Reactions of $[Fe_2(\eta\text{-dienyl})_2(CO)_{4-n}(CNR)_n]$ with Strong Acids. The Structure of *cis*-μ-Carbonyl-μ-methyliminiomethylene-bis[carbonyl(η-cyclopentadienyl)iron] Tetrafluoroborate

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Strong acids react with many $[Fe_2(\eta\text{-dienyl})_2(CO)_{4-n}(CNR)_n]$ complexes (dienyl = C_5H_5 or C_9H_7; R = alkyl or benzyl; n = 1 or 2) to give salts of the cations $[cis\text{-}Fe_2(\eta\text{-dienyl})_2(CO_t)_2(CO_\mu)\{CN(H)R_\mu\}]^+$ and $[cis\text{-}Fe_2(\eta\text{-dienyl})_2(CO_t)_2\{CN(H)R_\mu\}_2]^{2+}$. The reactions proceed rapidly in water or in tetrahydrofuran solution when R = n-alkyl, less rapidly when R is a secondary alkyl group, and do not take place when R = Bu^t. The constitution of the products has been determined from conductivity data, i.r. spectra, and an *X*-ray diffraction study on $[cis\text{-}Fe_2(\eta\text{-}C_5H_5)_2(CO_t)_2(CO_\mu)\{CN(H)Me_\mu\}][BF_4]$. Crystals of this are monoclinic, space group $P2_1/n$, $Z = 4$, $a = 8.26(1)$, $b = 15.65(2)$, $c = 13.41(2)$ Å, and $\beta = 100.5°$. The structure has been determined by heavy-atom methods from photographic data and refined by full-matrix least-squares to $R = 0.083$ for 1853 reflections.

IN many polynuclear metal carbonyl complexes the oxygen atoms of bridging carbonyl groups are basic sites. Alich *et al.*[1] have shown that strong non-protic Lewis acids such as BF_3 or $AlEt_3$ form $\mu\text{-CO}\rightarrow AlEt_3$ bonds to one or both bridging carbonyl groups of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ and related complexes. They have been able to isolate some of these adducts, and have determined the structure of one of them.[2]

Nitrogen tends to be more basic than oxygen. Consequently, it was reasonable to expect that the μ-RNC ligand in the appropriate isomers of $[Fe_2(\eta\text{-dienyl})_2(CO)_{4-n}(CNR)_n]$ complexes (dienyl = C_5H_5, C_5H_4Me, or C_9H_7; n = 1 or 2; R = alkyl or benzyl) would also be susceptible to attack by acids. Treichel *et al.*[3] have shown that this is so for $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3(CNMe)]$ which dissolves in dilute hydrochloric acid. They isolated $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3\{CN(H)Me\}][PF_6]$. We have extended this reaction, and show that it is limited by both the η-dienyl ligand and the nature of R.[4] Also we have determined the structure of $[cis\text{-}Fe_2(\eta\text{-}C_5H_5)_2(CO_t)_2(CO_\mu)\{CN(H)Me\}][BF_4]$.†

TABLE 1

Melting points and analyses for $[Fe_2(\eta\text{-dienyl})_2(CO)_3\{CN(H)R\}][X]$ and $[Fe_2(\eta\text{-dienyl})_2(CO)_2\{CN(H)R\}_2][X]_2$ salts

