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Structure and Chemical Behavior of an η^5-(1-Azapentadienyl)lithium Derivative Generated by Deprotonation Reactions Starting from 9-(*N-tert*-Butylaminomethyl)fluorene or 6-(*tert*-Butylamino)dibenzofulvene

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Abstract: Fluorenyllithium (**1**) adds to *tert*-butyl isocyanate to yield 9-(*N-tert*-butylcarboxamido)fluorenyllithium (**3**). Its reduction with LiAlH$_4$ followed by aqueous workup leads to the formation of the corresponding dibenzo-*N-tert*-butylaminofulvene **5**. Treatment of **5** with sodium cyanoborohydride furnishes 9-(*N-tert*-butylaminomethyl)-fluorene (**6**). Deprotonation of the fulvene **5** with *n*-butyllithium in ether yields the η^5-azapentadienyllithium derivative **11**. The X-ray crystal structure analysis of **11**·(Et$_2$O)$_2$ reveals a nearly planar U-shaped 1-azapentadienyl moiety that exhibits five close contacts to the lithium atom located above the ligand plane. Computational chemistry (PM3) has identified the η^5-(1-azapentadienyl)lithium derivative **11** as a global minimum. In solution compound **11** undergoes a dynamic degenerate rearrangement process that is rapid on the ^{1}H NMR time scale. It equilibrates the annulated arene moieties of **11**. The Gibbs activation energy of this symmetrization process is $\Delta G^{\ddagger}_{\text{enant}} = 11.8 \pm 0.3$ kcal mol^{-1}. A C_s-symmetric transition state geometry (**11**-TS) where the 1-azapentadienyl conjugation is interrupted between C9−C10 was identified by the PM3 calculation. Deprotonation of 9-(*N-tert*-butylaminomethyl)fluorene (**6**) gives rise to several competing pathways. Treatment with lithium hexamethyldisilazide leads to abstraction of the fluorenyl 9-H proton to produce the aminomethyl-substituted fluorenyl anion **7**. Subsequent treatment of **7** with *tert*-butyllithium gives the dilithio compound **10**. The reaction of **6** with *n*-butyllithium leads to the formation of a mixture of fluorenyllithium (**1**) and the η^5-(1-azapentadienyl)lithium derivative **11**. Deprotonation of **6** with *tert*-butyllithium furnishes **1** and the dilithiated compound **10**. Single crystals of **1**·Et$_2$O were analyzed by X-ray diffraction. The compound shows a polymeric "super-sandwich" structure with an alternating fluorenyl-Li·OEt$_2$ arrangement exhibiting inversion symmetry. The X-ray crystal structure analysis of **10**·(THF)$_3$ reveals an unsymmetrical arrangement of the lithium atoms at the amidomethylfluorenyl-"dianion" framework with one THF molecule bridging between the metal centers. The bonding features of the dilithiated system **10** derived by double deprotonation of **6** were also analyzed by computational chemistry.

Introduction

The cyclopentadienides are among the most important ligand systems in organometallic chemistry. The structural chemistry of their "anionic synthons", the alkali metal cyclopentadienides, is well understood and has been competently described on a sound experimental basis.[1] Less is known about the acyclic analogues of the Cp-ligands,[2] especially when heteroatoms are part of the five-atom conjugated π-system.[3] Experimental details of the corresponding 1-azapentadienyl anion systems (i.e., on their alkali metal salts or complexes) are rather scarce.[4] Detailed structural information on the basis of X-ray diffraction data seems to be lacking for η^5-(1-azapentadienyl)lithium and related systems altogether, but even other spectroscopic and quantum chemical evidence of their structural characteristics is limited[4] in contrast to many other lithiated carbanionic π-systems.[5] We have now found that a η^5-(1-azapentadienyl)lithium derivative is readily available by deprotonation of either 9-(*N-tert*-butylaminomethyl)fluorene or the related 6-(*tert*-butyl-amino)dibenzofulvene. To the best of our knowledge, our example represents the first U-shaped η^5-(1-azapentadienyl)-lithium derivative characterized by an X-ray crystal structure analysis. The mechanisms of the generation and some of the chemical properties of this interesting new species are reported in this article.

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§ Quantum chemical calculations.
⊗ Abstract published in *Advance ACS Abstracts,* October 15, 1997.
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Results and Discussion

Synthesis of the 9-(*tert*-Butylaminomethyl)fluorene System. *N*-Substituted aminomethyl substituents are readily introduced into organic systems by reduction of the respective *N*-substituted carboxamide with hydridic reagents. The carboxamido substituent can be introduced at cyclopentadienyl-type systems by treatment of a metal cyclopentadienide with one molar equivalent of the corresponding alkylisocyanate,[6,7] as we have recently demonstrated.

Therefore, we synthesized the title compounds by treating the fluorenyllithium reagent (**1**) with 1 molar equiv of *tert*-butyl isocyanate in THF at −50 °C. The addition presumably yields the 1:1 coupling product **2** which is rapidly converted to the more stable system **3** under the reaction conditions. Hydrolysis of an aliquot of the reaction mixture affords the carboxamido-substituted system **4** as the sole product.

Refluxing 9-(*N*-*tert*-butylcarboxamido)fluorenyllithium (**3**) with LiAlH₄ in THF for several days afforded the fulvene **5** in close to quantitative yield.[8] Further reduction of the aminofulvene **5** was achieved by treatment with sodium cyanoborohydride in acetic acid/methanol. After a reaction time of 2 days at ambient temperature followed by aqueous workup 9-(*N*-*tert*-butylaminomethyl)fluorene **6** was isolated in a 65% overall yield.[9]

Deprotonation Reactions. Deprotonations of the *N*-substituted aminomethylfluorene system **6** and related systems were carried out using strong bases (*n*-butyllithium, *tert*-butyllithium, LDA, or lithium hexamethyldisilazide). Since the reactions initially appeared to be rather complicated, the temperature and solvent (and sometimes co-ligands) were varied considerably to achieve clean reactions that allowed product identification and elucidation of the reaction pathways by which these products are formed.

In a typical experiment under optimized conditions the amine **6** was treated with *n*-butyllithium in an ether/hexane mixture (ca. 8:1) at −78 °C using ca. 2 molar equiv of the base. The mixture was then warmed to room temperature. The resulting bright orange precipitate shown to be lithio-9-(*N*-*tert*-butyl-aminomethyl)fluorenylidene **7** was isolated in ca. 30% yield. It contained 1 equiv of coordinated diethyl ether.

From the combined organic filtrates two different types of crystals appeared after 2 days at ambient temperature. Single crystals of both products were picked from this mixture and identified by X-ray crystal structure analyses (for details see below) as fluorenyllithium (**1**)·diethyl ether and the fluorene derived η⁵-(1-azapentadienyl)lithium compound **11**(·2Et₂O). The remaining mother liquor was hydrolyzed to give a white crystalline material that was identified as the aminofulvene **5**.

It appears that **11** may be formed by deprotonation of intermediate **5**. This is supported by the observation that the fulvene **5** is deprotonated with the strong base lithium hexamethyldisilazide (1 equiv) in ether to furnish the monolithiated compound **11**. The compound **11** was also obtained in almost quantitative yield as an oil by deprotonation of **5** in ether/pentane (1:1) at 0 °C using *n*-butyllithium.

In a control experiment, we treated the amine **6** with a 2-fold excess of lithium hexamethyldisilazide in THF-*d₈* at ambient temperature. The ¹H NMR spectrum showed that the monolithio compound **7** was formed and proved to be stable for a prolonged period of time under these reaction conditions.

We conclude that the deprotonation of **6** may lead to the formation of three monolithio fluorenyl-type compounds **7**, **1**, and **11**, that are formed in a series of competing reaction sequences. The neutral starting material **6** contains two acidic

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Scheme 1

Scheme 2
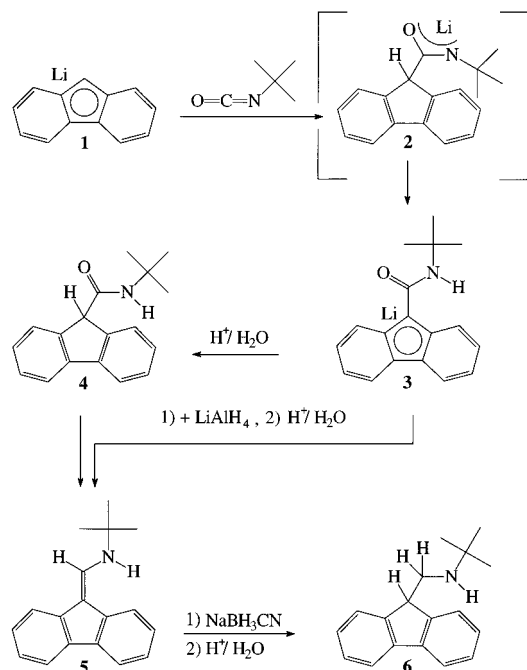
protons, albeit of quite different pK_a,[10] the N—H and the fluorenyl 9-H. Deprotonation at C9 directly results in the formation of **7**, identified as one of the major reaction products. This product appears to be stable under the typical reaction conditions. The N—H deprotonation product **8** appears to be unstable under the reaction conditions (see Scheme 2). The elimination of lithium hydride[11] affords fulvene **5**, which was not directly observed; under the basic reaction conditions this is then instantaneously deprotonated to give the η^5-(1-aza-pentadienyl)lithium derivative **11**. A competing fragmentation produces the isolable fluorenyllithium **1**.

