reactions have been found. In terms of differences in free energy changes for reactions 3, 5, and 9, this is certainly the case. While not necessarily anticipated by them, these results are compatible with our earlier findings from electrochemical and spectroscopic properties that variation of macrocycle structure in the series P = OEP, OEC, OEiBC results in only very slightly different cis effects.[15] As yet untested sources of possible reactivity differences of $Fe^{II,III}$(P)-type complexes are kinetic features of biologically relevant reactions such as ligand binding and electron transfer.

Supplementary Material Available: A listing of absorbance/p_{CO} data for the systems Fe(P)/CO (Table II) (4 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Organic Chemistry,
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# Chemistry of Some (η^5-Pyrrolyl)- and (η^1-N-Pyrrolyl)iron Complexes[1a]

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Azaferrocene undergoes a facile reaction with π-acidic ligands (L = CO, RNC, and R_2NPF_2) to afford η^1-N-pyrrolyl complexes of the type (η^5-C_5H_5)FeL$_2$(η^1-NC_4H_4). A similar reaction with σ-donor ligands such as Ph$_3$P, Ph$_2$MeP, and Me$_2$PhP resulted in the decomposition of the starting complex. In the presence of aluminum chloride, azaferrocene reacts with aromatic solvents to afford cationic complexes of the type (η^6-arene)(η^5-cyclopentadienyl)iron(1+). The thermal degradation of azaferrocene to "bare" iron and ferrocene is thought to involve an autodisproportionation process. The ^{13}C NMR spectra of azaferrocene and some of its substituted pyrrolyl analogues, as well as of certain (η^1-N-pyrrolyl)iron derivatives, have been obtained and analyzed.

Introduction

During the past 3 decades the chemistry of (cyclopentadienyl)metal complexes has received considerable attention. By contrast, the chemistry of the nearest heteroatom (π-pyrrolyl)metal system has been the subject of relatively few investigations. Azaferrocene,[1b,2] tricarbonyl(η^5-pyrrolyl)-manganese,[1b,3,4] and some of their derivatives were prepared[4-7] and investigated. Limited attention has also been placed on the study of certain η^1-pyrrolyl complexes of iron,[7] manganese,[8] titanium,[9] and zirconium.[9] The bonding modes of the pyrrolyl ligand are either π (I and II) or σ (III and IV). In general,
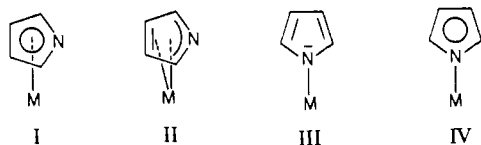
π-pyrrolyl is viewed as a symmetrically bonded ligand (I), though a certain ^{55}Mn NQR study[10] of (η^5-C_4H_4N)Mn(CO)$_3$ suggested an asymmetric bonding arrangement involving the η^3-azaallylic and η^2-olefinic systems, with the Mn–C(α) distances being shorter than the Mn–C(β) distances (II). Extremes in the degree of delocalization of the π-electron density in the σ-bonded pyrrolyl ligand are exemplified by III (localized) and IV (delocalized).

In the context of the area of heterocyclic π complexes,[11] the current study describes the chemistry and spectroscopic properties of certain (σ- and π-pyrrolyl)iron complexes.

Experimental Section

Microanalyses were performed by the Microanalytical Laboratory at the Weizmann Institute. Infrared spectra were recorded on a Perkin-Elmer 467 grating IR spectrometer and were calibrated with the aid of a polystyrene film. NMR spectra of samples dissolved in either CDCl$_3$ or other solvents as specified were recorded on the following instruments: ^{1}H spectra were obtained at 60 MHz (Varian A-60) and/or 90 MHz (Bruker HFX-10). ^{13}C spectra were obtained at 20 MHz on a Varian FT-80A spectrometer. Both ^{1}H and ^{13}C spectra were calibrated by using Me$_4$Si as a reference. ^{19}F spectra were recorded at 84.66 MHz on a Bruker HFX-10 spectrometer, with Freon-11 as a reference. Mass spectra were obtained on a MAT-ATLAS CH-4 spectrometer (inlet temperature 30–50 °C; ionization chamber temperature, 270 °C).

Argon atmosphere was routinely provided for the following operations: (i) carrying out reactions, (ii) admission to evacuated vessels, (iii) handling solutions of organometallic compounds, and (iv) storage of organometallic solids. Solvents used during the course of this investigation were dried, deoxygenated, and freshly distilled before being used. Azaferrocene (V),[1b] isocyanides,[12] and (dialkylamino)-difluorophosphines[13] were prepared according to known procedures.

Preparation of (Diisocyanide)(η^1-N-pyrrolyl)(η^5-cyclopentadienyl)iron Derivatives (VI). VI, L = (CH$_3$)$_3$CNC. Azaferrocene (0.5 g, 2.67 mmol) and *tert*-butyl isocyanide (0.64 g, 7.71 mmol) in benzene (50 mL) were stirred and refluxed for a period of 2 h. The reaction mixture was cooled to ambient temperature and filtered. The filtrate was stripped to dryness on a rotary evaporator [40 °C (30 torr)], and the excess of the isocyanide was removed under low pressure [40 °C (0.1 torr)]. Recrystallization of the crude product from a