Complex	M.p. (θ_c/°C) [a]	Analyses (%) [b] C	H	N	Yield (%)
$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3\{CN(H)Me\}][BF_4]$	110—117 (decomp.)	39.1 (39.5)	3.1 (3.1)	3.0 (3.1)	20
$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3\{CN(H)Et\}][PF_6]\cdot 2H_2O$	105—110 (decomp.)	34.1 (34.4)	2.7 (3.0)	2.6 (2.7)	32
$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3\{CN(H)Pr^i\}][PF_6]\cdot H_2O$	117—123 (decomp.)	36.1 (36.4)	3.6 (3.6)	2.5 (2.5)	5
$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3\{CN(H)Bu^n\}][PF_6]\cdot 2H_2O$	120—124 (decomp.)	36.3 (36.5)	3.2 (4.1)	2.4 (2.4)	26
$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3\{CN(H)C_6H_{11}\}][PF_6]\cdot H_2O$	>360	39.9 (40.0)	4.0 (4.0)	2.4 (2.3)	52
$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3\{CN(H)CH_2Ph\}][PF_6]$	25 (decomp.)	43.2 (43.0)	3.2 (3.1)	2.5 (2.4)	18
$[Fe_2(\eta\text{-}C_9H_7)_2(CO)_3\{CN(H)Me\}][PF_6]\cdot 2thf$	110—117 (decomp.)	48.7 (47.5)	4.4 (4.3)	2.2 (1.9)	1
$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2\{CN(H)Me\}_2][BF_4]_2$	125 (decomp.)	34.8 (34.5)	3.4 (3.2)	5.3 (5.0)	5
$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2\{CN(H)Me\}_2][PF_6]_2$	120—127	28.0 (28.5)	2.9 (2.7)	4.2 (4.2)	35
$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2\{CN(H)Me\}_2]Cl_2\cdot H_2O$	25 (decomp.)	40.6 (40.7)	3.9 (4.2)	6.1 (5.9)	16
$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2\{CN(H)Me\}_2]I_2\cdot 2H_2O$	32 (decomp.)	28.4 (28.6)	2.6 (3.2)	4.6 (4.1)	16
$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2\{CN(H)Et\}_2][PF_6]_2\cdot 2H_2O$	25 (decomp.)	28.7 (29.5)	3.9 (3.5)	3.7 (3.8)	31
$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2\{CN(H)CH_2Ph\}_2][PF_6]Cl\cdot H_2O$	110—120 (decomp.)	45.1 (44.8)	3.8 (4.0)	4.1 (3.7)	

[a] Measured in sealed tubes. [b] Calculated values are given in parentheses.

Under certain conditions, terminally co-ordinated RNC may also be protonated at the nitrogen atom. Thus *trans*-$[M(CNR)_2(dppe)_2]$ (M = Mo or W, dppe = $Ph_2PCH_2CH_2PPh_2$) forms $[trans\text{-}M\{CN(H)R\}_2(dppe)_2]^{2+}$ salts.[5] However, this has not occurred during our work.

EXPERIMENTAL

The complexes $[Fe_2(\eta\text{-dienyl})_2(CO)_4]$ (dienyl = C_5H_5,[6] C_5H_4Me,[6] or C_9H_7 [7]) and the isocyanide ligands [8] were prepared by standard methods. The complexes $[Fe_2(\eta\text{-dienyl})_2(CO)_{4-n}(CNR)_n]$ were obtained as described elsewhere.[9] Other chemicals were purchased. All the reactions were carried out under an atmosphere of nitrogen in purified solvents.

The protonated species were prepared by dissolving $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_{4-n}(CNR)_n]$ (1 mmol) in 18% hydrochloric acid (*ca.* 50 cm³). This mixture was stirred, and to it was added 40% aqueous HBF_4 or 60% aqueous HPF_6 (*ca.* 1 cm³). The precipitated red solids $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_{4-n}\{CN(H)R\}_n][X]_n$ (X = BF_4 or PF_6) were filtered off, washed with water, benzene, and pentane, and dried. Their low solubilities in suitable solvents generally prevented further purification. An alternative route was to dissolve $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNR)_2]$ in diethyl ether. Dry HCl gas or aqueous hydriodic acid was added, and the precipitated red $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2\{CN(H)R\}_2][X]_2$ (X = Cl or I) filtered off, washed with water, benzene, and pentane, and dried.

In a modification of the above method $[Fe_2(\eta\text{-}C_9H_7)_2(CO)_3(CNMe)]$ (1 mmol) was dissolved in tetrahydrofuran (75 cm³), and 60% aqueous HPF_6 (1 cm³) added. The resulting green solution was filtered. When its volume was reduced to *ca.* 30 cm³ by removal of the solvent at reduced pressure

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† The subscripts t and μ are used to indicate terminal and bridging ligands respectively.

it turned red. The addition of hexane precipitated a small amount of a red powder, $[Fe_2(\eta\text{-}C_9H_7)_2(CO)_3\{CN(H)Me\}][PF_6]$. This was washed and dried.