We further investigated the double deprotonation of the aminomethylfluorene starting material **6**. In view of the competing pathways after monodeprotonation (see above), it was expected that double deprotonation could afford complicated mixtures of anionic products. Initial studies with *tert*-butyl-lithium furnished mixed results. Thus, treatment of **6** with *tert*-butyllithium in THF at low temperature gave a bright orange colored precipitate that could not be adequately characterized directly due to its low solubility. Upon addition of [12]-crown-4 the product went into solution (THF-d_8) and was spectroscopically identified as the monodeprotonated species **7**·[12]-crown-4. However, a systematic change of the reaction conditions eventually afforded the doubly deprotonated product **10**. In the beginning, **10** was formed in addition to substantial amounts of the monolithio byproducts, especially the fragmentation product fluorenyllithium. **10** could best be obtained by mixing the starting material **6** with solid *tert*-butyllithium followed by addition of tetrahydrofuran at room temperature. A vigorous reaction takes place under these rather forcing conditions to give a clear, intensely orange colored solution. The ^{1}H NMR spectrum (THF-d_8) shows the signals of the dianion **10** [δ 4.54 (s, 2H, CH_2—N(R))] (in some experiments in addition to the signals of a fluorenyllithium contamination). Keeping such a
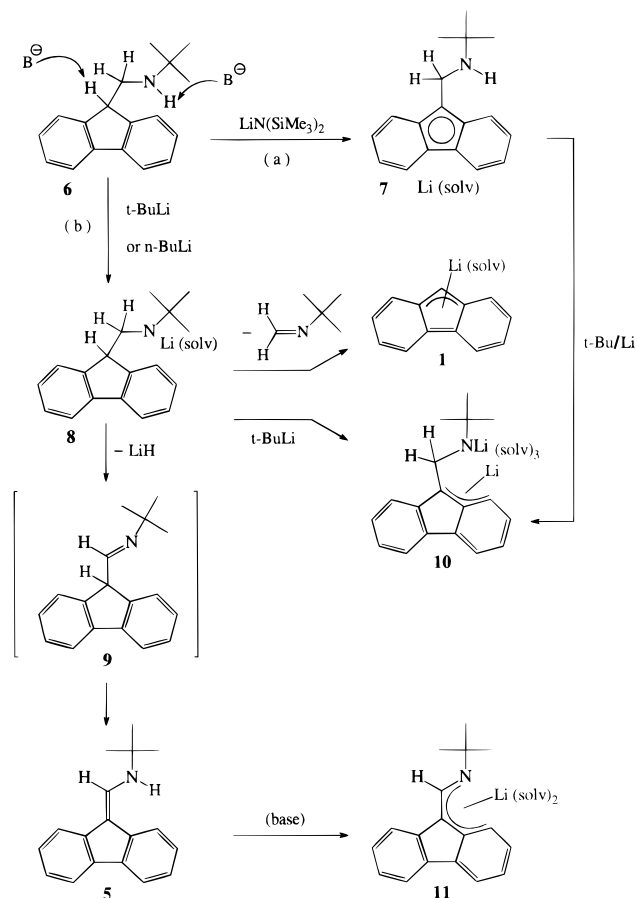
solution for several weeks at −30 °C produced single crystals of the dilithio compound **10** that were suited for an X-ray crystal structure determination. The dilithio compound **10** was also obtained by treatment of the monolithio compound **7** (generated in situ from the amine **6** by treatment with LDA in *tert*-butylmethyl ether) with *tert*-butyllithium. This afforded a ca. 2:1 mixture of the lithio compounds **7** and **10**. The latter was obtained completely free from the fragmentation products **1** and **11** (see Scheme 2).

X-ray Crystal Structure Analyses. X-ray crystal structure determinations were carried out for the anionic compounds **1**, **10**, and **11**.

Fluorenyllithium·diethyl ether (**1**) exhibits a polymeric chain structure in the solid state.[12] This compound represents one of the rare examples of a [(RCp)Li]$_n$ columnar structure.[13] A close inspection of the bonding features of the repeating fluorenyllithium·Et$_2$O unit[14,15] (see Figure 1) reveals an η^3-allyl type bonding mode between the Li·OEt$_2$ building block to both adjacent fluorenyl anion neighbors. The bonding between the lithium atom and both its η^3-fluorenyl ligands is of similar strength. The interaction between the C9 carbon atoms of both top and bottom C$_{13}$H$_9$ ligands is rather strong (Li—C9: 2.256(3) Å, Li—C9*: 2.249(3) Å). The lithium—carbon distance to the adjacent (proximal) five-membered ring carbon centers (C1A, C8A) is larger but still clearly within bonding range (2.56−2.78 Å, see Figure 1),[16] whereas the Li—C separation with the remaining distal five-membered ring carbon centers (C4A, C5A)

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and to the adjacent arene carbon atoms is clearly outside the range of any direct bonding interaction (3.2–3.6 Å). Along the polymeric chain the mutual arrangement of the individual fluorenyllithium·diethylether building blocks occurs with inversion symmetry. The adjacent ether ligands point to opposite sectors of the chain in a strictly alternating manner. Consequently, the arrangement of the fluorenyl ligands, whose planes are oriented normal to the polymer chain vector, repeats this alternating structural motif. A schematic representation of this arrangement is depicted in Scheme 3.

The lithiated dianion species **10** shows a rather unusual structure. Compound **10** exhibits isolated monomeric units in the crystal. It contains a single planar fluorenyl subunit to which a $-CH_2-N-CMe_3$ functional group is attached at carbon atom C9. There are two lithium centers, Li1 and Li2, that are bonded to the nitrogen atom. The lithium atoms are coordinated to a set of three THF ligands, two of which are η^1-coordinated, one to each of the Li-atoms, and one that is bridging between the

(14) For structures of solvent stabilized $(CpM)_n(solv)$ fragments see, e.g.: Sekiguchi, A.; Sugai, Y.; Ebata, K.; Kabuto, C.; Sakurai, H. *J. Am. Chem. Soc.* **1993**, *115*, 1144. Fritz, M.; Hiermeier, J.; Hertkorn, N.; Köhler, F. H.; Müller, G.; Reber, G.; Steigelmann, O. *Chem. Ber.* **1991**, *124*, 1531. Hiermeier, J.; Köhler, F. H.; Müller, G. *Organometallics* **1991**, *10*, 1787. Rabe, G.; Roesky, H. W.; Stalke, D.; Pauer, F.; Sheldrick, G. M. *J. Organomet. Chem.* **1991**, *403*, 11. Chen, H.; Jutzi, P.; Leffers, W.; Olmstead, M. M.; Power, P. P. *Organometallics* **1991**, *10*, 1282. Youngs, W. J.; Djebli, A.; Tessier, C. A. *Organometallics* **1991**, *10*, 2089. Hammel, A.; Schwarz, W.; Weidlein, J. *Acta Crystallogr.* **1990**, *C46*, 2337. Jutzi, P.; Leffers, W.; Pohl, S.; Saak, W. *Chem. Ber.* **1989**, *122*, 1449. Lorberth, J.; Shin, S.-H.; Wocadlo, S.; Massa, W. *Angew. Chem.* **1989**, *101*, 793; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 735. Stezowski, J. J.; Hoier, H.; Wilhelm, D.; Clark, T.; Schleyer, P. v. R. *J. Chem. Soc., Chem. Commun.* **1985**, 1263. Jutzi, P.; Schlüter, E.; Pohl, S.; Saak, W. *Chem. Ber.* **1985**, *118*, 1959. Lappert, M. F.; Singh, A.; Engelhardt, L. M.; White, A. H. *J. Organomet. Chem.* **1984**, *262*, 271. Jutzi, P.; Schlüter, E.; Krüger, C.; Pohl, S. *Angew. Chem.* **1983**, *95*, 1015; *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 994. Rogers, R. D.; Atwood, J. L.; Rausch, M. D.; Macomber, D. W.; Hart, W. P. *J. Organomet. Chem.* **1982**, *238*, 79. Rhina, W. E.; Stucky, G. D. *J. Am. Chem. Soc.* **1975**, *97*, 737. Brooks, J. J.; Rhine, W.; Stucky, G. D. *J. Am. Chem. Soc.* **1972**, *94*, 7339. Reviews: Stalke, D. *Angew. Chem.* **1994**, *106*, 2256, *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2168. Weiss, E. *Angew. Chem.* **1993**, *105*, 1565; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1501. Jutzi, P. *J. Organomet. Chem.* **1990**, *400*, 1. Paquette, L. A.; Bauer, W.; Sivik, M. R.; Bühl, M.; Feigel, M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1990**, *112*, 8776, and references cited therein. Theoretical studies: Lambert, C.; Schleyer, P. v. R. *Angew. Chem.* **1994**, *106*, 1187; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1129. Setzer, W. N.; Schleyer, P. v. R. *Adv. Organomet. Chem.* **1985**, *24*, 353. Jemmis, E. D.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1982**, *104*, 4781. Alexandratos, S.; Streitwieser, A., Jr.; Schaefer III, H. F. *J. Am. Chem. Soc.* **1976**, *98*, 7959. Malaba, D.; Tessier, C. A.; Youngs, W. J. *Organometallics* **1996**, *15*, 2918. Malaba, D.; Djebli, A.; Chen, L.; Zarate, E. A.; Tessier, C. A.; Youngs, W. J. *Organometallics* **1993**, *12*, 1266. Malaba, D.; Chen, L.; Tessier, C. A.; Youngs, W. J. *Organometallics* **1992**, *11*, 1007. Paver, M. A.; Russell, C. A.; Stalke, D.; Wright, D. S. *J. Chem. Soc., Chem. Commun.* **1993**, 1349. Dohmeier, C.; Baum, E.; Ecker, A.; Köppe, R.; Schnöckel, H. *Organometallics* **1996**, *15*, 4702.

