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A Precoordination Complex of 1,2,3-Trimethyl-1,3,5-triazacyclohexane with *tert*-Butyllithium as Key Intermediate in Its Methylene Group Deprotonation

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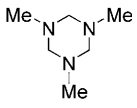
Abstract: α-Lithiated tertiary methylamines are important building blocks in all fields of chemistry, such as for the synthesis of new ligand or catalyst systems. However, the access to these compounds is still limited and the reaction mechanism, in general, not fully understood. We present herein X-ray diffraction analyses of organolithium compounds with 1,2,3-trimethyl-1,3,5-triazacyclohexane (**1**), such as a precoordination adduct of *tert*-butyllithium, $[(t\mathrm{BuLi})_3{\cdot}C_6H_{15}N_3]$, which represents a potential intermediate of the lithiation of the methylene group of this ligand. By means of molecular structures and computational studies, the regioselectivity of this deprotonation reaction can be understood. Furthermore, the *t*BuLi adduct gives a hint to an alternative deaggregation process of organolithium compounds.

Keywords: lithiation · lithium · N ligands · structure–activity relationships · structure elucidation

Introduction

The direct deprotonation of tertiary *N*-methylamines is a challenging task in organic and organometallic synthesis for gaining important building blocks.[1] These building blocks enable the facile introduction of a nitrogen function, which is of central interest in various fields of research, for example, in ligand or natural material syntheses. However, to date, only few amines are known to undergo this type of reaction, for instance, *N,N,N′,N′*-tetramethylethylenediamine (TMEDA), *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (PMDTA), and (1*R*,2*R*)-tetramethylcyclohexane-1,2-diamine [(*R,R*)-TMCDA].[1] Therefore, α-lithiated amines are usually only accessible by transmetalation or via aminoboranes, which can be deprotonated more readily.[2] In general, the hindered α-lithiation is assumed to be the result of the repulsion between the carbanion center and the lone pair of the nitrogen. However, the mechanism of this deprotonation often proceeds via precoordinated intermediates according to the complex-induced proximity effect (CIPE).[3] These complexes determine the reaction pathway and decrease the barrier, so that also the direct α-lithiation of *N*-methylamines becomes possible. X-ray diffraction analysis of potential intermediates is a crucial tool to get a more detailed insight into the ongoing processes, although there have only been few examples of structural analyses of such species, and the mechanism of many reactions is still unclear.[1e,f]

Recently, N. W. Mitzel and co-workers showed that the tridentate, cyclic ligand, 1,3,5-trimethylhexahydro-1,3,5-triazine (**1**), undergoes α-lithiation.[4] Here, deprotonation occurs not at the methyl group of the triazacyclohexane, but at its methylene bridge, resulting in the formation of the first doubly *N*-substituted carbanion.



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This fact raises two essential questions: 1) Do any intermediate structures exist, which enable deprotonation of the amine? 2) Can the regioselectivity of the deprotonation be explained by precoordination according to the CIPE model? First, we herein present molecular structures of **1** with phenyllithium (PhLi) and *tert*-butyllithium, whereby the latter represents a special type of aggregation. Subsequently, DFT studies based on the molecular structures give an explanation for the selectivity of the lithiation of the triazacyclohexane **1**.

Results and Discussion

Out of various mixtures of *tert*-butyllithium and **1** in *n*-pentane, $[(t\mathrm{BuLi})_3{\cdot}C_6H_{15}N_3]$ (**2**) crystallizes at −78 °C in the

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monoclinic crystal system, space group $P2_1$. Compound **2** contains three molecules of *tert*-butyllithium coordinated by the tridentate ligand to give the highly symmetric molecule (pseudo-C_{3v} symmetry). However, symmetry is broken arising from the disorder of one of the methyl groups (C15–C18), which was refined using a split model, describing all atoms of the methyl group in two positions with occupancies of 0.6 and 0.4. Figure 1 shows the main isomer of compound **2**. The Li–C distances range from 2.093(14) to 2.292(18) Å, the Li–N distances from 2.156(16) to 2.190(11) Å, and are thus comparable with monomeric and dimeric lithium alkyls.[5,6] The three lithium atoms form an almost equilateral triangle. Every lithium atom has three contacts: two to the carbanion centers and one to the nitrogen atom of the ligand. Contrary to the oligomeric lithium organics, in which the Li_3 surfaces of the polyhedron are μ^3-capped by the carbanionic units, the *tert*-butyl groups in **2** coordinate only to two lithium atoms, thus forming a Li–C six-membered ring. **2** is a rare example of a molecular structure formed by three alkyllithium groups. Generally, organolithium compounds tend to form structures, such as hexamers, tetramers, dimers, or monomers.[5,6,1f]

