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A Five-Membered Ring with Three Negative Charges and Solvent-Free Lithium Counterions**

David Scheschkewitz, Matthias Menzel,
Matthias Hofmann, Paul von Ragué Schleyer,
Gertraud Geiseler, Werner Massa,
Klaus Harms, and Armin Berndt*

Dianionic boron heterocycles like **1**–**3** and **7** are well characterized,[1] whereas triply and quadruply negatively charged systems such as **4** and **5** have only been known as ligands in transition metal triple decker complexes.[2] The derivative of **8** described here is the first five-membered ring with three formal negative charges.[3] Its η^5-bound lithium counterions exhibit remarkably short distances to the ring and are free from "external" π and n ligands.

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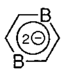

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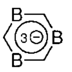

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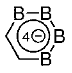

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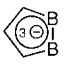

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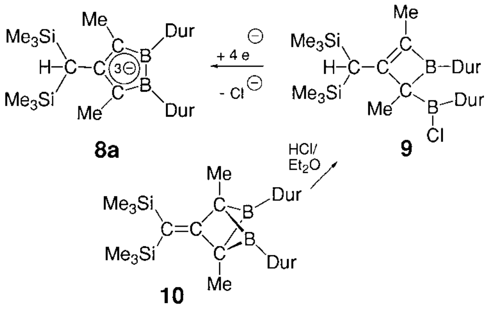
The orange-red trilithium compound **8a**·$\mathrm{Li_3\cdot 2\,Et_2O}$ (Dur = 2,3,5,6-tetramethylphenyl) with *one* solvent-free lithium cation is the only product (besides LiCl) from the reaction of chloroborylboretene **9** with lithium metal in $\mathrm{Et_2O}$. A similar reductive ring expansion in which a B–B bond was formed during the synthesis of a four-membered ring was reported recently.[4] We isolated **8a**·$\mathrm{Li_3\cdot Et_2O}$ with *two* solvent-free lithium counterions by crystallization from boiling toluene. Compound **9** is accessible from diborabicyclopentane **10**[5] and ethereal HCl. Its constitution was secured by



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X-ray structure determination.[6] Figure 1 displays the structures of **8a**$\cdot\mathrm{Li_3}\cdot\mathrm{Et_2O}$ and **8a**$\cdot\mathrm{Li_3}\cdot 2\,\mathrm{Et_2O}$ in the solid state.[7] Table 1 summarizes relevant atom distances compared to those calculated[8] for the unsubstituted **8u**$\cdot\mathrm{Li_3}$ and for the model compound **8b**$\cdot\mathrm{Li_3}\cdot\mathrm{Me_2O}$ (see Figure 2).