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(16) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S 1.
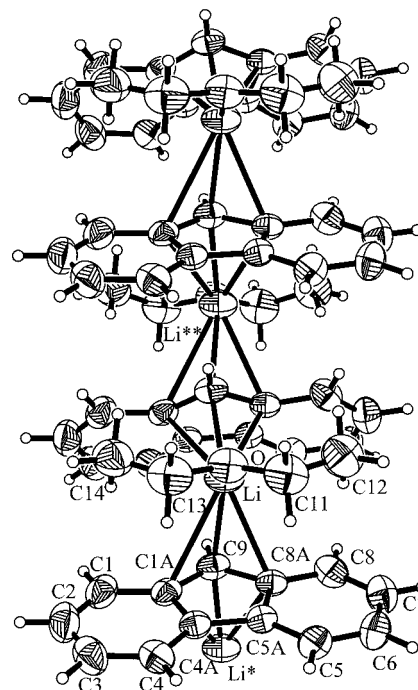
Figure 1. A view of the polymeric chain structure of fluorenyllithium· diethyl ether (**1**) in the solid state with atom numbering scheme (a section containing a sequence of four monomeric units is depicted). Selected bond lengths (Å) and angles (deg): C1A–C9 1.426(2), C9–C8A 1.434(2), C8A–C5A 1.438(2), C5A–C4A 1.431(2), C4A–C4 1.398(2), C4–C3 1.377(3), C3–C2 1.394(3), C1–C1A 1.407(2), C8A–C8 1.407(2), C8–C7 1.377(2), C7–C6 1.404(3), C6–C5 1.371(2), C5–C5A 1.395(2), Li–O 1.935(3), Li–C1A 2.770(3), Li–C1A* 2.784(3), Li–C8A 2.612(3), Li–C8A* 2.565(3), Li–C4A 3.341(3), Li–C4A* 3.304(3), Li–C5A 3.255(3), Li–C5A* 3.194(3), Li–C1 3.568(3), Li–C1* 3.643(3), Li–C8 3.307(3), Li–C8* 3.258(3), C1A–C9–C8A 107.48(13), C9–C8A–C5A 108.40(13), C4A–C1A–C9 108.67(13), C9–Li–O 112.50(14), Li–O–C11 123.81(14), Li–O–C13 119.38(15), C9–C8A–C8 132.87(14), C1–C1A–C9 132.67(15).

Scheme 3
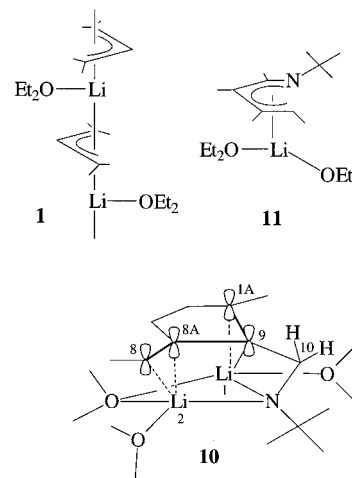
lithium atoms. Thus, in **10** there is a central core containing two lithiums, an oxygen, and a nitrogen atom that are found in a slightly puckered four-membered metallacyclic arrangement. The Li1···Li2 separation in this arrangement is 2.556(5) Å. The laterally coordinated THF ligands both exhibit an envelope-type deviation from planarity, whereas the central bridging THF ligand appears to be planar (see Figure 2).[17]

The relative orientation of the Li1–O31–Li2 core to the fluorenyl moiety is distinctly unsymmetric. The lithium atom Li1 exhibits a very strong bonding interaction with the central
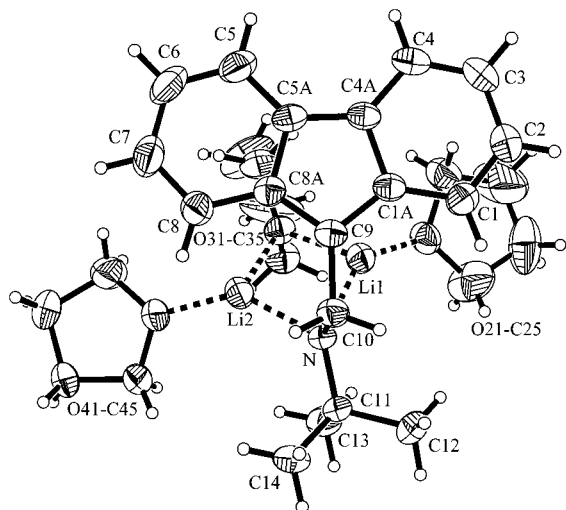
Figure 2. The molecular structure of compound **10** in the crystal (with atom numbering scheme). Selected bond lengths (Å) and angles (deg): C10−N 1.474(3), C9−C10 1.503(3), C9−C1A 1.422(3), C1A−C4A 1.447(3), C4A−C5A 1.421(3), C5A−C8A 1.447(3), C5A−C5 1.394(3), C5−C6 1.367(4), C6−C7 1.404(4), C7−C8 1.367(3), C8−C8A 1.414(3), C1A−C1 1.415(3), C1−C2 1.377(3), C2−C3 1.398(4), C3−C4 1.369(3), C4−C4A 1.401(3), Li1−N 1.969(4), Li1−O31 2.082(4), Li2−N 1.984(4), Li2−O31 2.041(4), Li1−O21 1.923(4), Li2−O41 1.915(4), Li1−C1: 3.022(4), Li1−C4A 3.342(4), Li1−C5A 3.632(4), Li1−C8A 3.089(4), N−C11 1.462(3), C11−C12 1.540(3), C11−C13 1.530(3), C11−C14 1.541(3), O21−C22 1.416(3), O21−C25 1.433(3), O31−C32 1.452(3), O31−C35 1.450(3), O41−C42 1.424(3), O41−C45 1.435(3), C8A−C9−C1A 106.6(2), C9−C1A−C4A 109.3(2), C1A−C4A−C5A 107.4(2), C4A−C5A−C8A 107.0(2), C8A−C9−C10 126.1(2), C1A−C9−C10 126.9(2), C8−C8A−C9 131.9(2), C7−C8−C8A 119.8(2), Li1−O21−C22 124.0(2), Li1−O21−C25 124.2(2), C22−O21−C25 109.3(2), Li2−O41−C42 128.3(2), Li2−O41−C45 124.3(2), C42−O41−C45 106.3(2), N−Li1−O31 99.0(2), Li1−O31−Li2 76.6(2), O31−Li2−N 99.8(2), Li2−N−Li1 80.6(2), C10−N−C11 113.8(2), Li1−N−C11 130.7(2), Li1−N−C10 95.2(2), Li2−N−C10 104.8(2), Li2-N−C11 124.6(2), C32−O31−C35 108.7(2), Li1−O31−C32 111.4(2), Li1−O31−C35 122.9(2), Li2−O31−C32 112.4(2), Li2−O31−C35 121.8(2).

fluorenyl carbon atom C9 (Li1−C9: 2.368(4) Å), and it also seems to have a pronounced interaction with the adjacent bridgehead carbon center C1A (Li1−C1A: 2.544(4) Å). The separation of Li1 with the adjacent fluorenyl sp²-carbon centers is substantially larger and probably outside of the direct bonding range (3.0−3.6 Å). We conclude that the lithium atom Li1 is strongly bonded to C9 and still shows a strong bonding interaction to C1A; however, other short contacts of Li1 to the fluorenyl π-system seem to be absent.

