Reactions of [Fe_2(η-dienyl)$_2$(CO)$_{4-n}$(CNR)$_n$] Complexes (dienyl = C_5H_5, C_5H_4Me, or C_9H_7; R = alkyl or benzyl; n = 1 or 2) with Alkyl Halides and Other Alkylating Agents. The Crystal Structure of *cis*-[Fe_2(η-C_5H_4Me)$_2$-(CO)$_3${C(NMe$_2$)$_\mu$}]I †

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The title complexes react with alkyl halides, R′X, to give the salts [Fe_2(η-dienyl)$_2$(CO_t)(CO_μ)(L_t){CN(R′)R_μ}][X] (L = CO or CNR). The ease of the reaction is affected by the nature of the dienyl ligand, *n*, R, R′, and X so that no reaction occurs when R or R′ = Bu^t or X = Cl, and it is much slower when R or R′ are secondary alkyl groups. Other alkylating agents may be used but give much less satisfactory results. The i.r. and ^1H and ^{13}C n.m.r. spectra of the salts suggest that isomerism occurs, but its nature is not clear. The structure of *cis*-[Fe_2(η-C_5H_4Me)$_2$-(CO_t)$_2$(CO_μ){C(NMe$_2$)$_\mu$}]I has been determined by an *X*-ray diffraction study. It has been solved using the heavy-atom method from photographic data and refined by full-matrix least squares to *R* = 0.078 for 724 non-zero unique reflections. Crystals of this compound are orthorhombic with space group *Pmn*2, *Z* = 2, *a* = 13.87(2), *b* = 9.03(1), and *c* = 8.05(1) Å.

THE basicity of the bridging CO groups in [Fe_2(η-C_5H_5)$_2$(CO)$_4$] has allowed the isolation of adducts such as [Fe_2(η-C_5H_5)$_2$(CO_t)$_2${CO(AlEt$_3$)$_\mu$}$_2$] (t indicates a terminal, μ a bridging group).[1] The μ-CNR ligands in [Fe_2(η-C_5H_5)$_2$(CO)$_{4-n}$(CNR)$_n$] derivatives (n = 1 or 2) are more basic and may be protonated by quite weak acids.[2] Here we describe the reactions of the isocyanide complexes with alkyl halides and other alkylating agents. The structure of one of the products, *cis*-[Fe_2(η-C_5H_4-Me)$_2$(CO_t)$_2$(CO_μ){C(NMe$_2$)$_\mu$}]I has been determined by an *X*-ray diffraction study.

TABLE 1

Melting points, yields, reaction times, and analyses for some [Fe_2(η-C_5H_5)$_2$(CO)$_3${CN(R′)R}]I salts

					Analysis (%) [b]			
R	R′	M.p. (θ_c/°C) [a]	Yield (%)	Time *t*/h	C	H	N	I
Me	Me	decomp. 235	72	4	38.0 (37.7)	3.3 (3.1)	2.8 (2.8)	25.5 (25.0)
Me	Et	212—216	21	4	39.1 (39.0)	3.5 (3.4)	2.9 (2.7)	24.1 (24.5)
Me	allyl	96—100	69	0.25	39.9 (40.3)	3.6 (3.4)	2.8 (2.6)	
Me	Bu^n	193—197	5	48	41.6 (42.6)	4.2 (3.9)	2.5 (2.5)	22.3 (22.4)
Me	CH_2Ph	decomp. 145	11	2	45.0 (45.1)	3.3 (3.4)	2.5 (2.4)	23.4 (21.7)
Me	CH_2Ph [c]	decomp. 185	36	5	47.6 (47.4)	4.5 (4.0)	2.5 (2.5)	
Et	Me	decomp. 210	54	6	38.5 (39.0)	3.4 (3.4)	2.6 (2.7)	24.1 (24.3)
Et	allyl	178—180	76	16	40.6 (41.6)	3.6 (3.6)	2.6 (2.6)	
Pr^i	Me	205—209	29	24	40.3 (41.2)	3.9 (3.7)	2.4 (2.6)	
CH_2Ph	Me	decomp. 183—185	32	20	45.4 (45.0)	3.4 (3.4)	2.6 (2.4)	
Me	Me [d]	decomp. 201	69	4	40.3 (40.0)	3.7 (4.1)	2.8 (2.8)	
Me	Me [e]		2	9	47.9 (47.4)	3.5 (3.3)	2.3 (2.3)	

[a] decomp. = Decomposes without melting. [b] Calculated values are given in parentheses. [c] I^- replaced by Br·H_2O. [d] C_5H_5 replaced by C_5H_4Me. [e] C_5H_5 replaced by C_9H_7.

Chatt *et al.*[3] have found that the terminal isocyanide ligand in *trans*-[M(CNR)$_2$(dppe)$_2$] complexes (M = Mo or W; dppe = $Ph_2PCH_2CH_2PPh_2$) is also susceptible to electrophilic attack at the N atom. Products such as [W(CNMe$_2$)(CNMe)(dppe)$_2$][BF$_4$] are formed which contain a terminal C=N(R′)R ligand.[3] We have not observed this type of behaviour.

EXPERIMENTAL

The [Fe_2(η-dienyl)$_2$(CO)$_{4-n}$(CNR)$_n$] complexes were prepared as described elsewhere,[4] whilst literature methods were used to obtain [CPh$_3$][BF$_4$] [5] and [OEt$_3$][BF$_4$].[6] Other chemicals were obtained from commercial sources.

