901(12)	Fe2–C5	1.906(12)
O2–C6	1.177(12)	Fe2–C8	1.766(12)
O4–C8	1.122(13)	O1–C5	1.179(12)
N3–C11	1.489(13)	O3–C7	1.144(13)
N3–C13	1.502(12)	N3–C9	1.572(12)
N4–C14	1.474(14)	N3–C12	1.500(12)
C9–C10	1.532(13)	N4–C10	1.457(12)
		N4–C15	1.442(13)
Bond angles (°)			
C6–Fe1–C5	95.0(5)	C7–Fe1–Fe2	102.8(4)
C7–Fe1–C5	87.4(5)	C7–Fe1–C6	90.7(5)
C6–Fe2–C5	95.8(5)	C8–Fe2–Fe1	102.9(5)
C8–Fe2–C5	88.6(5)	C8–Fe2–C6	89.4(5)
C11–N3–C9	110.9(8)	C12–N3–C9	108.6(8)
C12–N3–C11	106.9(8)	C13–N3–C9	113.5(8)
C13–N3–C11	108.9(8)	C13–N3–C12	107.8(8)
C14–N4–C10	113.7(9)	C15–N4–C10	120.7(9)
C15–N4–C14	112.7(9)	Fe2–C5–Fe1	81.3(5)
O1–C5–Fe1	139(1)	O1–C5–Fe2	140(1)
Fe2–C6–Fe1	81.6(5)	O2–C6–Fe1	139(1)
O2–C6–Fe2	140(1)	O3–C7–Fe1	176(1)
O4–C8–Fe2	179(1)	C10–C9–N3	112.5(8)
C20–C9–N3	108.6(8)	C20–C9–C10	122.4(8)
C9–C10–N4	118.0(9)	C21–C10–N4	117.4(8)
C21–C10–C9	111.0(8)		

Table 9
Selected bond lengths and bond angles for R,S-[$\mathrm{Fe_2\{\eta,\eta\text{-}C_5H_4\text{-}CH(NMe_2)CH(NMe_3)C_5H_4\}(CO)_2(\mu\text{-}CO)_2][SO_3CF_3]\cdot CH_2Cl_2}$

Bond lengths (Å)			
Fe1–Fe2	2.499(2)	Fe1–C1	1.913(14)
Fe1–C2	1.896(13)	Fe1–C3	1.737(15)
Fe2–C2	1.920(13)	Fe2–C1	1.891(13)
O2–C1	1.184(14)	Fe2–C4	1.683(14)
O4–C3	1.152(15)	O1–C2	1.196(13)
N1–C17	1.449(16)	O3–C4	1.210(15)
N2–C11	1.522(15)	N1–C10	1.467(15)
N2–C20	1.525(16)	N1–C18	1.468(16)
C10–C11	1.575(16)	N2–C19	1.493(15)
		N2–C21	1.512(16)
Bond angles (°)			
C2–Fe1–C1	95.2(6)	C3–Fe1–Fe2	103.5(5)
C3–Fe1–C1	90.5(6)	C3–Fe1–C2	89.6(6)
C2–Fe2–C1	95.2(6)	C4–Fe2–Fe1	101.4(5)
C4–Fe2–C1	88.9(6)	C4–Fe2–C2	88.3(6)
C18–N1–C10	119(1)	C17–N1–C10	115(1)
C19–N2–C11	114.9(9)	C18–N1–C17	112(1)
C20–N2–C19	106(1)	C20–N2–C11	108.8(9)
C21–N2–C19	108(1)	C21–N2–C11	113.0(9)
Fe2–C1–Fe1	82.1(5)	C21–N2–C20	105.2(9)
O2–C1–Fe2	140(1)	O2–C1–Fe1	137(1)
O1–C2–Fe1	141(1)	Fe2–C2–Fe1	81.8(5)
O4–C3–Fe1	176(1)	O1–C2–Fe2	137(1)
C9–C10–N1	117(1)	O3–C4–Fe2	178(1)
C11–C10–C9	111.4(9)	C11–C10–N1	116(1)
C12–C11–N2	111.3(9)	C10–C11–N2	111.4(9)
		C12–C11–C10	121.8(9)

SO_4Me. The reaction with $MeOSO_2CF_3$ is virtually instantaneous, but that with Me_2SO_4 does not take place unless $NH_4[PF_6]$ is present. Anion exchange with $[R_4N]X$ or $Na[BPh_4]$ allows the preparation [**4**]X and [**5**]X where $X^- = Cl^-$, Br^-, I^-, $[SO_3CF_3]^-$, $[PF_6]^-$, or $[BPh_4]^-$.

