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Monosubstituted nitrogen donors as ligands in cyclopentadienyliron complexes: synthesis, reactivity, ligand properties, and crystal structure of $[C_5H_5Fe(CO)_2(C_5H_5N)]SbF_6$

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Abstract

Cationic complexes $[C_5H_5Fe(CO)_2(L)]BF_4$, with L a monosubstituted nitrile, RCN, or a pyridine C_5H_4NR' have been prepared by oxidative cleavage of $[C_5H_5Fe(CO)_2]_2$ with $[(C_5H_5)_2Fe]BF_4$ in the presence of an excess of L. The coordinated nitriles act as relatively weak donors and the donor strength dependence of R as observed by NMR and IR spectroscopy is in good agreement with Taft's inductive factor δ^* for the uncoordinated ligand. These constants correlate roughly with the charge on the nitrogen atom of the uncoordinated RCN ligand as found by AM1 calculations. For the stronger donor ligands C_5H_4NR' there is no overall dependence of their donor strength, but for systems with substituents in the same ring position there is a correlation of the $\delta^{13}C$ CO shift of the complex with the pK_a value of the uncoordinated pyridine ligand. The lability of the coordinated nitrile has been demonstrated by ligand replacement with anionic nucleophiles ($X^- = I$ and CN) or Group Vb donor ligands ER_3 ($E = P$, $R = C_6H_5$, OCH_3, OC_6H_5; $E = As$, Sb, $R = C_6H_5$) to give the related $C_5H_5Fe(CO)_2X$ and $[C_5H_5Fe(CO)_2(ER_3)]BF_4$ complexes in high yields. Related substitutions are only found with X^- in the pyridine series. When $L = C_5H_4NR'$ with $R' = $ 3-4-CN or 4-$N(CH_3)_2$, a nonseparable mixture of isomeric complexes involving coordination of the pyridine–nitrogen or of the pyridine substituent R' are obtained. The observed ratio between these isomers depends on the pK_a value of the uncoordinated pyridine and on the reaction conditions.

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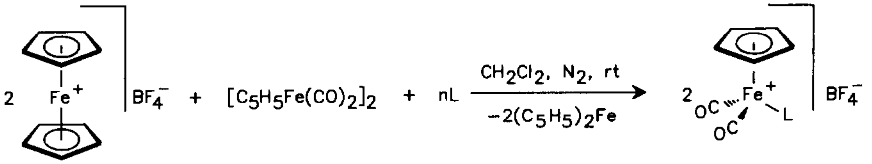
Introduction

In continuation of our research on cationic organometallic complexes [1] we have investigated the ligand properties of monosubstituted nitrogen donors of the nitrile and pyridine type towards the cyclopentadienyliron dicarbonyl system. A wide variety of organometallic complexes containing nitrogen donors are known [2], and nitrile complexes in particular have been successfully used as reactive starting materials for organometallic syntheses [3]. For the cyclopentadienyliron system, however, only a limited number of nitrile and pyridine complexes have been obtained and there has been no detailed investigation [4]; the X-ray structure of $[C_5H_5Fe(CO)_2(NCCH_3)]BF_4$ (VIa) has been discussed [5].

We now report our results on a spectroscopic investigation of these complexes which is used as a basis for a discussion about the donor/acceptor properties of these ligands. Synthetic applications of some of the obtained complexes as stable starting materials for organometallic syntheses are also outlined.

Results and discussion

All nitrogen ligands employed in this investigation react slowly at room temperature with ferricenium salt (I) and cyclopentadienyliron dicarbonyl dimer (II) to afford the desired complexes VI (L = RCN IV) or VII (L = C_5H_4NR' V) (eq. 1) [6].



(1)

I II IV/V VI/VII

L = RCN (IV (free L)/VI (complex)):

R = a CH_3, b C_2H_5, c n-C_3H_7, d $C_6H_5CH_2$, e $ClCH_2$, f CH_3 OC_2H_4, g BrC_2H_4, h C_6H_5, i CH_2=CH, j CH_2=$CHCH_2$

L = C_5H_4NR' (V free L)/VII (complex)):

R' = a H, b 2-Cl, c 2-CH_3O, d 3-Br, e 3-CH_3CO_2, f 3-CH_3C(=O), g 3-CH_3, h 4-$(CH_3)_2N$, i 4-CN, j 4-C_4H_9-t

Complexes VI and VII are obtained in good to excellent yields as dark yellow to light brown solids except for VIj, which is obtained as an unstable viscouse oil. All the compounds are readily soluble and give yellow to dark brown solutions, in polar aprotic solvents such as methylene chloride and nitromethane, but slowly decompose in donor solvents such as acetone or dimethylsulfoxide.

The stability of VI in polar solvents depends on the nature of R and decreases in the order: CH_3, C_2H_5, n-$C_3H_7 > C_6H_5CH_2 > C_6H_5 > BrC_2H_4$, $CH_3OC_2H_4 > ClCH_2 > CH_2{=}CH \gg CH_2{=}CHCH_2$; VIj decomposes in acetone solution at room temperature within 20 minutes. From IR and ^1H NMR data (see Tables 1 and 2), there is no evidence for the formation of an η^2-alkene complex in the case of R = CH_2=CH and CH_2=$CHCH_2$, either as intermediate or side product during the preparation, or as product from the decomposition of these complexes [7]. Attempts to coordinate the alkene unit in VIj by UV irradiation in methylene chloride to form a monocarbonyl complex like $[C_5H_5Fe(CO)(\eta^1,\eta^2\text{-}CH_2{=}CHCH_2CN)]BF_4$ were also