The salts isolated are summarised in Table 1 with their melting points and analyses. Product yields were between 1 and 50%.

Infrared spectra (Tables 2 and 3) were obtained on a Perkin-Elmer 337 spectrometer equipped with a Perkin-Elmer 56 readout recorder. They were calibrated using gaseous DCl, DBr, and H_2O,[10] so that peak positions are accurate to *ca.* ±1 cm^{-1}.

TABLE 2

Infrared spectra (cm^{-1}) of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3\{CN(H)R\}][X]$ salts between 1 500 and 2 200 cm^{-1} as Nujol mulls, unless stated otherwise

		Absorption bands [a]			
R	X	A	B	C	D
Me	BF_4	1 598(6.3)	1 814(10)	1.965(9.0), 1 996(10)	2 022(9.8br)
Me	BF_4 [b]		1 835(3.5)	1 990(2.3)	2 022(10)
Et	PF_6	1 574(4.4)	1 836(7.1)	1 995(7.7)	2 030(10br)
Pr^i	PF_6	1 596(5.5)	1 832(8.6)	1 988(8.8)	2 025(10br)
Bu^n	PF_6	1 591(5.8)	1 832(8.6)	1 988(8.8)	2 025(10br)
C_6H_{11}	PF_6	1 567(6.2)	1 822(8.7)	1 993(8.7)	2 025(10br)
C_6H_{11}	PF_6 [b]		1 833(3.3)	1 988(2.5)	2 020(10)
Me	PF_6 [c]	1 605(5.5)	1 844(7.4)	1 972(7.3)	1 997(10br)

[a] Peak positions (cm^{-1}) with relative peak heights in parentheses; br = broad. [b] Measured in *m*-cresol solution. [c] $[Fe_2(\eta\text{-}C_9H_7)_2(CO)_3\{CN(H)Me\}][PF_6]$.

TABLE 3

Infrared spectra of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2\{CN(H)R\}_2][PF_6]_2$ salts between 1 500 and 2 200 cm^{-1} as Nujol mulls, unless stated otherwise

	Absorption bands [a]		
R	E	F	G
Me	1 610(7.3)	2 032(10)	2 047(9.7 br)
Me[b]		2 022(3.8)	2 050(10)
Et	1 605(7.8)	2 031(10)	2 066(9.2 br)
CH_2Ph	1 588(5.4)	2 018(10)	2 040(9.6 br)

[a] Peak positions (cm^{-1}) with relative peak heights in parentheses; br = broad. [b] Measured in *m*-cresol solution.

Crystal Data.—$C_{15}H_{14}BF_4Fe_2NO_3$, $M = 454.8$, Monoclinic, $a = 8.26 \pm 0.01$, $b = 15.65 \pm 0.02$, $c = 13.41 \pm 0.02$ Å, $\beta = 100.5 \pm 0.1°$, $U = 1\,704.8$ Å^3, $D_m = 1.76$ (by flotation), $Z = 4$, $D_c = 1.772$ g cm^{-3}, $F(000) = 912$, $\mu(\text{Mo-}K_\alpha) = 17.8$ cm^{-1}. Systematic absences $0k0$ if $k = 2n$, $h0l$ if $h + l = 2n$, space group $P2_1/n$.

Cell parameters were determined from precession photographs using Mo-K_α radiation. Intensities were estimated visually from precession photographs for the layers 0—5, 0—4, and 0—3 about 010, 001, and 011 respectively. They were corrected for Lorentz and polarisation effects but not for absorption or extinction. The structure factors were placed on a common scale by internal correlation, and 1 853 non-zero unique reflections obtained. Scattering factors were taken from ref. 11, and all the calculations were carried out on a UNIVAC 1106 computer with programs written by F. S. S.