Similarly, $[Fe_2\{\eta,\eta\text{-}C_5H_4CH_2CH(NMe_3)C_5H_4\}(CO)_2(\mu\text{-}CO)_2]X$ salts, [**6**]X, are obtained from $[Fe_2\{\eta,\eta\text{-}C_5H_4CH_2CH(NMe_2)C_5H_4\}(CO)_2(\mu\text{-}CO)_2]$, **3**.

The salts are red solids. They are soluble in polar organic solvents or water, but [**4**]X and [**5**]X where $X^- = [PF_6]^-$ or $[BPh_4]^-$ and all [**6**]X are virtually insoluble in dichloromethane or chloroform. All are insoluble in non-polar solvents such as benzene. They are stable in air in the solid state but oxidise slowly in solution.

The infrared spectra of [**4**]X and [**5**]X are the same in the solid state as in solution. The most intense absorption bands at ca. 1780, 1820, 1970, and 2010 cm^{-1} (Table 2) are due respectively to the antisymmetric $\nu(CO\mu)$, symmetric $\nu(CO\mu)$, antisymmetric $\nu(CO_t)$ and symmetric $\nu(CO_t)$ vibrations of the *cis*-$Fe_2(CO)_2(\mu\text{-}CO)_2$ moiety (cf. Ref. [8]). The relative intensities of these absorption bands are similar to those for **1** and **2**, but there is a small increase in their frequency in going from **1** or **2** to $[\mathbf{4}]^+$ or $[\mathbf{5}]^+$, as might be expected from the presence of an $NMe_3{}^+$ moiety close to a cyclopentadienyl ligand.

In solution the spectra of [**6**]X between 1700 and 2100 cm^{-1} are similar to those of [**4**]X and [**5**]X. However, when $X^- = Cl^-$, Br^- and I^- the spectra are much more complicated in the solid state. They are similar to those of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ in *m*-cresol or *o*-chlorophenol solutions, where there are solvent-solute interactions of the type μ-CO...HOR [9]. The pattern of the $\nu(CO\mu)$ absorption bands is consistent with the presence of $Fe_2(\mu\text{-}CO)_2$ and $Fe_2(\mu\text{-}CO)(\mu\text{-}CO \rightarrow A)$ species in the solid (A = acceptor site) [9]. Unfortunately, we have not been able to grow crystals of these salts suitable for an X-ray study, which would determine unambiguously whether such interactions are present.

The spectra of $[\mathbf{4}]^+/[\mathbf{5}]^+$ and $[\mathbf{4}(CD_3)]^+/[\mathbf{5}(CD_3)]^+$ differ only in the presence of $\nu(CD)$ absorption bands 2250 and 2287 cm^{-1} in the latter. The $\nu(CH)$ bands of the CH_3 groups are found at 2794 and 2919 cm^{-1}.

The assignment of the ^1H- and ^{13}C-NMR spectra of the [**4**]X, [**5**]X and [**6**]X salts (Tables 3 and 4) are straight-forward, and based on those for **1**, **2** and **3** [1].

Variable temperature ^1H-NMR spectroscopy shows that in solution the three cations exist as a single species. The ^1H–^1H coupling constants across this bond [10] suggest that $[\mathbf{5}]^+$ and $[\mathbf{6}]^+$ have structures derived from **2** and **3** (Fig. 3) whilst $[\mathbf{4}]^+$ has the same structure as in the solid state (see below). None of them undergoes a partial rotation about its ring-linking C–C bond that would convert them into their other possible isomer (Fig. 3) (cf. **1** which does, and **2** and **3** which do not [1]). Both $[\mathbf{4}]^+$ and $[\mathbf{5}]^+$ cations undergo (i) rotation of the Me_3N group about the $CH\text{–}NMe_3$ bond and (ii) rotation–inversion of the NMe_2 group, both of which slow on cooling. The $\Delta G^{\neq}_{T_c}$ for these processes may be calculated from the coalescence temperatures T_c [11]. For all salts investigated the values for (i) lie between 39 and 42 kJ mol^{-1} and those for (ii) between 61 and 64 kJ mol^{-1}. They are independent of anion and the conformation of the cation. The $\Delta G^{\neq}_{T_c}$ values for (ii) are much greater than those found for the corresponding NMe_2 rotation–inversions in **1** or **2** (ca. 37 kJ mol^{-1}) [1]. It is possible that this is the result