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Table I. Some New $(\eta^1$-N-Pyrrolyl)iron Derivatives of the Type $(\eta^5$-$C_5H_5)FeL_2(\eta^1$-$NC_4H_4)^c$

| | | | Anal. | | | | |
L	yield, %	mp, °C	% C	% H	% N	mol wt^e	IR, cm^{-1}
							$\nu(NC)^f$
$(CH_3)_3CNC$	70	115	65.10^a	7.67	12.00	353	2105 (vs)
			(64.60)^b	(7.70)	(11.89)	(353)	2140 (vs)
$CH_3CH_2CH_2NC$	61	50	62.64	7.24	12.35	325	2120 (vs)
			(62.78)	(7.13)	(12.92)	(325)	2154 (vs)
$(CH_3)_2CHNC$	72	53	61.43	6.80	11.88	325	2110 (vs)
			(62.78)	(7.13)	(12.92)	(325)	2155 (vs)
$(CH_3)_2N(CH_2)_3NC$	15	43	60.64	8.56	16.58		2122 (vs)
			(61.31)	(8.09)	(17.02)		2150 (vs)
C_6H_5NC	8	dec^d	69.50	4.62	10.47		2125 (vs)
			(70.26)	(4.84)	(10.69)		2169 (vs)
							$\nu(PF)^g$
$(CH_3)_2NPF_2$	80	86	37.92	5.26	10.16	413	710–842 (s to vs)
			(37.80)	(5.12)	(10.17)	(413)	
$(C_2H_5)_2NPF_2$	85	54	43.71	6.20	8.96	469	710–842 (s to vs)
			(43.52)	(6.23)	(8.96)	(469)	

^{a} Found. ^{b} Calcd. ^{c} The colors of these complexes range from red to deep red. ^{d} Decomposes gradually on heating. ^{e} Determined mass spectrometrically. ^{f} Spectra taken in CH_2Cl_2 solution. ^{g} Spectra taken in Nujol.

Table II. ^{13}C, ^1H, and ^{19}F NMR Spectral Data of Certain η^5- and η^1-Pyrrolyl Complexes of Iron

| | chemical shift^d | | | | |
| | pyrrolyl | | | | |
complex	α	β	η^5-C_5H_5	CH_3	other L^a resonances
	^{13}C NMR Spectra $(\delta_C^{Me_4Si})$				
$(\eta^5$-$C_5H_5)Fe(\eta^5$-$C_4H_4N)$	90.0 (2 C, s)	72.6 (2 C, s)	68.7 (5 C, s)		
$(\eta^5$-$C_5H_5)Fe[\eta^5$-$C_4H_3(2$-$CH_3)N]$	87.3 (1 C, s, C-5)	71.1 (1 C, s C-4)	69.2 (5 C, s)	15.9 (1 C, s)	
	103.2 (1 C, s, C-2)	70.7 (1 C, s, C-3)			
$(\eta^5$-$C_5H_5)Fe[\eta^5$-$C_4H_2(2,5$-$(CH_3)_2)N]$	100.9 (2 C, s)	69.6 (2 C, s)	69.0 (5 C, s)	15.1 (2 C, s)	
$(\eta^5$-$C_5H_5)FeL_2(\eta^1$-$NC_4H_4)$					
L = $(CH_3)_3CNC$	135.3 (2 C, s)	107.1 (2 C, s)	80.5 (5 C, s)	31.4 (6 C, s)	
L = $CH_3CH_2CH_2NC$	135.3 (2 C, s)	107.4 (2 C, s)	80.4 (5 C, s)	11.2 (2 C, s)	46.8 (2 C, s, α'-CH_2)
					23.8 (2 C, s, β'-CH_2)
L = $(CH_3)_2CHNC$	135.2 (2 C, s)	107.3 (2 C, s)	80.6 (5 C, s)	24.3 (4 C, s)	49.1 (2 C, s, α'-CH)
L = $(CH_3)_2N(CH_2)_3NC$	135.2 (2 C, s)	107.6 (2 C, s)	80.4 (5 C, s)	28.4 (4 C, s)	56.1 (2 C, s, α'-CH_2)
					45.5 (2 C, s, β'-CH_2)
					43.1 (2 C, s, γ'-CH_2)
L = $(CH_3)_2NPF_2$	135.8 (2 C, s)	109.2 (2 C, s)	81.1 (5 C, s)	35.9 (4 C, m)	
L = $(C_2H_5)_2NPF_2$	135.6 (2 C, s)	109.0 (2 C, s)	80.8 (5 C, s)	13.9 (4 C, s)	38.9 (4 C, m, α'-CH_2)
	^1H NMR Spectra $(\delta_H^{Me_4Si})$				
$(\eta^5$-$C_5H_5)Fe(\eta^5$-$C_4H_4N)^b$	5.26 (2 H, s)	4.45 (2 H, s)	4.15 (5 H, s)		
$(\eta^5$-$C_5H_5)Fe(\eta^5$-$C_4H_4N)$ (in D_2O)	5.35 (2 H, s)	4.72 (2 H, s)	4.33^c (5 H, s)		
$(\eta^5$-$C_5H_5)FeL_2(\eta^1$-$C_4H_4N)$					
L = $(CH_3)_3CNC$	6.55 (2 H, m)	6.15 (2 H, m)	4.44 (5 H, s)	1.16 (18 H, t)	
L = $CH_3CH_2CH_2NC$	6.52 (2 H, m)	6.11 (2 H, m)	4.42 (5 H, s)	1.10 (6 H, t)	3.68 (4 H, t, α'-CH_2)
					1.82 (4 H, m, β'-CH_2)
L = $(CH_3)_2CHNC$	6.49 (2 H, m)	6.10 (2 H, m)	4.38 (5 H, s)	1.45 (12 H, d)	4.12 (2 H, m, α'-CH)
L = C_6H_5NC	6.43 (2 H, m)	6.03 (2 H, m)	4.63 (5 H, s)		7.10 (10 H, m, Ph)
L = $(CH_3)_2NPF_2$	6.30 (2 H, m)	6.07 (2 H, m)	4.59 (5 H, s)	2.66 (12 H, b)	
L = $(C_2H_5)_2NPF_2$	6.27 (2 H, m)	6.06 (2 H, m)	4.55 (5 H, s)	1.15 (12 H, t)	3.17 (8 H, b, α'-CH_2)
	^{19}F NMR Spectra $(\delta_F^{freon-11})$				
$(\eta^5$-$C_5H_5)FeL_2(\eta^1$-$NC_4H_4)$					
L = $(CH_3)_2NPF_2$		22.1 (m) $J(P-F) = 1231$ Hz			
		36.7 (m)			
L = $(C_2H_5)_2NPF_2$		21.6 (m) $J(P-F) = 1213$ Hz			
		36.0 (m)			