Table 1

IR and NMR data for the complexes VI

RCN	VI	IR (νCO) (cm^{-1}) [a]	^{1}H NMR (δ; ppm vs. TMS) [b]	^{13}C NMR (δ; ppm vs. TMS) [c]
CH_3CN	a	2036; 2081	2.51 (s, CH_3), 5.70 (s, C_5H_5)	4.55 (CH_3), 87.68 (C_5H_5), 137.10 (CN), 209.23(CO)
C_2H_5CN	b	2036; 2080	1.29 (t, J(HH) = 7.5, CH_3), 2.90 (q, CH_2), 5.71 (s, C_5H_5)	9.73 (CH_3), 13.96 (CH_2), 87.74 (C_5H_5), 137.60 (CN), 209.24
n-C_3H_7CN	c	2037; 2080	1.04 (t, J(HH) = 7.5, CH_3), 1.75 (q, CH_2CH_3), 2.87 (t, CH_2CN)	13.39 (CH_3), 19.10 (CH_2CH_3), 21.72 (CH_2CN), 87.74 (C_5H_5), 139.70 (CN), 209.71 (CO)
$C_6H_5CH_2CN$	d	2036; 2082	4.39 (s, CH_2), 5.71 (s, C_5H_5), 7.3–7.5 (m, C_6H_5)	26.08 (CH_2), 87.80 (C_5H_5), 128.73 (*p*-C), 128.96 (*m*-C), 129.72 (*o*-C), 130.46 (Cl), 209.10 (CO) [d]
$ClCH_2CN$	e	2038; 2082	4.87 (s, CH_2), 5.75 (s, C_5H_5)	27.70 (CH_2), 87.95 (C_5H_5), 133.16 (CN), 208.54 (CO)
$CH_3OC_2H_4CN$	f	2036; 2082	3.14 (m, CH_2CN), 3.37 (m, CH_2O) 3.70 (s, OCH_3), 5.71 (s, C_5H_5)	21.82 (CH_2CN), 58.57 (CH_2O), 66.76(OCH_3) 87.78 (C_5H_5), 138.38 (CN), 209.14 (CO)
BrC_2H_4CN	g	2038; 2082	3.56 (br m, CH_2CN), 3.77 (br m, CH_2Br), 5.72 (s, C_5H_5)	25.28 (CH_2CN), 25.71 (CH_2Br), 87.77 (C_5H_5), 137.40 (CN), 208.91 (CO)
C_6H_5CN	h	2039; 2082 [e]	5.84 (s, C_5H_5), 7.65/7.90/ 8.05 (m, 2/1/2H, C_6H_5)	88.07 (C_5H_5), 111.28 (Cl), 129.97 (*m*-C), 134.01 (*o*-C), 135.38 (*p*-C), 135.70 (CN), 208.90 (CO) [f]
CH_2=CHCN	i	2038; 2084	5.74 (s, C_5H_5), 6.02–6.28 (m, CH), 6.45–6.69 (m, CH_2)	88.00 (C_5H_5), 107.74 (CH=), 135.90 (CN), 143.46 (CH_2), 208.83 (CO)
CH_2=$CHCH_2CN$	j	2039; 2084	3.74 (m, CH_2), 5.38 (m, CH=), 5.6–5.75 (m, CH_2=), 5.73 (C_5H_5)	[g]24.12 (CH_2), 87.59 (C_5H_5), 119.70 (CH), 126.24 (CH_2=), 136.86 (CN), 209.27 (CO)

[a] In 1,2-$Cl_2C_2H_4$ solution (±2 cm^{-1}) between CaF_2 windows: νCN is normally not observed. [b] In acetone-d_6 solution; abbreviations: br broad, m multiplet, s singlet, t triplet, J given in Hz. [c] In acetone-d_6 solution; all signals are observed as singlets. The CN signal is observed as a broad, weak peak. [d] Data at −60 °C: 25.92 (CH_2), 87.79 (C_5H_5), 128.65 (*p*−C), 128.95 (*m*-C), 129.67 (*o*-C), 130.08 (Cl), 137.76 (CN), 209.42 (CO). [e] A weak νCN absorption is observed at 2290 cm^{-1}. [f] Data at −60 °C: 88.02 (C_5H_5), 111.18 (Cl), 129.90 (*m*-C), 133.90 (*o*-C), 135.32 (*p*-C), 135.67 (CN), 208.86 (CO). [g] Data at −60 °C; the complex decomposes during measurement at room temperature.

Table 2

IR and NMR data for the complexes VII

C_5H_4NR' (R')	V	IR (ν CO) (cm^{-1}) [a]	^1H NMR (δ; ppm vs. TMS) [b]	^{13}C NMR (δ; ppm vs. TMS) [b]
H	a	2022; 2068	5.65 (C_5H_5), 7.50 (dd, H4), 8.02 (tt, J(34) 7.5, J(33′) 1.5, H3), 8.85 (dt, J(23) 5, J(24) 1.6, H2	88.50 (C_5H_5), 127.63 (C3), 140.28 (C4), 159.87 (C2), 211.44 (CO)
2-Cl	b	2024; 2070	5.70 (C_5H_5), 7.47 (t, J 6, 1H), 7.82 (d, J 7.2, 1H), 8.08 (Br t, J 5.4, 1H), 9.25 (br d J 5.4, 1H)	88.77 (C_5H_5), 125.39 (C5), 129.52 (C3), 143.13 (C4), 158.60 (C6), 161.20 (C2), 210.99 (CO)
2-CH_3O	c	2020; 2066	4.23 (OCH_3), 5.58 (C_5H_5), 7.11 (t, J 6, 1H), 7.27 (d, J 8.7, 1H), 8.05 (td, J 6/2.1, 1H), 8.74 (dd)	57.98 (OCH_3), 88.03 (C_5H_5), 109.89 (C5), 119.81 (C3), 137.40 (C4), 143.79 (C6), 157.92 (C2), 212.08 (CO)
3-Br	d	2024; 2072	5.70 (C_5H_5), 7.50 (dd, J 6/5.7, 1H), 8.24 (d, J 6.9, 1H), 8.94 (d, J 6, 1H), 9.06 (s, 1H)	88.44 (C_5H_5), 121.96 (C3), 128.18 (C5), 142.90 (C4), 158.61 (C6), 159.56 (C2), 210.94 (CO)
3-CH_3CO_2	e	2023; 2070 1782 (CO_2)	2.32 (CH_3), 5.68 (C_5H_5), 7.58/7.90 (m/m, 1H each), 8.78 (d, J 5.4, 1H), 8.82 (d, J 2.1, 1H)	20.75 (CH_3), 88.59 (C_5H_5), 127.69 (C5), 134.21 (C3), 149.43 (C4), 153.70 (C6), 157.11 (C2), 169.85 (CO_2), 211.29 (CO)

3 – $CH_3C(=O)$	f	2022; 2070 1704 (C=O)	2.67 (CH_3), 5.71 (C_5H_5), 7.67 (br t, *J* 6.9, 1H), 8.50 (d, *J* 7.5, 1H), 9.09 (br d, *J* 5.1, 1H), 9.27 (br s, 1H)	26.96 (CH_3), 88.66 (C_5H_5), 127.43 (C5), 135.68 (C4), 139.42 (C3), 159.53 (C4), 162.69 (C2), 195.61 (C=O), 211.25 (CO)
3-CN	g	2028; 2070 (2036; 2083) [c] 2280 (br, CN)	5.73/5.80 (C_5H_5), 7.40/8.44/9.20/9.39 (all m, 1H each)	88.40/86.64 (C_5H_5, CN/py coord.), 127.67 (C5), 143.46 (C4), 161.92 (C2), 163.20 (C6), 208.99/210.82 (CO, CN/py coord) [d]
4-$(CH_3)_2N$ [f]	h	2015; 2064	3.09/3.32 (NCH_3), 5.00/5.58 (C_5H_5) 6.68 (d, *J* 7.2), 7.11 (br m), 8.07 (d, *J* 7.2), 8.31 (br m)	39.26/40.22 (NCH_3, py/NR_2 coord.), 88.33/89.27 (C_5H_5, py/NR_2 coord.), 108.09/110.51 (C3), 158.41 (C2), 212.45 (CO) [e]
4-CN	i	2028; 2072 (2040; 2084) [c]	5.69/5.82 (C_5H_5), 7.89 (d, *J* 6.6, 1H), 9.20 (d, *J* 6.6, 1H)	88.45/88.73 (C_5H_5, CN/py coord.), 128.93 (C3), 160.96/161.21 (C2), 208.50/210.88 (CO, CN/py coord.) [g]
4-C_4H_9-t	j	2020; 2068	1.30 (t-C_4H_9), 5.63 (C_5H_5), 7.52/9.10 (br m, 2H each)	30.19 ($C(CH_3)_3$), 35.00 ($C(CH_3)_3$), 88.44 (C_5H_5), 124.76 (C3), 159.16 (C2), 162.20 (C4), 211.15 (CO)