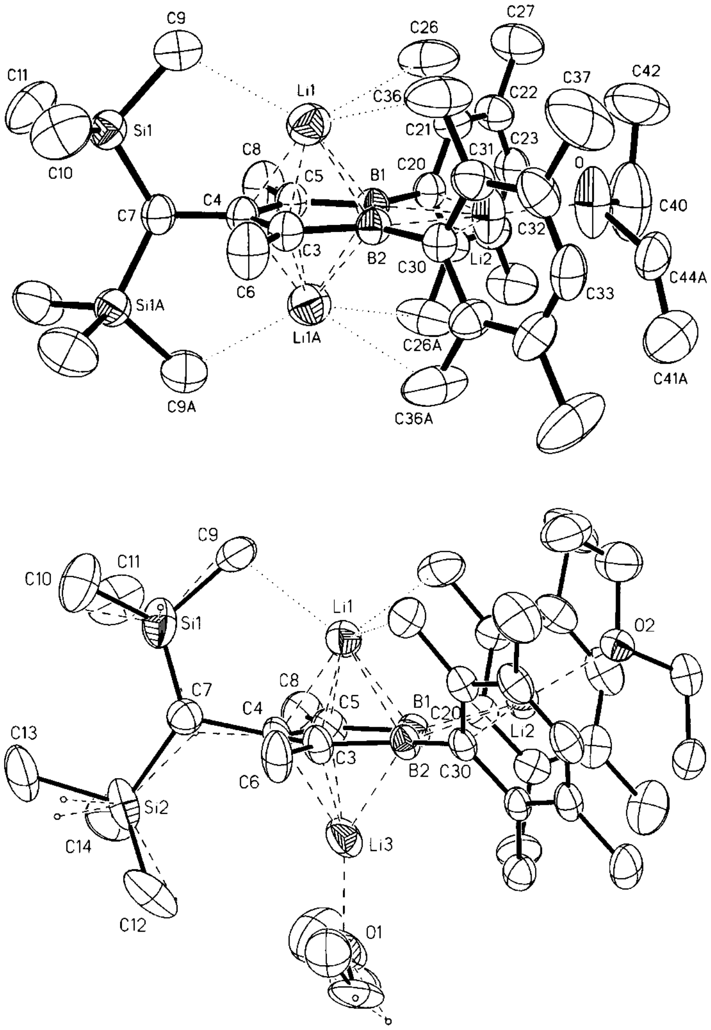

Figure 1. Structures of **8a**$\cdot\mathrm{Li_3}\cdot\mathrm{Et_2O}$ (top) und **8a**$\cdot\mathrm{Li_3}\cdot 2\,\mathrm{Et_2O}$ (bottom) in the crystal; thermal ellipsoids are shown at the 30% probability level. The alternative disordered location of the $\mathrm{CH(SiMe_3)_2}$ group is shown with dashed lines, and Li$\cdots$methyl contacts clearly beneath the sum of the van der Waals radii (r(Me) = 200 pm, r(Li) = 182 pm) are indicated with dotted lines. Selected distances [pm]: **8a**$\cdot\mathrm{Li_3}\cdot\mathrm{Et_2O}$: Li1–C9 265.8(6), Li1–C26 316.2(5), Li1–C36 316.3(5); **8a**$\cdot\mathrm{Li_3}\cdot 2\,\mathrm{Et_2O}$: Li1–C9/C9′ 238(2)/274(2) (disorder), Li1–C29 290.6(7), Li1–C39 315.9(8).

Whereas the lithium counterions of all experimentally characterized five-membered ring anions also are coordinated by π or n ligands (aromatic ligands, ethers, or amines) from the opposite side of the ring, such ligation is completely lacking in **8a**$\cdot\mathrm{Li_3}\cdot\mathrm{Et_2O}$ and partly lacking in **8a**$\cdot\mathrm{Li_3}\cdot 2\,\mathrm{Et_2O}$. Instead, the C–H bonds of the methyl groups of the bis(trimethylsilyl)methyl substituent act as σ ligands. This is shown by the short Li1–C9 and Li1–H(C9) distances of 265.8(6) and 219(4) pm, respectively, in **8a**$\cdot\mathrm{Li_3}\cdot\mathrm{Et_2O}$ as well as the short Li1–C9 distance of 238(2) pm in **8a**$\cdot\mathrm{Li_3}\cdot 2\,\mathrm{Et_2O}$.[9] Comparably short distances have been observed in many solvent-free lithium compounds as a consequence of agostic interactions.[10]

Table 1. Selected bond distances [pm] of **8a**$\cdot\mathrm{Li_3}\cdot 2\,\mathrm{Et_2O}$ and **8a**$\cdot\mathrm{Li_3}\cdot\mathrm{Et_2O}$ (crystal structures) as well as of **8u**$\cdot\mathrm{Li_3}$ and **8b**$\cdot\mathrm{Li_3}\cdot\mathrm{Me_2O}$ (//B3LYP/6-31G*).

	8a$\cdot\mathrm{Li_3}\cdot 2\,\mathrm{Et_2O}$	**8a**$\cdot\mathrm{Li_3}\cdot\mathrm{Et_2O}$	**8u**$\cdot\mathrm{Li_3}$	**8b**$\cdot\mathrm{Li_3}\cdot\mathrm{Me_2O}$
B–B	172.1(6)	169.3(4)	170.4	172.2
B–C	153.8(5)[a,b]	154.8(5)[a,b]	154.3	155.4
C–C	143.6(5)[a,b]	144.1(4)[a,b]	144.6	144.4
Li(η^2)–B	226.9(7)[a,c]	222.8(7)[a,c]	205.3	222.6
Li(η^5)–B	222.4(7)[a,d] 228.7(7)[a,c]	219.8(5)[a]	223.1	223.5
Li(η^5)–C(B)	209.9(7)[a,d] 216.6(8)[a,c]	208.4(5)[a,d]	214.7	209.2
Li(η^5)–C	207.7(7)[d] 212.2(8)[c]	205.2(5)[a,d]	210.8	204.2
Li(η^5)–ring	170.2(6)[d] 177.8(6)[c]	167.5(5)[d]	173.6	168.9

[a] Mean value. [b] In the five-membered ring. [c] For Li$\cdot\mathrm{Et_2O}$. [d] For Li without $\mathrm{Et_2O}$.