The structure was solved by the heavy-atom method. A difference map, phased by the cation, indicated the approximate positions for the hydrogen atoms and in subsequent calculations their contributions were included with optimised positions assuming C–H and N–H to be 1.0 Å. This map further showed that the anion was disordered and could be accounted for by the boron atom surrounded by 11 fluorine atoms. A series of difference syntheses was used to adjust the thermal parameter for boron and the occupancies of the fluorine atoms (for the latter B 10 Å^2) and a total occupancy of four was maintained. Refinement was by full-matrix least squares in which $\Sigma w\Delta^2$ was minimised. Weights were initially unity but in the final stages $w = (50.0 + 0.05|F_o|^2)^{-1}$. Reflections for which $|F_c| < 0.3|F_o|$ were omitted and only parameters for the cation were refined. Refinement was terminated when the maximum shift in any parameter was $<0.06\sigma$ and 1 842 reflections were included in the final cycle. The final R, based on 1 853 reflections, was 0.083 and R' [$= (\Sigma w\Delta^2/\Sigma w|F_o|^2)^{\frac{1}{2}}$] was 0.106. A final difference map showed no features $>|1.0|$e Å^{-3} and these were associated with the iron atoms. The final atomic parameters are given in Tables 4 and 5.

TABLE 4

Final atomic co-ordinates for the cation (fractional: × 10^4 for non-hydrogen atoms, × 10^3 for H) with estimated standard deviations in parentheses

	x/a	*y/b*	*z/c*
Fe(1)	2 543(2)	1 844(1)	231(1)
Fe(2)	1 321(2)	3 060(1)	1 081(1)
O(T1)	1 557(10)	2 343(7)	−1 874(6)
O(T2)	−203(13)	4 058(6)	−674(8)
O(B1)	−1 007(10)	1 721(6)	209(7)
N	4 502(10)	3 440(6)	511(7)
C(T1)	1 947(14)	2 153(7)	−1 058(10)
C(T2)	418(13)	3 669(8)	11(9)
C(B1)	291(13)	2 041(7)	428(8)
C(B2)	3 281(11)	2 952(6)	566(7)
C(M)	5 928(14)	3 183(9)	34(11)
C(11)	2 644(34)	539(10)	11(21)
C(12)	4 079(48)	894(18)	−135(22)
C(13)	4 779(22)	1 230(12)	789(31)
C(14)	3 760(40)	1 092(13)	1 415(13)
C(15)	2 412(23)	640(12)	923(22)
C(21)	200(26)	2 817(15)	2 329(13)
C(22)	−105(17)	3 638(16)	2 016(12)
C(23)	1 442(23)	4 056(10)	2 215(11)
C(24)	2 631(17)	3 538(13)	2 491(10)
C(25)	1 933(25)	2 728(11)	2 613(11)
H(N)	432	400	85
H(M1)	595	362	−50
H(M2)	543	274	−47
H(M3)	688	285	42
H(11)	186	24	−54
H(12)	461	93	−75
H(13)	592	152	102
H(14)	386	126	216
H(15)	140	41	115
H(21)	−67	238	235
H(22)	−124	390	186
H(23)	157	470	199
H(24)	384	368	263
H(25)	253	218	284

A list of structure factors and thermal parameters is available as Supplementary Publication No. SUP 22343 (13 pp.).*

RESULTS AND DISCUSSION

The neutral complexes $[Fe_2(\eta\text{-dienyl})_2(CO)_{4-n}(CNR)_n]$ react with protic acids to give salts of the $[Fe_2(\eta\text{-dienyl})_2(CO)_{4-n}\{CN(H)R\}_n]^{n+}$ cations ($n = 1$ or 2), but not of $[Fe_2(\eta\text{-dienyl})_2(CO)_2(CNR)\{CN(H)R\}]^+$. Although the counter anions may be Cl^- or I^-, where they are $[BF_4]^-$ or $[PF_6]^-$ the complexes are crystallised more readily.