^{a} The terms α', β', and γ' designate the positions of the alkanic moieties in L in relationship to the coordinated functionality. ^{b} Data by King and Bisnette.[2] ^{c} This resonance was wrongly quoted as δ 4.62 in the preliminary communication of this work. ^{d} Abbreviations: s, singlet; m, multiplet; t, triplet; d, doublet; b, broad (unresolved multiplet).

cold (−78 °C) toluene–hexane mixture gave an analytically pure sample of VI, L = (CH₃)₃CNC, in 70% yield.

The other isocyanide derivatives of VI (with L = CH₃CH₂CH₂NC, (CH₃)₂CHNC, (CH₃)₂NCH₂CH₂CH₂NC, and C₆H₅NC) were prepared by essentially the same procedure.

Select data pertaining to the characterization of the new complexes are furnished in Tables I–III.

Preparation of Bis[(dialkylamino)difluorophosphine](η^1-N-pyrrolyl)(η^5-cyclopentadienyl)iron Derivatives (VI). VI, L =
(CH₃)₂NPF₂. Azaferrocene (0.86 g, 4.6 mmol), (dimethylamino)-difluorophosphine (1.5 g, 15.1 mmol), and benzene (10 mL) were placed in a glass reactor, which was cooled to −198 °C, evacuated, and sealed. The reaction mixture was warmed slowly to 70 °C, at which temperature it was left to stir for 2 h. After completion, the reaction mixture was left to reach ambient temperature, and both the solvent and excess (CH₃)₂NPF₂ were removed under reduced pressure [35 °C (0.2 torr)]. The dry crude product was extracted with pentane, and the pentane extracts were combined, reduced in

Table III. Intensities (I) and Relative Currents (RC) of Group Ions with Intact Ligands in the Mass Spectra (at 70 eV) of Some (η^1-N-Pyrrolyl)iron Derivatives of the Type (η^5-C_5H_5)FeL$_2$(η^1-NC$_4$H$_4$)

ion[a]	L = (CH$_3$)$_3$CNC m/z	%I	L = CH$_3$CH$_2$CH$_2$NC m/z	%I	L = (CH$_3$)$_2$CHNC m/z	%I	L = (CH$_3$)$_2$NPF$_2$ m/z	%I	L = (C$_2$H$_5$)$_2$NPF$_2$ m/z	%I
CpPyFeL$_2$$^+$	353	15	325	12	325	9	413	42	469	5
CpFeL$_2$$^+$	287	9	259	2	259	6	347		403	
PyFeL$^+$	205	6	191	1	191	1	235		263	
CpFeL$^+$	204	10	190	4	190	10	234	3	262	
CpPyFe$^+$	187	100	187	100	187	100	187	100	187	100
PyFe$^+$	122	11	122	6	122	7	122	5	122	6
CpFe$^+$	121	95	121	98	121	86	121	99	121	91
Fe$^+$	56	18	56	43	56	38	56	27	56	25

group ions[c]	% RC[b] L = (CH$_3$)$_3$CNC	L = CH$_3$CH$_2$CH$_2$NC	L = (CH$_3$)$_2$CHNC	L = (CH$_3$)$_2$NPF$_2$	L = (C$_2$H$_5$)$_2$NPF$_2$
CpFe containing	87	81	82	88	86
PyFe containing	50	45	46	53	49
FeL containing	15	7	10	16	2

[a] Cp = η^5-C$_5$H$_5$; Py = η^5-C$_4$H$_4$N. The absence of PyFeL$_2$$^+$ and the presence of PyFeL$^+$ and PyFe$^+$ were confirmed by examining peaks of ions due to some minor naturally occurring isotopes, especially ^{13}C, ^{54}Fe, and ^{57}Fe. [b] Computed from ($\Sigma I_i/I_t$) × 100, where ΣI_i is the sum of intensities of the group ions type i, and I_t is the total sum of intensities of all of the ions with intact ligands in each spectrum. [c] Average RC values: CpFe (85%); PyFe (49%); FeL (10%).

volume on a rotary evaporator [25 °C (30 torr)], and cooled to −78 °C to afford the desired product VI, L = (CH$_3$)$_2$NPF$_2$ in 80% yield.

The related derivative VI, L = (C$_2$H$_5$)$_2$NPF$_2$, was prepared by essentially the same procedure.

Selected data pertaining to the characterization of the new complexes are furnished in Tables I–III.

