

Monomeric 'Benzyl Lithium' in 2,5-Dimethyltetrahydrofuran. NMR Spectroscopic Studies of ^6Li and $^{13}\text{C}_2$ Labelled Ferrocenophanyl Lithium using ^{13}C - ^6Li Coupling and ^6Li Decoupling

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Abstraction of the C-11 proton in [11,12- $^{13}\text{C}_2$][1,1](1,1'';1',1''') ferrocenophane **1** by n-butyl[^6Li]lithium in 2,5-dimethyltetrahydrofuran (DMTHF)[†] results in ferrocenophanyl lithium **2** with lithium bonded to C-11 as shown by observed ^{13}C - ^6Li couplings and ^6Li decoupling.

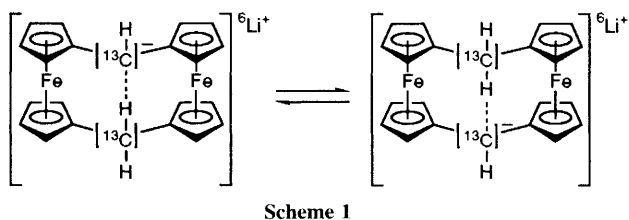
It has been shown by dynamic NMR spectroscopy that the carbanion formed in the reaction of ferrocenophane with n-butyl lithium in tetrahydrofuran (THF) undergoes rapid intramolecular 11,12-proton transfer (*c.f.* Scheme 1).¹

Indications of lithium coordination to the carbanion have also been obtained.²

The degenerate rearrangement in Scheme 1 constitutes to our knowledge the first example of an alkali metallation reaction with an intramolecular proton transfer. We are investigating the mechanism of this reaction in detail by isotopic labelling and multinuclear NMR spectroscopy; in particular we are elucidating the roles of the cation and solvent in this metallation reaction.

Organolithium compounds in solution show a strong tendency to aggregate *i.e.* to form dimers, tetramers *etc.* and it

[†] DMTHF consists of a *cis/trans* mixture.



has been found that the degree of oligomerization affects the rate of reaction of such reagents.³

Nuclear spin-spin couplings between ^6Li and ^{13}C have been used extensively to investigate the aggregation of organolithium compounds in solution.⁴ The splitting pattern of the signal from the carbanionic carbon shows the number of lithiums bonded to that very carbon *i.e.* about the state of aggregation.

In order to clarify the nature of ferrocenophanyl lithium the $^{13}\text{C}_2$ labelled precursor **1** with 99 atom% ^{13}C of the carbons at positions 11 and 12 respectively was synthesized⁵ and the corresponding ^6Li salt was prepared in 2,5-dimethyltetrahydrofuran (DMTHF).

The solvent DMTHF was used rather than THF, since we have found that in the former solvent the 11,12-proton transfer in **2** is much slower than in THF. Thus in DMTHF the NMR spectrum of **2** at room temperature corresponds to a 'frozen' structure rather than to a rapidly equilibrating species as in THF. Therefore DMTHF is a more suitable solvent for the present aggregation study than THF, since couplings between carbanionic ^{13}C and ^6Li are searched for.

In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum \ddagger of **2** in DMTHF at 100 MHz obtained using a Varian VXR 5000 spectrometer the signal from H^{13}C^- appears as a broader singlet than that from H_2^{13}C at 20 °C. This indicates the presence of coupling between ^6Li and the carbanionic carbon of H^{13}C^- . Upon lowering the temperature to -45 °C the H^{13}C^- signal split into a 1 : 1 : 1 triplet as shown in Fig. 1.

The coupling constant J is 4.0 Hz. These results suggest that each carbanionic carbon is bonded to only one ^6Li *i.e.* that **2** is mainly monomeric in DMTHF at -45 °C.

In order to obtain more support for this conclusion further experiments were carried out using a Varian 500 Unity spectrometer equipped with a triple resonance probe. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum \ddagger was obtained at 125 MHz. At this higher magnetic field the H^{13}C^- signal was not resolved at -45 °C as previously observed at 100 MHz but appeared as a broad signal ($W_{1/2}$ 10.8 Hz). Irradiation of a ^6Li signal at 73

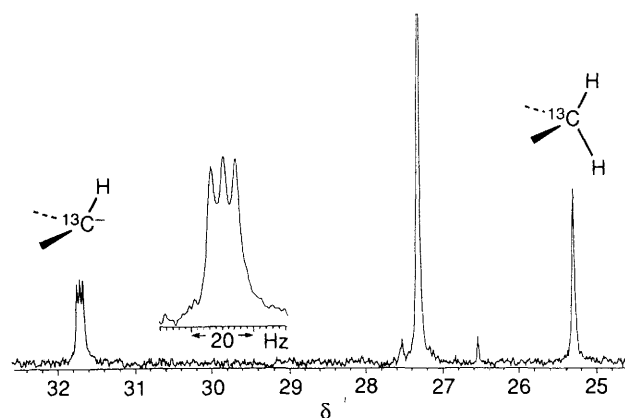


Fig. 1 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum \ddagger of **2** in DMTHF obtained at 100 MHz at -45 °C using a Varian VXR 5000 spectrometer. The most high frequency signal from DMTHF, which was set to δ 75.6, was used as a reference.

MHz changed the H^{13}C^- carbon signal to a sharp singlet with the same width as that of the H_2^{13}C signal. This confirms the conclusion that lithium is bonded to the carbanionic carbon.

The above results unambiguously show that the carbanionic carbon of the benzylic like carbanion in **2** is bonded to only one lithium in DMTHF and that **2** is mainly monomeric at the salt concentration and temperature used in the experiments.

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- 5 Synthesized by M. Löwendahl at the Department of Organic Chemistry University of Göteborg, Göteborg, Sweden; to be published.

\ddagger Waltz decoupling was used.