

Self-assembling of bis-*ortho* chelated diaminobenzyl- (NC'N) and butyl-lithium units to give 2 : 2 mixed alkyl lithium aggregates (NC'N)Li₂Bu₂Li₂(NC'N) with a ladder structure

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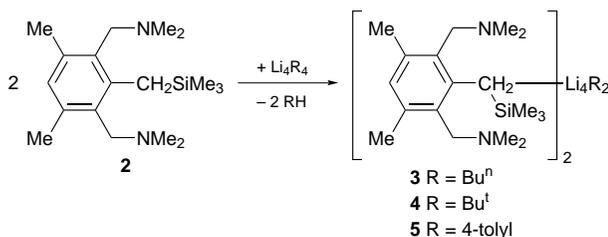
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The lithiation reaction of 1,3-bis(dimethylaminomethyl)-4,6-dimethyl-2-(trimethylsilylmethyl)benzene **2** with BuⁿLi (2 equiv.) affords a unique aggregated species **3** of the parent lithiated compound and BuⁿLi in a 2 : 2 ratio in which the bridging carbon atoms and the lithium atoms are arranged in an unprecedented ladder-type arrangement with exclusively bridging alkyl groups.

Heteroatom-assisted lithiation of the bis(*ortho*-amino) substituted 2-methyl group in 1,3-bis(dimethylaminomethyl)-2,4,6-trimethylbenzene (NC'N-H)[†] with BuⁿLi resulted in the formation of an unprecedented 2 : 2 mixed alkyl lithium aggregate (NC'N)₂Li₄Bu₂ **1**.¹ The structure of **1** suggests considerable stability for the [(NC'N)₂Li₄]²⁺ dication, which comprises a lithium tetrahedron of which two faces are capped by two NC'N terdentate monoanionic ligands, leaving two faces open for the binding of a C-monoanion *via* η³-coordination (in **1**, two η³-bonded Bu groups).

As a possible approach to overcome the formation of tetrahedral Li₄ aggregates like **1** we explored the effect an α-Me₃Si group would have on the aggregate formation. We now report that lithiation of 1,3-bis(dimethylaminomethyl)-4,6-dimethyl-2-(trimethylsilylmethyl)benzene **2** (NC'N-SiMe₃)¹ with BuⁿLi likewise results in the formation of a 2 : 2 mixed alkyl lithium aggregate having (NC'N-SiMe₃)₂Li₄Bu₂ stoichiometry, but with a novel structure comprising a ladder type frame-work with exclusively bridging alkyl groups.

The 1 : 2 molar reaction of **2** with BuⁿLi in pentane afforded a pale yellow crystalline solid. According to its ¹H NMR spectrum this material appeared to be a mixed alkyl species **3** of α-lithiated **2** and BuⁿLi in a 1 : 1 molar ratio (Scheme 1), suggesting that **3** would have a similar 2 : 2 mixed alkyl aggregate structure as found earlier for **1**. Interestingly, the X-ray crystal structure determination[‡] of **3** revealed that the 2 : 2 mixed aggregate was comprised of four lithium atoms and four carbon atoms, but now arranged in a unique ladder-type C-Li₂-C'-Li₂-C framework [see Fig. 1(a)]. It should be noted that X-Li-C-Li structural units have been reported before,²⁻⁴ but **3** is the first heteroleptic organolithium aggregate containing a ladder framework consisting of only lithium and carbon atoms.[§]



Scheme 1

The 2 : 2 mixed alkyl lithium aggregate **3** may be regarded as consisting of two (NC'N-SiMe₃)Li₂ cationic units linked together by two butyl anions. The two cationic units are symmetry-related by a crystallographic centre of symmetry. In the (NC'N-SiMe₃)Li₂ unit the benzylic carbon atom, C(7), is asymmetrically bonded to Li(1) [2.456(6) Å] and Li(2) [2.152(7) Å], while the two nitrogen atoms of the NC'N-SiMe₃ anion are each coordinating to one lithium atom, *i.e.* Li(1) [2.140(6) Å] and Li(2) [2.032(7) Å].