Preparation of (η^6-Arene)(η^5-cyclopentadienyl)iron Tetrafluoroborate Cationic Complexes (VII). [(η^6-C$_6$H$_6$)(η^5-C$_5$H$_5$)Fe]$^+$BF$_4^-$. Azaferrocene (0.39 g, 2.08 mmol) and aluminum chloride (0.43 g, 3.23 mmol) in benzene (80 mL) were stirred and refluxed for a period of 2 h. The solvent was removed under low pressure [25 °C (0.1 torr)] and the dry residue treated with a methanolic solution (35 mL) containing sodium tetrafluoroborate (0.5 g, 4.54 mmol). The yellow solid obtained after the evaporation of the methanol was extracted with CH$_2$Cl$_2$, the extracts were combined and reduced in volume, and the desired product, [(η^6-C$_6$H$_6$)(η^5-C$_5$H$_5$)Fe]$^+$BF$_4^-$, was precipitated by the addition of benzene. A pure sample of this complex was obtained by recrystallization from a benzene–acetone mixture. The product, obtained in 30% yield, was characterized by its melting point (mp 174–175 °C) and ^{1}H NMR spectrum [(acetone-d_6) τ 3.48 (6 H, s) and 4.72 (5 H, s)], which are essentially identical with those reported for the original complex.[14]

The other arene derivatives of type VII were prepared under thermal conditions (80–90 °C) by essentially the same procedure. These products were characterized by comparison with the original complexes.[14]

VII, toluene: 50% yield; mp 159–161 °C; ^{1}H NMR (acetone-d_6) τ 3.62 (5 H, s), 4.83 (5 H, s), and 7.45 (3 H, s).

VII, m-xylene: 55% yield; mp 168–170 °C; ^{1}H NMR (acetone-d_6) τ 3.71 (4 H, s), 4.90 (5 H, s), and 7.48 (6 H, s).

VII, p-xylene: 57% yield; mp 192–195 °C; ^{1}H NMR (acetone-d_6) τ 3.65 (4 H, s), 4.88 (5 H, s), and 7.48 (6 H, s).

VII, mesitylene: 80% yield; mp 207–210 °C; ^{1}H NMR (acetone-d_6) τ 3.74 (3 H, s), 4.96 (5 H, s), and 7.50 (9 H, s).

Attempted Synthesis of VI, L = Ph$_3$P, Ph$_3$As, Ph$_2$MeP, and Me$_2$PhP. Azaferrocene ($\sim$2 mmol) and the appropriate tertiary phosphine ($\sim$5 mmol) were heated (40–80 °C) in benzene (50 mL) for periods of 2–24 h. The reaction mixture was filtered off, and the filtrate was checked for products. Products identified in the filtrate were unreacted tertiary phosphine, some azaferrocene, and ferrocene. The products were separated on a neutral alumina column.

Thermal Decomposition of Azaferrocene. Azaferrocene (0.23 g, 1.23 mmol) in benzene (30 mL) was refluxed for a period of 12 h. The black precipitate formed was filtered off, and the filtrate was chromatographed on a neutral alumina column. Ferrocene (0.06 g) was eluted with a 1:2 (v/v) benzene–hexane mixture, while unreacted azaferrocene (0.074 g) was eluted with ether. On the basis of the
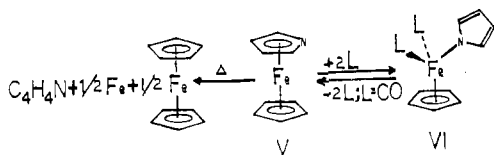
(14) Khand, I. U.; Pauson, P. L.; Watts, W. E. *J. Chem. Soc. C* **1968**, 2257 and pertinent references therein.

amount of azaferrocene that decomposed (0.156 g, 0.83 mmol), ferrocene is formed in about 39% yield.

Carbonylation of Azaferrocene. Azaferrocene (0.43 g, 2.3 mmol) in benzene (20 mL) was placed in a glass reactor. The reaction vessel was cooled (−78 °C) and then degassed under vacuum. The evacuated reaction vessel was filled with carbon monoxide, whose pressure was kept constant at 2.5 atm. The stirred reaction mixture was warmed to 50 °C for a period of 2 h. The initially orange solution turned deep red upon reaction with carbon monoxide; this occurred in the absence of any detectable precipitation, which normally signifies decomposition in this system. The infrared spectrum of the product mixture shows ν(CO) at 2020 and 1975 cm^{-1}, consistent with that of VI, L = CO.[7] ^{1}H NMR analysis of the products mixture indicates a near-equimolar ratio of azaferrocene and VI, L = CO; this corresponds to a 50% carbonylation yield.

Results and Discussion

The chemical and spectroscopic properties of azaferrocene (V) and some of its derivatives provide interesting information concerning the relationship between the π-pyrrolyl and π-cyclopentadienyl ligands. At the outset, a few remarks may be warranted concerning the comparison between ferrocene and its nearest heteroatom analogue azaferrocene (V). In sharp contrast with the pronounced stability of ferrocene, azaferrocene has been observed to thermally degrade to ferrocene and metallic iron. For instance, in boiling benzene for 12 h approximately 67% of V decomposes, to afford ferrocene in $\sim$39% yield. Under more rigorous thermal conditions, in boiling toluene, V decomposes nearly completely within 2 h. Recognition of this decomposition process is of importance with regard to both the synthesis of V and the understanding of its chemical reactions. According to the original procedure of Pauson et al.,[1b,7] the synthesis of V by the decarbonylation of the (η^1-N-pyrrolyl)iron complex VI, L = CO, affords better results if carried out under mild thermal conditions ($\sim$60 °C). Reactions of V that are carried out under thermal conditions invariably afford either small or significant amounts of ferrocene. The extent of ferrocene formation can be minimized by the choosing of mild thermal conditions or, alternatively, limiting the duration of reactions carried out under somewhat more rigorous conditions.