* For details see Notice to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

The salts are red to brown solids which tend to decompose slowly even at −20 °C in the solid state. This is especially marked where the counter ions are Cl^- or I^-, R is other than methyl, or dienyl = C_9H_7. The $[BF_4]^-$ and $[PF_6]^-$ salts are the most stable, but suffer from low solubilities in most organic solvents. Where they do dissolve they tend to decompose more or less rapidly. Thus in methanol $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3\{CN(H)Me\}][BF_4]$ forms $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)_2][BF_4]$. In favourable instances we have obtained conductivity data using nitromethane solutions: $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3\{CN(H)Me\}][BF_4]$, concentration $c = 0.99 \times 10^{-3}$ mol dm^{-3}, $\Lambda = 82$ S cm^2 mol^{-1}; $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3\{CN(H)C_6H_{11}\}][BF_4]$, $c = 0.99 \times 10^{-3}$ mol dm^{-3}, $\Lambda = 77$ S cm^2 mol^{-1}; and $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2\{CN(H)Me\}_2][BF_4]_2$, $c = 1.6 \times 10^{-3}$ mol dm^{-3}, $\Lambda = 214$ S cm^2 mol^{-1}. These compare with values of Λ *ca.* 1—8 S cm^2 mol^{-1} at *c ca.* 10^{-3} mol dm^{-3} obtained for the neutral complexes $[Fe_2(\eta\text{-dienyl})_2(CO)_{4-n}(CNR)_n]$. They are consistent with formulation of the protonated complexes as 1 : 1 and 1 : 2 electrolytes.

TABLE 5

Final atomic co-ordinates (fractional × 10³) and occupancies for the anion

Atom	Occupancy	x/a	y/b	z/c
B	1.00	603	526	204
F(1)	0.70	641	451	250
F(2)	0.65	449	517	147
F(3)	0.55	692	603	209
F(4)	0.50	597	505	107
F(5)	0.30	521	557	279
F(6)	0.35	431	557	207
F(7)	0.26	653	589	272
F(8)	0.25	709	544	137
F(9)	0.24	731	484	264
F(10)	0.20	533	609	207
F(11)	0.10	544	471	275

X-Ray diffraction studies show that protonation of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3(CNMe)]$ occurs at the nitrogen atom of the bridging isocyanide ligand (see later) to give [*cis*-$Fe_2(\eta\text{-}C_5H_5)_2(CO_t)_2(CO_\mu)\{CN(H)Me\}][BF_4]$. The lone pair of electrons on the nitrogen atom in a μ-(C=N–R) ligand is utilised to form a N→H dative bond.

The i.r. spectra of this salt, and its relatives in Table 1, between 1 500 and 2 200 cm^{-1} (Table 2) are consistent with this structure both in the solid state and in solution. These spectra were generally run on solid samples because no suitable solvents covered the complete range, although solution spectra were obtained for the range 1 700—2 200 cm^{-1} where $\nu(CO_\mu)$, $\nu(CO_t)$, and $\nu(CNR_t)$ vibrations give rise to absorption bands. In no case was there evidence for isomers. Using the arguments advanced elsewhere for $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$,[12] these spectra (Table 2) may be assigned as follows. Absorption band A is due to $\nu[C{=}N(H)R_\mu]$, B to $\nu(CO_\mu)$, C to the antisymmetric $\nu(CO_t)$, and D to the symmetric $\nu(CO_t)$.

Protonation of the $[Fe_2(\eta\text{-dienyl})_2(CO)_3(CNR)]$ derivatives causes the C–N stretching band to shift from *ca.* 1 720—1 740 cm^{-1} for $\nu(CNR_\mu)$ to *ca.* 1 570—1 600 cm^{-1} for $\nu[CN(H)R_\mu]$. At the same time the wavenumbers of $\nu(CO_t)$ and $\nu(CO_\mu)$ increase by *ca.* 30 cm^{-1}. These changes are similar to those which occur on going from $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ to $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3(CO{\cdot}AlEt_3)]$.[1] They reflect an increase of the overall electron-withdrawing ability of the bridging iminium ligand μ-[C=$\overset{+}{N}$(H)R] as opposed to μ-CNR.