All reactions were carried out in purified solvents under an atmosphere of nitrogen at room temperature unless it is stated otherwise.

The appropriate alkyl halide (*ca.* 10—30 mmol) was added to a stirred solution of [Fe_2(η-dienyl)$_2$(CO)$_{4-n}$(CNR)$_n$] (*ca.* 1 mmol) in tetrahydrofuran (thf) or diethyl ether (*ca.* 75 cm^3). When the product precipitated it was filtered off, recrystallized from chloroform–hexane, methylene chloride–hexane, or methanol, or it was washed with benzene and pentane. When dienyl = C_9H_7 (indenyl) no reaction took place unless the mixture was irradiated for *ca.* 9 h (Philips HPR 125-W lamp).

Reactions with Me_2SO_4, Et_2SO_4, $MeSO_3F$, [OEt$_3$][BF$_4$], and [CPh$_3$][BF$_4$] were carried out similarly, but for the first two reagents Na[BF$_4$] was added to the reaction mixture and for the third benzene or hexane was used as the solvent.

A representative selection of products is listed in Tables 1 and 2 together with their melting points, analyses, reaction yields, and reaction times. Infrared spectra are given in Tables 3 and 4 for the 1 500—2 200 cm^{-1} region. They were determined as described elsewhere.[2] N.m.r. spectra (Tables 5 and 6) were run on a JEOL 100s Fourier-transform pulsed n.m.r. spectrometer or a Perkin-Elmer R.12 spectrometer.

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† μ-Carbonyl-μ-dimethyliminiomethylene-bis[carbonyl(η-methylcyclopentadienyl)iron] iodide.

TABLE 2

Melting points, yields, reaction times, and analyses for some $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNR)\{CN(R')R\}]I$ salts

R	R′	M.p. (θ_c/°C) [a]	Yield (%)	Time t/h	Analysis (%) [b] C	H	N
Me	Me [c]	205	53	3	35.8 (36.0)	3.2 (3.6)	4.7 (4.8)
Me	Me [d]	>200			37.5 (37.6)	3.2 (3.5)	4.9 (5.2)
Me	Et	>206	59	16	39.7 (40.4)	3.8 (3.9)	5.2 (5.2)
Me	Et [e]	191—196	29	16	43.6 (43.2)	4.3 (4.3)	5.9 (5.7)
Me	Pr^n	197—200	21	48	41.0 (41.2)	4.4 (4.7)	5.1 (5.1)
Me	Pr^i	235	1	1 year	41.5 (41.2)	4.7 (4.7)	5.2 (5.1)
Me	allyl	>206	30	8	41.5 (41.6)	4.1 (3.8)	5.2 (5.1)
Et	Me	190—195	43	1	41.1 (41.2)	4.2 (4.2)	4.9 (5.1)
Et	Et	187—190	14	7	42.2 (42.6)	4.5 (4.4)	4.9 (4.9)
Pr^i	Me	decomp. 140	5	16	41.4 (41.6)	4.8 (4.8)	5.0 (4.6)

[a] Determined in sealed tubes. [b] Calculated values are given in parentheses. [c] With ½ $CHCl_3$ of crystallization. [d] I^- replaced by $[PF_6]^-$. [e] I^- replaced by Br^-.

TABLE 3

Infrared spectra (cm^{-1}) between 1 500 and 2 200 cm^{-1} of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3\{CN(R')R\}]I$ complexes in chloroform

R	R′	Absorption bands [a] A	B		C	D
Me	Me	1 599 (1.7)	1 827 (2.1)	1 840 (2.1)	1 989 (1.7)	2 023 (10)
Me	Me [b]	1 599 (1.6)	1 822 (2.3)	1 832 (2.3)	1 983 (1.7)	2 014 (10)
Me	Me [b,c]	1 605 (2.0)	1 823 (3.9)	1 830 (sh)	1 970 (2.2)	1 992 (10)
Me	Et	1 589 (1.6)	1 829 (2.0)	1 838 (2.0)	1 991 (1.7)	2 022 (10)
Me	Bu^n	1 588 (1.6)	1 828 (2.1)	1 838 (2.1)	1 992 (2.0)	2 023 (10)
Me	CH_2Ph	1 576 (1.2), 1 588 (0.8), 1 602 (sh)	1 825 (2.4)	1 836 (2.4)	1 988 (1.9)	2 019 (10)
Et	Me	1 587 (1.6)	1 825 (2.0)	1 836 (2.0)	1 990 (1.7)	2 021 (10)
Et	allyl	1 588 (1.7)	1 828 (sh)	1 838 (2.2)	1 988 (1.8)	2 019 (10)
Pr^i	Me	1 572 (1.5, br)	1 827 (2.2)	1 838 (2.2)	1 988 (1.7)	2 020 (10)

[a] Relative peak heights are given in parentheses; br = broad, sh = shoulder. [b] C_5H_5 replaced by C_5H_4Me. [c] Tetrahydrofuran solvent.