Azaferrocene (V) undergoes carbonylation to VI, L = CO, in benzene at 50 °C under a carbon monoxide pressure of 2.5 atm. This reaction, which is $\sim$50% completed in 2 h, involves a $\pi \rightarrow \sigma$ rearrangement of the pyrrolyl ligand. The carbonylation of V and the decarbonylation of VI, L = CO, constitute a reversible process, in which the equilibrium concen-
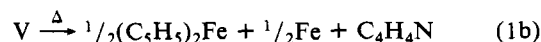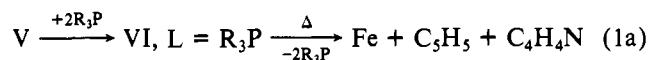
$$C_4H_4N+\tfrac{1}{2}Fe+\tfrac{1}{2}Fe \xleftarrow{\;\;\Delta\;\;} Fe \xrightarrow[-2L;L=CO]{+2L} Fe$$

$$V \qquad\qquad VI$$

tration ratio [VI, L = CO]/[V] should be proportional to P_{CO}^2. In general, the $\pi \rightarrow \sigma$ rearrangment of the η^5-pyrrolyl ligand in V has been shown to be effected by a variety of π-acidic ligands such as CO, PF_3, R_2NPF_2 (R = CH_3, C_2H_5), CH_3N-$(PF_2)_2$, t-C_4H_9NC, $CH_3CH_2CH_2NC$, $(CH_3)_2CHNC$, $(CH_3)_2NCH_2CH_2NC$, and C_6H_5NC. Selected data pertaining to the characterization of certain new VI derivatives and information concerning their NMR (^1H, ^{13}C, and ^{19}F) and mass spectral properties are furnished in Tables I–III. The derivatives of VI are easily prepared and purified with the exception of the complexes L = PF_3 and $CH_3N(PF_2)_2$, where we have encountered difficulties in the purification of the samples. The new complexes can be handled briefly (several hours) in air with no apparent decomposition. During a longer exposure to air at ambient temperature most of these complexes slowly decompose. These complexes can be preserved for a long period of time (several years) when sealed under argon and kept below 0 °C.

The spectroscopic properties of the new $(\eta^1$-N-pyrrolyl)iron derivatives VI are consistent with their assigned structures. The two strong $\nu(NC)$ stretching frequencies found in the IR spectra of the VI, L = RNC, derivatives are the expected A′ and A″ active modes in a system having an approximate C_s local symmetry. These bands appear in the region (Table I) assigned to terminal isocyanide ligands. Strong to very strong bands found in the 700–850-cm^{-1} region of the IR spectra of the VI, L = R_2NPF_2, derivatives are characteristic of the P–F stretching frequencies. Both the ^1H and ^{13}C NMR spectra of the VI derivatives are presented and analyzed in Table II. Specially interesting are the ^{13}C NMR spectra, which reveal large differences between V and VI. The η^1-N-pyrrolyl carbon atoms in VI are greatly deshielded as compared with the respective carbon atoms of the η^5-pyrrolyl ligand in azaferrocene (V). A much smaller deshielding effect has been observed for the cyclopentadienyl carbon atoms in VI as compared with that of V. The analogy between the various VI derivatives is also quite apparent from their similar ^1H NMR spectra. The respective H(α) and H(β) protons in VI resonate at similar fields and are significantly deshielded as compared with the nuclei of azaferrocene. Noteworthy is the ^1H NMR spectrum of azaferrocene in D_2O, which shows shifts downfield from those found in the spectrum taken in $CDCl_3$. These shifts of 0.09 [H(α)], 0.27 [H(β)], and 0.18 ppm (C_5H_5) may be attributed to solvent effects rather than to the protonation of the basic site in azaferrocene. Protonation would have been expected to result in greater downfield shifts as compared to those observed. The ^{19}F NMR chemical shifts ($\delta_F^{Freon-11}$ 29.4 and 28.8) and coupling constants [J(P–F) = 1231 and 1213 Hz] found in the spectra of the VI, L = $(CH_3)_2NPF_2$ and $(C_2H_5)_2NPF_2$, derivatives are in agreement with available data of such coordinated ligands.[15]

The mass spectra of azaferrocene[16–18] and tricarbonyl(η^5-pyrrolyl)manganese[19] have already been reported. It is therefore of interest to compare the mass spectra of the (η^1-N-pyrrolyl)iron derivatives (VI) with those of the (η^5-pyrrolyl)metal complexes. Most of the ion currents in the mass spectra of VI arise from the presence of metal-containing ions

