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Preliminary communication

METALLATION OF AZAFERROCENE

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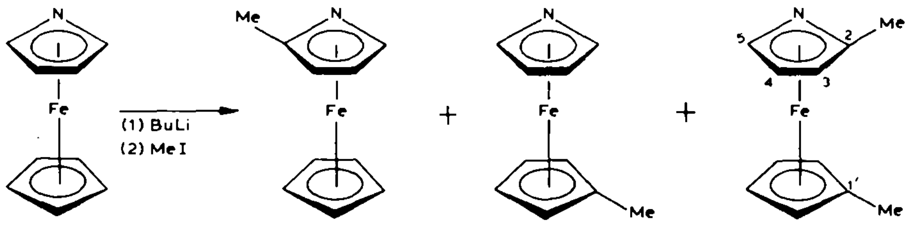
Summary

The first substitution reactions in azaferrocene have been found to be metallation with n-butyllithium. Substitution of hydrogen for lithium occurs both in the cyclopentadienyl and pyrrolyl (α-position) ligands of the complex at comparable rates.

Nearly two decades have elapsed since azaferrocene (I) was prepared for the first time [1] but knowledge about its reactivity is still very limited and extends only to reactions involving breaking of the π-bond between the pyrrolyl ligand and the iron atom [2,3]. No data are available on substitution reactions in this complex*.

We have found that I is readily metallated with n-butyllithium in THF solution at −50°C. Reaction of I with a double excess of BuLi for 2 h, followed by treatment with MeI, leads to a mixture of methylazaferrocenes II—IV as a viscous red-colored oil in a total yield close to the theoretical value.



(I) (II) (III) (IV)

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*In one of the early works there was mention of unsuccessful attempts to carry out electrophilic substitution of azaferrocene [4].

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Unfortunately, it is impossible to separate these products chromatographically because their R_F values are very close to each other. Fractional distillation is also difficult. Nevertheless, using the NMR technique we have been able to identify each of the compounds II—IV. In the ^{1}H NMR spectrum*, 2-methylazaferrocene (II) gave the signals (δ): 2.244 (3H, H(Me)), 4.152 (5H, H(Cp)), 4.377 (1H, H(3)), 4.398 (1H, H(4)) and 5.220 (1H, H(5)); 1′-methylazaferrocene (III) gave: 1.936 (3H, H(Me)), 4.087 (2H, H(2′,5′)), 4.117 (2H, H(3′,4′)), 4.447 (2H, H(3,4)) and 5.290 (2H, H(2,5)) ppm; and dimethylazaferrocene (IV) gave: 1.918 (3H, H(1′-Me)), 2.219 (3H, H(2-Me)), 4.020 (4H, H(Cp)), 4.310 (2H, H(3,4)) and 5.166 (1H, H(5)) ppm**. These results show that under these experimental conditions both the cyclopentadienyl and pyrrolyl ligands of I are lithiated, but only α-hydrogen is substituted in the latter; substitution of the second H-atom takes place in the unsubstituted ligand and yields a heteroannular dilithium derivative of I. On the basis of the ratio of integral intensities of methyl signals in the ^{1}H NMR spectrum, we evaluated the concentrations of each of the compounds II—IV in the mixture. The mixture was found to contain 49% II, 36% III and 15% IV. Interestingly, the reaction of I with BuLi, carried out for a period of 15 minutes under the same conditions and followed by treatment with MeI, produces a mixture consisting only of the monomethyl isomers II and III (with theoretical yields) in the same ratio as in the previous case. What can be concluded from this is that both the pyrrolyl and cyclopentadienyl ligands in I are metallated rapidly (the first one the more rapidly), and the yield of product equals the theoretical amount for the equilibrium mixture of monolithiated isomers of I. Longer reaction times favor formation of dilithiated I, probably, owing to further metallation of both isomers at close rates.

It is noteworthy that 2-methylazaferrocene (II) had been obtained earlier, then by reaction of the potassium salt of 2-methylpyrrol with CpFe(CO)$_2$I [5]. The ^{1}H NMR parameters given above for II agree with those reported in the literature. In the mass spectrum of the mixture of II—IV there are contributions from two molecular ions at *m/e* 215 and 201, corresponding to di- and monomethyl derivatives of IV and II+III, as well as of the fragment ions (Me$_5$C$_5$H$_4$Fe)$^+$ (135) and (CpFe)$^+$ (121).

Similar results were obtained when a mixture of lithiated azaferrocenes was treated with D$_2$O or Me$_3$SiCl. However, the obtained mono-substituted trimethylsilylazaferrocenes were unstable, brown-colored oils which decomposed into the corresponding ferrocenes as soon as they were separated. They were identified according to their mass spectra: $(M)^+$ (259), $(M-\text{Me})^+$ (244). Di-substituted trimethylsilylazaferrocene (V) is more stable and we have been able to obtain it as an orange oil. The ^{1}H NMR spectrum of V shows the following signals: 0.249 (s, 9H, H(1′-SiMe$_3$)), 0.361 (s, 9H, H(2-SiMe$_3$)), 4.141 (t, J 1.22 Hz, 2H, H(2′,5′)), 4.277 (t, J 1.22 Hz, 2H, H(3′,4′)), 4.513 (d, $J_{3,4}$ 2.44 Hz, 1H, H(3)), 4.676 (dd, $J_{4,3}$ 2.44 Hz, $J_{4,5}$ 0.61 Hz, 1H, H(4)) and 5.649 (s, 1H, H(5))

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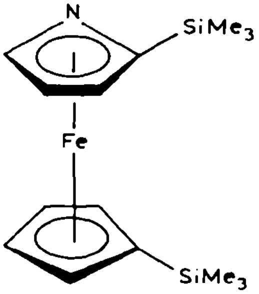
*The NMR spectra were taken in CDCl$_3$ with a Bruker-WP-200-SY instrument (200.13 MHz).

**The presence of minor amounts of paramagnetic impurities caused signal broadening and hampered determination of the spin—spin interaction constants.

ppm. In the mass spectrum of V there are peaks due to molecular $(M)^+$ (331) and fragment $(M-\text{Me})^+$ (316) ions.



(V)

The aim of our further research will be to determine the conditions under which selective lithiation of azaferrocene takes place.

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