The third lithium ion (Li2) in **8a**$\cdot\mathrm{Li_3}\cdot\mathrm{Et_2O}$ and **8a**$\cdot\mathrm{Li_3}\cdot 2\,\mathrm{Et_2O}$ is η^2-coordinated to the B1–B2 σ bond.[11] In addition Li2 is coordinated to the *ipso*-C atoms of the duryl substituents as π ligands and to one ether molecule as an n ligand.

The η^5-π-coordinated lithium ions without external ligands display remarkably short distances to the ring C and B atoms (i.e., to the plane of the five-membered ring; see Table 1): 167.5 (5) pm (**8a**$\cdot\mathrm{Li_3}\cdot\mathrm{Et_2O}$) and 170.2(5) pm (Li1; **8a**$\cdot\mathrm{Li_3}\cdot 2\,\mathrm{Et_2O}$). The Li3–ring distance of 177.8 (5) pm for **8a**$\cdot\mathrm{Li_3}\cdot 2\,\mathrm{Et_2O}$, which is 8 pm longer than for Li1 due to the $\mathrm{Et_2O}$ coordination, is still among the shortest on record between five-membered rings and lithium ions.[12] Lithium–ring distances in lithium cyclopentadienides **6**$\cdot$Li vary from 178[12a] to 201 pm,[12b] and in the **7a**$\cdot\mathrm{Li_2}\cdot$TMEDA dimer[13] (**7a**: $\mathrm{C_4H_4BNEt_2}$, TMEDA = *N,N,N′,N′*-tetramethylethylenediamine) from 179.5 to 186.9 pm. To evaluate the influence of the magnitude of the negative charge in the unsubstituted five-membered rings on the distances to the η^5-π-coordinated (but otherwise bare) lithium ions, we calculated the neutral series **6u**$\cdot$Li, **7u**$\cdot\mathrm{Li_2}$, and **8u**$\cdot\mathrm{Li_3}$ as well as the model compound **8b**$\cdot\mathrm{Li_3}\cdot\mathrm{Me_2O}$ (Figure 2) and also the charged "inverse sandwich" analogues D_{5h}-$[\mathrm{C_5H_5Li_2}]^+$ (i.e., [**6u**$\cdot\mathrm{Li_2}]^+$) and C_{2v}-$[\mathrm{C_3B_2H_5Li_2}]^-$ (i.e., [**8u**$\cdot\mathrm{Li_2}]^-$) at the B3LYP/6-31G* level of density functional theory.[14]

The Li–ring distance in dianionic **7u**$\cdot\mathrm{Li_2}$ (171.9 pm) is in between those in monoanionic **6u**$\cdot$Li (173.0 pm) and trianionic **8u**$\cdot\mathrm{Li_3}$ (170.6 pm). The effect of increasing negative charge is also reflected by the isoelectronic series [**6u**$\cdot\mathrm{Li_2}]^+$ (185.3 pm), **7u**$\cdot\mathrm{Li_2}$ (171.9 pm), and [**8u**$\cdot\mathrm{Li_2}]^-$ (164.9 pm). The progression in the Li–ring distances within the series [**8u**$\cdot\mathrm{Li_2}]^-$ (164.9 pm), **8b**$\cdot\mathrm{Li_3}\cdot\mathrm{Me_2O}$ (168.8 pm), and **8u**$\cdot\mathrm{Li_3}$ (170.6 pm) is particularly instructive. The third lithium ion, located in the plane of the five-membered ring, increases the distances of the η^5-coordinated lithium ions significantly, more when it is bare (in **8u**$\cdot\mathrm{Li_3}$) than when it is complexed with *n* and π ligands (e.g. in **8b**$\cdot\mathrm{Li_3}\cdot\mathrm{Me_2O}$). Hence, the short Li–ring distances found experimentally in **8a**$\cdot\mathrm{Li_3}\cdot\mathrm{Et_2O}$ and