The two butyl anions connecting the two (NC'N-SiMe₃)Li₂ cationic units are each binding to three lithium atoms in an asymmetric manner: C(19) to Li(1) 2.386(9) Å, to Li(1a) 2.274(8) Å and to Li(2) 2.088(8) Å. As a consequence of different bonding modes of the NC'N-SiMe₃ and butyl bridging carbon atoms the coordination geometry of Li(1) is distorted tetrahedral and that of Li(2) more or less trigonal [see Fig. 1(b)]. This difference in coordination number and geometry is nicely

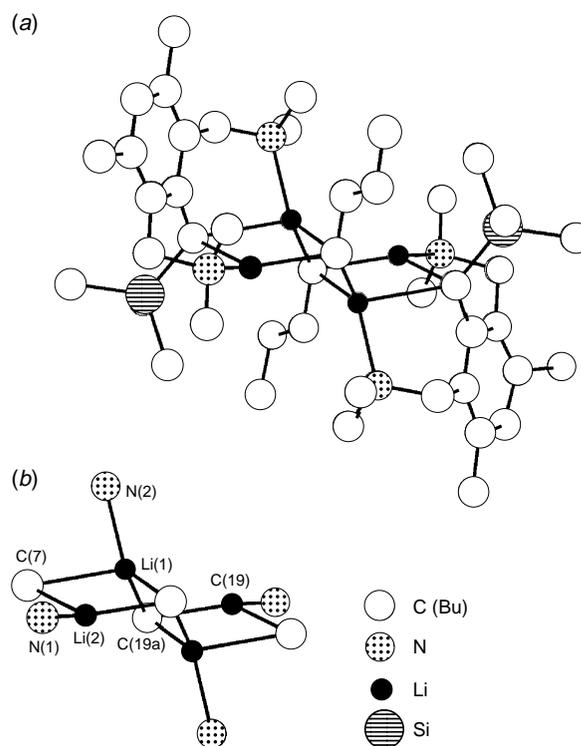


Fig. 1 (a) Overall molecular geometry of **3**. (b) Schematic structure showing the ladder type structure with the arrangement of the lithium atoms, the multi-centre bonded carbon atoms and the coordinating nitrogen atoms. Important bond lengths (Å): Li(1)-C(7), 2.456(6); Li(1)-C(19), 2.386(9); Li(1)-C(19a), 2.274(8); Li(1)-N(2), 2.140(6); Li(2)-C(7), 2.152(7); Li(2)-C(19), 2.088(8); Li(2)-N(1), 2.032(7).

reflected in the shorter bonding interactions ($\Delta\text{Li}-\text{C}_{\text{av}}$, 0.23 Å; $\Delta\text{Li}-\text{N}$, 0.1 Å) around Li(2) as compared to Li(1).

Comparison of the closed tetrahedral-Li₄ **1** and the open ladder-Li₄ structure **3** leads to the following conclusions. α -Substitution leads to a change of the **4c-2e** CLi₃ bonding in **1** to **3c-2e** CLi₂ bonding in **3**. Although the charge at the α -C anion changes considerably on introduction of the α -Me₃Si substituent it is most likely for steric reasons that instead of three (see **1**), only two lithium cations are bonded by the NC'N-SiMe₃ anion. This makes the NC'N-SiMe₃ anion unsuited to forming a well-defined dicationic species [(NC'N-SiMe₃)₂Li₄]²⁺ similar to **1**, but stabilises [(NC'N-SiMe₃)Li₂]⁺ monocationic building blocks instead.

The observed single resonance pattern in the ¹³C NMR spectrum of **3** at room temperature comprises two CH₂N resonances (δ 58.0 and 59.6), two ArMe resonances (δ 21.7 and 21.9) and four NMe resonances (δ 42.6, 43.1, 46.7 and 47.5). These observations indicate the lack of a symmetry plane, both in-plane and perpendicular to the plane of the aryl moiety of the benzylic ligand, and is, moreover, evidence that Li-N coordination is inert on the NMR timescale at this temperature. Also the ¹H NMR spectrum of **3** clearly illustrates the asymmetric fashion in which the benzylic ligand is bonded to two lithium atoms. Two AB patterns were observed for the two NCH₂ groups (δ 3.00 and 3.40, ²J_{HH} 14 Hz, and δ 3.10 and 3.95, ²J_{HH} 14 Hz). In the region between δ 1.60 and 2.10 several overlapping broad lines, attributed to the two NMe₂ and two ArMe groups were observed. ¹H, ¹³C and ⁶Li NMR spectra recorded at lower temperatures (+10 down to -80 °C) did not provide further information, and only extensive line broadening was observed. At higher temperatures a fluxional process becomes operative on the NMR timescale, generating a symmetry plane perpendicular to the aryl moiety of the benzylic ligand. The observation of only one resonance pattern for the two NMe₂ groups (one singlet) and the NCH₂ (one AB pattern) indicates that a process involving Li-N dissociation/association becomes fast on the NMR timescale. However, the fact that the CH₂ protons are still diastereotopic is proof for the configurational stability of the stereogenic α -C atom which is bound to the lithium atoms.