Absorption bands due to $\nu(CO_\mu)$, $\nu(CNR_t)$, and $\nu(CNR_\mu)$ vibrations are absent from the i.r. spectra of solid or dissolved samples of the protonated adducts of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNR)_2]$. On the other hand, those due to $\nu[C\overset{+}{N}(H)R_\mu]$ (E) and $\nu(CO_t)$ (F and G) are observed (Table 3). Thus it is reasonable to suggest that both μ-CNR ligands have been protonated. The relative intensities of F and G are consistent with formulation of the cations as [*cis*-$Fe_2(\eta\text{-}C_5H_5)_2(CO_t)_2\{CN(H)R_\mu\}_2]^{2+}$ with G assigned to their symmetric $\nu(CO_t)$ modes and F to their antisymmetric vibrations {*cf.*[12] $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$}.

Although there is no evidence against the presence of the *trans* isomer, its concentration must be low. Only one of its two $\nu(CO_t)$ vibrations would be i.r. active, the antisymmetric stretch of lowest frequency. Comparison with other systems, *e.g. cis-* and *trans*-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$,[12] suggests that it would be coincident with F, which is weak (Table 3).

The decreases in wavenumber in going from $\nu(CNR_\mu)$ to $\nu[CN(H)R_\mu]$ on protonation, *ca.* 110 cm^{-1}, are slightly less than for the monosubstituted series. However, the increases in $\nu(CO_t)$ are much greater, *ca.* 60 cm^{-1}. The presence of two powerful electron-withdrawing ligands μ-[C=$\overset{+}{N}$(H)R] rather than one is probably sufficient to account for these.

Not all $[Fe_2(\eta\text{-dienyl})_2(CO)_{4-n}(CNR)_n]$ complexes protonate readily. Those which are reluctant to adopt the isocyanide-bridged forms [9] tend to give unstable products in low yields, *e.g.* $[Fe_2(\eta\text{-}C_9H_7)_2(CO)_3(CNR)]$. Alternatively, like $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3(CNBu^t)]$, they may not react. The bulk of the Bu^t group does not allow the existence of μ-RNC isomers for this complex.[13,14] Consequently it does not dissolve in aqueous mineral acids and decomposes in tetrahydrofuran–hexafluorophosphoric acid mixtures. Steric factors also contribute to the reluctance of the $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNR)_2]$ complexes to adopt bis-μ-RNC forms where R is a secondary alkyl group such as cyclohexyl or Pr^i. Although these may be protonated, the products are unstable and decompose readily during preparation. Consequently consistent analyses could not be obtained, but their i.r. spectra are consistent with their formulation as $[Fe_2(\eta\text{-}C_5H_5)_2(CO_t)_2\{CN(H)R_\mu\}_2][X]_2$. The protonation reactions may be reversed by shaking the salts with aqueous ammonia. It is probable that this reaction is quantitative since we were able to isolate the neutral complexes in *ca.* 60% yields even from 0.06 g of the salt and with a relatively crude recrystallisation procedure.

Discussion of the Structure of [*cis*-$Fe_2(\eta\text{-}C_5H_5)_2(CO_t)_2(CO_\mu)\{CN(H)Me_\mu\}][BF_4]$.—The geometry of the cation [15] and the atom labelling is shown in Figure 1. Figure 2 shows the packing of the ions. Although hydrogen bonding of the $[BF_4]^-$ ion to the N atom is evident [NH · · · F distances are 2.84 to F(4), 3.00 to F(2), and 3.30 Å to F(1)] there is ample space for the anions to adopt several orientations and the B–F distances (1.32—1.50 Å) suggest that the B atom may occupy more than one site.