with intact ligands and the "bare" iron ions (Table III). Under electron-impact conditions, the most facile fragmentation sequence of the molecular ions in VI involves the elimination of 2L [L = $(CH_3)_3CNC$, $CH_3CH_2CH_2NC$, $(CH_3)_2CHNC$, $(CH_3)_2NPF_2$, and $(C_2H_5)_2NPF_2$] to afford azaferrocenium (m/z 187). Ions of the types $CpFeL_2^+$, $PyFeL^+$, and $CpFeL^+$ (abbreviations: Cp = η^5-C_5H_5; Py = η^5-C_4H_4N), are found in low abundances in some of the spectra (Table III). This observation implies that the cleavage of the cyclopentadienyl or pyrrolyl prior to the L ligands, though possible, is of a rather low probability. The decay of azaferrocenium to "bare" iron ions proceeds via a two-step sequence of pyrrolyl elimination and decyclopentadienylation as was originally reported[16] for azaferrocene. The formation of metal-containing ions with partial ligands is also evident from the mass spectra of VI. Though not listed in Table III, such ions originate, primarily, from azaferrocenium by processes analogous to those that were already characterized from the mass spectrum of azaferrocene.[16] Relative currents (RC) of group ions in the mass spectra of certain organometallic complexes were shown[20] to provide useful information concerning the relative order of metal-to-ligand ionic bond dissociation energy. According to this approach, the RC of the CpFe-, PyFe-, and FeL-containing group ions present in the mass spectra of VI were computed and compared (Table III). The results of this treatment suggest a relative bond strength order Cp > Py > L. The ratio RC(PyFe)/RC(CpFe) $\approx$ 0.58 should reflect the greater probability of cleavage of the Py–Fe$^+$ than the Cp–Fe$^+$ bond in the fragment ions generated under electron-impact conditions. Despite some relative differences, both ligands in azaferrocenium are expected to be rather strongly bonded to the central iron atom, and this is supported by both appearance potential and ion intensity data. Azaferrocenium (m/z 187) is the base peak in the mass spectra of V and VI; this may reflect upon its unusual stability. The ionization potential of azaferrocene (IP, 7.17 ± 0.1 eV)[18] and the appearance potential (AP) of CpFe$^+$ in its spectrum (AP, 12.6 ± 0.2 eV)[18] are similar, with one exception, to those reported for ferrocene (IP, 6.99 ± 0.1,[21] 7.05 ± 0.1;[22] AP, 12.8 ± 1.0,[21] 14.38 ± 0.3[22] eV). On the basis of the average data, the [Py–FeCp]$^+$ ionic bond dissociation in azaferrocenium can be estimated to be some 20% lower than that of [Cp–FeCp]$^+$ in ferrocenium. This conclusion is consistent with the presence of strongly bonded η^5-pyrrolyl and η^5-cyclopentadienyl ligands in azaferrocenium, with the latter metal-to-ligand bond being of a somewhat greater strength.

The $\pi \rightarrow \sigma$ rearrangement of the pyrrolyl ligand in V only takes place in the presence of π-acidic ligands. Attempts to effect similar reactions with σ-donor ligands such as Ph_3P, Ph_3As, Ph_2MeP, and Me_2PhP invariably resulted in an extensive decomposition of the starting iron complex to "bare" iron metal and some ferrocene. The amounts of ferrocene formed in these reactions have been found to be significantly smaller than those obtained under similar thermal conditions but in the absence of the σ-donor ligands. The accelerated decomposition of V (eq 1a) in the presence of σ-donor ligands

$$V \xrightarrow{+2R_3P} VI, L = R_3P \xrightarrow[-2R_3P]{\Delta} Fe + C_5H_5 + C_4H_4N \quad (1a)$$

$$V \xrightarrow{\Delta} {}^1/_2(C_5H_5)_2Fe + {}^1/_2Fe + C_4H_4N \quad (1b)$$

may be explained by the formation of labile intermediates of the type VI, L = R_3P, which then degrade further to "bare" iron and the free ligands. The thermal degradation of V (eq

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Table IV. Change in the ^{13}C Chemical Shifts on Complexation of the Pyrrolide and Cyclopentadienide Anions

	$\Delta\delta_C$(pyrrolyl)^a			
	C(α)	C(β)	C(α and β)^c	$\Delta\delta_C(\eta^5\text{-}C_5H_5)^b$
η^5-Pyrrolyl and/or η^5-Cyclopentadienyl				
(η^5-C$_5$H$_5$)Fe(η^5-C$_4$H$_4$N)	37.2	34.0	35.6	34.3
(η^5-C$_5$H$_5$)Fe[η^5-C$_4$H$_3$(2-CH$_3$)N]	32.8 (C-2)	33.8 (C-3)	35.1	33.8
	38.2 (C-5)	35.6 (C-4)		
(η^5-C$_5$H$_5$)Fe[η^5-C$_4$H$_2$(2,5-(CH$_3$)$_2$)N]	33.7	36.8	35.2	34.0
(η^5-C$_5$H$_5$)$_2$Fe				32.9,^{d} 35.1^e
(η^5-C$_4$H$_4$N)Mn(CO)$_3$	20.3^e	20.1^e	20.2	
(η^5-C$_5$H$_5$)Mn(CO)$_3$				27.0,^{d} 19.9^e
(η^5-C$_5$H$_5$)FeL$_2$(η^1-NC$_4$H$_4$)^f				
L = (CH$_3$)$_3$CNC	−8.1 [−16.7]	−0.5 [1.1]		22.5
L = CH$_3$CH$_2$CH$_2$NC	−8.1 [−16.7]	−0.8 [0.8]		22.6
L = (CH$_3$)$_2$CHNC	−8.0 [−16.6]	−0.7 [0.9]		22.4
L = (CH$_3$)$_2$N(CH$_2$)$_3$NC	−8.0 [−16.6]	−1.0 [0.6]		22.6
L = (CH$_3$)$_2$NPF$_2$	−8.6 [−17.2]	−2.6 [−1.0]		21.9
L = (C$_2$H$_5$)$_2$NPF$_2$	−8.4 [−17.0]	−2.4 [−0.8]		22.2