TABLE 4

Infrared spectra (cm^{-1}) between 1 500 and 2 200 cm^{-1} of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNR)\{CN(R')R\}]I$ complexes in chloroform

R	R′	Absorption bands [a] E	F		G		H	
Me	Me	1 590 (4.5)	1 806 (5.8)	1 821 (sh)	1 984 (10)	2 011 (sh)	2 173 (8.6)	2 196 (sh)
Me	Me [b]	1 591 (4.5)	1 806 (5.8)	1 818 (sh)	1 984 (10)	2 010 (sh)	2 173 (8.2)	2 196 (sh)
Me	Et	1 576 (3.4)	1 808 (5.8)	1 822 (sh)	1 984 (10)	2 009 (sh)	2 173 (7.5)	2 195 (sh)
Me	Pr^n	1 574 (3.3)	1 806 (5.5)	1 819 (sh)	1 986 (10)	2 010 (sh)	2 173 (7.5)	2 195 (sh)
Me	Pr^i [c]		1 809 (5.2)	1 822 (sh)	1 981 (10)	2 009 (sh)	2 176 (9.4)	2 210 (sh)
Me	allyl	1 573 (3.8)	1 809 (5.8)	1 821 (sh)	1 985 (10)	2 012 (sh)	2 173 (7.4)	2 194 (sh)
Et	Me	1 575 (3.1)	1 806 (5.4)	1 818 (sh)	1 983 (10)		2 159 (7.7)	2 180 (sh)
Et	Et	1 558 (3.2)	1 807 (5.6)	1 820 (sh)	1 982 (10)		2 158 (7.0)	2 180 (sh)
Pr^i	Me [c]		1 807 (5.4)	1 821 (sh)	1 981 (10)		2 150 (7.1)	2 162 (sh)

[a] Relative peak heights are given in parentheses. [b] I^- replaced by Br^- [c] Absorption band E obscured by the solvent.

Crystal Data.—$C_{18}H_{20}Fe_2INO_3$, $M = 537.0$, Orthorhombic, $a = 13.87 \pm 0.02$, $b = 9.03 \pm 0.01$, $c = 8.05 \pm 0.01$ Å, $U = 1\,007.1$ Å^3, $D_m = 1.77$ (by flotation), $Z = 2$, $D_c = 1.771$ g cm^{-3}, $F(000) = 528$, μ(Mo-K_α) = 30.4 cm^{-1}. Systematic absences $h0l$ if $h + l \neq 2n$, space group $Pmn2$ or $Pmnm$.

TABLE 5

N.m.r. spectra * of some $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3\{CN(R')R\}]I$ salts

R	R′	
		^1H spectra
Me	Me	5.50 (s, C_5H_5), 4.41 (s, μ-CH_3)
Me	Et	5.52 (s, C_5H_5), 5.06—4.54 (br m, μ-CH_2CH_3), 4.34 (s, μ-CH_3), 1.61 (t, J = 7.2 Hz, μ-CH_2CH_3)
		^{13}C spectra
Me	Me	90.08 (s, C_5H_5), 55.43 (s, μ-CH_3)
Me	Et	90.08 (s, C_5H_5), 63.87 (s, μ-CH_2CH_3), 51.25 (s, μ-CH_3), 13.20 (s, μ-CH_2CH_3)

* In $CDCl_3$ solution as p.p.m. downfield from $SiMe_4$; s = singlet, t = triplet, br m = broad multiplet.

Cell parameters were determined from precession photographs using Mo-K_α radiation. Intensities were estimated visually from precession photographs for the layers 0—4 about 100 and 110 and 0—3 about 010. They were corrected for Lorentz and polarization effects but not for absorption or extinction. The structure factors were placed on a common scale by internal correlation, and 724 non-zero unique reflections obtained. Scattering factors were taken from ref. 7, and all calculations were carried out on a UNIVAC 1106 computer with programs written by F. S. S.

With $Z = 2$, symmetry constraints are imposed by both the space-group symmetries for the non-centric group m and for the centric group mm. Only the former group is chemically realistic and hence the space group is $Pmn2$. The structure was solved by the heavy-atom method. Refinement was by full-matrix least squares in which $\Sigma w\Delta^2$ was minimized. Weights were initially unity but in the final stages $w = (15.0 + 0.5\,F_o + 0.05F_o^2)^{-1}$. When refine-

TABLE 6

N.m.r. spectra of some $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNR)\{CN(R')R\}]I$ salts

R	R′	^1H spectra *
Me	Me	5.26 (s, C_5H_5), 5.20 (s, C_5H_5), 4.42 (s, μ-CH_3), 4.35 (s, μ-CH_3), 3.23 (s, t-CH_3)
Me	Et	5.25 (s, C_5H_5), 5.21 (s, C_5H_5), 5.19 (s, C_5H_5), 4.93—4.53 (vbr m, μ-CH_2CH_3), 4.35 (s, μ-CH_3), 4.28 (s, μ-CH_3), 3.23 (s, t-CH_3), 1.66 (br t, J = 7.5 Hz, μ-CH_2CH_3)
Et	Me	5.25 (vb s, C_5H_5), 4.94—4.49 (br m, μ-CH_2CH_3), 4.36 (s, μ-CH_3), 4.31 (s, μ-CH_3), 3.57 (q, J = 7.5 Hz, t-CH_2CH_3), 1.64 (br t, J = 7.0 Hz, μ-CH_2CH_3), 1.12 (br t, J = 7.5 Hz, t-CH_2CH_3)
		^{13}C spectra
Me	Me	88.51 (s, C_5H_5), 88.14 (s, C_5H_5), 34.55 (br s, μ-CH_3), 31.74 (s, t-CH_3)
Me	Et	88.64 (s, C_5H_5), 88.43 (s, C_5H_5), 88.24 (s, C_5H_5), 88.05 (s, C_5H_5), 62.32 (s, μ-CH_2CH_3), 50.48 (s, μ-CH_3), 31.76 (s, t-CH_3), 13.78 (s, t-CH_2CH_3)
Et	Me	88.80 (s, C_5H_5), 88.63 (s, C_5H_5), 88.41 (s, C_5H_5), 88.31 (s, C_5H_5), 62.71 (s, μ-CH_2CH_3), 50.67 (s, μ-CH_3), 40.77 (s, t-CH_2CH_3), 15.24 (s, t-CH_3), 13.69 (t-CH_2CH_3)