In contrast, Li2 shows a slightly weaker interaction with the fluorenyl π-system as judged from the respective interatomic distances.[18] Reasonably close contacts are found between Li2 and C8 (2.648(5) Å) and Li2 and C8A (2.823(5) Å), but both are longer than the short Li1−fluorenyl distances mentioned above. The Li2−C9 (2.927(5) Å) and Li2−C7 (3.619(5) Å) separations are even larger. There are two rather short contacts between the lithium atoms and the saturated carbon atom C10 (Li1−C10: 2.564(4) Å, Li2−C10: 2.758(4) Å), but the "closeness" of these atoms follows from the spatial arrangement of metal centers at the chelating organic ligand system, not necessarily from a pronounced electronic interaction between

(17) See for a comparison: Armstrong, D. R.; Barr, D.; Brooker, A. T.; Clegg, W.; Gregory, K.; Hodgson, S. M.; Snaith, R.; Wright, D. S. *Angew. Chem.* **1990**, *102*, 443; *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 410.

(18) Similar orientations are sometimes found in the structures of lithiated stabilized carbanions: Raabe, G.; Gais, H.-J.; Fleischhauer, J. *J. Am. Chem. Soc.* **1996**, *118*, 4622, and references cited therein.

Scheme 4
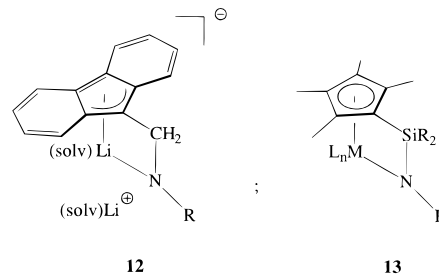
the respective centers. The arrangement of the Li₂ON core relative to the fluorenyl π-system (see Figure 2) suggests that it formally derives from the (C_s-symmetric) anionic heteroatom containing ansa-lithiocene-anion equivalent **12** to which a donor ligand-stabilized lithium cation was added. It is similar to many lithium amide aggregate structures.[19] The lateral connection of the lithium cation lowers the local symmetry of fragment **12**, leading to the structural distortion of **10**. However, it could also be that crystal packing forces are responsible for this structural detail. Compound **10** seems to be an intramolecular analogue of a lithio metallocene salt,[15] only that one of the Cp-rings is substituted by the pendant amido ligand. The novel compound **10** can, therefore, be regarded as a close relative to the family of nitrogen-analogues **13** of the ansa-metallocenes[20] (see Scheme 4). It remains to be studied, whether **10** can serve as a direct precursor to the carbon (instead of silicon) containing analogues of this important class of homogeneous Ziegler-catalyst precursors.[21]

The most remarkable structure is that of compound **11**. It represents to the best of our knowledge the first structurally characterized example of a U-shaped η⁵-(1-azapentadienyl)-lithium derivative. In contrast to the solid state polymer fluorenyllithium·Et₂O (**1**) the aminofulvene deprotonation product (**11**) exhibits independent monomeric molecular entities in the solid state. The lithium atom of **11** has two diethylether molecules coordinated to it. The remaining coordination of the lithium atom is made of a strong interaction with the nitrogen atom and by an arrangement of the carbon atoms C10, C9, C8A, and C8 within a pronounced bonding interaction (2.65−2.86 Å). All other adjacent sp²-hybridized carbon atoms are too remote from the lithium center to indicate any significant bonding contact. Thus the N−C10−C9−C8A−C8 π-system has to be regarded as an equivalent to a U-shaped 1-azapenta-dienyl ligand system[4] that is η⁵-coordinated to the central lithium center. The azapentadienyl moiety of **11** is oriented in a close to planar arrangement. Only the nitrogen center N11 is placed slightly out of this plane toward the lithium center (deviation of N11 from the C10−C9−C8A−C8 plane: 0.347 Å, dihedral angles C8A−C9−C10−N11 −15.6(6)°, C8−C8A−C9−C10

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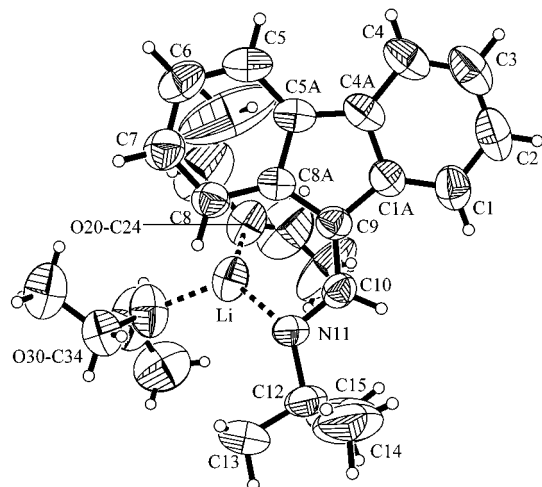
Figure 3. A projection of the molecular structure of **11** in the crystal with atom numbering scheme. Selected bond lengths (Å) and angles (deg): N11−C12 1.479(4), C1A−C9 1.439(5), C1A−C4A 1.424(5), C4A−C5A 1.442(5), C5A−C8A 1.428(4), C5A−C5 1.397(5), C5−C6 1.383(5), C6−C7 1.386(5), C7−C8 1.378(5), C1A−C1 1.403(5), C1−C2 1.390(6), C2−C3 1.393(7), C3−C4 1.355(6), C4−C4A 1.393(5), Li−O20 1.939(7), Li−O30 1.947(7), Li−N11 2.031(7), Li−C10 2.645(7), Li−C9 2.862(7), Li−C8A 2.810(7), Li−C8 2.654(7), N11−C10 1.306(4), C10−C9 1.399(4), C9−C8A 1.443(4), C8A−C8 1.395(5), N11−C10−C9 125.8(3), C10−C9−C8A 128.7(3), C9−C8A−C8 132.9(3), C8A−C8−C7 120.0(3), N11−Li−O30 119.9(4), N11−Li−O20 131.8(3), N11−Li−C8 86.7(3), C9−C1A−C4A 109.0(3), C1A−C4A−C5A 107.7(3), C4A−C5A−C8A 107.9(3), C5A−C8A−C9 108.6(3), C8A−C9−C1A 106.8(3), Li−O20−C21 116.9(3), Li−O20−C23 129.4(4), Li−O30−C31 121.6(4), Li−O30−C33 122.4(3), Li−N11−C10 102.7(3), Li−N11−C12 130.8(3), C10−N11−C12 117.5(3), N11−C10−C9 125.8(3), C10−C9−C8A 128.7(3), C9−C8A−C8 132.9(3).

−4.8(6)°) to induce a helical chirality element into the (η^5-1-azapentadienyl)Li-substructure of compound **11** (see Figure 3, additional projections of **11** are provided with the Supporting Information).

Dynamic Behavior of the η^5-(1-Azapentadienyl)lithium Compound 11. The η^5-(1-azapentadienyl)lithium derivative **11** exhibits the same structural type in solution as was observed in the crystal. This is evident from its very typical ^{1}H NMR spectrum in THF-d_8 at low temperature (600 MHz, 203 K). It shows signals of pairwise diastereotopic hydrogens at the fluorenyl nucleus at δ 6.63/6.54; 6.93/6.86 corresponding to the 2-H/7-H and/or 3-H/6-H pairs, respectively. The 4-H/5-H pair of signals is just separated under these conditions (overlapping pair of doublets centered at δ 7.76, see Figure 4), whereas the 1-H/8-H hydrogen pair gives rise to a large splitting: their ^{1}H NMR resonances are found at δ 8.57 and 7.52 ppm.

However, compound **11** shows dynamic NMR spectra upon increasing the monitoring temperature. A pairwise coalescence of the 1-H/8-H, 2-H/7-H, 3-H/6-H, and 4-H/5-H signals is observed, leading to a much simpler, symmetrized appearance of the spectrum at high temperature (298 K, see Figure 4). The N−C(CH_3)$_3$ signal (δ 1.28 ppm) and the 10-H resonance at δ 8.85 ppm are not affected by this spectral change.

