Self-assembling of bis-*ortho* chelated diaminobenzyl- (NC′N) and butyl-lithium units to give 2 : 2 mixed alkyllithium aggregates (NC′N)$Li_2Bu_2Li_2$(NC′N) with a ladder structure

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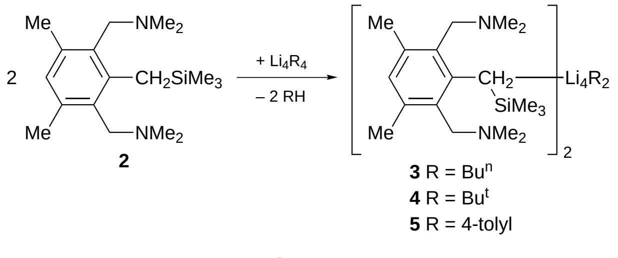
The lithiation reaction of 1,3-bis(dimethylaminomethyl)-4,6-dimethyl-2-(trimethylsilylmethyl)benzene 2 with Bu^nLi (2 equiv.) affords a unique aggregated species 3 of the parent lithiated compound and Bu^nLi in a 2 : 2 ratio in which the bridging carbon atoms and the lithium atoms are arranged in an 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 Bu^nLi resulted in the formation of an unprecedented 2 : 2 mixed alkyllithium aggregate $(NC'N)_2Li_4Bu_2$ **1**.[1] The structure of **1** suggests considerable stability for the $[(NC'N)_2Li_4]^{2+}$ 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* η^3-coordination (in **1**, two η^3-bonded Bu groups).

As a possible approach to overcome the formation of tetrahedral Li_4 aggregates like **1** we explored the effect an α-Me_3Si 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–$SiMe_3$)[1] with Bu^nLi likewise results in the formation of a 2 : 2 mixed alkyllithium aggregate having $(NC'N–SiMe_3)_2Li_4Bu_2$ 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 Bu^nLi 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 Bu^nLi 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–Li_2–C'_2–Li_2–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 alkyllithium aggregate **3** may be regarded as consisting of two $(NC'N–SiMe_3)Li_2$ cationic units linked together by two butyl anions. The two cationic units are symmetry-related by a crystallographic centre of symmetry. In the $(NC'N–SiMe_3)Li_2$ 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–$SiMe_3$ 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 $(NC'N–SiMe_3)Li_2$ 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–$SiMe_3$ 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

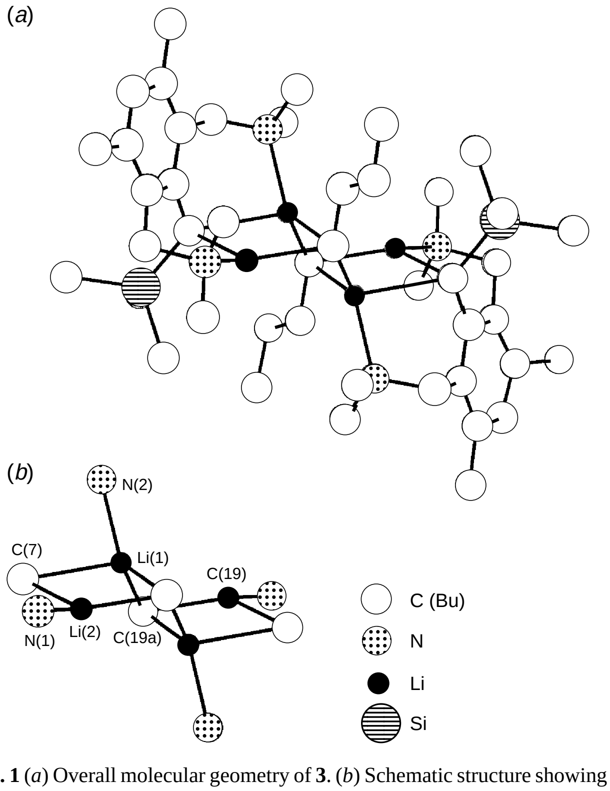


Fig. 1 (*a*) Overall molecular geometry of **3**. (*b*) Schematic structure showing the ladder type structure with the arrangement of the lithium atoms, the multi-centre bonded carbon atoms and the coordinating nitrogen atoms. Important bond lengths (Å): Li(1)–C(7), 2.456(6); Li(1)–C(19), 2.386(9); Li(1)–C(19a), 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 (ΔLi–C$_{av}$, 0.23 Å; ΔLi–N, 0.1 Å) around Li(2) as compared to Li(1).