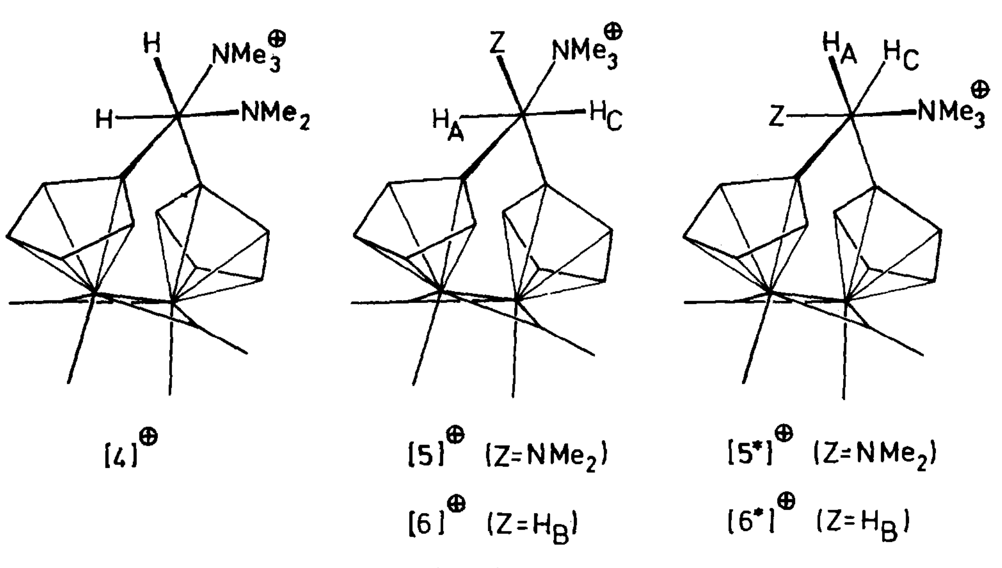

Fig. 3. Newman projections along the ring-linking C–C bonds of $[\mathbf{4}]^+$, $[\mathbf{5}]^+$ and $[\mathbf{6}]^+$ cations and the alternative, non-observed rotamers $[\mathbf{5}^*]^+$ and $[\mathbf{6}^*]^+$, together with proton labelling.

of an interaction of the lone pair of the NMe_2 group with the $CHNMe_3^+$ group in the cations. Circumstantial evidence for this is found in the case of [**6**][PF_6], for which rotation of the Me_3N group about the CH–NMe_3 bond cannot be slowed even at 223 K in $(CD_3)_2CO$ solution (also see below).

The most interesting feature of the ^{1}H-NMR spectra of [4]$^+$, [5]$^+$ and [6]$^+$ salts is that the chemical shifts, but not the coupling constants, of some of their resonances vary markedly with solvent and counteranion, whereas others do not. The only chemical shifts and coupling constants listed in Table 3 are for the H atoms bound to the ring-linking carbon atoms. The full ^{1}H-NMR spectra may be obtained from the authors on request. Although the appearance of the spectra in the cyclopentadienyl region change, the largest chemical shift variations are those of the Me_3NC–H protons which have been assigned unambiguously by $^{13}C/^1H$ correlated double resonance (COSY). In [**4**]X its chemical shift decreases along the anion series $X^- = Cl^- > Br^- > I^- > [SO_3CF_3]^- > [PF_6]^-$, e.g. from 5.99 ppm for [**4**]Cl to 4.43 ppm for [**4**][SO_3CF_3] (CD_2Cl_2 solution), and the solvent series $CD_2Cl_2 \sim CDCl_3 > CD_3CN$ for a given X^-, e.g. from 5.52 ppm in CD_2Cl_2 to 4.26 ppm in CD_3CN for [**4**]I. In contrast the chemical shift for the Me_2NC–H proton only changes from 4.46 to 4.52 ppm, and the Me_3NCH–Me_2NCH coupling (J = ca. 6.3 Hz) is constant. The anion effects are less marked in CD_3CN than in CD_2Cl_2 or $CDCl_3$. Comparable results were obtained with the [**5**]X and [**6**]X salts, but NMR spectra of the latter in $CDCl_3$ or CD_2Cl_2 solutions could not be obtained because of low solubility, and so CD_3CN and CD_3OD were used instead. For [**6**]X in CD_3CN solution the chemical shift of Me_3NC–H_A decreases along the series $X^- = Cl^- > Br^- > I^- \gg [BPh_4]^- \sim [CF_3SO_3]^- \sim [PF_6]^-$, but those of H_B and H_C hardly change (labelling of these protons is given in Fig. 3). In CD_3OD solution the anion effect is less marked. However, on changing from CD_3CN to CD_3OD all chemical shifts are more or less affected, but those of H_A are affected most.