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[a] In 1,2-$Cl_2C_2H_4$ solution (±2 cm^{-1}) between CaF_2 windows. [b] In acetone-d_6 solution at 20±2 °C; for abbreviations see Table 1. [c] νCO data for isomer with coordination of the CN group. [d] Data at −60 °C: 88.17/88.37 (C_5H_5), 115.40 (CN), 112.42/123.87/127.20/143.02/161.64/162.82 (all C_5H_4N), 208.70/210.68 (CO, CN/py coordination). [e] Data at −60 °C: 156.20/158.12 (br, C4 py/NR_2 coord.), 211.80/212.45 (CO, py/NR_2 coord). [f] NMR data for the pure NR_2-coordinated isomer (from reaction with III): ^1H: 3.09 (NCH_3), 5.57 (C_5H_5), 6.70 8.10 (br m, 2H each); ^{13}C: 39.24 (NCH_3), 88.32 (C_5H_5), 110.19 (C3), 155.45 (C4), 157.63 (C2), 212.40 (CO) IR: 2016; 2064 (νCO). [g] Data at −60 °C: 115.89 (CN), 122.74 (C4); all other shifts are identical with those observed at room temperature.

unsuccessful; only starting material VIj and decomposition products of unknown structure were observed.

In the case of the more stable pyridine complex series VII, decomposition occurs after longer times in polar solvents, the decomposition rate being greater for complexes with electronegative substituents on the pyridine moiety regardless of their position. In the solid state however, all complexes are stable under nitrogen and in the dark for longer periods, but some decomposition is found after exposure to air for a week.

Nitriles and most substituted pyridines are known to be weaker ligands than the related amines; this is also indicated by the slow oxidative cleavage of the Fe–Fe bond in $[C_5H_5Fe(CO)_2]_2$ by ferricenium ions (eq. 1): In the presence of good donor/acceptor ligands like phosphanes, phosphites, arsanes and dimethylchalcogenides, a nearly instantaneous reaction without observable R dependency takes place [1b]. Oxidation in the presence of the strong donor ligand $NR_{3-n}H_n$ ($n = 0$–3, $R = CH_3$ and/or C_6H_5) affords only inorganic coordination compounds of iron with elimination of CO and C_5H_5 [8]. In both ligand series IV/V (compare Tables 3 and 4), a strong R dependance on the oxidation rate is observed: L = RCN (VI): R (t_{ox}) = n-C_3H_7 (5 min) > C_2H_5, CH_3 (ca. 10 min) > $C_6H_5CH_2$, $CH_3OC_2H_4$ (15 min) > CH_2=$CHCH_2$ (25 min) > BrC_2H_4, C_6H_5, CH_2=CH (ca. 30 to 40 min) ≫ $ClCH_2$ (ca. 60 min) and L = C_5H_4NR' (VII): R' (t_{ox}) = 4-$(CH_3)_2N$ (instantaneous, exothermic reaction) ≫ 4-C_4H_9-t, H (2 to 5 min) > 3-CH_3C(=O), 3-CH_3CO_2, 3-Br, 2-CH_3O (ca. 10 min) > 3-/4-CN (ca. 20 min) ≫ 2-Cl (ca. 30 to 40 min).

Infrared CO stretching absorptions for complexes VI are observed in a region typical for relatively weak donor ligands like ketones, aldehydes, or phosphaneoxides coordinated to a cyclopentadienyliron dicarbonyl unit [4], but almost no R dependence is observed. In the complex series VII, the related absorptions are shifted by 10 to 15 cm^{-1} to lower frequencies, indicating the stronger donor properties of these ligands in comparison with nitrile ligands, but there is almost no variation of the CO stretching vibration with R'. The $\delta^{13}C$ CO shifts of complexes VI also indicate the coordination of a relatively weak donor ligand, with only small changes of the chemical shift on variation of R (see ref. 9 for a discussion of the application of $\delta^{13}C$ CO NMR shifts as a sensitive probe for ligand properties). For the complexes VII there is a larger $\delta^{13}C$ CO shift range, but no overall correlation with the pK_a values of the uncoordinated pyridines C_5H_4NR' is observed (see Tables 3 and 4 for data of the uncoordinated ligands L). For systems containing substituents on the same ring position, there is a progressive shift to lower field of the $\delta^{13}C$ CO signals with increasing basicity (as expressed by the pK_a value) of the monosubstituted pyridine:

3-R'($\delta^{13}C$ CO; pK_a): CN (210.82; 1.39) < Br (210.94; 2.99) < CH_3C(=O) (211.29; 3.18) < H(211.44; 5.25)

4-R'($\delta^{13}C$ CO; pK_a): CN (210.88; 1.90) < 6-C_4H_9 (211.15; 5.99) < $(CH_3)_2N$ 212.45; 9.70)

A much more sensitive probe for the iron–nitrile interaction in the complex series VI is the ^{13}C NMR shift of the cyano group: The CN signal is observed over a range of ca. 7 ppm with a strong R dependence, which is also evident to a smaller extent in the ^1H and ^{13}C NMR shift of the cyclopentadienyl group (see Table 1). Electron-donating groups R on the RCN moiety either in the coordinated or uncoordinated state shift the $\delta^{13}C$ CN resonance to lower field, as clearly shown in