* Measured in $CDCl_3$ solutions as p.p.m. downfield from $SiMe_4$; s = singlet, m = multiplet, t = triplet, q = quartet, v = very, br = broad; μ signifies a bridging ligand, t a terminal ligand.

TABLE 7

Final atomic co-ordinates (fractional, $\times 10^3$) with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c
I	0	261.1(3)	0
Fe	409.6(3)	193.7(3)	−129.8(5)
O(B)	500	479(3)	−71(4)
O(T)	365(2)	207(3)	216(3)
N	500	−90(2)	−41(2)
C(B)	500	345(3)	−94(3)
C	500	48(3)	−87(3)
Me(N)	412(2)	−176(2)	−12(4)
C(T)	383(2)	207(3)	85(3)
C(1)	300(2)	325(3)	−249(3)
C(2)	268(2)	163(7)	−200(6)
C(3)	336(3)	78(4)	−315(4)
C(4)	392(4)	179(8)	−402(4)
C(5)	374(3)	304(5)	−357(4)
Me(C)	262(3)	472(4)	−201(7)

ment was terminated the shift in the minimization function was <0.4%. The final R was 0.078 and $R'[=(\Sigma w\Delta^2/\Sigma wF_o^2)^{\frac{1}{2}}]$ was 0.101. A final difference map showed no features >|1.1|e Å^{-3} and these were associated with the iodide ion and the iron atom. The final atomic parameters are given in Table 7, bond lengths and angles in Table 8, and least-squares planes in Table 9. A list of structure factors and thermal parameters is available as Supplementary Publication No. SUP 22618 (8 pp.).*

RESULTS AND DISCUSSION

Alkyl halides R′X react with the purple neutral $[Fe_2(\eta\text{-dienyl})_2(CO)_2L(CNR)]$ complexes [dienyl = C_5H_5, C_5H_4Me, or C_9H_7; R = alkyl or benzyl; in L = CO (1) or CNR (2)] in diethyl ether or benzene solutions. Red to brown crystalline solids or oils precipitate which analyze as 1 : 1 adducts. The solids are stable in air, but their solutions in polar organic solvents decompose more or less rapidly. This often hampered their purification and in many instances the initial precipitate could only be washed with non-polar solvents such as benzene or light petroleum in which they were insoluble.

Solutions (*ca.* 10^{-3} mol dm^{-3}) of the adducts in nitromethane have conductivities Λ which vary from 64 to 94 ohm^{-1} cm^2 mol^{-1} (for $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3\{CN(Me)Et\}]I$ the value is 77.3 ohm^{-1} cm^2 mol^{-1} at 0.917 × 10^{-3} mol dm^{-3}). These compare with values of Λ = 8 for $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3(CNCH_2Ph)]$, 82.3 for $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3\{CN(H)Me\}][BF_4]$, and 214 ohm^{-1} cm^2 mol^{-1} for $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2\{CN(H)Me\}_2][BF_4]_2$ in *ca.* 10^{-3} mol dm^{-3} nitromethane solution.[2] Thus the products are formulated as 1 : 1 electrolytes. Their spectra and an *X*-ray diffraction

TABLE 8

Bond lengths and angles [a] with estimated standard deviations in parentheses

(*a*) Distances (Å) [b]

Fe···Fe′	2.51(1)		
Fe–C(T)	1.77(2)	Fe–C	1.85(2)
Fe–Cp	1.76	Fe–C(B)	1.88(2)
C(1)–Me(C)	1.47(4)	C(T)–O(T)	1.08(3)
C(1)–C(2)	1.57(6)	C(B)–O(B)	1.22(3)
C(2)–C(3)	1.53(6)	C–N	1.30(3)
C(3)–C(4)	1.39(7)	N–Me(N)	1.46(2)
C(4)–C(5)	1.21(6)		
C(5)–C(1)	1.36(4)		

(*b*) Angles (°) [b]

C(T)–Fe–Cp	131	C(T)–Fe–C(B)	87(1)
C(B)–Fe–Cp	125	C(T)–Fe–C	90(1)
C–Fe–Cp	128	C(B)–Fe–C	92(1)
Me(C)–C(1)–C(2)	132(4)	Fe–C(T)–O(T)	176(2)
Me(C)–C(1)–C(5)	124(4)	Fe–C(B)–Fe′	84(1)
C(2)–C(1)–C(5)	104(3)	Fe–C(B)–O(B)	138(1)
C(3)–C(2)–C(1)	99(3)	Fe–C–Fe′	85(1)
C(4)–C(3)–C(2)	109(3)	Fe–C–N	137(1)
C(5)–C(4)–C(3)	110(4)	C–N–Me(N)	123(1)
C(1)–C(5)–C(4)	119(5)	Me(N)–N–Me(N′)	113(1)

[a] Cp is the centroid of the cyclopentadienyl ring. [b] Atoms marked with a prime are related to those at (x, y, z) by the mirror plane at $x = \frac{1}{2}$.