This dynamic behavior indicates a rapid process at higher temperatures on the 600 MHz ^{1}H NMR time scale in the course of which the specific Li−C8 and C8a interaction is lost and becomes equilibrated with a symmetry-equivalent η^5-coordination that involves the symmetry counterparts of these atoms on the other side of the fluorenyl framework, namely C1 and C1a. The details of the intramolecular automerization pathway and a description of the possible transition state geometry was
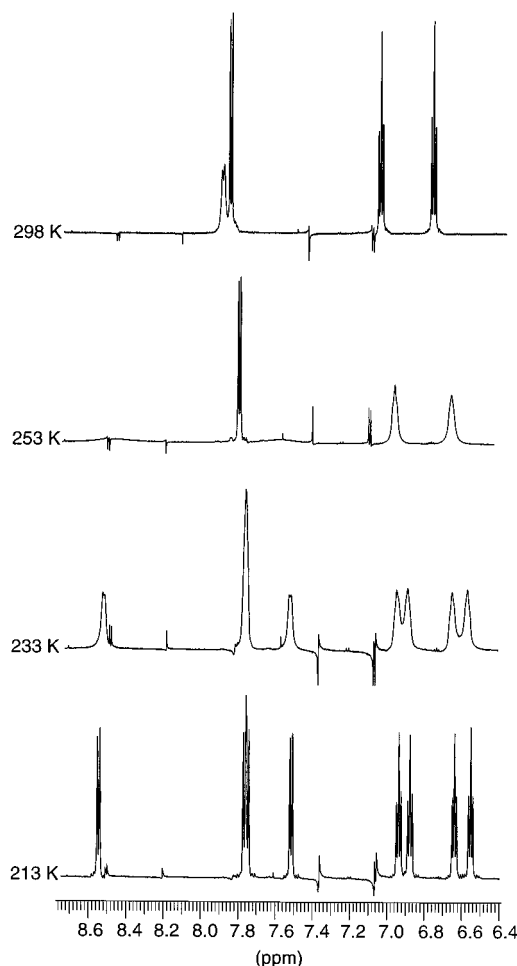

Figure 4. Temperature dependent dynamic ^{1}H NMR spectra (600 MHz, THF-d_8) of **11**; only the signals of the "fluorenyl-hydrogens" 1-H to 8-H are shown.

obtained from a computational investigation (see below). From the dynamic ^{1}H NMR spectrum the activation barrier of the thermally induced intramolecular enantiomerization process was determined. From the ^{1}H NMR coalescence of the 1-H/8-H pair of resonances ($\Delta\delta$ = 624 Hz, $T_{coal.}$ = 260 K) a Gibbs activation energy of $\Delta G^{\ddagger}_{enant}$ (260 K) = 11.8 ± 0.3 kcal/mol was obtained[22] for this dynamic process of **11**.

Computational Analysis

The dynamic behavior of **11** prompted us to investigate the preferred reaction pathway by computational methods. To gain confidence in the applied methodology we first turned to a description of the ground state structures of the organolithium systems prepared in the course of this study. The semiempirical method PM3[23] was used throughout. Due to the recently derived lithium parameters of Anders et al.[24] this method has proven to be of enormous value in predicting and interpreting organolithium structures.[25] The MOPAC 6.0 program package[26] was used for complete geometry optimizations of the full molecules with the complexing ether or THF ligands being substituted by

(22) Green, M. L. H.; Wong, L.-L.; Seela, A. *Organometallics* **1992**, *11*, 2660 and references cited therein.
(23) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209, 221.
(24) Anders, E.; Koch, R.; Freunscht, P. *J. Comput. Chem.* **1993**, *11*, 1301.
(25) Gertzmann, R.; Möller, M. H.; Rodewald, U.; Fröhlich, R.; Grehl, M.; Würthwein, E.-U. *Tetrahedron* **1995**, *51*, 3767. Gertzmann, R.; Fröhlich, R.; Grehl, M.; Würthwein, E.-U. *Tetrahedron* **1995**, *51*, 9031.
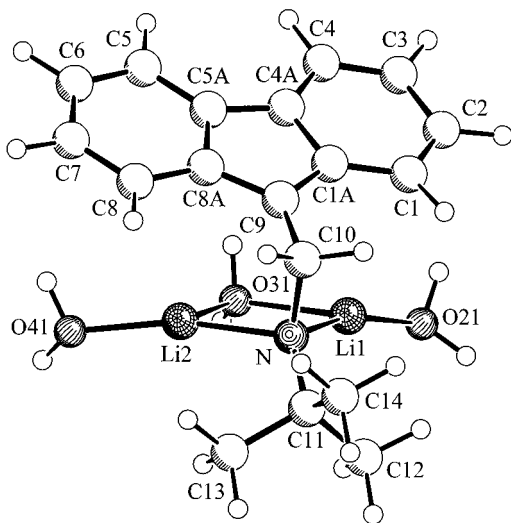(26) MOPAC6: Stewart, J. J. P. QCPE 455, 1990.

An η^5-(1-Azapentadienyl)lithium Derivative

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Figure 5. Calculated molecular structure of compound **10**·3H$_2$O (PM3; local minimum, calc. ΔH_f = −131.9 kcal/mol, crystallographic numering).

Figure 6. Calculated structure of compound **7**·2H$_2$O (PM3; atom numbering analogous to the related X-ray crystal structures).

Table 1. Comparison of Bond Lengths (Å) and Bond Angles (deg) around the Lithium Atoms from X-ray and PM3 for Compound **11**[a]

bond/angle	X-ray	PM3	bond/angle	X-ray	PM3
Li−C8	2.654(7)	2.560	N11−C10−Li	48.5(2)	34.18
Li−C8A	2.810(7)	3.088	C8A−C8−Li	81.5(2)	98.10
Li−C9	2.862(7)	3.298	C9−C10−Li	84.1(2)	90.85
Li−C10	2.645(7)	2.969	C10−N11−Li	102.7(3)	123.68
Li−N11	2.031(7)	2.004	C12−N11−Li	130.8(3)	116.86
Li−O20	1.939(7)	2.011	O20−Li−O30	103.0(3)	103.84
Li−O30	1.947(7)	1.958	O20−Li−N11	131.8(3)	112.20
C7−C8−Li	132.7(3)	127.62	O30−Li−N11	119.9(4)	140.62

[a] Atom numbering as in Figure 2.

H$_2$O molecules. This allowed for a good comparison between the experimentally obtained X-ray structures and the structures calculated for independent molecules in the gas phase, thus *inter alia* allowing the evaluation of the specific influences of the crystal lattice.

Compound 10. The computational results for the dilithio compound **10** are somewhat complicated to interpret. Complete geometry optimizations starting from various initial geometries without including the water molecules as models for the etheral solvents yield essentially two minima. One corresponds to a four-membered ring involving Li1−N−Li2−C1, positioned perpendicular to the fluorene moiety (see Figure 2 for a comparison). This is ca. 10 kcal/mol higher in energy than the global minimum. The latter resembles the X-ray structure of **10**, showing bridging of the lithium cations between the nitrogen atoms and the carbon atoms C1 and C8, respectively. Including three molecules of water to simulate the X-ray structure leads to an asymmetric structure, having one lithium ion coordinated with two molecules of water, the other one with only one molecule of water. This structural type came out to be lowest in energy (global minimum, calc. ΔH_f = −139.2 kcal/mol). Introducing a preformed L1−N−Li2−O four-membered ring as found in the X-ray diffraction study led to a second minimum, ca. 7 kcal/mol higher in energy (calc. ΔH_f = −131.9 kcal/mol, see Figure 5), showing close structural analogies to the experimentally found geometry. Both lithium ions have close contacts to the nitrogen atom and to the oxygens of the solvent molecules (ca. 2.0 Å) with additional weaker interactions to the carbon atoms C1 and C8 (2.7 Å). The Li1−Li2 interaction is calculated to be much weaker than experimentally observed (calc. distance: 3.11 Å). The main disagreement with the experiment is the calculated perfectly perpendicular position (90°) of the dilithiated CH$_2$−N−tBu unit with respect to the fluorene plane. However, bending of this unit from 90° to 98° costs only 0.1 kcal/mol, indicating a very soft potential energy hypersurface. This suggests that crystal lattice forces cause this bending, since no obvious intramolecular steric effects are detectable. A direct comparison between X-ray and calculational data is therefore misleading. The central four-membered ring seems to cause problems to PM3 regarding the calculated heat of formation, but still the parameter set used is suitable to model such structures.