Table 3

IR and NMR data for the uncoordinated ligands RCN IV

RCN	IV	IR ν CN (cm^{-1}) [a]	^1H NMR (δ; ppm vs. TMS) [b]	^{13}C NMR (δ; ppm vs. TMS) [b]
CH_3CN	a	2250 (vs), 2292 (s)	2.01 (s, CH_3)	1.80 (CH_3), 116.61 (CN)
C_2H_5CN	b	2242 (br, m)	1.30 (t, J(HH) = 7, CH_3), 2.38 (q, CH_2)	10.60 (CH_3), 11.10 (CH_2), 121.10 (CN)
n-C_3H_7CN	c	2240 (br, m)	1.10 (t, J(HH) ca. 7.5, CH_3), 1.70 (br q, $CH_3\mathit{C}H_2$), 2.35 ($\mathit{C}H_2CN$)	14.35 (CH_3), 20.06 ($CH_3\mathit{C}H_2$), 20.26 ($\mathit{C}H_2CN$) 120.65 (CN)
$C_6H_5CH_2CN$	d	2246 (br, w)	3.67 (s, CH_2), 7.27–7.37 (m, C_6H_5)	23.84 (CH_2), 117.10 (CN), 127.56 (*m* + *p*-C), 128.73 (*o*-C), 129.60 (Cl)
$ClCH_2CN$	e	2256 (br, w)	4.13 (s, CH_2)	24.72 (CH_2), 114.44 (CN)
$CH_3OC_2H_4CN$	f	2244 (m)	2.61 (t, J(HH) = 6.3, CH_2CN), 3.41 (s, OCH_3), 3.52 (t, CH_2O)	17.92 ($\mathit{C}H_2CN$), 57.88 (OCH_3), 66.29 (CH_2O), 117.52 (CN)
BrC_2H_4CN	g	2250 (m-s)	3.00 (t, J(HH) = 6.6, CH_2CN), 3.54 (t, CH_2Br)	21.83 ($\mathit{C}H_2CN$), 24.81 (CH_2Br), 117.34 (CN)
C_6H_5CN	h	2230 (s)	7.41–7.48 (m, 2H)/7.55–7.62 (m, 3H, C_6H_5)	111.86 (Cl), 118.37 (CN), 128.67 (*m*-C), 131.57 (*p*-C), 132.33 (*o*-C)
$CH_2{=}CHCN$	i	2226 (br, vw)	5.67 (m, CH), 6.14 (m, CH_2)	106.97 (CH=), 116.56 (CN), 136.68 (CH_2=)
$CH_2{=}CHCH_2CN$	j	2244 (br, m)	3.15 (dt, J(HH) 5.4/3.3, CH_2), 5.32/5.60 (dm/dm, J(HH) = 9.3/m, 16.8/m, CH_2=), 5.5 (m, CH=)	21.42 (CH_2), 116.91 (CN), 119.34 (CH=), 125.67 (CH_2=)

[a] In 1,2-$Cl_2C_2H_4$ solution (±2 cm^{-1}) between CaF_2 windows; see Table 1 for abbreviations. [b] In $CDCl_3$ solution.

Table 4

NMR data for the uncoordinated ligands C_5H_4NR' V

C_5H_4NR' R′ (pK_a)	V	^1H NMR (δ; ppm vs. TMS) [a]	^{13}C NMR (δ; ppm vs. TMS) [a]
H (5.11 to 5.25)	a	6.60 (td, $J = 6/1.5$, 2H), 7.05 (m, 1H), 8.04 (br s, 2H)	122.68 (C3), 134.88 (C4), 148.60 (C2)
2-Cl (0.49 to 0.72)	b	7.24/7.30/7.65/8.36 (all m/1H)	122.37 (C5), 124.44 (C3), 138.83 (C4), 149.73 (C6), 151.38 (C2)
2-CH_3O (3.28)	c	3.35 (OCH_3), 6.16 (m, 2H), 6.97/7.59 (br s, 1H each)	52.52 (OCH_3), 110.42 (C5), 116.01 (C3), 137.77 (C4), 146.40 (C6), 163.67 (C2)
3-Br (2.84 to 2.99)	d	6.50 (dd, $J = 3.6/4.8$, 1H), 7.10 (dd, $J = 3.6/1.5$, 1H), 7.86 (d, $J = 4.8$, 1H), 8.02	120.01 (C3), 123.89 (C5), 137.55 (C4), 146.93 (C6), 150.01 (C2)
3-CH_3CO_2 [b] (–)	e	2.26 (CH_3), 7.29/7.46/8.50 (all m, 2/1/1H)	20.79 (CH_3), 124.09 (C5), 129.60 (C3), 139.83 (C4), 143.25 (C6), 146.60 (C2)
3-$CH_2C(=O)$ [c] (3.18)	f	1.75 (CH_3), 6.35 (dd, $J = 8.1/4.8$, 1H), 7.31 (m, 1H), 7.87 (dd, $J = 5.3/1.5$, 1H), 8.25 (d, $J = 2.1$, 1H)	25.47 (CH_3), 122.48 (C5), 131.01 (C3), 134.23 (C4), 148.69 (C6), 152.28 (C2), 195.53 (C=O)
3-CN [d] (1.36 to 1.39)	g	7.33 (t, $J = 7.2$, 1H), 7.70 (d, $J = 7.2$, 1H), 8.66 (d, $J = 4.2$, 1H), 8.73 (br s, 1H)	109.37 (C3), 116.01 (CN), 123.15 (C5), 139.78 (C4), 151.80 (C2), 152.40 (C6)
4-$(CH_3)_2N$ (9.70)	h	2.95 (NCH_3), 6.45/8.21 (t/t, $J = 2.5$, 2H each)	38.90 (NCH_3), 106.57 (C3), 149.70 (C2), 154.08 (C4)
4-CN (1.90)	i	7.58/8.84 (m, 2H each)	116.44 (CN), 120.37 (C4), 125.30 (C3), 150.79 (C2)
4-C_4H_9-t (5.99)	j	1.29 (C_4H_9-t), 7.25/8.55 (d, $J = 4.8$m, 2H each)	30.05 ($C(CH_3)_3$), 34.13 ($C(CH_3)_3$), 120.02 (C3), 148.95 (C2), 159.00 (C4)

[a] In $CDCl_3$ solution; for abbreviations see Table 1. *IR data (in 1,2-$Cl_2C_2H_4$)*: [b] 1770 (νCO_2) cm^{-1}; [c] 1690 ($\nu C=O$) cm^{-1}. [d] 2234 (νCN) cm^{-1}.

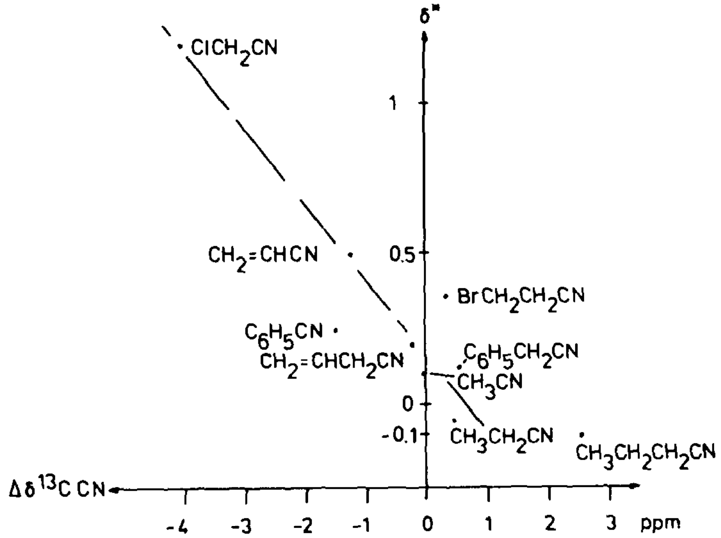


Fig. 1. Plot of the ^{13}C NMR shift (δ(VI CN) − δ(VIa CN)) vs. Taft's inductive factor δ* for the uncoordinated nitriles IV.

