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Novel Features in the Chemistry of Azaferrocene: Comparison Between the π-Pyrrolyl and π-Cyclopentadienyl Ligands

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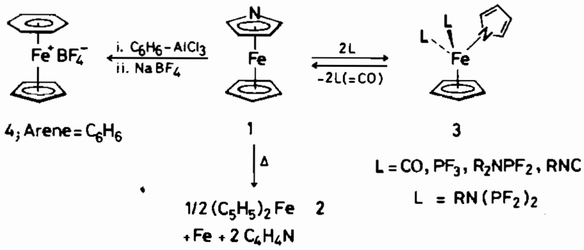
Since the discovery of ferrocene [1] and the recognition of its unique chemical properties [2], much attention has been focused on the study of this novel system. By contrast, the chemistry of its nearest heteroatom analog azaferrocene [3] has not yet been explored in any detail. Comparison of the chemical properties of azaferrocene (*1*) and ferrocene (*2*) was thought to be of fundamental interest, especially with regards to the relationship between the π-pyrrolyl and π-cyclopentadienyl ligands. In this communication we wish to report both different as well as similar features in the chemistry of *1* and *2*.

In contrast with the distinct chemical stability of *2*, the inherent lability of *1* appears to originate from the pyrrolyl ligand. Noteworthy in this context are the reactions of *1* with certain π-acidic ligands which effect the π → σ rearrangement of the pyrrolyl. A typical example of such a reaction is described below.

Treatment of *1* (0.86 g; 4.6 mmol) dissolved in benzene (10 ml) with $(CH_3)_2NPF_2$ (1.5 g; 15.1 mmol) in an evacuated glass tube at 70 °C for 2 hr gave, after separation, the red crystalline complex *3*; L = $(CH_3)_2NPF_2$ [m.p., 86 °C] in 40% yield. *Anal.* Calcd. for $C_{13}H_{21}N_3F_4P_2Fe$: C, 37.80; H, 5.12; N, 10.17; Mol. Wt., 413. Found: C, 37.92; H, 5.26; N, 10.16; Mol. Wt., 413 (Mass spect.). IR in $CHCl_3$; strong ν(P–F) absorptions in the 710–842 cm^{-1} region. ^1H NMR in $CDCl_3$: τ 3.70(2H, m); 3.93(2H, m); 5.41(5H, s); 7.34(12H, broad). ^{13}C NMR in $CDCl_3$: δ 35.9(m); 81.1(s); 109.2(s); 135.8(s). ^{19}F NMR in $CDCl_3$: δ (relative to Freon) 22.1(m); 36.7(m) [J(P–F) = 1230 Hz].

The facile π → σ rearrangement of the pyrrolyl in *1* was shown to be effected by a variety of π-acidic ligands including CO, PF_3, R_2NPF_2 (R = CH_3, C_2H_5), $CH_3N(PF_2)_2$, C_6H_5NC, t-C_4H_9NC, $CH_3CH_2CH_2NC$, and $(CH_3)_2NCH_2CH_2CH_2NC$. New complexes of the type *3* prepared during the course of this investigation were fully characterized. The known carbonyl analog *3*; L = CO was characterized by comparison with an authentic sample [4]. Azaferrocene has been observed to disproportionate to ferracene under thermal conditions. For example, in boiling toluene *1* degrades completely within 2 hrs, whereas in refluxing benzene for 12 hr approximately half of the starting complex converts to *2*. In contrast with π-acidic ligands, the reactions of *1* with σ-donor ligands of the type Ph_3M (M = P, As, Sb) have been noticed to only accelerate the conversion of *1* to *2*. In analogy with ferrocene, azaferrocene reacts with boiling aromatic solvents in the presence of two-fold excess $AlCl_3$ to afford known cations [5] of the type $[(\pi\text{-}C_5H_5)Fe(\pi\text{-Arene})]^+$; isolated in the form of the tetrafluoroborate salts (*4*) in yields of 30% (benzene), 50% (toluene), 55% (*m*-xylene), 57% (*p*-xylene) and 80% (mesitylene). In the absence of products type $[(\pi\text{-Pyrrolyl})Fe(\pi\text{-Arene})]^+$, this reaction appears to exclusively involve the more weakly bonded pyrrolyl ligand.



Significant information concerning the bonding of pyrrolyl in *1* and *3* has been obtained from the ^{13}C NMR spectra of these complexes. The spectrum of *1*, in $CDCl_3$, exhibits singlets at δ 68.7 (C_5H_5), 72.6 (pyrrolyl β carbons), and 90.0 (pyrrolyl α carbons). The chemical shifts of the C_5-rings in *1* and *2* differ by 0.8 ppm; the π-pyrrolyl in *1* appears to exert only a slight deshielding effect. In general, substantial shielding effects have been noted on π-complexation of unsaturated ligands, and this was attributed to an increase in the electron density at the carbon sites due to extensive back-bonding interaction [6] (*e.g.*, upfield shift of 40 ppm is recorded on moving from cyclopentadienide to ferrocene). Compared with free pyrrole [7], the upfield shifts of the α and β carbon atoms of the π-pyrrolyl in *1* are 28.4 and 35.6 ppm, respectively. These shifts are expected to be somewhat smaller (2–4 ppm) if comparison could be made with the pyrrolide anion, for which data is not available. The foregoing considerations suggest that the cyclopentadienyl in *1* is more strongly π-bonded than is the pyrrolyl ligand. This conclusion appears to be consistent with the above discussed chemical properties of azaferrocene.

In sharp contrast with *1*, the ^{13}C NMR spectrum of the N-bonded σ-pyrrolyl (*e.g.*, *4*, L = $(CH_3)_2NPF_2$) shows chemical shift changes of −14.6 (downfield) and 1.7 ppm for the α and β carbon atoms, respectively, as compared with those of free pyrrole.

These results suggest a substantial decrease in the electron density at the carbon sites, whereas the β carbon atoms seem to experience a rather slight increase in density. Extensive withdrawal of electron density from the α position can be explained by a strong (N)pπ → (Fe)dπ interaction. An increase in the dπ density at the iron site according to this mechanism is expected to effect further strengthening of bonding to the π-acidic ligands in *3*. In fact, the relative stability displayed by these complexes is perhaps a manifestation of the above considered bond strengthening effect.

Azaferrocene exhibits considerable solubility in water, and its ^{1}H NMR spectrum, in D_2O relative to $(CH_3)_3SiCD_2CD_2COO^-Na^+$, shows singlets at τ 4.65(2H), 5.28(2H), and 5.38(5H). Compared with the spectrum in $CDCl_3$, the most pronounced change is the downfield shift (~0.5 ppm) of the cyclopentadienyl protons. The aqueous chemistry of azaferrocene and some of its derivatives is currently under investigation.

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