The incremental addition of Y^- ions as [n-Bu_4N]Y to solutions of [**4**]X or [**5**]X results in spectra which, at first, are intermediate between those of [**4**]X or [**5**]X and [**4**]Y or [**5**]Y, may become comparable with those of [**4**]Y or [**5**]Y, and may finally go beyond those of [**4**]Y or [**5**]Y (Table 3). The addition of more [**4**]X or [**5**]X partially reverse these changes. In related experiments, the addition of [Me_4N][PF_6] or [**6**][CF_3SO_3] to a solution of [**6**]I in CD_3CN causes the Me_3NC–H_A resonance to move upfield with accompanying small changes in the cyclopentadienyl resonances. The chemical shift for H_A (and H_B and H_C) in a 1:1 molar mixture of [Me_4N][PF_6] and [**6**]I are very close to the mean of the shifts for pure [**6**][PF_6] and [**6**]I whilst at 3:1 ratio the spectrum is virtually identical with that of [**6**][PF_6]. However, even the addition of large amounts of [**6**][CF_3SO_3] (δH_A = 3.90 ppm) to its I^- counterpart did not induce the chemical shift of H_A to move upfield of 4.15 ppm.

These observations may be rationalized if it assumed that solutions of [**4**]X, [**5**]X and [**6**]X contain (i) cation–anion pairs, (ii) solvated cations, (iii) solvated anions and (iv) free cations in facile equilibria which cannot be slowed on the NMR timescale above 183 K. The observed ^{1}H chemical shifts are then the average of those for the various species in the solutions. It is possible that there are two types of ion pairs (i) and solvated cations (ii). In the first there is a purely electrostatic interaction between the positively charged part of the cation and the anion or negatively charged part of the solvent molecule. There is no independent evidence for this in the systems described here but observations by others suggest that it occurs [12] and it would be unwise for us to neglect it. In the second there is a specific, strong, Lewis base–Lewis acid interaction between the anion or solvent molecule and the Me_3NC–H hydrogen atom of the cation. This hydrogen bonding is responsible for the variation of the chemical shift of the latter and, as a secondary effect, of the cyclopentadienyl protons. The anion → H interactions would be expected to decrease in importance and the equilibria shift away from (i) so that the chemical shift of the Me_3NC–H hydrogen atom would move upfield along the series for $X^- = Cl^- > Br^- > I^- \gg [SO_3CF_3]^- > [PF_6]^- > [BPh_4]^-$, and for solvent = CD_2Cl_2 or $CDCl_3 > CD_3CN > CD_3OD$. Both acetonitrile and methanol would be expected to compete with the anion for this hydrogen bonding, but the greater effect of methanol may be a result of its added ability to solvate the anion, at which acetonitrile is notoriously poor. (iv) is more subtle and applies to [**4**]X and [**5**]X only. The very high barriers to Me_2N rotation–inversion (vs. [1] and [2], see above) and NMe_3 rotation (vs. [**6**]X, see above) may indicate that the lone pair on the Me_2N group in [**4**]$^+$ and [**5**]$^+$ interacts with the Me_3N^+CH part of the cation (see above) and competes with (i) and (ii). However, although this could be $Me_2N \rightarrow H$-$CNMe_3$ in [**5**]$^+$, these are not possible in [**4**]$^+$ where Me_2N and H are transoid to one another (see below).

The specific nature of the suggested interaction between the cations and solvent or anion implies that the relevant hydrogen atom is very acidic. This would be expected because the adjacent NMe_3 moiety is able to stabilize the resulting partial negative charge on the saturated carbon atom.

The addition of [R_4N]Y (R = Me or n-Bu) to solutions of [**4**]X, [**5**]X or [**6**]X are also explicable on the basis of our proposals. The [R_4N]$^+$ ions are less effective at hydrogen bonding than are [**4**]$^+$, [**5**]$^+$ or [**6**]$^+$, so when Y = Br^- or I^- the proportion of the organometallic cations which are hydrogen bonded to these anions may be greater than in the absence of added $[R_4N]Y$. However, when $Y^- = [PF_6]^-$ and $X^- = I^-$ in CD_3CN solution, the $[R_4N]^+$ will compete with the organometallic cations for the donor X^- ions and the spectra will tend towards those of the $[PF_6]^-$ salts of $[\mathbf{4}]^+$, $[\mathbf{5}]^+$ or $[\mathbf{6}]^+$.