the case of IV/VIa–c. These results are in good agreement with related investigations on uncoordinated nitriles using ^{13}C or ^{14}N NMR shifts of the cyano group [10] or hydrogen bonding to methanol or phenol (as observed by IR shift of the CN stretching vibration) [11] as probe. There is a good correlation between the ^{13}C shift (δ(VI CN) − δ(VIa CN)) and the Taft inductive factor δ* for the uncoordinated nitriles IV (data from ref. 12) (see Fig. 1 and ref. 13). The derivations in in Fig. 1 are not larger for groups R capable for possible π-interaction with the cyano group, such as C_6H_5, CH_2=CH and to a lesser extent for CH_2=$CHCH_2$, indicating in our opinion the dominance of inductive (σ-donor) effects on the electron density at the cyclopentadienyl iron center. This is also in agreement with results from AM1 calculations of a series of nitriles (see Table 5), for which the charge localized at the nitrogen atom correlates roughly with Taft's inductive factor δ* and the observed δ^{13}C CO shift of the related complexes VI. This is also supported by the observed correlation between the δ^{13}C CO NMR shift and the pK_a value of the uncoordinated pyridine ligand for the complex series VII. A test system for this interpretation is provided by the pyridine complexes VII with R′ = 3-CN, 4-$(CH_3)_2N$ and 4-CN (Vg–i): The ratio of observed pyridine-*N* R′ coordination (R′ = cyano or amino nitrogen) should be determined in the absence of other sterical or electronical factors only by the relative donor properties of both functional sites. Based on the known pK_a values of the uncoordinated pyridines, the following order of increasing pyridine-*N* coordination would be expected for the ligands Vg–i (pK_a values):

VIIg (1.39) < VIIi (1.90) ≪ VIIh (9.70)

The observed ratios, which are independent of the reaction temperature (range −20 to 40 °C) and solvent (methylene chloride, 1,2-dichloroethane or acetone), were observed by integration of the ^{1}H C_5H_5 NMR signals:

(pyridine-*N*/R′) VIIg 1/2 VIIh 2/3 VIIi 10/3

Table 5

Selected results from AM1 calculations on uncoordinated ligands RCN IV

R	IV	d_{C-N} (Å)	X–C–N (°)	ΔH_f (kcal/mol)	IP (eV)	ChD. N(sp_x) [a]	Charge N [b]	^{13}C CN [c] (δ: ppm vs. TMS)
CH_3	a	1.163346	179.99991	19.27805	12.4642	−0.388138	−0.0501	137.10
C_2H_5	b	1.16294	180.00292	13.02129	11.9886	−0.388139	−0.0505	137.60
n-C_3H_7	c	1.16299	180.00605	6.13646	11.7542	−0.388121	−0.0512	139.76
$C_6H_5CH_2$	d	1.16285	179.87127	46.77165	9.7536	−0.388052	−0.0467	137.76
$ClCH_2$	e	1.16259	179.98405	14.61531	11.8181	−0.388153	−0.0082	133.16
$CH_3OC_2H_4$	f	1.16294	180.02324	−26.42931	10.7980	−0.388023	−0.0446	138.38
BrC_2H_4	g	1.16274	180.02396	18.92489	11.14595	−0.387997	−0.0335	137.40
C_6H_5	h	1.16357	180.00951	53.37547	10.0203	−0.388165	−0.0382	135.70
CH_2=CH	i	1.16398	180.04757	44.95751	10.8572	−0.388101	−0.0387	135.90
CH_2=$CHCH_2$	j	1.16276	180.00654	38.29710	10.5038	−0.388119	−0.0464	136.88

[a] Electron density in nitrogen sp_x orbital. [b] Sum of charge on nitrogen. [c] See Table 3 for experimental conditions.

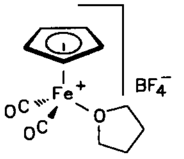
These ratios are not in agreement with those expected. Two possible explanations of the observed results can be considered: (a) strong electronic interaction between the group R′ and the π-system of the pyridine moiety, which weakens the donor ability of R′ and increases that of the pyridine-*N* site or (b) the "preference" of one coordination site by the reactive intermediate from the oxidation of $[C_5H_5Fe(CO)_2]_2$ by ferricenium ions in the presence of L. To confirm the later hypothesis, IVg–i were treated with $[C_5H_5Fe(CO)_2(THF)]BF_4$ (III; THF = C_4H_8O) under low rate conditions (suspension in ether; compare experimental part). The observed ratios were:

VIIg 1/2 VIIh 0/1 VIIi 2/1

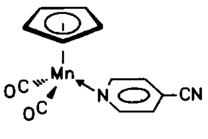
These ratios for Vg/Vi are in better agreement with those expected, and do indicate some "preference" of one coordination site over the other arising from the method of preparation for complexes VIIg–i. Due to the lower substitution rate of THF in III by the incoming ligand V, this complex is more selective than the $[C_5H_5Fe(CO)_2]^+$ fragment (possibly solvent or anion coordination [14]) generated via Fe–Fe bond cleavage. The exclusive coordination of the $(CH_3)_2N$ group in complex VIIh (prepared via complex III) indicates only minor interaction of the lone electron pair on the amino nitrogen with the pyridine π-system because otherwise, due to the high pK_a value of Vh, a dominance of pyridine-*N* site coordination due to a decreasing amino nitrogen basicity would be expected.

While this work was in progress, Keim [15] reported related results for the methylcyclopentadienylmanganese dicarbonyl system; depending on the basicity and steric requirements of these ligands, 2-, 3- and 4-cyanopyridine react with $CH_3C_5H_4Mn(CO)_2(THF)$ in the dark to give up to 3 complexes, A–C.

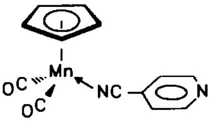
The weak coordination of RCN ligand IV in the related complexes VI is also revealed by ligand exchange reactions: VIa (R = CH_3) undergoes ligand exchange with anionic nucleophiles X or neutral Group Vb donor ligands at room temperature in 12 to 24 h in high yields. In the case of VIIa (R′ = H), only substitution reactions with X^- are found; no substitution is observed with Group Vb ligands used in this investigation (eq. 2).



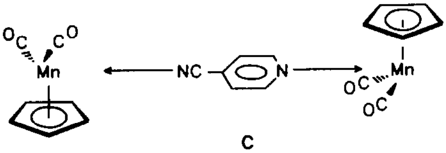
III



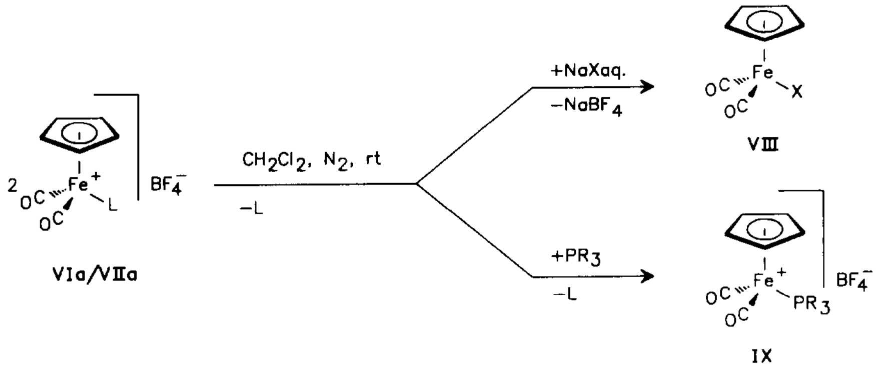
A



B



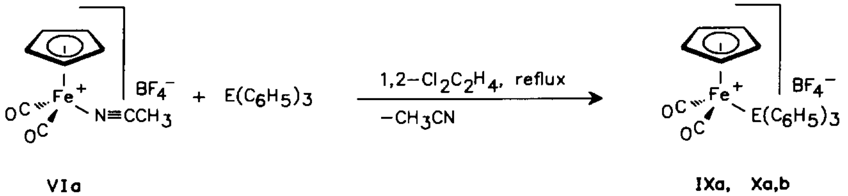
C



(2)

VIII: a X = I (80% yield), b X = CN (85% yield; both independent of L)
IX: a R = C_6H_5 (78% yield), b R = OCH_3 (92%), c R = OC_6H_5 (83%).