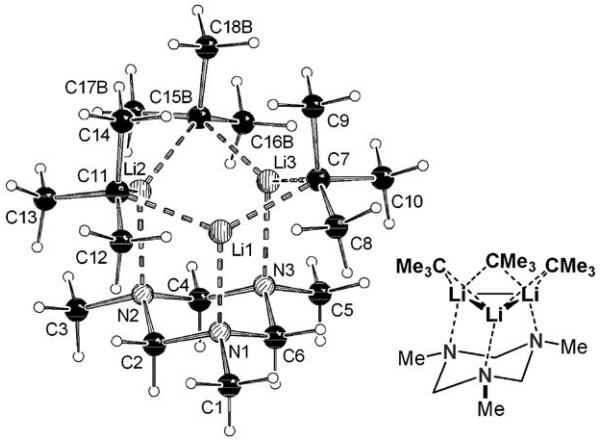

Figure 1. Left) Molecular structure of $[(t\text{BuLi})_3{\cdot}C_6H_{15}N_3]$ (**2**) in the crystal. Only the main isomer of the disordered methyl group is depicted. Selected bond lengths [Å] and angles [°]: Li1-C7 2.169(16), Li1-C11 2.168(15), Li2-C11 2.211(15), C(15B)-Li(3) 2.093(14), C(15B)-Li(2) 2.292(18), Li3-C7 2.182(13), Li1-N1 2.163(6), Li2-N2 2.156(16), Li3-N3 2.190(11) Li1-Li3 2.563(13), Li1-Li2 2.536(14), Li2-Li3 2.529(8), C7-C6 3.616(13), C7-C1 4.371(11), C7-C5 4.38415; Li1-C7-Li3 72.2(4), Li1-C11-Li2 70.8(4), Li3-C15B-Li2 70.3(4). Right) Representation of the molecular structure of compound **2**.

Abstract in German: α-Lithiierte tertiäre Methylamine sind wichtige Bausteine in allen Bereichen der Chemie, wie beispielsweise zur Synthese neuer Liganden oder Katalysatorsystemen. Ihr synthetischer Zugang ist jedoch sehr beschränkt und der Reaktionsmechanismus im Allgemeinen nicht völlig verstanden. Röntgenstrukturanalysen von Organolithiumverbindungen mit dem dreizähnignen Liganden 1,2,3-trimethyl-1,3,5-triazacyclohexan, darunter ein außergewöhnliches Aggregat von *tert*-Butyllithium, $[(t\text{BuLi})_3{\cdot}C_6H_{15}N_3]$, geben Hinweis auf mögliche Mechanismen der Deprotonierung der Methylenbrücke des Liganden. Die Regioselektivität dieser Deprotonierungsreaktion kann mit Hilfe der Molekülstrukturen und quantenchemischen Studien erklärt werden. Darüber hinaus deutet das *t*BuLi-Addukt auf einen weiteren möglichen Daggregationsprozess der oligomeren Lithiumorganyle hin.

With its three *tert*-butyllithium groups coordinated by one ligand, compound **2** represents an extraordinary type of molecular structure.[7] In a thought experiment, this structure suggests a further possibility for the deaggregation of organolithium compounds. In general, it is assumed that the cleavage of the oligomeric structures of organolithium compounds, such as tetramers and hexamers, proceeds via the dimeric compounds, which again break into monomers. However, compound **2** suggests another possibility for this process. Based on the tetrameric structure of $(t\text{BuLi})_4$, the *tert*-butyllithium monomer can be formed by cutting off one edge from the $(t\text{BuLi})_4$ tetrahedron. For instance, this can be achieved by adding (−)-sparteine or (*R,R*)-TMCDA as Lewis base, which are known to build monomers with *t*BuLi in the crystal. The three remaining *tert*-butyllithium groups can then be stabilized by a tridentate ligand as found in an experiment with triazacyclohexane **1** (Figure 2).