TABLE 9

Least-squares planes and their equations, given by $lX + mY + nZ - p = 0$ where X, Y, and Z are the atomic co-ordinates in Å.* The deviations (Å) of the most relevant atoms from the planes are given in square brackets

	l	m	n	p
Plane (1): Fe, C, C(B)	0.2442	−0.0202	−0.9695	2.3642
Plane (2): C(1)—C(5)	0.6770	−0.0367	0.7351	1.2643
[C(1) −0.03, C(2) 0.02, C(3) <|0.01|, C(4) −0.02, C(5) 0.03, Me(C) −0.15]				
Plane (3): C, N, Me(N), Me(N′)	0	−0.2422	−0.9702	0.5420
[C 0.03, N −0.03, Me(N), Me(N′) <|0.01|, Fe 0.05]				
Plane (4): Fe, Fe′, C	0	−0.2518	−0.9678	0.5703
[N −0.05, Me(N) −0.07]				
Plane (5): Fe, Fe′, C(B)	0	−0.2051	−0.9787	1.3809

Dihedral angles (°): (1)–(2) 123, (1)–(1′) 152, (4)–(5) 26, and (3)–(4) <1

* For atoms marked with a prime see footnote *b* to Table 8.

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

study suggest that all are of the general type $[Fe_2(\eta\text{-dienyl})_2(CO)_2(L)\{CN(R')R\}][X]$. The reaction in which they are formed may be regarded as a nucleophilic displacement of X^- from R'X in which the nucleophile is the nitrogen atom of a CNR ligand of one of the isomers of (1) or (2). Alternatively it may be thought of as an electrophilic attack on the bridging isocyanide ligand. In this the reaction resembles closely the protonation of the CNR groups in (1) or (2) and like them is reversible. Liquid ammonia converts $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2L\{C(NMe_2)\}]I$ (L = CO or CNMe) into $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2L(CNMe)]$ in *ca.* 60% yield although some unchanged salt remained.

No kinetic studies have been made, but it is clear that the ease of the reactions, and the yields and stabilities of the products, are affected by both the nucleophile, $[Fe_2(\eta\text{-dienyl})_2(CO)_{4-n}(CNR)_n]$, and the electrophile, R'X. In general the π-indenyl salts are much less readily formed (*i.e.* require u.v. irradiation of the reaction mixtures) and are much less stable than their $\eta\text{-}C_5H_5$ counterparts. For example, $[Fe_2(\eta\text{-}C_9H_7)_2(CO)_3(CNR)]$ reacted with MeI but not EtI, and then only when R = Me or Et but not cyclohexyl or CH_2Ph. Consequently we devoted most of our efforts towards the $\eta\text{-}C_5H_5$ and, to a lesser extent, $\eta\text{-}C_5H_4Me$ complexes.

The effect of changes in the RNC ligand is well illustrated by the formation of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3\{CN(Et)R\}]I$ in 21% yield after *ca.* 4 h from $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3(CNR)]$ and EtI when R = Me, whereas when R = Et only traces of the salt could be detected after 3 d, and when R = Pr^i or Bu^t no reaction occurred. The ease with which both series of compounds, (1) and (2), form salts declines for R = Me > Et > Ph > CH_2Ph > Pr^i > Bu^t so that the last are unaffected or decomposed by even the most powerful alkylating agents. This appears to be predominantly a steric effect; the steric interaction between the planar μ-{C=N(R')R} ligand which lies in the $Fe(C_\mu)Fe$ plane (see later) and the terminal $Fe(\eta\text{-dienyl})(L_t)$ moieties would increase with increasing bulk of R and would tend to discourage salt formation. It is unlikely to be an electronic effect since, although electron-withdrawing groups R such as CH_2Ph tend to favour the formation of μ-CNR isomers in (1) and (2),[4] the $CNCH_2Ph$ derivatives react far less rapidly with EtI than do their CNMe counterparts. Alternatively it might be argued that replacing μ-CNMe by μ-CNEt would increase the N atom nucleophilicity (*cf.* pK_b of $NMeH_2$ and $NEtH_2$),[8a] but the rate of the reaction declines.

Increasing the number, *n*, of isocyanide ligands in the covalent molecules increases the nucleophilicity of the μ-CNR ligand even though the second isocyanide group in the reacting isomer of (2) is a terminal ligand. This is well illustrated by the reactions of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2L(CNEt)]$ with EtI which give only traces of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2L\{C(NEt_2)\}]I$ after 3 d when L = CO, but the related product in 14% yield after 7 h when L = CNEt. This is probably an electronic effect since the steric requirements of terminal CO and CNEt groups probably do not differ greatly, but the latter is the stronger σ donor/poorer π acceptor. It will tend to give rise to a greater negative charge upon the N atom of the μ-CNR ligand and make it a stronger nucleophile.