At higher temperatures, the ligand exchange in complex VIa is faster, and can be used for the preparation of other $[C_5H_5Fe(CO)_2(L)]BF_4$ systems in about 90% yield (eq. 3).



(3)

Due to the high yield, the ease of preparation, and the stability towards air and moisture, complex VIa is a good substitute for $[C_5H_5Fe(CO)_2(THF)]BF_4$ in most substitution reactions or in cases in which the reaction shown in eq. 1 cannot be used.

Attempts to investigate the relative donor properties of coordinated RCN ligands in complex series VI through exchange reactions with uncoordinated R′CN were unsuccessful. While no exchange was observed at room temperature, rapid decomposition was found at higher temperature. Furthermore, attempts to determine δ ^{15}N NMR shifts for complexes VI were unsuccessful due to limited solubility and/or stability in polar solvents [8].

For a more detailed understanding in the bonding of nitrogen donors, the crystal structure of $[C_5H_5Fe(CO)_2(C_5H_5N)]SbF_6$ (VIIa; SbF_6 salt) was determined (see Experimental section). Atomic coordinates are given in Table 6 and selected bond distances and angles for each of the two independent molecules in Table 7. The structure of complex VIIa is shown in Fig. 2 and stereoview in Fig. 3. The structure is composed of discrete cations $[C_5H_5Fe(CO)_2(C_5H_5N)]^+$ and anions SbF_6^- without any interactions between them. The anions have the usual octahedral geometry, and are not shown in the Figs. The two independent cations have almost identical geometries. The coordination about the iron atom is pseudooctahedral ("three-legged piano-stool geometry"), with the carbonyl (C(7) and C(9)) and pyridine ligands occupying three of the six positions and the cyclopentadienyl ring, acting as a tridentate ligand, occupying the remaining three positions.

Table 6

Atomic positional and vibrational parameters (with esd's)

Atom	x	y	z	$100 \times U_{eq}$ (Å^2)
Cation A				
Fe	0.13229(9)	0.5807(1)	−0.1128(1)	2.10(5)
N	0.1373(4)	0.7193(5)	−0.1041(6)	2.2(3)
C(2)	0.1786(9)	0.7657(9)	−0.0179(9)	5.2(5)
C(3)	0.183(1)	0.861(1)	−0.013(1)	7.7(8)
C(4)	0.1457(9)	0.9124(9)	−0.098(1)	5.7(7)
C(5)	0.1023(9)	0.8667(9)	−0.190(1)	5.4(6)
C(6)	0.0991(7)	0.7702(8)	−0.1889(9)	4.2(4)
C(7)	0.1305(8)	0.5631(8)	0.011(1)	4.3(5)
O(8)	0.1317(8)	0.5458(8)	0.0902(8)	8.0(6)
C(9)	0.0194(7)	0.5804(7)	−0.1740(10)	3.9(5)
O(10)	−0.0520(5)	0.5784(7)	−0.2117(8)	6.2(4)
C(11)	0.204(1)	0.458(1)	−0.092(1)	7.0(7)
C(12)	0.2538(9)	0.536(2)	−0.079(2)	9.6(10)
C(13)	0.227(1)	0.585(1)	−0.170(2)	8.(1)
C(14)	0.156(1)	0.539(2)	−0.239(1)	11.(1)
C(15)	0.1462(10)	0.459(1)	−0.185(1)	6.3(7)
Sb	0.08229(4)	0.21676(6)	0.00534(6)	3.46(3)
F(1)	0.1584(8)	0.1210(8)	0.027(1)	12.7(7)
F(2)	0.0898(6)	0.246(1)	−0.1175(7)	11.0(5)
F(3)	0.1750(7)	0.2953(7)	0.0711(9)	10.8(5)
F(4)	0.0120(8)	0.3152(10)	−0.013(1)	14.6(8)
F(5)	−0.0054(8)	0.1394(10)	−0.062(1)	13.8(7)
F(6)	0.0766(8)	0.1983(9)	0.1288(9)	12.3(7)
Cation B				
Fe	0.37164(9)	0.1714(1)	0.8414(1)	2.10(5)
N	0.3920(5)	0.3042(6)	0.8202(7)	1.6(3)
C(2)	0.3386(8)	0.3522(9)	0.7390(9)	4.2(5)
C(3)	0.349(1)	0.444(1)	0.721(1)	6.4(7)
C(4)	0.417(1)	0.492(1)	0.790(2)	7.7(10)
C(5)	0.472(1)	0.445(1)	0.873(2)	7.5(9)
C(6)	0.4579(8)	0.3518(9)	0.886(1)	4.4(5)
C(7)	0.4829(9)	0.1349(9)	0.8900(9)	4.3(5)
O(8)	0.5485(5)	0.1095(8)	0.9178(7)	2.8(4)
C(9)	0.3585(7)	0.1379(9)	0.710(1)	5.0(5)
O(10)	0.3525(6)	0.1122(8)	0.6360(7)	3.1(4)
C(11)	0.298(1)	0.215(1)	0.920(2)	6.8(9)
C(12)	0.2477(8)	0.171(2)	0.831(1)	7.0(7)
C(13)	0.276(1)	0.082(1)	0.833(2)	7.9(10)
C(14)	0.340(1)	0.065(1)	0.922(2)	7.7(9)
C(15)	0.3579(9)	0.152(2)	0.979(1)	7.5(8)
Sb	0.38396(4)	0.69851(5)	0.27675(6)	3.15(3)
F(1)	0.3239(6)	0.8011(7)	0.2116(7)	8.7(4)
F(2)	0.4470(6)	0.5964(6)	0.3429(8)	9.0(5)
F(3)	0.4825(6)	0.7508(8)	0.2779(9)	10.5(6)
F(4)	0.4046(9)	0.758(1)	0.3981(7)	14.4(7)
F(5)	0.3625(7)	0.643(1)	0.1530(9)	16.0(7)
F(6)	0.2862(7)	0.649(1)	0.278(1)	18.(1)

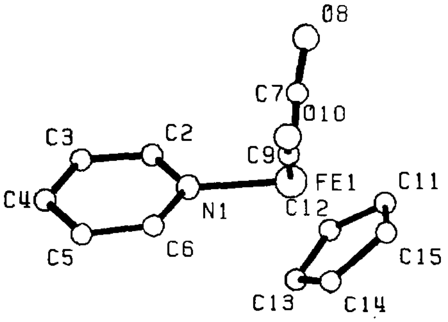


Fig. 2. The structure of one cation showing the atom numbering scheme. The two independent molecules are denoted by A and B.