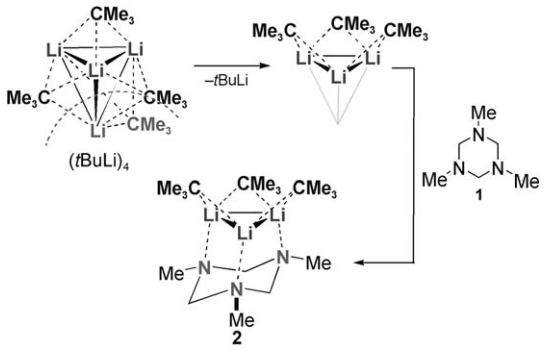

Figure 2. Hypothetical formation of compound **2** by cutting off one edge of the $(t\text{BuLi})_4$ tetrahedron and stabilizing the remaining *tert*-butyl groups by **1**.

Out of an equimolar mixture of **1** and phenyllithium in *n*-pentane/dibutylether, the dimeric compound $[\text{PhLi}{\cdot}C_6H_{15}N_3]_2$ (**3**) crystallizes in the monoclinic crystal system, space group $P2_1/c$ (Figure 3). The molecule possesses an inversion center. Thus, the central four-membered Li–C–Li–C ring, which is typical for dimeric alkyllithium compounds, shows no deformation towards an envelope conformation (sum of angles of 360°), although this deformation is generally observed in dimeric organolithium compounds.[5b,7,8] The Li–C distances in the central four-membered ring amount to 2.211(3) and 2.237(3) Å, the Li–N distances to 2.133(3), 2.439(3), and 2.457(3) Å, with two distances being significantly longer than in analogous dimeric compounds. Altogether, the lithium centers have five con-

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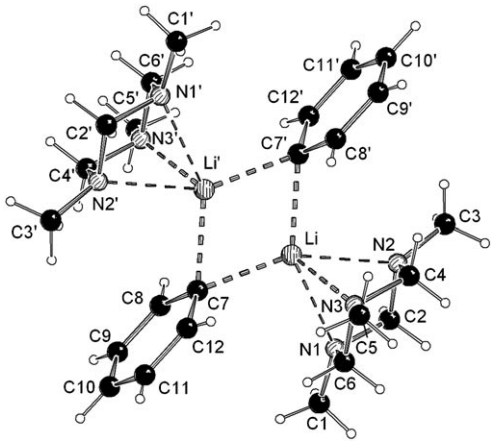

Figure 3. Molecular structure of $[PhLi{\cdot}C_6H_{15}N_3]_2$ (**3**) in the crystal. Selected bond lengths [Å] and angles [°]: Li-C7' 2.237(3), C7-Li 2.211(3), Li-N1 2.457(3), Li-N2 2.439(3), Li-N3 2.133(3), C6-C7 3.579(4), C5-C7 4.294(5), C1-C7 4.115(6); Li-C7-Li' 66.42(12), C7-Li-C7' 113.58(12).

tacts each, whereas two of them are considerably elongated. Besides [PhLi·(−)-sparteine]$_2$, a sparteine-surrogate,[8c] and the TMEDA adduct, compound **3** is a rare example of a dimeric phenyllithium structure.[9] Interestingly, the tridentate ligand PMDTA forms a monomeric structure with PhLi, in which the lithium atoms are coordinated by all three nitrogen atoms of the ligand.[10] In contrast, triazacyclohexane **1** forms a dimer with phenyllithium, in which only one of the three nitrogen centers is coordinated at the lithium atoms.

Considering *t*BuLi, an analogous symmetric, dimeric structure is not possible because of the sterical hindrance of the *t*BuLi groups. This is confirmed by DFT studies, which showed no stationary point for a dimeric structure $[t\text{BuLi}{\cdot}C_6H_{15}N_3]_2$.[11] Nevertheless, besides the crystal structure **2**, also a monomeric molecular structure $t\text{BuLi}{\cdot}C_6H_{15}N_3$ and a coordination polymer with central *t*BuLi dimers, coupled by two ligand molecules, are imaginable. Such a polymeric *t*BuLi structure was recently discovered in our working group with *N,N'*-dimethylpiperazine as ligand.[1f] Calculations at the B3LYP/6-31+G(d) level showed that **2** is the most stable type of structure, being energetically favored by 27 kJ mol^{-1} over $^3/_4$ of the tetrameric $(t\text{BuLi})_4$ and one molecule of triazacyclohexane **1** (Figure 4). Monomeric $t\text{BuLi}{\cdot}C_6H_{15}N_3$ **4** is also 6 kJ mol^{-1} more favorable than $^1/_4$ $(t\text{BuLi})_4$ plus one molecule of triazacyclohexane **1**, and the addition of two monomers to the unsymmetrical dimer $[(t\text{BuLi})_2{\cdot}(C_6H_{15}N_3)_2]$ (model system for the coordination polymer) yields additional 19 kJ mol^{-1}.[12] Altogether, **2** is the thermodynamically most stable adduct between *tert*-butyllithium and triazacyclohexane **1**, as found in experiment.