The reactivity of the halide R'X with either (1) or (2) (R = Me in most instances) declines along the series R' = allyl ~ benzyl ~ Me > Et > Pr^i > $Bu^t \gg Pr^i \gg$ Ph or Bu^t so that the last two compounds fail to react. This is the series found for most nucleophilic substitution reactions except for the position of Bu^tX,[8b] and here the limitation is probably steric. The Bu^t group is too bulky for it to form part of a μ-CN(R')R or μ-CNR ligand. Also, the consequences of changing *n* are further illustrated by the failure of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2L(CNMe)]$ to react with Pr^iI when L = CO but to react slowly (*ca.* 1 year) when L = CNMe.

For both MeX and $PhCH_2X$ the reactivities decrease in the order X = I > Br $\gg$ Cl. The chlorides do not react with either (1) or (2) (R = Me). This is the usual behaviour of alkyl halides in nucleophilic substitution reactions.[8b]

Other, more powerful, alkylating agents were used in place of the alkyl halides, but were rarely satisfactory. Thus, $[OEt_3][BF_4]$ acted as a protonating rather than an ethylating agent. Similar behaviour has been observed in the $[Mo(dppe)_2(N_2)_2] + [OEt_3][BF_4]$ reaction which gives $[Mo(dppe)(N_2H_2)F][BF_4]\cdot CH_2Cl_2$.[9] We do not know whether this is an intrinsic property of $[OEt_3][BF_4]$ or whether small quantities of protons are present arising from reagent hydrolysis despite our efforts to prevent this.

Old samples of either Me_2SO_4 or Et_2SO_4 also protonated (1) or (2), but freshly distilled reagents in the presence of $Na[BF_4]$ gave $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2L\{CN(R')R\}][BF_4]$ (L = CO or RNC). Both $MeSO_3F$ and $EtSO_3F$ occasionally gave products which appeared to be those we anticipated, but analytical data were not consistent, and more often the results were confusing and irreproducible. The salt $[CPh_3][BF_4]$ reacted with $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNMe)_2]$ but the product was unstable and could not be characterized satisfactorily although its i.r. spectrum suggested that it was of the type $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNMe)\{CN(R')Me\}][X]$.

It should be noted that the $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2L\{CN(R')R\}]^+$ salts failed to react with strong acids or alkylating agents except to undergo anion exchange. When L = CNR there was no evidence for its protonation or alkylation. We attribute this to steric effects; although these molecules can accommodate one μ-{C=N(R')R} and one μ-CO, or two μ-{C=N(H)R} ligands with their attendant μ-ligand–$Fe(\eta\text{-}C_5H_5)(L_t)$ interactions, two μ-{C=N(R')(R)} or one μ-{C=N(R')R} and one μ-{C=N(H)R} ligands cannot be introduced.

The i.r. spectra in the 1 500—2 200 cm^{-1} region are summarized in Tables 3 and 4 for a selection of the salts. The absorption bands A and E at *ca.* 1 600 cm^{-1} are assigned to $\nu(C{=}N_\mu)$, B and F at *ca.* 1 830 cm^{-1} to $\nu(CO_\mu)$, C, D, and G at 2 000 cm^{-1} to $\nu(CO_t)$, and F at *ca.* 2 180 cm^{-1} to $\nu(CN_t)$ stretching vibrations. Salts of the

$[\mathrm{Fe_2(\eta\text{-}dienyl)_2(CO)_3\{CN(R')R\}}]^+$ cations have spectra which are broadly similar in the solid state and in solution. They are consistent with the *cis*-$[\mathrm{Fe_2(\eta^2\text{-}dienyl)_2(CO_t)_2(CO_\mu)\{CN(R')R\}}]^+$ structure found for one of them in the solid state (see later). However, there are aspects of their i.r. spectra which have no obvious explanation. In chloroform solution, absorption bands B clearly have two components of comparable intensities which are not resolved but give rise to a very broad envelope with a flat top. This may be due to the presence of isomers, but there is no other supporting evidence. We feel that it is probably due to interactions of the cation with the anion or solvent. There is a slight change in the shape of B for $[\mathrm{Fe_2(\eta\text{-}C_5H_5)_2(CO)_3\{C(NMe_2)\}}]\mathrm{X}$ in going from X = I to Br with a relative decline in the importance of the high-frequency component. A similar but more marked change in this peak shape for $[\mathrm{Fe_2(\eta\text{-}C_5H_4Me)_2(CO)_3\{C(NMe_2)\}}]\mathrm{I}$ is produced by varying the solvent along the series $\mathrm{CHCl_3} > \mathrm{MeCN} >$ thf so that in the last solvent the high-frequency component is scarcely visible. These changes are reflected in (*a*) a decline in peak width of B at half-height (27 > 23 > 18 cm^{-1}) whilst those of D remain constant at 13.5—14 cm^{-1}, and (*b*) an increase in the relative peak heights of B (Table 3). Consequently it seems probable that the doublet nature of B is due largely to solvent-dependent solvent–cation interactions with cation–anion interactions being much less important. The second unusual feature of these spectra which we are not able to explain is the multiplet nature of absorption band A in some instances, *e.g.* $[\mathrm{Fe_2(\eta\text{-}C_5H_5)_2(CO)_3\{CN(R)Me\}}]\mathrm{X}$ where R = allyl and X = I, or R = benzyl and X = Br or I. It appears to vary slightly from sample to sample, but we are not sure whether it is an artifact. Normally A is a sharp singlet (Table 3).