Data from the X-ray structural determinations of complexes VIa (L = CH_3CN [5]) and VIIa (L = C_5H_5N) allow a direct comparison of Fe–N bonding properties. In acetonitrile complexes, the Fe–N bond distance varies between 1.91(1) Å and VIa and 1.881(5) Å in $[C_5H_5Fe[(C_6H_5)_2PCH_2]_2(NCCH_3)]B(C_6H_5)_4$ [22], which is about the sum of the covalent radii of Fe and N (1.78 Å), and the Fe–N–C angle is close to linear at 176(2)° and 171.9(1)° for these complexes. These data are in agreement with the suggested dominance of σ-donor over π-acceptor properties for nitriles as discussed in ref. 24 and indicated by *ab initio* calculations [25]. In contrast, the Fe–N distance in cyclic ligands is somewhat elongated: the average value for the two independent molecules of VIIa (SbF_6 salt) is 1.980 Å, which is shorter than the related value observed on $Fe(CO)_4(C_5H_5N)$ (2.046(5) Å) and $Fe(CO)_4(C_4H_8N_2)$ (2.031(2) Å; $C_4H_8N_2$ = pyrazine) [23]. Due to the weak interaction between the coordinating lone pair on N and the π-system of the heterocycle, pyridine acts mainly as donor ligand towards transition metals [26].

In summary, nitrogen ligands of the nitrile and pyridine type act as σ-donor towards the $[C_5H_5Fe(CO)_2]^+$ fragment: While nitriles are weakly coordinated, with the strength of the Fe–N bond considerably depending on the nature of the group R in RCH_2CN ligands, monosubstituted pyridines are generally strongly bound and

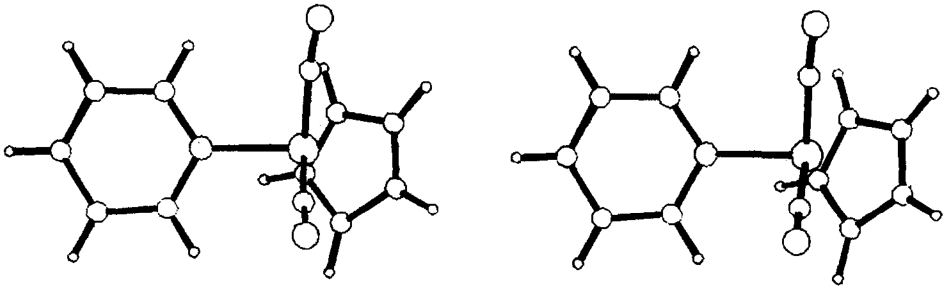


Fig. 3. Stereoview of the cation $[(C_5H_5)Fe(CO)_2(C_5H_5)]^+$.

their dominant bonding site (pyridine-*N* vs R coordination) depends on the relative basicity of both sites and the method of preparation.

Experimental

Preparations were carried out under nitrogen by Schlenk tube techniques. Solvents were purified by standard methods, $[(C_5H_5)_2Fe]BF_4$ (I), $[(C_5H_5)_2Fe]SbF_6$ [16] and $[C_5H_5Fe(CO)_2(THF)]BF_4$ (III) [1b] were prepared as previously described. $(C_5H_5)_2Fe$ (Aldrich), $[C_5H_5Fe(CO)_2]_2$ (Strem Chemicals) and the ligands RCN and C_5H_4NR' (Aldrich) were obtained from commercial sources and used as received. Analysis were performed by Desert Analytics, Tucson, AZ.

NMR spectra were recorded in $CDCl_3$ (uncoordinated ligands) or acetone-d_6 solutions (complexes) on Varian XL-300 spectrometers (300 MHz for ^1H and 75.5 MHz for ^{13}C) and were referenced to internal $Si(CH_3)_4$; IR spectra were recorded as $1,2-Cl_2C_2H_4$ solutions in 0.1 mm CaF_2 cells on a Perkin Elmer 298 IR spectrometer. Theoretical calculations on selected RCN ligands were performed at an Apollo workstation using the AM1 program [17] as implemented in AMPAC 1.0 [18].

General procedure for the preparation of VI / VII

To a CH_2Cl_2 solution (25 ml) of $[C_5H_5Fe(CO)_2]_2$ (II, 1.0 g; 2.8 mmol) and $[(C_5H_5)_2Fe]BF_4$ (I, 1.5 g; 5.5 mmol) was added a solution of 22 mmol of L (IV or V) in CH_2Cl_2. The mixture was stirred for 0.2 to 1.5 h at room temperature, during which the colour of the solution changed from deep blue (I) to dark orange–brown (traces of II, $(C_5H_5)_2Fe$ and VI or VII). The solution was filtered, ether (100 ml) was added, and the resulting yellow–brown precipitates were filtered off and washed several times with ether and pentane to remove starting material and ferrocene. All compounds were recrystallized from CH_2Cl_2/ether (1/1 to 1/3) except for VIj, which could only be obtained as a thermolabile, viscous oil. Yields:
VI: a 84%, b 87%, c 82%, d 90%, e 77%, f 82%, g 84%, h 92%, i 67% and j 60%.
VII: a 90%, b 78%, c 80%, d 68%, f 74%, g 83%, h 88%, i 85% and j 92%.

Analytical data:

VIa: Found: C, 35.58; H, 2.55; N, 4.31. $C_9H_8BF_4FeNO_2$ calc.: C, 35.43; H, 2.62; N, 4.59%.

VIh: Found: C, 45.45; H, 2.58; N, 3.51. $C_{14}H_{10}BF_4FeNO_2$ calc.: C, 45.80; H, 2.73; N, 3.82%.

VIIa: Found: C, 41.65; H, 2.90; N, 4.37. $C_{12}H_{10}BF_4FeNO_2$ calc.: C, 42.00; H, 2.92; N, 4.08%.

VIIf: Found: C, 42.97; H, 3.17; N, 4.02. $C_{14}H_{12}BF_4FeNO_3$ calc.: C, 43.65; H, 3.11; N, 3.64%.

The purities of all other complexes VI/VII were checked by NMR and IR spectroscopy, see Tables 1 and 2 for data on complexes VI/VII and Tables 3–5 for data on the uncoordinated ligands IV/V.

Attempted preparation of $[C_5H_5Fe(CO)(\eta^1,\eta^2-CH_2{=}CHCH_2CN)]BF_4$

A CH_2Cl_2 solution (40 ml) of VIj (0.5 g; 1.5 mmol) was irradiated for 12 hours at 25 ° C under nitrogen ($\lambda > 300$ nm; Hanovia medium pressure Hg lamp). After work up as described for VI/VII, only starting material VIj (0.21 g; 40% recovery) was isolated, and identified by IR and NMR spectroscopy.