During the lithiation of **2** a stereocentre at the benzylic position, having either (*R*) or (*S*) stereochemistry, is formed in equal amounts. The observation of only one resonance pattern in the ¹H and ¹³C NMR spectra of **3** indicates that, most likely as a consequence of differences in thermodynamic stability of the possible aggregates, a diastereoselective aggregation to **3** [*i.e.* (*R,S*)] as found in the solid state has occurred.

That anionic organic groups other than primary alkyl anions are also capable of linking two cationic (NC'N-SiMe₃)Li₂ units to a ladder type arrangement may be concluded from the independent synthesis of the corresponding Bu^t and 4-MeC₆H₄ aggregates **4** and **5**, respectively (see Scheme 1). The observed ¹H and ¹³C NMR spectra of **4** and **5** are almost identical (with respect to the benzylic ligand) to that of **3**, suggesting a close structural resemblance. Obviously, the formation of these mixed hetero-aggregates from the homo-aggregates is driven by the difference in their thermodynamic stability. The observed selectivity of the self-assembling process in the present study is connected to the use of well-designed heteroatom-containing ligands such as NC'N in **1** and NC'N-SiMe₃ in **2**.

For synthetic purposes the present findings are relevant as ample evidence exists in the literature⁵ that for the *in situ* preparation of various LiR species excess metallating reagent is often required.¶ When this is due to the formation of stable aggregates like **1** or **3**, subsequent reactions will be hampered as a consequence of the presence of trapped, but still reactive, Bu groups, *e.g.* with transition metals both MR as well as often unstable MBu may be formed. The use of Bu^tLi, for example, can sometimes solve this problem, most probably not because of the higher nucleophilicity of the Bu^tLi anion but because of the lower stability of species such as **1** and **3** containing bridging Bu^t instead of Buⁿ groups as compared with the respective parent alkyllithiums.

Footnotes and References

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† The NC'N abbreviation is used to distinguish this monoanionic benzylic ligand from the monoanionic NCN ligand [C₆H₃(CH₂NMe₂)₂-2,6]- we commonly use in our studies.

‡ *Crystal data* for **3**: C₄₄H₈₄Li₄N₄Si₂, triclinic, $P\bar{1}$, $a = 10.309(2)$, $b = 10.3220(13)$, $c = 12.890(3)$ Å, $\alpha = 103.85(2)$ $\beta = 101.19(2)$, $\gamma = 106.293(15)^\circ$, $V = 1227.0(4)$ Å³, $D_{\text{calc}} = 1.019$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 1.0$ cm⁻¹, $Z = 1$, 4333 unique reflections ($1.7 < \theta < 25.0^\circ$), 3046 with $F_o > 4.0 \sigma(F_o)$. Enraf-Nonius CAD4T/rotating anode diffractometer, graphite monochromated Mo-K α radiation, $\lambda = 0.71073$ Å, $T = -123$ °C. Solution by direct methods (SHELXS86), refinement on F^2 with SHELXL-93 converged at R_1 (wR_2) = 0.066 (0.1779), $w = 1/[(\sigma^2(F_o) + (0.0736P)^2 + 1.0293P)]$, $P = (F_o^2 + 2F_c^2)/3$, for 260 refined parameters (anisotropic temperature factors for the non-hydrogen atoms). Hydrogen atoms were included on calculated positions, riding on their carrier atoms. The structure contains some unresolved disorder as indicated by the anisotropic displacement parameter of C(19), the nature of which is unclear. CCDC 182/578.

§ One example of a homoleptic alkyllithium compound exhibiting a cyclic 'ladder' structure is (c-HexLi)₆ (ref. 6).

¶ In this respect it should be noted that we have proposed earlier, based on chemical evidence, that a mixed aryl-butyl aggregate [2-Me₂NCH(Me)C₆H₄]₂Bu₂Li₄ **6** is formed during the heteroatom assisted lithiation of Me₂NCH(Me)C₆H₅, irrespective the molar ratio of amine and BuLi used, *i.e.* excess amine is not reacting further with **6** (ref. 7). Furthermore (C₆H₂Bu^t₃-2,4,6)₂Li₄Bu₂, obtained as one of the products from the reaction of C₆H₂BrBu^t₃-2,4,6 with BuⁿLi, represents the first example of a well characterised mixed aryl-alkyllithium aggregate (ref. 8).

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