Similar observations have been reported for [Me(Ph)(α-naphthyl)(PhCH$_2$)P]X salts [13]. Their ^{1}H-NMR spectra are a function of both the solvent and X^-. In particular, the two benzylic protons give rise to a singlet in the polar solvent dimethylsulphoxide or in the less polar solvent $CDCl_3$ with large anions, e.g. $[I_3]^-$. However they become distinguishable and couple in chloroform solution when X^- is a coordinating anion and their chemical shift separation decreases $X^- = Cl^-$, $Br^- > [NO_3]^-$. Mixtures of the salts give a single set of resonances with intermediate chemical shift differences. The H–H coupling constant is independent of the anion. These effects were attributed to ion-pairing in solution. Although this is correct, in light of our results it seems likely that there is a more specific interaction between the anion and one of the benzylic hydrogen atoms which does not take place with the larger anions because of the more diffuse nature of its negative charge and, perhaps, steric effects.

In subsequent papers in the same series it was reported that the $[BPh_4]^-$ anion caused very low chemical shifts for the methylene protons in various $[R_3M\text{-}CH_2R']^+$ and related cations (M = N, P, As, or Sb; R′ = aryl, CO_2Et, or CN) as compared with, for example, Cl^- or Br^-. This was attributed to aromatic ring current effects in the ion pair [14]. This does not appear to be the case for the [**6**]X salts as the effects of the $[BPh_4]^-$ anion does not differ greatly from those of the $[SO_3CF_3]^-$ and $[PF_6]^-$, whereas all three are very different from Cl^-, Br^- and I^-.

There have been many other examples of the involvement of C-H bonds in hydrogen bonding [15]. For example, Mautner has suggested that they are important in complexes of polyethers [16], and a recent study [17] of the [n-Bu$_4$N][BH$_4$] system using nuclear Overhauser effects suggest that in $CDCl_3$ solution there is a strong anion–cation interaction of each of three BH_4^- hydrogens with two α-CH$_2$ and one β-CH$_2$ protons in a pyramidal created by N and three n-Bu groups of the cation. Even in unfavourable cases these interactions appear to be present, e.g. calculations have shown that the binding energies for the model systems $H_3C\text{-}H \cdots \text{Y-I-Y}^-$ are 1.1, 1.3 and 1.6 kcal mol^{-1} for Y = I, Br and Cl respectively [18], whilst in more favourable circumstances they are significant, e.g. the $-C\text{–}H \cdots O$ interactions between $[Me_4N]^+$ and water or acetone have strengths > 9 kcal mol^{-1} [16].

The effects of anion or solvent on the various ^{13}C chemical shifts of the $[\mathbf{4}]^+$ cation are small (Table 4). The largest variation is that of the CHNMe$_3$ atom. Its chemical shift decreases along the series $X^- = Br^- > I^- > [SO_3CF_3]^- > [PF_6]^-$ in CD_3CN and $X^- = I^- > [SO_3CF_3]^-$ in CD_2Cl_2, and for $CD_2Cl_2 > CD_3CN$ when $X^- = I^-$ or $[SO_3CF_3]^-$. The same is true for [**6**]X salts in CD_3CN and CD_3OD solutions (Table 4). This is the behaviour expected for specific interactions between the Me$_3$NC–H hydrogen atom and the anion or solvent [15].

There are two other noteworthy features of the room temperature ^{13}C-NMR spectra of the [**4**]X and [**5**]X. The NMe$_2$ groups normally give rise to two singlets which are sharp in some spectra and broad in others but in one case are not observed. This is consistent with Me/Me site exchange (cf. ^{1}H-NMR spectra). The second feature is our inability to detect resonances due to t and μ-CO groups under conditions where they are readily observed in the precursors **4** and **5**. The exception is [**4**]Br in CD_3CN which shows two very broad resonances at 209.8 and 267.5 δ. This implies fast CO exchange.

In contrast, the ^{13}C resonances of the four distinguishable CO groups of [**6**]X salts have been detected. They are sharp and there is no evidence for CO/CO site exchange at room temperature. We have no explanation for these differences and have not investigated the system further.