The i.r. spectra of the second series of salts (Table 4) are consistent with a $[\mathrm{Fe_2(\eta\text{-}dienyl)_2(CO_t)(CO_\mu)(CNR_t)\{CN(R')R_\mu\}}]^+$ structure for the cation, but it is not possible to determine whether it has a *cis* or *trans* conformation. Invariably the absorption bands are either asymmetric or have marked shoulders, except for E [due to ν(C=N)], and have two components with those at higher frequencies being the weaker. These effects are real and may be due to the presence of *cis* and *trans* isomers. If this is the case, the n.m.r. spectra discussed later suggest that the isomers are fluxional and interconvert rapidly at room temperature.

Replacing a μ-RNC ligand in the $[\mathrm{Fe_2(\eta\text{-}dienyl)_2(CO_t)(CO_\mu)(L_t)(CNR_\mu)}]$ isomers of (1; L = CO) and (2; L = CNR) by $\mu\text{-}\{\mathrm{C\overset{+}{N}(R')R}\}$ results in a *ca.* 35 cm^{-1} increase in the wavenumbers of the stretching vibrations of the remaining $\mathrm{C{\equiv}O_t}$, $\mathrm{C{\equiv}NR_t}$, and $\mathrm{C{=}O_\mu}$ groups. This suggests that the $\mu\text{-}\{\mathrm{C\overset{+}{N}(R')R}\}$ ligands, like $\mu\text{-}\{\mathrm{C\overset{+}{N}(H)R}\}$, are much more effective electron-withdrawing groups than μ-CNR. This is reflected in the much lower $\nu\{\mathrm{C{=}N(R')R_\mu}\}$ frequencies at *ca.* 1 600 cm^{-1} as compared with $\nu(\mathrm{C{=}NR_\mu})$ at *ca.* 1 730 cm^{-1}. Normally, σ donation from similar unsaturated nitrogen atoms results in a decrease in the relevant stretching frequency so that for imines, $\mathrm{R_2C{=}NR'}$, ν(C=N) occurs at *ca.* 1 620—1 660 cm^{-1} whereas for iminium cations, $[\mathrm{R_2C{=}NR'_2}]^+$, ν(C=N) occurs at *ca.* 1 640—1 690 cm^{-1}.[10] Also, in going from a μ-CO group in $[\mathrm{Fe_2(\eta\text{-}C_5H_5)_2(CO)_4}]$ to a CO group in acetone, $\mathrm{Me_2CO}$, there is a marked decrease in the ν(CO) frequency (*ca.* 1 790 to *ca.* 1 715 cm^{-1}), whereas in going from a $\mu\text{-}\{\mathrm{C\overset{+}{N}(R')R}\}$ group in our salts to one in iminium salts, $[\mathrm{R_2C{=}NR'_2}]^+$, there is a marked increase in ν(C=N). These observations point to the $\mu\text{-}\{\mathrm{C\overset{+}{N}(R')R}\}$ group being a very effective electron-withdrawing ligand and a much more powerful π acceptor than either μ-CNR or μ-CO.

Although we have regarded $\{\mathrm{CN(R')R}\}^+$ as a bridging iminium ligand $\mathrm{{>}C{=}\overset{+}{N}(R')R}$, it may also be formulated as a bridging carbyne $\mathrm{{>}\overset{+}{C}{-}N(R')R}$. Compounds containing such ligands have been reported recently, *e.g.* $[\mathrm{Fe_2(\eta\text{-}C_5H_5)_2(CO_t)_2(CO_\mu)(CR)}]$.[11] However, in our salts the frequencies of the $\nu\{\mathrm{C{=}N(R')R}\}$ vibrations and the $\mathrm{C_\mu{-}N}$ bond lengths (see later) are only consistent with a $\mathrm{C_\mu{-}N}$ bond order close to two.

The relatively low solubilities of the salts, their tendencies to decompose in solution, and the difficulties that we often encountered in their purification made it difficult to obtain reliable n.m.r. data. Thus, weak resonances which vary in importance from sample to sample may be real but we cannot be sure. Generally only the cyclopentadienyl resonances were reliable and so in most instances we will limit our discussion to these.*

Superficially at least, the ^{1}H and ^{13}C n.m.r. spectra of the $[\mathrm{Fe(\eta\text{-}C_5H_5)_2(CO)_3\{CN(R')R\}}]^+$ salts (Table 5) are consistent with their proposed structures. They show only a singlet cyclopentadienyl resonance even when R and R′ are different and the two $\eta\text{-}\mathrm{C_5H_5}$ ligands are nominally in different environments. However, it may be that the molecules are fluxional with rapid rotation about $\mathrm{C_\mu{=}N}$.