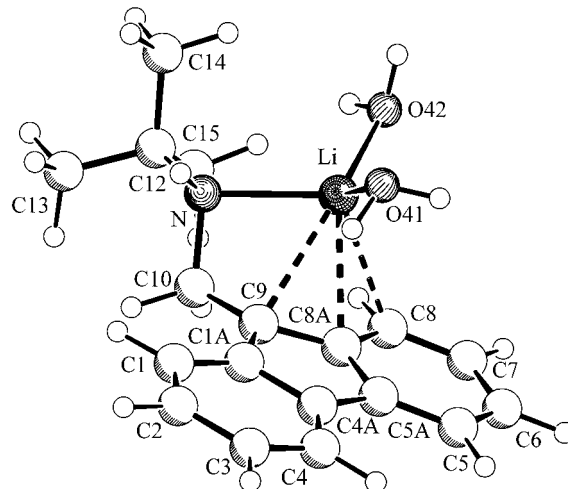Based on the experience with the PM3 calculations for **10**, we also suggest a molecular structure for compound **7***2H$_2$O

as predicted by the PM3 method (Figure 6), of which no X-ray data are available. Since **7** is prepared from fluorene **6**, initially a lithiocene-like structure was expected. However, by starting with different geometries, the coordination of the lithium cation to the nitrogen atom (2.191 Å) seems to be the predominant interaction, thus allowing short contacts only to C8 (2.471 Å), C8a (2.467 Å), and C9 (2.535 Å) but not to the center of the five-membered ring of the fluorenyl moiety. Two more short distances to the oxygen atoms of the model solvents (O41: 2.000 Å and O42: 1.978 Å) produce a six-coordinate lithium cation, whose chemical environment resembles very much that of compound **11** (see below).

Compound 11. A careful investigation of the possible conformers of **11** revealed a U-shape structure which very closely resembles the X-ray results (Figure 7, top; see Figure 3 for a comparison). Several starting geometries placing the lithium cation above the central five-membered ring or in the neighborhood to nitrogen, all led to the same U-shaped conformer. A local minimum with the lithium cation on the face of a six-membered fluorene ring was ca. 20 kcal/mol higher in energy. The strong preference of the U-shape structural type is not surprising. The few reported experimental and theoretical studies on 1-azapentadienyl lithium compounds[4] point to the predominance of U-shaped structures with an η^3-1,5 bridging lithium cation, allowing the participation of the lone pair on nitrogen to be involved in stabilizing the metal ion. A detailed analysis of the calculated structure of **11** (see Table 1) leads to the same principal interactions of the lithium atom as obtained from the X-ray diffraction study. Thus, the shortest contacts of lithium are to the two ether oxygens and to the nitrogen atom, followed by a weaker interaction to C8. PM3 gives a significantly weaker interaction to C10 as found experimentally.
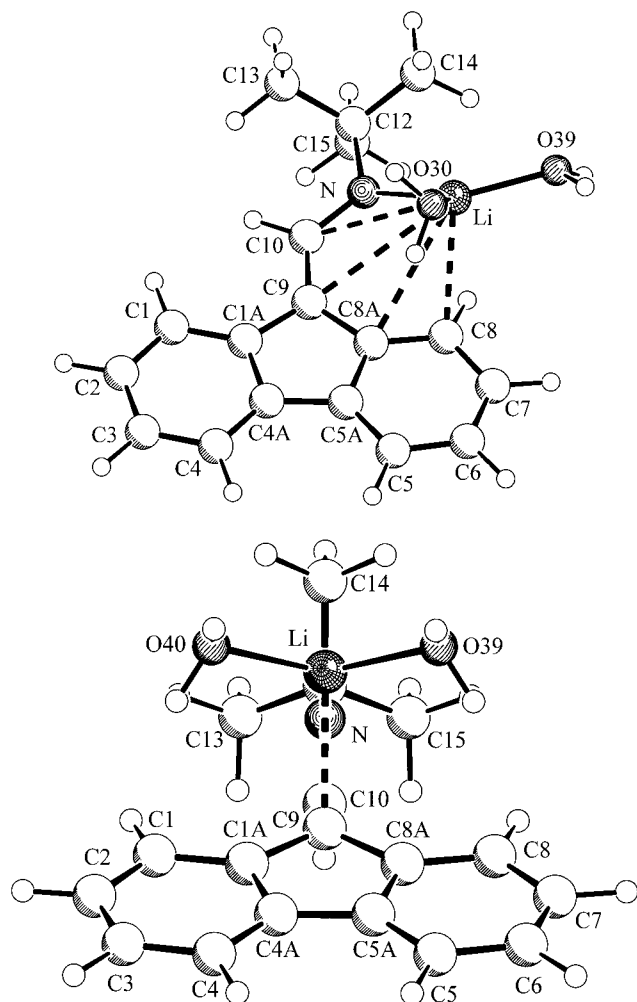
Figure 7. Calculated structure of **11** (top) and calculated transition state structure of **11**-TS (bottom) of the automerization reaction of **11** (both PM3).

In slight difference to the X-ray structure, PM3 calculates the lithium cation to be essentially four coordinate, placed in the center of a distorted tetrahedron. This indicates minor problems of PM3 in balancing the bonding of lithium to different types of nitrogen and carbon atoms. Nevertheless, the overall structure is reproduced very well by PM3, considering the soft potential around lithium. Special crystal lattice effects seem to be absent.

A temperature dependent NMR study revealed a dynamic behavior of **11** in solution (see above). According to the symmetry properties of **11** obtained by NMR a degenerate equilibrium is taking place rapidly on the NMR time scale at higher temperatures (>250 K) potentially involving a transition state of higher symmetry compared to the established ground state structure of **11**. To investigate this behavior the PM3 method was applied in a search for a transition state showing C_s symmetry. We were able to localize such a transition structure **11**-TS (NIMAG = 1, -38.20 cm^{-1}) with a calculated relative energy of 8.7 kcal/mol compared to **11**. This energy does not differ significantly from the experimentally observed barrier of ca. 12 kcal/mol. As indicated in Figure 7, the 1-azaallyllithium moiety of **11**-TS (i.e., Li−N, C10, C9) now adopts a perpendicular orientation with respect to the fluorene plane (C_s symmetry), placing the lithium cation above the central five-membered ring of the fluorene system and resulting in electronic decoupling of the C10−C9 π-interaction.

Conclusions

Our study has shown that the (1-azapentadienyl)lithium derivative **11** is readily available by deprotonation of the fulvene **5**. Alternatively, **11** is available from the mechanistically more complicated reaction sequence initiated by treatment of the aminomethylfluorene derivative **6** with suitable bases. Other structurally very interesting products form as well (e.g., **10**). **11** probably is formed via the fulvene **5** which is subsequently deprotonated. The X-ray crystal structure analysis of **11** has revealed a U-shaped η^5-1-azapentadienyl substructure. There is a tendency toward a slight asymmetry in the η^5-interaction, favoring the N−Li and the Li−C8/C8a interaction, but the C9 and C10 centers are clearly within bonding contact with the metal. A PM3 computational study reveals the same substructures, suggesting that crystal packing forces are not a major factor in determining the observed bonding geometry of **11** in the solid state.

Our study also points to the energetic limits of the Li−1-azapentadienyl bonding interaction of **11**. In solution, a rapid equilibration of the two symmetry-equivalent η^5-(1-azapentadienyl)Li-type structures is observed. The activation barrier ($\Delta G^{\ddagger}_{enant}$) of this process is ≈12 kcal/mol. The computational analysis (PM3) has located a C_s-symmetric transition state structure with a calculated activation barrier that is in accord with the experimental value. Thus, the observed $\Delta G^{\ddagger}_{enant}$ value maybe a good estimate of the magnitude of the "extra stabilization" of a η^5-(1-azapentadienyl)lithium unit in **11**. Whether this provides an estimate of the general range of an energetic separation between different types of (1-azapentadienyl) anion isomers in their respective alkali metal compounds will be investigated.

Experimental Section

The reactions involving organometallic substrates or reagents were carried out in an inert atmosphere (argon) using Schlenk-type glassware or in a glovebox. Solvents were dried and distilled under argon prior to use. The following instruments were used for physical characterization of the compounds: Bruker AC 200 P and Bruker AM 360 NMR spectrometers (atom numbering schemes used are analogous as in Figures 2 and 3); Nicolet 5 DXC FT-IR spectrometer; DuPont 2910 (STA instruments) DSC; elemental analyses: Foss-Heraeus CHN-O Rapid; X-ray crystal structure analyses: data were collected on Enraf-Nonius CAD4- (**1, 11**) or MACH3-diffractometers (**10**). Structures were solved with the program SHELXS-86 and refined with SHELXL-93. Graphics were done with XP and SCHAKAL. *tert*-Butyl isocyanate was distilled prior to use.