^{a} $\delta_{C(i)}^{Me_4Si}$(pyrrolide anion) − $\delta_{C(i)}^{Me_4Si}(\eta^5$-pyrrolyl). Data for the 2-methyl- and 2,5-dimethylpyrrolide anions were computed from the chemical shifts of the respective free pyrroles^{27c} by invoking known additivity relationships.^{29} The parameters used are 8.6 [C(α)] and −1.6 ppm [C(β)]. ^{b} 103 − $\delta_C^{Me_4Si}(\eta^5$-cyclopentadienyl). The value of 103 ppm is that for C$_5$H$_5$Na.^{30} ^{c} Average value of all of the co-ordinated carbon nuclei. ^{d} On the basis of the data by Lauterbur and King.^{31} ^{e} On the basis of the data by Nesmeyanov et al.^{26} ^{f} Data in brackets pertains to free pyrrole: $\delta_{C(i)}^{Me_4Si}$(free pyrrole) − $\delta_{C(i)}^{Me_4Si}[(\eta^1$-N-pyrrolyl)iron].

1b) and its decomposition in the presence of σ-donor ligands do not necessarily proceed by the same mechanism. Due to the presence of a basic nitrogen atom in azaferrocene,^{1b} a plausible bimolecular mechanism to explain its thermal degradation to ferrocene may be suggested to involve intermediates of the types VIII, IX, and X. In this autodecomposition
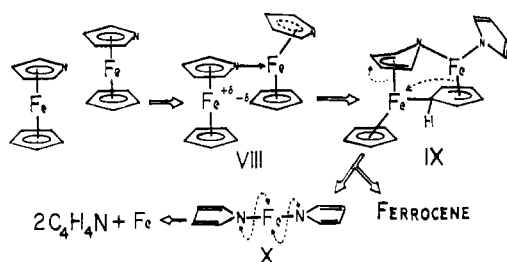
process, the σ-coordination bond in VIII is thought to facilitate the C$_5$H$_5$ ligand transfer^{23} by the enhancement of the electrophilicity of the iron atom and the nucleophilicity of the cyclopentadienyl ligand. Initiation of the ligand transfer by the creation of a C−Fe bond as in IX, followed by a stepwise transfer process, would explain the formation of ferrocene in 50% yield or less. Homolytic cleavage of X may account for the formation of "bare" iron metal in this reaction.

By analogy with ferrocene, azaferrocene (V) has been observed to react with aromatic solvent in the presence of aluminum chloride at 80–90 °C to afford known cationic complexes of the type (η^6-arene)(η^5-cyclopentadienyl)iron(1+), which were isolated in the form of the tetrafluoroborate salts VII. These complexes were characterized by their ^{1}H NMR spectra and melting points which were compared with those of authentic samples.^{14} The possibility that the VII complexes are formed indirectly from ferrocene, rather than V, can be ruled out on several grounds. Under the thermal conditions employed in this synthesis, a 2-h reaction could have resulted, at best, in several percent (3–5%) degradation of V to ferrocene. The lowest yield of formation of a VII derivative (30%; arene = benzene) would have necessitated a ~60% degradation of V in order to account for the formation of the product from ferrocene. The extent of decomposition of V during the formation of VII has been judged to be relatively small also on the basis of the "bare" iron metal precipitate formed during these reactions. Other reasonable products anticipated from

these reactions are the cationic complexes (η^6-arene)(η^5-pyrrolyl)iron(1+) tetrafluoroborate(1−) (XI). The ^{1}H NMR
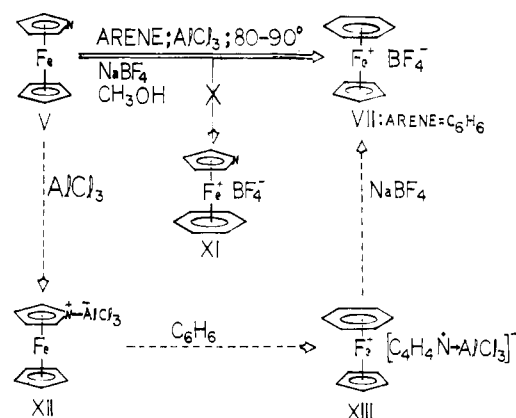

spectra of the reaction products unequivocally rule out the presence of even trace amounts of such complexes. In the absence of XI, it would be pertinent to point out the exclusive exchange of η^5-pyrrolyl by η^6-arene during the course of these reactions. This exchange does not necessarily imply a weaker iron to η^5-pyrrolyl than to η^5-cyclopentadienyl bond in the parent azaferrocene complex. Under the conditions of these ligand-exchange reactions, labilization of the η^5-pyrrolyl ligand in V most probably occurs by the formation of an aza-ferrocene–AlCl$_3$ adduct of the type XII. A subsequent reaction of XII with the arene is envisaged to result in the preferential exchange of the pyrrolyl ligand to afford XIII, which is then solvolyzed in the presence of NaBF$_4$ to give VII. This is probably another example in which the course of a reaction is dictated by the basic properties of azaferrocene. Viewed in a wider context, the formation of plausible intermediates of the type XII, and alike, may explain the failure to effect electrophilic substitution reactions with azaferrocene.^{1b} A preferential attack by electrophiles at the basic nitrogen site in azaferrocene will most probably weaken the pyrrolyl to iron bond and thus accelerate decomposition. Attempts to effect electrophilic substitutions with azaferrocene, similar to those reported with ferrocene,^{24} have resulted in the extensive decomposition of the starting complex.^{25}

