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Preliminary Communication

Deprotonation of decamethylferrocenium cation — new approach to alkyl group functionalization in transition metal complexes

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Abstract

Deprotonation of decamethylferrocenium tetrafluorborate (20°C, THF, ^tBuOK or $^iPr_2NH$, Et_3N) proceeds via intermediate formation of nonamethylferrocenylmethyl radical and results in the products of butoxylation and amination of methyl groups.

The deprotonation of transition metal π-complexes containing acidic hydrogen atoms at α-positions in its substituents has hitherto only been studied for 18-electron complexes [1]. The acidity of such protons and the ease of their deprotonation should be expected to increase on going from 18-electron to 17-electron complexes. In line with these expectations we have begun systematic study of the deprotonation of 17-electron alkyl substituted transition metal sandwich complexes for the purpose of alkyl group functionalization. In this paper we report on the deprotonation of decamethylferrocenium tetrafluorborate $(\mathbf{I}^{+\cdot})BF_4$.

Potassium tert-butoxide, diisopropylamine and triethylamine were used as deprotonating bases. All reactions of $(\mathbf{I}^{+\cdot})BF_4$ with an excess of deprotonating base (two-fold for ^tBuOK and approximately twenty-fold for amines) were carried out in THF at room temperature. Because of the low solubility of $(\mathbf{I}^{+\cdot})BF_4$ in THF the conditions were heterogeneous, but intense stirring was continued during the course of reactions. The dissolution of $(\mathbf{I}^{+\cdot})BF_4$ was taken as indicating completion of the reaction. After removing the volatiles *in vacuo* the reaction products were isolated by reprecipitation from ether by heptane at −10°C. The deprotonation process (Scheme 1) leads to a rather complex mixture of products which are of very similar chromatographic characteristics and solubilities. This restricts the use of 1H NMR spectroscopy for direct determination of the structure and composition of the reaction products. Therefore the most useful information was obtained from FAB mass spectroscopy (KRATOS CONSEPT instrument, energy of bombarding atoms 8 Kev, 2-nitrobenzylic alcohol as a matrix). The appearance of molecular ion peaks (M^+) in mass spectra was taken as the criterion for determination of the composition of the mixture of reaction products.

We believe the deprotonation of $(\mathbf{I}^{+\cdot})BF_4$ to proceed according to Scheme 1. In our opinion the structure of the deprotonation product is best represented as the nonamethylferrocenylmethyl radical $\mathbf{III}^{\cdot}$. This radical can undergo a series of further transformations; abstraction of hydrogen atoms from the medium (i), dimerization (ii) and formation of adduct $\mathbf{III}\cdot B$ ($\mathbf{V}^{\cdot}$) (iii). The further transformation of $\mathbf{V}^{\cdot}$ and the ratio of reaction products are determined by the deprotonating base. In line with Scheme 1 mass spectra of the reaction products should demonstrate M^+ resulting from transformation of **I**, **IV** and the products of adducts $\mathbf{V}^{\cdot}$.

Deprotonation of $(\mathbf{I}^{+\cdot})BF_4$ by potassium tert-butoxide gives a mixture of tert-butoxymethyl(nonamethyl) ferrocene (**VI**, M^+ 398) and decamethyl-ferrocene (**I**, M^+ 326) as the main reaction products. The dimer **IV** is formed in considerably lower yield, the approximate ratio **VI**:**I**:**IV** being 7:6:1. We believe that electron transfer between anion-radical adduct $(\mathbf{VI})^{-\cdot}$ and ferrocenium cation $\mathbf{I}^{+\cdot}$ (Scheme 2) rather than abstraction of hydrogen from the solvent (Scheme 1, i) is mainly responsible for the formation of **I** in this case. Nevertheless the formation of **I** due to partial reduction of $\mathbf{I}^{+\cdot}$ by ^tBuOK cannot be completely excluded. The mass spectrum also showed peaks of low intensity which can be tentatively assigned to products of the introduction of one additional tert-butoxy group in **VI** (**VII**, M^+ 470), and of one (**VIII**, M^+ 722) and two (**IX**, M^+ 794) tert-butoxy groups in dimer **IV** as well as to an ether type dimer $[(C_5Me_5)Fe(C_5Me_4CH_2)]_2O$ (**X**, M^+ 666) and to the product of its butoxylation (**XI**, M^+ 722).