Reaction of Fluorenyllithium with *tert*-Butyl Isocyanate. *n*-Butyllithium (48 mL of a 1.55 M solution in *n*-hexane, 74.4 mmol) was added dropwise with stirring at −78 °C to a solution of 12.3 g (73.8 mmol) of fluorene in ca. 200 mL of tetrahydrofuran. The cooling bath was then removed, and the mixture allowed to warm to room temperature. After 4 h of stirring the reaction mixture was cooled to −50 °C. *tert*-Butyl isocyanate (6.4 g, 64.9 mmol) in 50 mL of THF was added dropwise. Then the cooling bath was removed, and the mixture stirred overnight at ambient temperature. The resulting solution of **3** was directly subjected to the reduction reaction using LiAlH$_4$ (see below). For characterization, a small amount of the solution was hydrolyzed by adding it to a saturated aqueous sodium chloride solution. The mixture was extracted with dichloromethane. The organic phase was washed with water and dried over magnesium sulfate. The solvent was removed in vacuo to give **4**, mp 194 °C: HRMS calcd for C$_{18}$H$_{19}$-NO 265.1466, found 265.1474. ^{1}H NMR (CDCl$_3$): δ 7.75 (m, 2H), 7.67 (m, 2H, 1-H, 8-H, 4-H, 5-H), 7.37 (m, 4H, 2-H, 7-H, 3-H, 6-H), 5.01 (br. s, 1H, NH), 4.66 (br. s, 1H, 9-H), 1.19 (s, 9H, C(CH$_3$)$_3$). ^{13}C NMR (CDCl$_3$): δ 169.7 (*C*ONH), 141.8, 141.2 (C1a, C8a, C4a, C5a), 128.1, 127.6, 125.1, 120.2 (C1, C8; C2, C7; C3, C6; C4, C5), 57.1 (C9), 51.1, 28.5 (*C*(CH$_3$)$_3$). IR (KBr): $\tilde{\nu}$ = 3257 cm^{-1} (NH), 3064, 2965, 1645 (C=O), 1549, 1450, 1327, 1262, 1225, 1098, 1023, 803, 742.

6-(*tert*-Butylamino)dibenzofulvene 5. To the remaining solution of **3** in THF (see above) was added LiAlH₄ (20.0 g, 527 mmol) in several portions. The mixture was kept at reflux temperature with stirring for 40 h and then hydrolyzed by pouring the solution in several portions (each of ca. 10 mL volume) into a vigorously stirred mixture of 300 mL of ice-water and 100 mL of ether. The phases were separated, and the aqueous layer was extracted with 70 mL of ether. The organic layers were combined, and the solvent removed in aspirator vacuum. The residue was taken into a minimum amount of ether, washed with brine, and dried over MgSO₄. Removal of the solvent in vacuo gave **5** in a quantitative yield (15.9 g). Crystallization from a saturated ethereal solution at −30 °C gave a spectroscopically pure fraction of the fulvene **5**, mp 72 °C: HRMS calcd for C₁₈H₁₉N 249.1517, found 249.1512. ¹H NMR (CDCl₃): δ 7.86, 7.78, 7.57, 7.50 (each d, ³*J* = 7.8 Hz, each 1H, 1-H, 4-H, 5-H, 8-H), 7.41 (d, ³*J* = 14 Hz, 1H, =C*H*-N), 7.28 (1H), 7.18 (2H), 7.08 (1H, each pseudo-t, 2-H, 3-H, 6-H, 7-H), 5.28 (br. d, ³*J* = 14 Hz, 1H, NH), 1.42 (s, 9H, C(CH₃)₃). ¹³C NMR (CDCl₃): δ 140.1, 137.2, 136.2, 134.6 (C1a, C4a, C5a, C8a), 132.9 (=CH−N), 123.7 (double intensity), 122.9, 120.6, 120.1, 120.0, 119.6, 116.5 (C1−C8), 105.9 (C9), 52.3, 30.4 (C(CH₃)₃). IR (KBr): ν̃ = 3422 cm⁻¹ (NH), 3051, 2958, 2925, 1638, 1606, 1446, 1367, 1313, 1296, 1209, 1032, 930, 917, 767, 722.

N-*tert*-Butyl-9-fluorenylmethylamine 6. The fulvene **5** (15.9 g, 63.8 mmol) was dissolved in 800 mL of methanol with the aid of ca. 50 mL of tetrahydrofuran. A total of 6.2 g (98.7 mmol) of sodium cyanoborohydride was added in several portions. The pH was brought to ca. 4−5 by adding a few milliliters of glacial acetic acid. The mixture was stirred for 2 days at room temperature with care being taken that the pH remained constant. The reaction mixture was then poured into 500 mL of saturated aqueous sodium chloride solution. Solid KOH was added to adjust the solution to pH 11. The white precipitate was extracted into 300 mL of ether, and the aqueous phase extracted again with 70 mL of ether. The combined ethereal phases were treated with 300 mL of 2 N aqueous HCl. The acidic aqueous phase was washed with ether (70 mL) and then pentane (70 mL). The organic phases were discarded. Solid KOH was added to the aqueous phase until pH 11 was reached, and the product then extracted with ether (5 × 100 mL). The combined ethereal phases were dried over anhydrous magnesium sulfate. Solvent was removed in vacuo to give 10.6 g (overall yield 65%) of **6** as a white solid, mp 57 °C. Anal. Calcd for C₁₈H₂₁N (251.37) C, 86.01; H, 8.42; N, 5.57. Found C, 85.69; H, 8.40; N, 5.56%. HRMS calcd for C₁₈H₂₁N 251.1674, found 251.1679. ¹H NMR (CDCl₃): δ 7.78, 7.65 (m, each 2H, 1-H, 8-H, 4-H, 5-H), 7.40 (m, 4H, 2-H, 7-H, 3-H, 6-H), 4.02 (t, ³*J* = 7 Hz, 1H, 9-H), 2.96 (d, ³*J* = 7 Hz, 2H, −CH₂−N), 1.15 (br. s, 1H, NH), 1.04 (s, 9H, C(CH₃)₃). ¹³C NMR (CDCl₃, APT): δ 146.1, 140.9 (C4a, C5a, C8a, C1a), 127.1, 126.8, 124.6, 119.9 (C1, C8; C2, C7; C3, C6; C4, C5), 50.4 (C9), 46.3 (−CH₂−N), 48.4, 28.9 (C(CH₃)₃). IR (KBr): ν̃ = 3302 cm⁻¹ (NH).

Deprotonation of the Amine 6 Using *n*-Butyllithium in Diethyl Ether. A suspension of the amine **6** (2.30 g, 9.2 mmol) in 80 mL of ether was cooled to −78 °C. A 1.55 M solution of *n*-butyllithium in *n*-hexane (11.8 mL, 18.3 mmol) was added dropwise with stirring. The mixture was allowed to warm to room temperature over night. During that time an orange-colored precipitate was formed that was isolated by filtration, washed with pentane (3 × 20 mL), and dried in vacuo: yield of **7·Et₂O** 860 mg (29%). ¹H NMR (THF-*d₈*): δ 7.96, 7.36 (m, each 2H, 1-H, 8-H, 4-H, 5-H), 6.94, 6.53 (m, each 2H, 2-H, 7-H, 3-H, 6-H), 4.32 (d, ³*J* = 7.6 Hz, 2H, −CH₂−N), 1.40 (t, ³*J* = 7.6 Hz, 1H, NH), 1.31 (s, 9H, C(CH₃)₃). ¹³C NMR (THF-*d₈*, APT): δ 135.5, 123.6 (C1a, C8a, C4a, C5a), 120.6, 119.6, 113.1, 109.8 (C1−C8), 87.2 (C9), 38.7 (CH₂−N), 51.1 and 29.5 (CMe₃). From the combined filtrate two different looking types of crystals appeared after 2 days at ambient temperature, that were both characterized by X-ray crystal structure analyses and identified as fluorenyllithium (**1·Et₂O**) and **11·(Et₂O)₂**, respectively. X-ray crystal structure analysis of **1·Et₂O**: formula C₁₇H₁₉OLi, *M* = 246.26, 0.4 × 0.2 × 0.1 mm, *a* = 9.698(1), *b* = 19.785(3), *c* = 7.814(1) Å, *β* = 106.21(1)°, *V* = 1439.7(3) Å³, ρ₍calc₎ = 1.136 g cm⁻³, *μ* = 5.14 cm⁻¹, empirical absorption correction via *ψ*-scan data (0.916 ≤ *C* ≤ 0.999), *Z* = 4, monoclinic, space group *P*2₁/*c* (no. 14), *λ* = 1.54178 Å, *ω*/2*θ* scans, 3158 reflections collected (±*h*,−*k*,+*l*), [(sin *θ*)/*λ*]₍max₎ = 0.62 Å⁻¹, 2939 independent and 2033

observed reflections [*I* ≥ 2σ(*I*)], 175 refined parameter, *R* = 0.046, *wR*² = 0.122, max. residual electron density 0.21 (−0.15) e Å⁻³, hydrogens calculated and riding. X-ray crystal structure analysis of **11·(Et₂O)₂**: formula C₂₆H₃₈NO₂Li, *M* = 403.51, 0.7 × 0.35 × 0.1 mm, *a* = 8.080(1), *b* = 32.585(5), *c* = 9.770(3) Å, *β* = 94.08(2)°, *V* = 2565.8(9) Å³, ρ₍calc₎ = 1.045 g cm⁻³, *μ* = 4.911 cm⁻¹, no absorption correction, *Z* = 4, monoclinic, space group *P*2₁/*n* (no. 14), *λ* = 1.54178 Å, *ω*/2*θ* scans, 4922 reflections collected (−*h*,−*k*,±*l*), [(sin *θ*)/*λ*]₍max₎ = 0.62 Å⁻¹, 4586 independent and 2287 observed reflections [*I* ≥ 2σ(*I*)], 279 refined parameter, *R* = 0.078, *wR*² = 0.223, max. residual electron density 0.47 (−0.29) e Å⁻³, hydrogens calculated and riding. The remaining mother liquor was then hydrolyzed by the addition of water. The phases were separated and the aqueous layer extracted with ether (30 mL). From the combined organic solutions white crystals were formed after several days at room temperature, that were identified to contain the aminofulvene derivative **5** (characterization see above).