The ^{1}H and ^{13}C n.m.r. spectra of the $[\mathrm{Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNR)\{CN(R')R\}}][\mathrm{X}]$ salts are also consistent with the proposed structure where R = R′ = Me or Et. The two $\mathrm{Fe(\eta\text{-}C_5H_5)(L_t)}$ moieties have different $\mathrm{L_t}$ ligands and as a consequence two ^{1}H or ^{13}C resonances are observed for the cyclopentadienyl ligands, and there are two proton resonances due to the two Me groups of the $\mu\text{-}\mathrm{CNMe_2}$ ligand which are in different environments. However, when $\mathrm{R} \neq \mathrm{R'}$ the spectra become more complicated. This is especially clear for the ^{13}C spectrum where, when R = Me, R′ = Et or R = Et and R′ = Me, two pairs of cyclopentadienyl resonances are observed which vary in importance from sample to sample but are unaffected by lowering the solution

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* Typical chemical shifts for the ^{13}C n.m.r. resonances of CO and CN ligands (p.p.m. downfield from $\mathrm{SiMe_4}$ in $\mathrm{CDCl_3}$) are: $[\mathrm{Fe_2(\eta\text{-}C_5H_5)_2(CO_t)_2(CO_\mu)\{C(NMe_2)_\mu\}}]\mathrm{I}$, **315.59** ($\mathrm{CN_\mu}$), **267.74** ($\mathrm{CO_\mu}$), and **207.45** ($\mathrm{CO_t}$); $[\mathrm{Fe_2(\eta\text{-}C_5H_5)_2(CO_t)(CO_\mu)(CNMe_t)\{C(NMe_2)\}}]\mathrm{I}$, 322.39 ($\mathrm{CN_\mu}$), 261.89 ($\mathrm{CO_\mu}$), 210.17 ($\mathrm{CO_t}$), and 153.38 ($\mathrm{CN_t}$). All resonances are singlets.

temperature. It would be tempting to assign them to two isomers arising from hindered rotation about the C_{μ}=N bond, but this was not observed with the tricarbonyl salts due either to non-hindered rotation or to the R and R′ not providing distinguishably different cyclopentadienyl environments (see above). There are other possibilities. The cations lack a plane of symmetry and hence optical isomerism is possible, but this is independent of the nature of R and R′ and in any event would not be expected to be observable. The *cis–trans* isomerism, which is the best way of accounting for the i.r. spectra, is also independent of the nature of R and R′. Since it produces no observable effect on the n.m.r. spectra of for example $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNMe)\{C(NMe_2)\}]I$, either it does not occur or the interconversion of the two isomers is rapid on the n.m.r. time scale in some instances but not in others.

Structure of *cis*-$[Fe_2(\eta\text{-}C_5H_4Me)_2(CO_t)_2(CO_{\mu})\{C(NMe_2)\mu\}]I$.—The geometry of the cation[12] and the atom labelling is shown in Figure 1. Figure 2 shows the packing of the ions. The bond lengths and angles of the cation are given in Table 6. The structure of the cation has space-group imposed *m* (C_s) symmetry and has the expected carbonyl–isocyanide bridging system with a *cis* configuration of the cyclopentadienyl rings. The bond distances and angles within the cation are in good agreement with corresponding ones in the analogous $\{CN(H)Me_{\mu}\}$ complex cation.[2] The $\{C(NMe_2)_{\mu}\}$ group is planar (see Table 9) and the C–N bond length of 1.30 Å agrees well with the sum of the double-bond radii for the atoms (1.29 Å).[13] Hence the $\{C(NMe_2)\}^+$ is acting as a bridging iminium group rather than a bridging carbyne group.

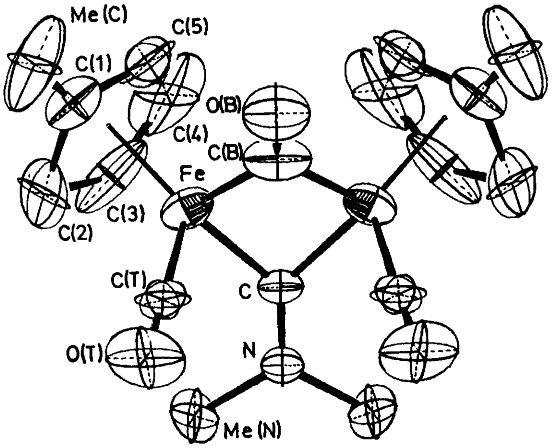

FIGURE 1 Perspective drawing of the cation and the atom-labelling system. Thermal ellipsoids are scaled to include 35% probability

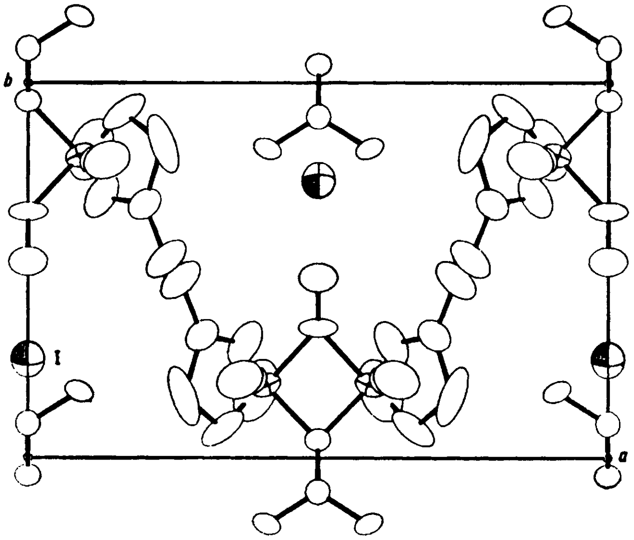

FIGURE 2 The packing in the crystal

The iron atom has an octahedral environment similar to that defined for compounds of the type $[Fe(\eta\text{-}C_5H_5)(CO)_2Y]$.[14] The cation is made up of two such octahedra sharing an edge [C · · · C(B) direction] and the angle of tilt along the common edge is 152°.

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