Investigations of the reactivity of triazacyclohexane **1** conducted by N. W. Mitzel and co-workers showed selective deprotonation of the ligand by *t*BuLi at the methylene bridge, and not at the methyl group.[4a] Therefore, we wanted to know if this selective reaction can be explained by the isolated molecule **2** or further possible intermediates built during the deprotonation process. DFT calculations were

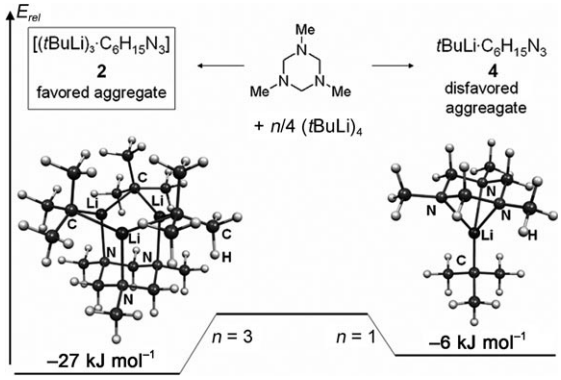

Figure 4. Relative energies (ΔH) of compound **2** and monomer $t\text{BuLi}{\cdot}C_6H_{15}N_3$ (**4**) in comparison to triazacyclohexane **1** and $(t\text{BuLi})_4$.

performed to gain a more detailed insight into possible mechanisms of this reaction.[10] At the B3LYP/6-31+G(d) level, the reaction barriers of the deprotonation of the methyl group and the methylene bridge were calculated. Furthermore, reaction pathways via compound **2** and a monomer-based transition state were calculated.[12] Based on compound **2**, the lithiation of the methylene bridge turned out to be favored by 21 kJ mol^{-1} over the lithiation of the methyl group via the monomeric transition states by 7 kJ mol^{-1}. Both the monomer-based mechanism and the mechanism via compound **2** possess barriers sufficiently low for the process of the reaction (Figure 5), so that both reaction pathways should be possible. Whether the reaction proceeds via compound **2** or via a monomeric transition state depends on the existence of an equilibrium between both species. If the barrier between compound **2** and monomer **4** is too high, the reaction will only proceed via the more favored compound **2** (Figure 5). However, both pathways prefer the deprotonation of the methylene bridge as seen in the experiment.[4a]

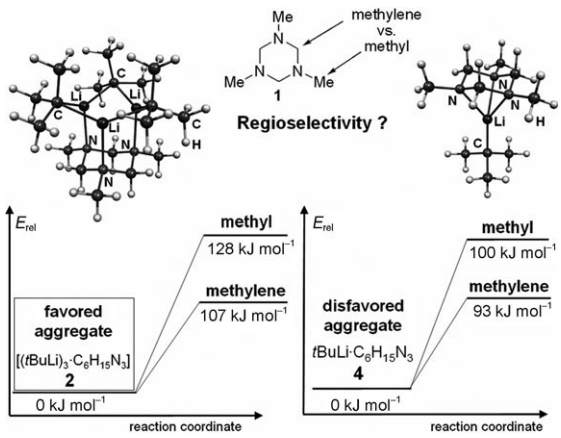

Figure 5. Comparison of the barriers ($\Delta H^{\#}$) of the lithiation of the methyl group and the methylene bridge of triazacyclohexane **1** via **2** and the monomer-based mechanism; B3LYP/6-31+G(d).

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The differences in the reaction barriers of the lithiation of the methyl group and the methylene bridge are easy to explain by means of the crystal structures. In compound **2**, the carbanion center and the hydrogen atom of the methylene bridge, which is located directly below the carbanion center, come close to each other. In the crystal, the carbanionic center C7 shows a closer contact to the methylene bridge C6 of 3.616(13) Å than to the methyl groups [C1: 4.371(11); C5: 4.384 (15) Å]. Arising from this spatial proximity the barrier is decreased and deprotonation becomes possible. An analogous proximity for the deprotonation of the methyl group is not observed in compound **2**. This is also true for the hypothetic monomeric compound *t*BuLi·$C_6H_{15}N_3$ (**4**). For the deprotonation of the methyl group via monomer **4**, even a conformational change of the methyl group from the equatorial to the axial position is required (Figure 6). Consequently, the regioselectivity of the deprotonation reaction of triazacyclohexane **1** can be explained by means of precoordination according to the CIPE.[3]