Preparation of VIg–i via [$C_5H_5Fe(CO)_2(THF)]BF_4$ (III)

A suspension of III (1.0 g; 3 mmol) in ether (40 ml) was stirred for 24 h with 5 mmol L (IVg–i), during which the color of the suspension changed from deep red (III) to red–brown. The products were filtered off, washed with ether, and pentane and recrystallized from CH_2Cl_2/ether (1/3). The yields in all cases were ca. 85%.

Ligand exchange reactions with VIa / VIIa

(a) Room temperature exchange. Complex VIa (or VIIa; 1.5 mmol) was stirred in CH_2Cl_2 solution with NaX (4.8 mmol in H_2O (5 ml); X = I, CN) or PR_3 (only VIa; 4.8 mmol, R = C_6H_5, OCH_3, OC_6H_5) at room temperature for 12 hours. After evaporation of the solvent, the products were extracted with acetone and isolated by evaporation of the extract *in vacuo*.

(b) Ligand exchange at 350 K (VIa only). To a 1,2-$Cl_2C_2H_4$ solution (5 ml) of VIa (0.5 g; 1.6 mmol), $E(C_6H_5)_3$ (4.8 mmol; E = P, As, Sb) was added and the resulting light yellow–brown solution was then placed in a preheated oil bath (T = 350 ± 5 K) for 2 to 3 min during which the color changed to dark yellow. After dilution with CH_2Cl_2 and filtration, the products were precipitated by addition of ether and dried *in vacuo*. The complexes were identified by comparison of their IR (CO stretching vibration in CH_2Cl_2) and/or their ^1H NMR data (in acetone-d_6) with published data $C_5H_5Fe(CO)_2X$ [19], $[C_5H_5Fe(CO)_2(P(OR)_3)]BF_4$ [20] and $[C_5H_5Fe(CO)_2(E(C_6H_5)_3)]BF_4$ [21].

Synthesis and structure determination of [$C_5H_5Fe(CO)_2(C_5H_5N)]SbF_6$

The SbF_6 salt of cation VIIa was obtained from the reaction of $[C_5H_5Fe(CO)_2]_2$ and $[(C_5H_5)_2Fe]SbF_6$ in methylene chloride solution in the presence of pyridine by the general procedure outlined above. Spectroscopic data, except for those depending on the anion, were identical with those obtained for $[C_5H_5Fe(CO)_2(C_5H_5N)]BF_4$ (VIIa).

Crystal data. $[(C_5H_5)(CO)_2Fe(C_5H_5N)][SbF_6]$, monoclinic, space group $P2_1/c$, with the cell dimensions $a = 17.201(2)$, $b = 14.280(2)$, $c = 14.236(1)$ Å, $\beta = 113.00(1)°$, $V = 3218.5(7)$ Å^3, $M_r = 491.80$, $Z = 8$, $D_c = 2.03$ g cm^{-3}, μ (Cu-K_α) = 216.40 cm^{-1}, Cu-K_α radiation. Standard experimental and computational details are given in [27]. The crystal ($0.20 \times 0.50 \times 0.52$ mm) was obtained by slow diffusion of ether/pentane (1 : 1) into a dilute solution in methylene chloride at room temperature during 4 days. Unit cell dimensions are from reflexions with $28° < \theta < 66°$. Intensity data for 23984 reflections (a complete sphere up to $\theta = 70°$) were collected with a scan-speed of 16°/min, comprising 6096 unique reflections, of which 4305 were observed ($R_{merge} = 0.21$). The low quality of the data was partly the result of the poor quality of the crystal and partly due to the lack of an accurate absorption correction procedure. The structure was solved by automated Patterson interpretation methods (program PATSYS [28]). Hydrogen atoms were placed at calculated positions. Semi-empirical absorption correction (EMPABS [28]; correction factors in the range 0.76 to 1.00) was followed by another empirical absorption correction (DIFABS [28]; correction factors in the range 0.60 to 1.6). Least-squares refinement gave $R = 0.061$ and $R_W = 0.076$. The cell contains two independent molecules. Other programs used in this structure determination were SHELX, PLUTO and PARST [28]. Final structural parameters are given in Table 6 and selected bond distances and angles in Table 7. Lists of thermal parameters and structure factors are available from the authors.

Table 7
Selected bond lengths (Å) and angles (°)

	Cation A	Cation B
Fe–N	1.983(28)	1.973(31)
Fe–C(7)	1.789(48)	1.838(49)
Fe–C(9)	1.791(41)	1.853(55)
Fe–C(11)	2.088(44)	2.089(48)
Fe–C(12)	2.056(46)	2.080(42)
Fe–C(13)	2.093(45)	2.056(53)
Fe–C(14)	2.075(49)	2.100(47)
Fe–C(15)	2.075(48)	2.078(49)
N–C(2)	1.329(46)	1.348(48)
N–C(6)	1.341(42)	1.341(50)
C(2)–C(3)	1.358(63)	1.364(61)
C(3)–C(4)	1.356(70)	1.379(83)
C(4)–C(5)	1.390(68)	1.368(86)
C(5)–C(6)	1.380(55)	1.383(63)
C(7)–O(8)	1.150(52)	1.101(52)
C(9)–O(10)	1.132(44)	1.085(56)
C(11)–C(12)	1.371(87)	1.372(81)
C(11)–C(15)	1.308(77)	1.371(80)
C(12)–C(13)	1.379(92)	1.356(84)
C(13)–C(14)	1.403(94)	1.340(91)
C(14)–C(15)	1.409(91)	1.445(85)
Sb–F(1)	1.833(37)	1.823(30)
Sb–F(2)	1.851(34)	1.842(31)
Sb–F(3)	1.874(31)	1.846(31)
Sb–F(4)	1.806(37)	1.829(36)
Sb–F(5)	1.811(35)	1.831(37)
Sb–F(6)	1.817(40)	1.830(33)
N–Fe–C(7)	95.5(15)	96.3(16)
N–Fe–C(9)	92.6(13)	93.0(16)
C(7)–Fe–C(9)	92.6(20)	90.3(17)
Fe–N–C(2)	123.3(25)	121.2(27)
Fe–N–C(6)	119.3(24)	122.1(29)
C(2)–N–C(6)	117.3(32)	116.7(37)
N–C(2)–C(3)	123.1(41)	123.8(46)
C(2)–C(3)–C(4)	120.0(45)	118.6(51)
C(3)–C(4)–C(5)	118.9(41)	119.0(48)
C(4)–C(5)–C(6)	117.7(43)	119.2(52)
N–C(6)–C(5)	123.1(39)	122.7(49)
Fe–C(7)–O(8)	175.3(39)	177.2(44)
Fe–C(9)–O(10)	178.5(38)	175.1(42)
C(12)–C(11)–C(15)	108.0(58)	108.4(57)
C(11)–C(12)–C(13)	109.3(59)	108.6(54)
C(12)–C(13)–C(14)	106.6(55)	109.9(59)
C(13)–C(14)–C(15)	105.2(49)	106.9(49)
C(11)–C(15)–C(14)	110.7(56)	106.1(49)

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