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In an attempt to ascertain bonding effects in (η^1-*N*-pyrrolyl)- and (η^5-pyrrolyl)metal complexes, the ^{13}C NMR spectra of the relevant complexes were examined and compared with those of the free ligands and certain analogous (η^5-cyclopentadienyl)metal derivatives. In general, substantial shielding effects are produced on π complexation of olefinic ligands,[26] and this has been attributed to an increase in the electron density at the ligand nuclei sites during such bonding interactions. Therefore, a comparison between the ^{13}C NMR chemical shifts of free and π-complexed ligands provides a useful qualitative measure of the extensiveness of the π-bonding interactions in various π complexes. Upfield chemical shifts created by the η^5-complexation of certain pyrrolide ions (e.g., $C_4H_4N^-$, 2-$CH_3C_4H_3N^-$, and 2,5-$(CH_3)_2C_4H_2N^-$) and cyclopentadienide ($C_5H_5^-$) are listed in Table IV. This table also provides information concerning the differences in the ^{13}C NMR chemical shifts between the pyrrolide anion (or free pyrrole)[27a] and certain (η^1-*N*-pyrrolyl)iron derivatives of the type VI. The chemical shifts of the substituted pyrrolide anions 2-$CH_3C_4H_3N^-$ and 2,5-$(CH_3)_2C_4H_2N^-$ were calculated from those of the respective substituted pyrroles[26b,28] by invoking the additivity relationship described by Pugmire and Grant.[27c,29] The chemical shift of the cyclopentadienide carbon nuclei used in calculating $\Delta\delta_C$(η^5-C_5H_5) was 103[30] rather than 108[26] or 109.5 ppm.[31]

On the basis of the information furnished in Table IV, the average increase in the shielding of the C(α) and C(β) pyrrolide anion nuclei on π complexation to azaferrocene corresponds to 35.6 ppm. Similar values have also been found for the π complexation of the substituted pyrrolide anions 2-$CH_3C_4H_3N^-$ (35.1 ppm) and 2,5-$(CH_3)_2C_4H_2N^-$ (35.2 ppm). Shifts encountered between free pyrrolide anions and η^5-pyrrolyls in azaferrocenes are about the same or slightly larger than those between the cyclopentadienide anion and the η^5-cyclopentadienyl ligand in certain azaferrocenes (34.3, 33.8, and 34.0 ppm) and ferrocene (32.9[31] and 35.1[26] ppm). In contrast with azaferrocenes, significantly smaller shifts have been found for the η^5-pyrrolyl and η^5-cyclopentadienyl ligands in (η^5-C_4H_4N)Mn(CO)$_3$ [C(α), 20.3; C(β), 20.1 ppm][26] and (η^5-C_5H_5)Mn(CO)$_3$ (27.0[31] and 19.9[26] ppm). The results of this comparative study are of interest from several points of view. In reference to azaferrocenes, this study suggests similar π-bonding interactions for the η^5-pyrrolyl and η^5-cyclopentadienyl ligands in the ground-state neutral molecules. Moreover, this π-bonding interaction appears to be of the order found in ferrocene. Comparison between the η^5-pyrrolyl and η^5-cyclopentadienyl ligands in the manganese and iron com-

plexes suggests significantly weaker π-bonding interactions with the former metal. Another noteworthy result relates to the near-identical $\Delta\delta_C$ terms (Table IV) found for (η^5-C_4H_4N)Mn(CO)$_3$ [C(α), 20.3; C(β), 20.1 ppm], which rule out the previously proposed[10] asymmetric bonding model II. Evidently, the longer Mn–C(β) than Mn–C(α) bonds, which were postulated according to this model, should have resulted in the greater shielding of the C(α) nuclei. Such an effect has not been detected from the ^{13}C NMR spectral data.

In contrast with the shielding effect caused by π complexation, the formation of (η^1-*N*-pyrrolyl)iron complexes of the type VI has been observed to cause the deshielding of the C(α) nuclei, whereas the C(β) nuclei remain little affected. Differences between the ^{13}C chemical shifts of the (η^1-*N*-pyrrolyl)iron nuclei in VI and either the pyrrolide anion or the free pyrrole are given in Table IV. While the comparison between π- and σ-pyrrolyl is best examined in reference to the pyrrolide anion, the effects of the metal on the σ-bonded ligand may be ascertained in relationship to free pyrrole. This way, it should be possible to monitor relative effects created by the changing from H–NC$_4$H$_4$ to Fe–η^1-NC$_4$H$_4$. Compared with free pyrrole, the average shifts of C(α) $\approx$ –16.8 and C(β) $\approx$ +0.3 ppm observed for the VI derivatives cannot be explained in terms of either bonding model IV or bonding model III. A plausible bonding model (XIV) which is consistent with both
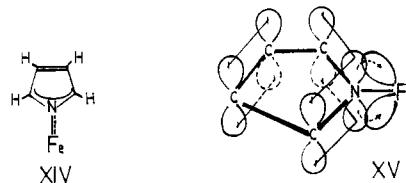
the ^{13}C NMR data and the chemical properties of VI is suggested to consist of localized η^1-*N*-azaallylic and olefinic systems. An extensive pπ(N) $\rightarrow$ dπ(Fe) interaction (XV), by which the π-electron density on the iron is increased, may account for the significant deshielding effects at the C(α) nuclei. Furthermore, this interaction should enhance the π basicity of the iron atom and this is expected to effect the strengthening of bonds with the other π-acidic ligands in VI. The failure to obtain complexes of type VI, where L are σ-ligands, coupled with the pronounced stabilization effect created by the presence of π-acidic ligands in such a system, lends circumstantial support to the above-considered bonding model XIV.

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