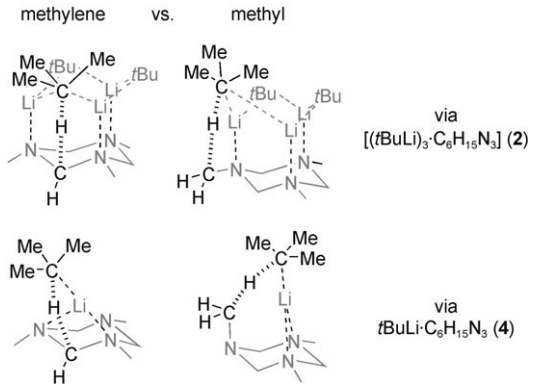

Figure 6. Illustration of the relevant transition states.

The same tendencies can be found for a dimeric structure of triazacyclohexane **1** analogous to [PhLi·$C_6H_{15}N_3$]$_2$ (**3**). Such a dimer is not possible for *tert*-butyllithium because of the sterical hindrance, however, it can be formed by smaller organolithium bases. Calculations at the B3LYP/6-31+G(d) level with methyllithium as lithiumalkyl (Figure 7) showed also a favoritism by 37 kJ mol^{-1} of the deprotonation of the methylene bridge over the deprotonation of the methyl group with a barrier of only 99 kJ mol^{-1}. This favoritism by the dimer-based mechanism is also caused by the spatial proximity between the carbanionic center and the methylene bridge. Although phenyllithium does not undergo such a readily deprotonation and methyllithium, no deprotonation of the ligand at all, in comparison to *tert*-butyllithium or *n*-butyllithium, the spatial proximity can also be found in the molecular structure of **3**: the carbanionic center C7 shows a closer contact to the methylene bridge C(6) of 3.579(4) Å and a farther contact to the methyl groups C5 and C1 of 4.294(5) and 4.115(6) Å. Altogether, the regioselectivity of the deprotonation of 1,2,3-trimethyl-1,3,5-triazacyclohexane (**1**) can be understood by the spatial proximity of reactive groups according to the CIPE independent of the aggregation type of the intermediate (monomer, dimer, aggregate).

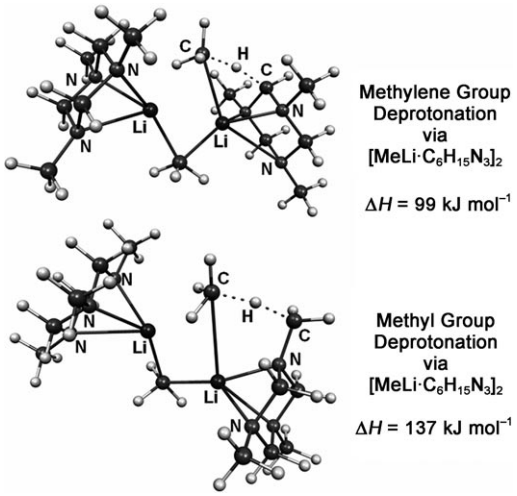

Figure 7. Illustration of the relevant transition states of the dimer-based mechanism; B3LYP/6-31+G(d).

Conclusions

In conclusion, we present herein molecular structures with the tridentate ligand 1,3,5-trimethylhexahydro-1,3,5-triazine (**1**): [(*t*BuLi)$_3$·$C_6H_{15}N_3$] (**2**) and [PhLi·$C_6H_{15}N_3$]$_2$ (**3**). Compound **2** exhibits an extraordinary type of aggregation, which gives hint to a deaggregation process of tetrameric organolithium compounds by breaking into a monomer unit and three alkyllithium groups coordinated by a tridentate ligand. Based on the presented structures, DFT studies of the lithiation of the ligand show that monomer- and dimer-based mechanisms, as well as a mechanism via compound **2** are possible. All pathways show an energetic favoritism of the deprotonation of the methylene bridge over the deprotonation of the methyl group. This regioselective deprotonation of the methylene bridge can be explained by the spatial proximity of the reactive groups in the precoordinated complexes according to the CIPE.

Experimental Section

Deprotonation Reactions

All experiments were carried out under a dry, oxygen-free argon atmosphere by using standard Schlenk techniques. Involved solvents were dried over sodium and distilled prior to use.