Deprotonation of 6 with Lithium Hexamethyldisilazide. The deprotonation of **6** with LiN(SiMe₃)₂ was carried out as an NMR experiment in THF-*d₈*. The solid components **6** and LiN(SiMe₃)₂ were mixed at room temperature. Then ca. 0.5 mL of THF-*d₈* was added. The dark red colored solution was characterized by its ¹H NMR spectrum after 25 min. The spectrum showed that only the mono-deprotonated product **7** was present in the solution.

Deprotonation of the Aminofulvene System 5. (a) The amino-fulvene **5** (660 mg, 2.7 mmol) and LiN(SiMe₃)₂ (530 mg, 3.8 mmol) were mixed as solids, then 100 mL cooled (0 °C) ether was added, and the mixture was stirred over night. The reaction mixture was then concentrated in vacuo to a volume of ca. 20 mL. Pentane (100 mL) was added to the suspension. The resulting precipitate was collected by filtration and washed several times with pentane to give 200 mg (27%) of **11** that contains some coordinated ether (ca. 0.5 equiv, indentified by ¹H NMR). The compound **11** could also be obtained in near to quantitative yield by deprotonation of **5** (3.25 g, 13 mmol) in ether/pentane (1:1, 140 mL) at 0 °C with *n*-butyllithium in *n*-hexane (8 mL of a 1.71 M solution, 13.7 mmol). In this case **11** was obtained as a very sensitive red oil: ¹H NMR (THF-*d₈*/benzene-*d₆*, 1:5): δ 9.06 (s, 1H, -C*H*=N-), 8.31, 8.10 (m, each 2H, 1-H, 8-H; 4-H, 5-H), 7.39, 7.19 (m, each 2H, 2-H, 7-H; 3-H, 6-H), 1.44 (s, 9H, C(CH₃)₃). ¹³C NMR (THF-*d₈*/benzene-*d₆*, 1:5): δ 153.2 (−CH=N-), 138.7, 130.0 (C1a, C8a, C4a, C5a), 124.0, 120.3, 116.4, 114.5 (C1−C8), 97.6 (C9), 65.8 and 31.7 (CMe₃). (b) To a mixture of 15 mg (60 μmol) of the aminofulvene **5** and 7 mg (65 μmol) of LDA was added 0.4 mL of THF-*d₈*. The bright yellow solution was transferred to a 5-mm NMR tube and used for a dynamic ¹H measurements (see Figure 4). ¹H NMR (THF-*d₈*, 599.9 MHz, 203 K): δ 8.85 (s, 1H, 10-H), 8.57 (d, ³*J* = 8.0 Hz, 1H, 1-H/8-H), 7.78−7.75 (m, 2H, 4-H, 5-H), 7.52 (d, ³*J* = 8.0 Hz, 1H, 1-H/8-H), 6.93 (pt, *J* = 7 Hz, 1H) / 6.86 (pt, *J* = 7 Hz, 1H) / 6.63 (pt, *J* = 7 Hz, 1H) / 6.54 (pt, *J* = 7 Hz, 1H, 2-H, 3-H, 6-H, 7-H), 1.28 (s, 9H, CH₃-H) ppm. The following individual Δ*G*‡₍enant₎ values were obtained: 11.8 kcal/mol (260 K, 1-H/8-H equilibration), 12.1 kcal/mol (240 K, 243 K, from both the 2-H/7-H and 3-H/6-H equilibration).

Deprotonation of 6 with *tert*-Butyllithium. Two types of experiments were carried out under somewhat different reaction conditions that led to substantially different product mixtures. (a) A solution of the amine **6** (1.95 mg, 7.8 mmol) in 50 mL of tetrahydrofuran was cooled to −78 °C. Then 8.6 mL of a 1.84 M solution of *tert*-butyllithium (15.8 mmol) in pentane was added dropwise with stirring. After 3 h of stirring at −78 °C a brightly orange-red colored precipitate had formed that was collected by filtration (yield 3.01 g, 95%). The product turned out to be almost insoluble even in THF-*d₈* but could be characterized as **7·(THF)₂** after dissolving it with the aid of a slight excess of the Li-specific crown ether [12]crown-4. ¹H NMR of **7·[12]crown-4** (THF-*d₈*): δ 7.92, 7.40 (m, each 2H, 1-H, 8-H; 4-H, 5-H), 6.86, 6.42 (m, each 2H, 2-H, 7-H; 3-H, 6-H), 4.25 (d, ³*J* = 6.4 Hz, 2H, −C*H₂*−N−), 2.9−2.7 (m, ca. 16H, CH₂ of [12]crown-4), 1.29 (s, 9H, C(CH₃)₃), 0.75 (t, ³*J* = 6.4 Hz, 1H, NH). (b) A sample of the amine **6** (20 mg, 80 μmol) was mixed with solid *tert*-butyllithium (20 mg, 320 μmol). Then THF-*d₈* (0.5 mL) was added at once at ambient temperature. A vigorous reaction was observed to take place that resulted in the formation of clear deeply orange colored solution. After 15 min an ¹H NMR spectrum was recorded that showed two sets of signals, one belonging to fluorenyllithium **1** (see above), the other to

the dilithiated species **10**. Several experiments were carried out under similar conditions, in a few cases solutions were obtained that showed only the ^{1}H NMR signals of the pure compound **10**: ^{1}H NMR (THF-d_8): δ 8.01, 7.36 (m, each 2H, 1-H, 8-H; 4-H, 5-H), 6.97, 6.53 (m, each 2H, 2-H, 7-H; 3-H, 6-H), 4.54 (s, 2H, -CH_2−N−), 1.26 (s, 9H, C(CH_3)$_3$). In the sealed NMR tube crystals of **10**·(THF)$_3$ were formed during several weeks at −30 °C that were used for the X-ray crystal structure determination. X-ray crystal structure analysis of **10**·(THF)$_3$: formula $C_{30}H_{43}NO_3Li_2$, $M = 479.53$, $0.7 \times 0.5 \times 0.3$ mm, $a = 10.418(1)$, $b = 18.174(1)$, $c = 15.521(2)$ Å, $\beta = 107.88(1)°$, $V = 2796.8(5)$ Å^3, $\rho_{calc} = 1.139$ g cm^{-3}, $\mu = 0.71$ cm^{-1}, empirical absorption correction via ψ-scan data ($0.979 \leq C \leq 0.999$), $Z = 4$, monoclinic, space group $P2_1/n$ (no. 14), $\lambda = 0.71073$ Å, $\omega/2\theta$ scans, 5112 reflections collected ($\pm h, -k, +l$), [$(\sin\theta)/\lambda]_{max} = 0.62$ Å^{-1}, 4925 independent and 3172 observed reflections [$I \geq 2\sigma(I)$], 328 refined parameter, $R = 0.054$, $wR^2 = 0.149$, max. residual electron density 0.31 (−0.31) e Å^{-3}, hydrogens calculated and riding.

Generation of 10 by Deprotonation of 7. The monolithiate compound **7** was generated in situ by treatment of 430 mg (1.7 mmol) of the amine **6** with 185 mg (1.7 mmol) of LDA in 20 mL of *tert*-butyl methyl ether at 0 °C. The mixture was stirred for 1 h at this temperature and then cooled to −78 °C. A 1.7 M *tert*-butyllithium solution (1.05 mL, 1.8 mmol) in pentane was added dropwise with stirring. The mixture was then allowed to warm to room temperature during 2 h. Solvent was removed in vacuo. The ^{1}H NMR analysis of the residue revealed the presence of a 2:1 mixture of **7** and **10**. Neither of the fragmentation products **1** or **11** was observed in the product mixture under these conditions.

Supporting Information Available: Details of the X-ray crystal structure analyses of compounds **1**, **10**, and **11**, including additional projections of the molecular structures, listings of bond lengths and angles, positional parameters, and the quantum chemical calculations (MOPAC6-Archive entries) (46 pages). See any current masthead page for ordering and Internet access instructions.

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