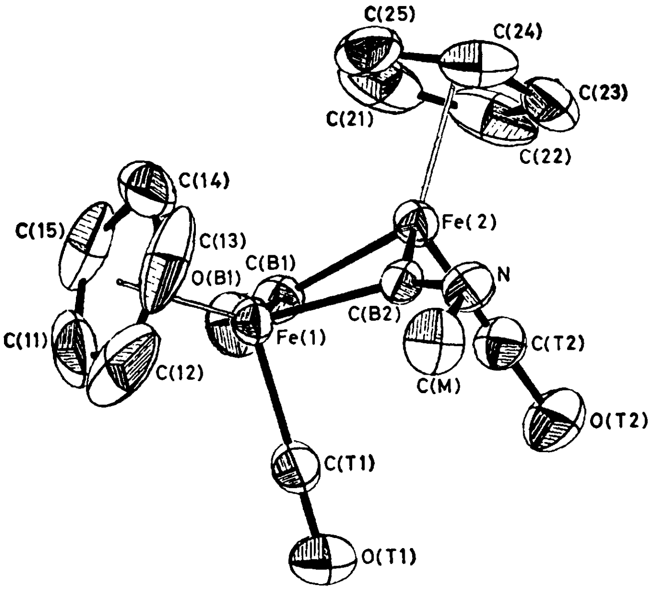

FIGURE 1. Perspective drawing of the cation and the atom-labelling system. Thermal ellipsoids are scaled to include 35% probability

TABLE 6

Bond lengths and angles * with estimated standard deviations in parentheses

(*a*) Distances (Å)

Fe(1) · · · Fe(2)	2.521(2)		
Fe(1)–C(T1)	1.78(1)	Fe(2)–C(T2)	1.77(1)
Fe(1)–Cp(1)	1.75	Fe(2)–Cp(2)	1.73
Fe(1)–C(B1)	1.95(1)	Fe(2)–C(B1)	1.94(1)
Fe(1)–C(B2)	1.87(1)	Fe(2)–C(B2)	1.88(1)
C(T1)–O(T1)	1.12(1)	C(B2)–N	1.28(1)
C(T2)–O(T2)	1.14(1)	N–C(M)	1.49(1)
C(B1)–O(B1)	1.17(1)		
C(11)–C(12)	1.36(3)	C(21)–C(22)	1.36(3)
C(12)–C(13)	1.37(3)	C(22)–C(23)	1.42(2)
C(13)–C(14)	1.31(3)	C(23)–C(24)	1.30(2)
C(14)–C(15)	1.38(3)	C(24)–C(25)	1.41(2)
C(15)–C(11)	1.28(3)	C(25)–C(21)	1.42(2)

(*b*) Angles (°)

C(B1)–Fe(1)–C(B2)	95.7(4)	C(B1)–Fe(2)–C(B2)	95.6(4)
C(B1)–Fe(1)–C(T1)	89.2(5)	C(B1)–Fe(2)–C(T2)	89.5(5)
C(B2)–Fe(1)–C(T1)	90.2(5)	C(B2)–Fe(2)–C(T2)	90.8(5)
C(B1)–Fe(1)–Cp(1)	120.5	C((B1)–Fe(2)–Cp(2)	123.9
C(B2)–Fe(1)–Cp(1)	128.3	C(B2)–Fe(2)–Cp(2)	124.6
C(T1)–Fe(1)–Cp(1)	122.9	C(T2)–Fe(2)–Cp(2)	122.9
Fe(1)–C(B1)–Fe(2)	80.8(4)	Fe(1)–C(B2)–Fe(2)	84.6(4)
Fe(1)–C(B1)–O(B1)	139(1)	Fe(1)–C(B2)–N	140(1)
Fe(2)–C(B1)–O(B1)	140(1)	Fe(2)–C(B2)–N	135(1)
Fe(1)–C(T1)–O(T1)	179(1)	C(B2)–N–C(M)	124(1)
Fe(2)–C(T2)–O(T2)	178(1)		
C(15)–C(11)–C(12)	112(2)	C(25)–C(21)–C(22)	107(2)
C(11)–C(12)–C(13)	105(2)	C(21)–C(22)–C(23)	107(1)
C(12)–C(13)–C(14)	108(2)	C(22)–C(23)–C(24)	111(2)
C(13)–C(14)–C(15)	110(2)	C(23)–C(24)–C(25)	108(1)
C(14)–C(15)–C(11)	106(2)	C(24)–C(25)–C(21)	107(1)

* Cp is the centroid of a cyclopentadienyl ring.