2: 1,3,5-Trimethylhexahydro-1,3,5-triazine (**1**) (160 mg, 1.24 mmol) was dissolved in *n*-pentane (5 mL) and cooled to −40 °C. At this temperature, *t*BuLi (1.7 M solution in *n*-pentane, 1.5 mL, 2.55 mmol) was carefully added. Cooling to −78 °C gave colorless needles of **2**. Compound **2** was also obtained with 1 equivalent and 3 equivalents of *t*BuLi. At temperatures higher than −20 °C, deprotonation of the ligand and thus transformation of the compound was observed.

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3: 1,3,5-Trimethylhexahydro-1,3,5-triazine (**1**) (160 mg, 1.24 mmol) was dissolved in *n*-pentane (5 mL) and cooled to −60 °C. At this temperature, PhLi (2.0 M in dibutylether, 0.7 mL, 1.40 mmol) was carefully added to give two phases. Cooling to −78 °C gave colorless crystals of **3** at the phase interface after 12 h. Phenyllithium also undergoes deprotonation of the triazacyclohexane ligand **1**, however, less readily than *tert*-butyllithim. After 5 days at room temperature, one third of the ligand was deprotonated. The lithiated species were trapped with acetophenone according to N. W. Mitzel and co-workers.[4a] With methyllithium, no deprotonation of the ligand was observed.

X-ray Measurements

X-ray measurements were performed on a Bruker APEX-CCD [Mo-K_α: $\lambda = 0.71073$ Å, $T = 173$ K] diffractometer. The crystals of both compounds were mounted in an inert oil (perfluoropolyalkylether) at −60 °C (N_2 stream), by using the X-TEMP 2 device.[13] Crystal structures were solved with direct methods, and refined against F^2 with the full-matrix least-squares method by using SHELXS-90 (G. M. Sheldrick, University of Göttingen 1990) and SHELXL-97 (G. M. Sheldrick, SHELXL97, University of Göttingen 1997). Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 676876 for **2**, and CCDC 676877 for **3**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk/data_request/cif. Ortep plots of both molecular structures in the crystal are available in the Supporting Information.

Crystallographic data of **2**: Colorless needle crystals from *n*-pentane, $0.5 \times 0.5 \times 0.2$ mm^3: $C_{18}H_{42}Li_3N_3$, $M = 321.37$, monoclinic, space group $P2_1$, $a = 9.104(7)$, $b = 14.593(10)$, $c = 9.480(5)$ Å, $\beta = 116.599(10)°$, $V = 1126.2(12)$ Å^3, $Z = 2$, $\rho = 0.948$ Mg m^{-3}. 6239 reflections measured with 2θ in the range 2.50–24.00°, 3459 unique reflections ($R_{int} = 0.0341$). $R_1 = 0.0686$, $wR_2 = 0.1638$ (all data). The methyl group (C15−C18) is disordered, and therefore all atoms are refined over two sites with occupancies of 0.6 and 0.4. The split atoms were not refined anisotropically. Thus, pseudosymmetry element *m* is broken by this disorder resulting in space group $P2_1$ and not $P2_1/m$.

Crystallographic data for compound **3**: Colorless needles from *n*-pentane, $0.5 \times 0.3 \times 0.1$ mm^3: $C_{24}H_{40}Li_2N_4$, $M = 426.50$, monoclinic, space group $P2_1/c$, $a = 7.764(10)$, $b = 18.85(2)$, $c = 9.401(13)$ Å, $\beta = 109.25(5)°$, $V = 1299(3)$ Å^3, $Z = 4$, $\rho = 1.091$ Mg m^{-3}. 9878 reflections measured with 2θ in the range 2.16–25.0°, 2276 unique reflections ($R_{int} = 0.0368$). $R_1 = 0.0450$, $wR_2 = 0.1039$ (all data).

Computational Studies

If not otherwise mentioned, all calculations were done without symmetry restrictions. Starting coordinates were obtained with Chem3DUltra 10.0. Optimization and additional harmonic vibrational frequency analyses (to establish the nature of stationary points on the potential energy surface) were performed with the software package Gaussian 03 (Revision D.01) at the B3LYP/6–31+G(d) level.[12] The vibrational frequency analyses showed one imaginary frequency for the transition states representing the corresponding vibration for the deprotonation. For the educts, no imaginary frequencies were obtained. Coordinates of all calculated structures are available in the Supporting Information.

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