lytical absorption correction. Crystal data are as follows: $C_{18}H_{14}O_4S_2$, monoclinic, $C_{2/c}$, $a = 6.636$, $b = 9.758$, $c = 24.510$ Å, $\beta = 90.29^\circ$, $V = 1587.1$ Å³, $Z = 4$, $R = 0.035$. The mean interplanar distance between the hydroxyphenyl moiety and benzoquinone skeleton was 3.13 Å, and the O...O distance in the hydrogen bonds was 2.743(2) Å. Further details of the crystal structure investigation are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, GB-Cambridge CB21EW (UK), on quoting the full journal citation.

- [9] The bond lengths of benzoquinone itself [10] and of the benzoquinone components in **5** are: a) C=C bonds 1.334, 1.327; b) C-C bonds 1.474, 1.479; c) C=O bonds 1.222, 1.228.
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Fig. 1. Structure of the reactive intermediate $[(Me_3Si)_2NAIH_3Li \cdot 2Et_2O]_2$. Selected distances [pm] and angles $^\circ$: Al1-H2 163(4), Al1-H3 158(4), Al2-H4 166(4), Al2-H5 161(4), Al1-H1 158(5), Al2-H6 161(4), Li1-H2 181(4), Li1-H4 174(4), Li2-H3 180(4), Li2-H5 176(4), Al1-N1 185.5(3), Al2-N2 186.0(3), average Li-O 193.1(8), average Si-N 171.3(3), average H-Al-H 107(2), average H-Li-H 107(2), average Al-H-Li 157(3), average Si-N-Si 125.6(2), average Al-N-Si 117.2(2).

Structures of Two Highly Reactive Intermediates upon $LiAlH_4$ Reduction in the Solid State and in Solution: $[(Me_3Si)_2NAIH_3Li \cdot 2Et_2O]_2$ and $[(Me_3Si)_2N]_2AlH_2Li \cdot 2Et_2O^{**}$

By Andreas Heine and Dietmar Stalke*

Lithium aluminum hydride $LiAlH_4$ is a versatile reducing and hydrogenating reagent in both inorganic and organic synthesis.^[1, 2] Although more than 60 functional groups are known to react with $LiAlH_4$, very little is known of the reactive intermediates involved in these syntheses. We report here the isolation of the intermediates **1** and **2**.

The overall reaction to form the trisubstituted aluminum compound **3**^[3, 4] proceeds stepwise, whereby the reactive mono-substituted intermediate **1** and the disubstituted intermediate **2** can be isolated. Although the isolation of **1** and **2** does not necessarily prove that these compounds are intermediates in the reaction pathway suggested above, this is, however, chemically plausible. $LiAlH_4$ was allowed to react with hexamethyldisilylamine in diethyl ether. The reaction mixture was stirred for 24 h at room temperature and filtered, whereupon crystals of **1** were obtained after 3 d at $-35^\circ C$. The crystals were directly mounted onto the diffractometer from mother-liquor at ca. $-50^\circ C$, thus permitting an X-ray structure analysis. At approximately $-30^\circ C$ the colorless crystals start to "effervesce" and turn into a white insoluble powder. We assume that they lose hydrogen. **1** (Fig. 1) is a dimer in the solid state.^[5] The aluminum atoms in the central eight-membered $Al_2H_4Li_2$ ring are each coordinated by three hydrogen atoms and a $N(SiMe_3)_2$ ligand. The lithium atoms form two bridges between the two $(Me_3Si)_2NAIH_3$ units via Li-H contacts. Each of them is also coordinated to two ether molecules. The average Li-H

distance in **1** is 177.7 pm and therefore significantly shorter than in solid LiH (204.0 pm)^[6] or even $LiAlH_4$ (188–216 pm).^[7] To our knowledge, a shorter Li-H contact has only been found (168 and 192 pm, determined by X-ray structure analysis) in $[tBu_3AlHLi]_2$.^[8] The shortest Li-H contact (159.6 pm) is found by spectroscopic techniques in molecular LiH .^[9] The average Al-H distance of 161.0 pm is in good agreement with the values quoted in the literature.^[8, 10–12] Addition of $HN(SiMe_3)_2$ to $LiAlH_4$ in diethyl ether and subsequent refluxing for 3 h followed by stirring for 12 h at room temperature leads to formation of the disubstituted intermediate **2**. Crystals were grown in good yield at $-18^\circ C$. Under these conditions the reaction is stopped after substitution of two equivalents of bis(trimethylsilyl)-amine rather than allowing the trisubstituted product **3** to be formed. Crystals of **2** were mounted on the diffractometer at ca. $-10^\circ C$ and started to effervesce above $+5^\circ C$. Presumably they also lose hydrogen. Figure 2 shows the monomeric structure of **2** in the solid state. The most striking feature is the central AlH_2Li four-membered kite-shaped ring, in which the lithium atom bridges the two aluminum-bound hydrogen atoms. The bond angles show that **2** has a relatively strained structure. The average H-Al-H bond an-

