

Direct observation of an internally π -complexed alkenyllithium compound in THF solution

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NMR studies have shown that the hexenyllithium compound **4** exists at $-80\text{ }^\circ\text{C}$ in THF solution as two distinct species: the 'normal' THF solvated alkenyllithium compound **4a** and the internally π -complexed species **4b** in a ratio of 5.5:1.

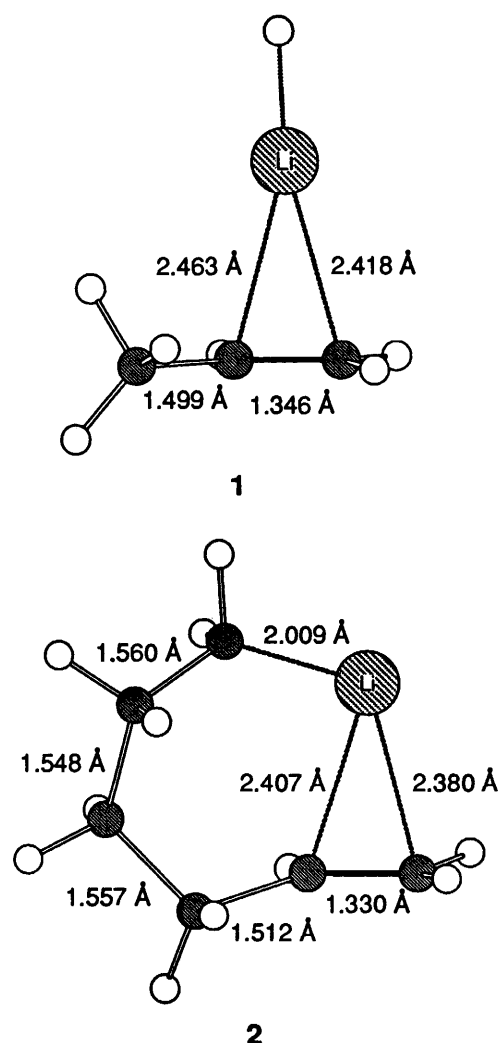
Inter- and intra-molecular carbolithiation reactions have found much interest in recent years.^{1,2} The lithium cation must play a specific role in this process, since hex-5-enyllithium cyclizes readily, its sodium or potassium counterparts refuse to do so.³ For this reason specific interactions of the lithium cation with the double bond have been discussed.^{2,3} In fact, *ab initio* calculations show that intermolecular interactions between unsolvated lithium hydride and ethene^{2,4} is stabilizing by 36.5 kJ mol^{-1} . We carried out MP2(full)/HF 6-311G** calculations on the interaction between propene and lithium hydride, which show that the complex **1** is more stable by 49.3 kJ mol^{-1} than its constituents. The geometry of the complex **1** is very similar to the internal complex of unsolvated hexenyllithium **2**, calculated by Wiberg and co-workers.²

Coordination of a lithium cation to a π -system can also be seen in several crystal structures of organolithium compounds.⁵ Such π -complexes are probably necessary intermediates in carbolithiation reactions and may be important for directing the stereochemical outcome of several organolithium reactions.⁶ Nevertheless, it remains open whether such π -complexes are observable species in the usual donor solvents such as tetrahydrofuran (THF) or diethyl ether. In fact, early NMR investigations suggested⁷ that but-3-enyllithium is internally coordinated in cyclopentane as solvent, but that π -complexation is disrupted on addition of dimethyl ether. It is therefore of interest that we observed both the internally π -coordinated as well as the π -uncoordinated form of the hexenyllithium derivative **4** in THF by ^1H , ^6Li HOESY experiments.

4,4-Dimethyl-1-(phenylsulfanyl)hex-5-enyllithium **4** was generated[†] from 4,4-dimethyl-1-(phenylsulfanyl)hex-5-enyl-(trimethyl)stannane **3** at $-78\text{ }^\circ\text{C}$ in THF by *tert*-butyllithium. The organolithium compound **4** is monomeric in THF at $0\text{ }^\circ\text{C}$, its aggregation number was found to be 1.07 ± 0.1 by vapour pressure osmometry.

Investigations at $-80\text{ }^\circ\text{C}$ of **4**, generated from the tin compound **3** and butyl- ^6Li in [$^2\text{H}_8$]THF revealed the presence of two major components A and B, as well as a minor constituent C. Integration of the ^1H and ^6Li NMR spectra gives their ratio as $(80 \pm 5):(15 \pm 3):(5 \pm 3)$.

The major components A and B show no differences in the 500 MHz ^1H NMR spectra with H_c at $\delta = 4.72$ and H_i at $\delta = 4.74$ ppm. Both compounds show the lithium-bearing carbon atom with a signal at $\delta = 18.7$ ppm in the 126 MHz ^{13}C NMR spectrum, with $J_{\text{C-H}} = 124\text{ Hz}$, indicative of an



sp^3 -hybridized carbon atom. Compound A ($\delta = 109.2$ and 150.8 ppm) and compound B ($\delta = 111.3$ and 148.0 ppm) differ in the chemical shifts of the alkenic carbon atoms. The two compounds also show distinct signals in the 74 MHz ^6Li NMR spectrum. Compound A gives a singlet at $\delta = 1.0$ ppm (relative to external 1 mol dm^{-3} LiCl in D_2O), compound B gives a singlet at $\delta = 2.7$ ppm. The fact that two distinct signals are observed at $-80\text{ }^\circ\text{C}$ shows that the interconversion between compounds A and B is slow at this temperature, the individual lifetime τ of these species should be equal to or larger than 0.3 s.