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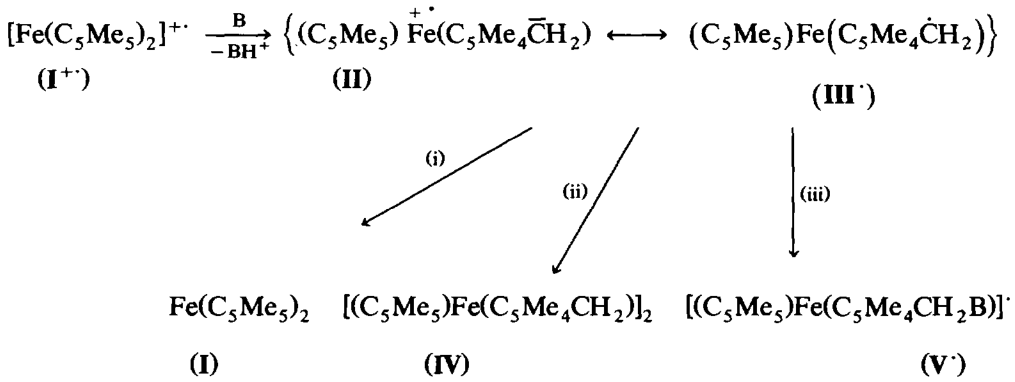


Scheme 1.

$$[(C_5Me_5)Fe(C_5Me_4CH_2O^tBu)]^{-\cdot} + I^{+\cdot} \longrightarrow VI + I$$

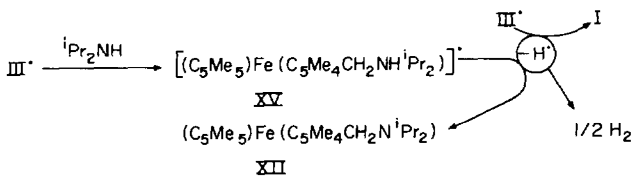
$(VI^{-\cdot})$

Scheme 2.

We believe the formation of **VII–IX** to be caused by the fact that $I^{+\cdot}$ which presents as a solid in reaction mixture can oxidize complexes **VI**, **IV** and **VIII** to corresponding ferrocenium salts which in their turn undergo further deprotonation and butoxylation accordingly to Scheme 1. The complex **XI** is probably formed in the same way from **X**.

The outcome of deprotonation of $I^{+\cdot}$ by amines is determined by the nature of the amine. In the case of $^iPr_2NH$ the products of one-fold (**XII**, M^+ 425), two-fold (**XIII**, M^+ 524) and three-fold (**XIV**, M^+ 623) amination of **I** are mainly produced, whereas the dimer **IV** is not formed. Both the mass spectra data and the solubility of reaction products in ether indicate that ammonium salt $[(C_5Me_5)Fe(C_5Me_4CH_2NH^iPr_2)]^+$ is not formed in this process. The most intensive peak M^+ 325 corresponding to $[(C_5Me_5)Fe(C_5Me_4CH_2)]^+$ is observed in the mass spectrum. Its appearance being thought to result from breakage of the C–N bond in the amination product **XII**. We believe that this amination product is formed according to Scheme 3. Splitting of hydrogen atoms from ammonium radicals of type **XV** is a well established process of their stabilization which results in formation of corresponding amines [2].

In doing so, the hydrogen radical can either dimerize or be caught by the nonamethylferrocenylmethyl radical **III**· to form decamethylferrocene **I**.



Scheme 3.

In the case of triethylamine the decamethylferrocene (**I**) was found to be strongly predominant among the products, and again the formation of dimer **IV** was not observed. In terms of Scheme 1, this means that the predominant transformation of radical **III**· is the abstraction of hydrogen from the medium (Scheme 1, i) since the reduction of $I^{+\cdot}$ by triethylamine is doubtful.

Thus in this paper it has been shown that deprotonation of decamethylferrocenium tetrafluorborate by ^tBuOK or $^iPr_2NH$ results in introduction of ^tBuO- and $^iPr_2N$-groups into the methyl substituents. The formation of such derivatives is thought to result from interaction of primary deprotonation product, *i.e.* nonamethylferrocenyl radical **III**·, with deprotonating base to give adducts of the type **V**·, the rate of this process being higher than the rate of dimerization of **III**·. It follows from these results that deprotonation of 17-electron transition metal π-complexes can be the basis of a new approach to alkyl group functionalization in these complexes. We are now clarifying the synthetic potential of this approach.

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