Comparison of the closed tetrahedral–Li_4 **1** and the open ladder-Li_4 structure **3** leads to the following conclusions. α-Substitution leads to a change of the **4c–2e** CLi_3 bonding in **1** to **3c–2e** CLi_2 bonding in **3**. Although the charge at the α-C anion changes considerably on introduction of the α-Me_3Si substituent it is most likely for steric reasons that instead of three (see **1**), only two lithium cations are bonded by the NC′N–$SiMe_3$ anion. This makes the NC′N–$SiMe_3$ anion unsuited to forming a well-defined dicationic species $[(NC'N–SiMe_3)_2Li_4]^{2+}$ similar to **1**, but stabilises $[(NC'N–SiMe_3)Li_2]^+$ monocationic building blocks instead.

The observed single resonance pattern in the ^{13}C NMR spectrum of **3** at room temperature comprises two CH_2N 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 ^{1}H 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 NCH_2 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 NMe_2 and two ArMe groups were observed. ^{1}H, ^{13}C and ^{6}Li 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 NMe_2 groups (one singlet) and the NCH_2 (one AB pattern) indicates that a process involving Li–N dissociation/association becomes fast on the NMR timescale. However, the fact that the CH_2 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 ^{1}H and ^{13}C 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 $(NC'N–SiMe_3)Li_2$ units to a ladder type arrangement may be concluded from the independent synthesis of the corresponding Bu^t and 4-MeC_6H_4 aggregates **4** and **5**, respectively (see Scheme 1). The observed ^{1}H and ^{13}C 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–$SiMe_3$ in **2**.

For synthetic purposes the present findings are relevant as ample evidence exists in the literature[5] 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^{t}Li, for example, can sometimes solve this problem, most probably not because of the higher nucleophilicity of the Bu^{t}Li anion but because of the lower stability of species such as **1** and **3** containing bridging Bu^t instead of Bu^n 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 $[C_6H_3(CH_2NMe_2)_2\text{-}2,6]^-$ we commonly use in our studies.

‡ *Crystal data* for **3**: $C_{44}H_{84}Li_4N_4Si_2$, triclinic, $P\bar{1}$, a = 10.309(2), b = 10.3220(13), c = 12.890(3) Å, α = 103.85(2) β = 101.19(2), γ = 106.293(15)°, V = 1227.0(4) Å^3, D_{calc} = 1.019 g cm^{-3}, μ(Mo-Kα) = 1.0 cm^{-1}, Z = 1, 4333 unique reflections ($1.7 < \theta < 25.0°$), 3046 with $F_o > 4.0\ \sigma(F_o)$. Enraf-Nonius CAD4T/rotating anode diffractometer, graphite monochromated Mo-Kα radiation, λ = 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 $(c\text{-}HexLi)_6$ (ref. 6).

¶ In this respect it should be noted that we have proposed earlier, based on chemical evidence, that a mixed aryl-butyl aggregate $[2\text{-}Me_2NCH(Me)C_6H_4]_2Bu_2Li_4$ **6** is formed during the heteroatom assisted lithiation of $Me_2NCH(Me)C_6H_5$, irrespective the molar ratio of amine and BuLi used, *i.e.* excess amine is not reacting further with **6** (ref. 7). Furthermore $(C_6H_2Bu^t_3\text{-}2,4,6)_2Li_4Bu_2$, obtained as one of the products from the reaction of $C_6H_2BrBu^t_3$-2,4,6 with Bu^{n}Li, represents the first example of a well characterised mixed aryl-alkyllithium aggregate (ref. 8).

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