Fig. 2. Structure of the intermediate $[(Me_3Si)_2N]_2AlH_2Li \cdot 2Et_2O$. Selected distances [pm] and angles $^\circ$: Al-H40 162(2), Al-H50 155(2), Li-H40 189(2), Li-H50 197(2), average Li-O 194.4(6), Al-N1 186.7(3), Al-N2 185.7(2), average Li-H50-Al 96(1), H40-Li-H50 74(1), O1-Li-O2 120.6(3), N1-Al-N2 117.5(1).

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gle in **2** (94.3°) is 12.9° smaller than that in **1** (107.2°). The average H–Li–H angle (73.6°), however, is even 33.8° smaller than that in **1** (107.4°). The intramolecular bridging of the lithium atom leads to a longer Li–H distance (average 193.3 pm; but 177.7 pm in **1**), which is comparable to the distance in LiAlH₄.^[7] The hydrogen atoms are forced close together to the transannular distance of 233.1 pm. Despite this steric strain the molecule does not dissociate in solution. The ⁷Li-NMR spectrum of **2** shows a ¹J(Li,H) coupling constant of 10.5 Hz (Fig. 3). This is in good agreement with

Fig. 3. Experimental ⁷Li-NMR spectra of **2** at various temperatures. The chemical shift at –50 °C is 0.4, the coupling constant ¹J(Li,H) 10.5 Hz.

the only other known ¹J(Li,H) coupling (8.4 Hz) detected in the ¹H/⁷Li-NMR spectra of [Cp*IrH₃Li(pmdeta)] (pmdeta = (Me₂NCH₂CH₂)₂NMe).^[13] This supports our suggestion^[14] that there is more covalent character in bonds to lithium than was previously considered likely. In **2** the ⁷Li–¹H coupling is only resolvable in the temperature window –30 °C to –70 °C. Outside this window the triplet structure of the signal is lost (Fig. 3), at higher temperatures as a result of exchange and at lower temperatures probably as a result of ⁷Li quadrupole effects. The coupling could not be verified in the ¹H-NMR experiment because the hydride signals are too broad. Furthermore, the ¹J(Li,H) coupling could not be observed in **1** at any temperature between room temperature and –120 °C in [D₈]toluene. **1** is fluxional in solution. This fluxionality could indicate a monomer/dimer equilibrium superposed on a μ₁ and/or μ₂ and/or μ₃ hydride bridging exchange.

Experimental

1: HN(SiMe₃)₂ (7 mL, 33.3 mmol) was added over 8 h to a suspension of LiAlH₄ (1.26 g, 33.3 mmol) in diethyl ether (30 mL). The mixture was stirred for 24 h at room temperature. Subsequent filtration furnished a clear solution, storage of which at –35 °C afforded colorless crystals after about one week. ¹H NMR ([D₈]toluene, ca. 25 °C): δ = 0.35 (s, 36H of SiMe₃), 1.08 (t, 24H of CH₂CH₃), 3.35 (q, 16H of CH₂CH₃); ⁷Li NMR ([D₈]toluene, ca. 25 °C): δ = –0.37.

2: A solution of HN(SiMe₃)₂ (8 mL, 38.1 mmol) in diethyl ether (20 mL) was added to a suspension of LiAlH₄ (0.71 g, 18.7 mmol) in diethyl ether (20 mL). The mixture was stirred for 12 h at room temperature. After the precipitate was filtered off, colorless crystals separated from the clear solution after several days at –18 °C. ¹H NMR ([D₈]toluene, ca. 25 °C): δ = 0.47 (s, 36H of SiMe₃), 0.94 (t, 12H of CH₂CH₃), 3.19 (q, 8H of CH₂CH₃); ⁷Li NMR ([D₈]toluene, ca. 25 °C): δ = 0.31, (–50 °C): 0.4, ¹J(Li,H) = 10.5 Hz; IR: ν̄ (AlH) = 1754 cm^{–1} (s).

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1, 141612-14-8; **2**, 141634-70-0; HN(SiMe₃)₂, 999-97-3; LiAlH₄, 16853-85-3.

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Total Synthesis of the Carbohydrate Fragments of Esperamicin A₁**

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Esperamicin A₁^[1] (**1**) is one of the most prominent members of the naturally occurring enediyne anticancer antibiotics.^[2] In this communication, we report the total synthesis of both its carbohydrate chains **2** and **3**^[3] (Scheme 1) in their

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