[†] The starting material **3** was prepared from 4,4-dimethylhex-5-enal by addition of trimethyltin lithium in THF at $-78\text{ }^\circ\text{C}$. After hydrolysis with aqueous NH_4Cl solution the resulting stannylated alcohol was treated with diphenyl disulfide and tributylphosphine in DMF at $0\text{ }^\circ\text{C}$ to yield 68% of **3**, for details see ref. 8.

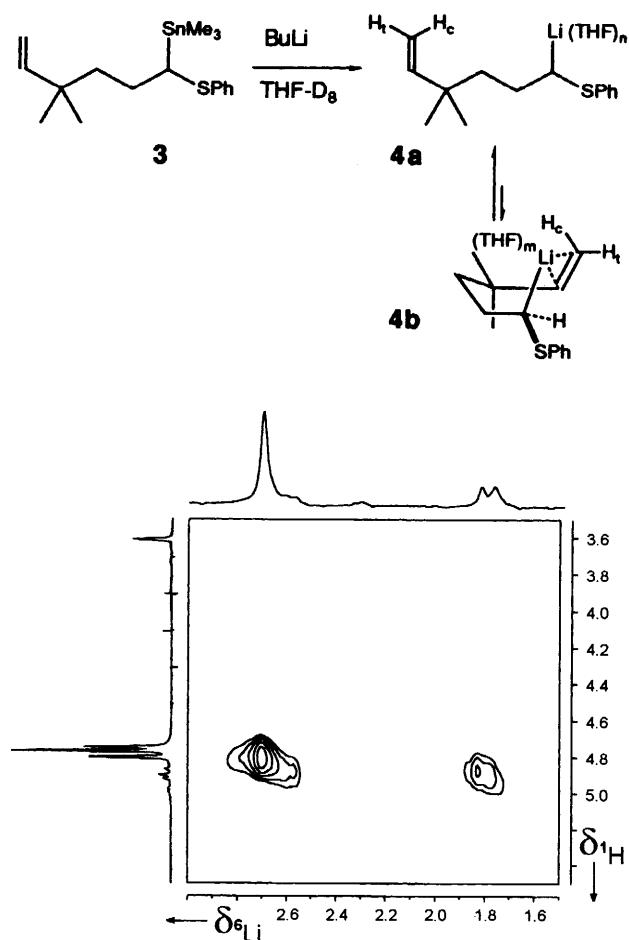


Fig. 1 $^1\text{H}, ^6\text{Li}$ HOESY data for the lithium compound **4**

$^1\text{H}, ^6\text{Li}$ HOESY experiments ‡ suggest that compound **A** is the π -uncomplexed species **4a** and that compound **B** the internally coordinated organolithium compounds **4b**, cf. Fig. 1: the lithium signal of the major species **A** at $\delta = 1.0$ ppm shows no cross peak to the alkenic proton signals. In turn, the lithium signal of the species **B** at $\delta = 2.7$ ppm shows a strong cross peak to H_c , the vinylic proton in the *cis*-position. We therefore conclude that the hexenyllithium compound **4** exists in THF solution as two distinct species, the normal THF solvate **4a** and the internally π -complexed species **4b** in a 5.5:1 ratio. It is conceivable that the *gem*-dialkyl effect 10 stabilizes **4b** to the point that it becomes observable in THF solution.

‡ The HOESY spectrum was recorded in the phase-sensitive mode using a relaxation delay of 5.0 s and a mixing time of 4.0 s. 128 free induction decays were recorded on 512 data points using a spectral width of 6.8 ppm in F_2 and 8.0 ppm in F_1 . The data matrix was processed to give 512×512 real datapoints using an exponential window in F_2 and a $\pi/2$ -shifted sinusoidal window in F_1 .

As a sideline, we would like to comment on the minor constituent **C** observed to *ca.* 5%. It is characterized by different ^1H NMR signals for H_c and H_t at 4.84 and 4.82 ppm as well as by two ^6Li NMR signals at $\delta = 1.7$ and 1.8 ppm. Both ^6Li signals show a cross peak to the terminal alkene protons of compound **C** in the $^1\text{H}, ^6\text{Li}$ HOESY experiment, cf. Fig. 1.

While **4** is monomeric in THF, butyllithium is a dimer in this solvent. 11 Residual butyllithium should form a mixed dinuclear aggregate in the presence of an excess of **4**. Such a mixed dimer would contain two magnetically distinct Li atoms, both of which could interact with the π -electrons of the double bond. The data recorded for the minor constituent **C** are therefore consistent with it being a mixed dimer between **4b** and butyllithium.

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