The bond distances and angles of the cation are given in Table 6. The structure of the cation has the expected carbonyl–isocyanide bridging system with the cyclopentadienyl rings in a *cis* configuration. The angle between the two FeCFe bridging planes is 161.5° and protonation of the nitrogen atom of the isocyanide occurs.

Table 7 gives a comparison of structural data for closely related complexes. In the present structure the distances and angles closely parallel the corresponding ones in the parent carbonyl- [16] and isocyanide-bridged [17] complexes with the exception that the distance of 1.87 Å to the isocyanide group is significantly shorter than that of 1.94 Å in the parent. The protonation of the nitrogen of the isocyanide is accompanied by a significant lengthening of the C–N distance from 1.22 Å in the parent [17] to 1.28 Å. Whereas the addition of $AlEt_3$ to the parent carbonyl-bridged complex [2] results in a

TABLE 7

Comparison of structural data for complexes closely related to *cis*-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CO_\mu)\{CN(H)Me_\mu\}]^+$; distances in Å, angles in degrees

	(1) [a]	(2) [b]	(3) [c]	(4) [d]
Fe . . . Fe	2.531(2)	2.538(1)	2.491(8)	2.521(2)
Fe–$(CO)_t$ [e]	1.745(8)	1.714(8)	1.70(2)	1.77(1)
Fe–$(CO)_b$	1.917(7)			1.94(1)
Fe–$(CX)_b$ [f]		1.937(7)	1.89(2)	1.87(1)
Fe–Cp	1.746(5)	1.753	1.72	1.74
C–N		1.221(8)		1.28(1)
Fe–$(CO)_b$–Fe	82.6(3)			80.8(4)
Fe–$(CX)_b$–Fe		81.8(3)	82	84.6(4)
C_b–Fe–C_b	96.0(3)	95.8(5)	96	95.6(4)
C_b–Fe–Cp	123.2	124.8	124	124
C_t–Fe–Cp	124.4	124.8	120	123
Dihedral angle	164	157.9	167	161.5

[a] *cis*-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CO_\mu)_2]$.[16] [b] *cis*-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2\text{-}(CNMe_\mu)_2]$.[17] [c] *cis*-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CO{\cdot}AlEt_{3\mu})_2]$.[2] [d] This work. [e] Subscripts t and b refer to terminal and bridging groups respectively and Cp is the centroid of the C_5H_5 ring. [f] X = NMe for (2), $OAlEt_3$ for (3), and NHMe for (4).

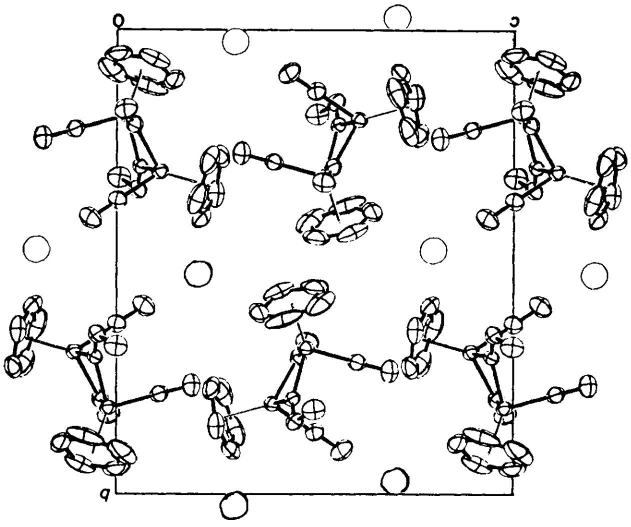

FIGURE 2 The packing in the crystal. The $[BF_4]^-$ ions are represented by a single circle

shortening of 0.04 Å in the Fe · · · Fe distance, there is no such significant variation in the present structure.

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