3.1. *The reaction of [4][SO$_3$CF$_3$] and [5][SO$_3$CF$_3$] with [Et$_4$N]F · 2H$_2$O*

The F^- salts of $[\mathbf{4}]^+$ and $[\mathbf{5}]^+$ could not be prepared. Addition of excess [n-Bu$_4$]F in tetrahydrofuran to a solution of [**4**][SO$_3$CF$_3$] gave a ca. 80% yield of [**4**][H$_4$F$_5$], whilst [**5**][SO$_3$CF$_3$] and [Et$_4$N]F · 2H$_2$O in dichloromethane gave a 10% yield of [**5**][H$_5$F$_6$] and extensive decomposition. The $[H_4F_5]^-$ and $[H_5F_6]^-$ anions are formulated from elemental analyses only. They are very stable and survive chromatography (alumina/methanol). The ^{1}H-NMR spectra of these salts show that the anions are more akin to $[PF_6]^-$ than Cl^-.

In acetonitrile solution, as a consequence of the very strong H–F bond [19] coupled with the limited anion solvation, [Et$_4$N]F · 2H$_2$O acts as source of OH^- which arises from the reaction between F^- ions and H_2O molecules which also gives HF. The presence of OH^- ions is confirmed by the isolation of [**6**]OH from the reaction of [**6**][SO$_3$CF$_3$] with [Et$_4$N]F · 2H$_2$O. No further reaction occurs in this case, but if [**6**][SO$_3$CF$_3$] is replaced by [**4**][SO$_3$CF$_3$], the enamine [Fe$_2${η,η-C$_5$H$_4$CHC(NMe$_2$)C$_5$H$_4$}(CO)$_2$(μ-CO)$_2$] is formed by elimination of H$^+$ and Me$_3$N, and if replaced by [**5**][SO$_3$CF$_3$] the amine [Fe$_2${η,η-C$_5$H$_4$CH$_2$CH(NMe$_2$)C$_5$H$_4$}(CO)$_2$(μ-CO)$_2$], **3**, is formed in a water-gas shift mediated

Me_3N displacement by H^-. The reactions of OH^- with [4][SO_3CF_3] and [5][SO_3CF_3] to give the same products have been discussed in detail in Ref. [1].

3.2. Structures of the R,S-[$Fe_2\{\eta,\eta'-C_5H_4CH(NMe_2)CH(NMe_3)C_5H_4\}(CO)_2(\mu-CO)_2$]X salts ($X^- = I^-$ and $[SO_3CF_3]^-$)

Because of their very different ^{1}H-NMR spectra, it was not clear that these two salts possessed the same cation, and so the structures of both were determined. Crystals of [4]I · 2MeCN were grown from acetonitrile whilst those of [4][SO_3CF_3] · CH_2Cl_2 were grown from dichloromethane-hexane mixtures. X-ray diffraction shows that the unit cells contain anions and cation together with the appropriate solvent of crystallization. The structures of the [$Fe_2\{\eta,\eta-C_5H_4CH(NMe_2)CH(NMe_3)C_5H_4\}(CO)_2(\mu-CO)_2]^+$ cations are illustrated in Figs. 1 and 2, and their bond lengths and bond angles summarised in Tables 8 and 9.

The $[4]^+$ cations in both salts are very similar with bond lengths and bond angles close to those found for **1** [20], **2** [1] and related molecules [21]. There has been no change in configuration of the two ring-linking carbon atoms on methylation; one has the *R* configuration and the other *S* as in **1** itself. In the cations illustrated (Figs. 1 and 2) the *C*HNMe$_2$ carbon is *R* and the *C*HNMe$_3$ carbon is *S*. The NMe_3 group is transoid to a cyclopentadienyl group and the NMe_2 transoid to H rather than vice versa as in the alternative *R,S* isomer which has not been detected (cf. Fig. 3). The H–C–C–H dihedral angle in [4]I is 57°, in [4][SO_3CF_3] it is 63.4°, and in **4** it is 79°. In both cations the NMe_2 is oriented so that its Me groups point away from and, presumably, its lone pair points towards the $NMe_3{}^+$ group. This is consistent with the presence of $NMe_2 \rightarrow CHNMe_3{}^+$ interactions postulated above to account for the ^{1}H-NMR spectra of the cations.

A detailed comparison of the C–N distances show that those of the $CNMe_3$ moiety are longer than those of the $CNMe_2$ moieties in both $[4]^+$ cations and **1** (1.460(12)–1.497(10) Å [20]). Although the C–N(3)Me$_3$ distance appears to be longer than the N(3)–Me distances in [4]I, the same is not true for [4]SO_3CF_3. The reasons for this minor difference between the two cations is not clear.

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