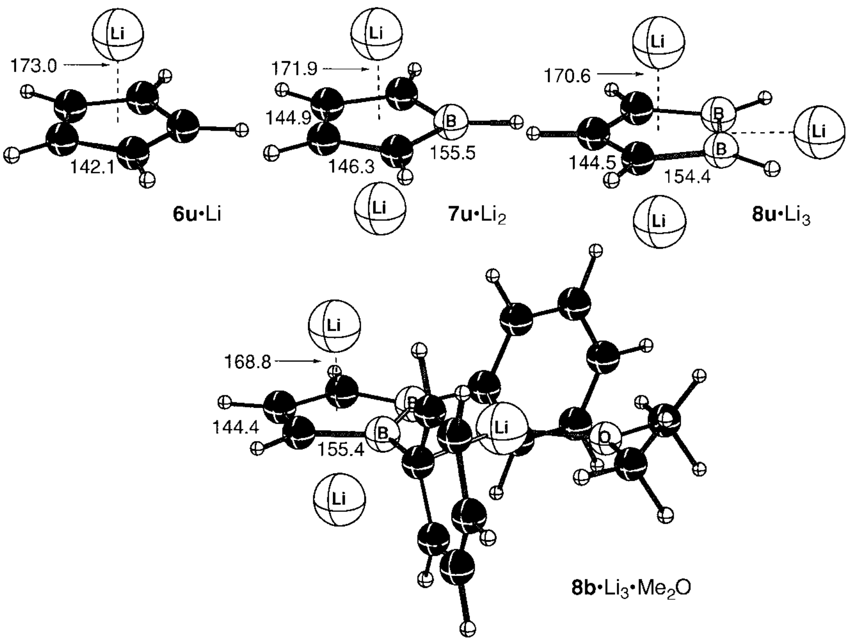

Figure 2. The B3LYP/6–31G* optimized structures of **6u** · Li, **7u** · Li$_2$, **8u** · Li$_3$, and **8b** · Li$_3$ · Me$_2$O.

8a · Li$_3$ · 2Et$_2$O are due to the accumulation of negative charge in the five-membered ring, to the lack of external ligands at the η^5-coordinated lithium ions, and, as the comparison with **8u** · Li$_3$ shows, to the n and π coordination of the lithium ion in the ring plane.

Schnöckel et al. noted that calculated Li–C distances in substituted cyclopentadienes are shorter than in the parent molecule.[15] This also is true for **8b** · Li$_3$ · Me$_2$O and **8u** · Li$_3$ (Table 1). Whereas Schnöckel et al. found that Li–C distances calculated with HF/TZP are generally 2–4% longer than experimentally observed values,[15] we determined that the Li–C and Li–B distances calculated at B3LYP/6-31G*[14] for **8b** · Li$_3$ · Me$_2$O are in very good agreement with those experimentally recorded for **8a** · Li$_3$ · Et$_2$O. The B3LYP/6-31G* optimized geometry of **8u** · Li$_3$ has Li–C and Li–B distances that are 2–3 pm shorter than those given by MP2(fc)/6-31G* and MP2(fc)/6-31+G* calculations. The experimentally observed distances for the ring atoms were fairly well reproduced by B3LYP/6-31G*, even for the unsubstituted model **8u** · Li$_3$ (Table 1).

When the expected substituent effects are taken into account, the computed chemical shifts (GIAO-SCF/6-31G*//B3LYP/6-31G*[14]) of the skeleton atoms for **8b** · Li$_3$ · Me$_2$O ($\delta(^{13}\mathrm{C}) = 105.9, 105.8, 105.9$; $\delta(^{11}\mathrm{B}) = 20.0$) are in reasonable agreement with those measured for **8a** · Li$_3$ · 2Et$_2$O ($\delta(^{13}\mathrm{C}) = 103.7, 116.2, 104.1$; $\delta(^{11}\mathrm{B}) = 14$ and 16).[16] The strong shielding of the η^5-π-coordinated lithium ions ($\delta(^7\mathrm{Li}) = -4.6$, calcd: $\delta(^7\mathrm{Li}) = -3.2$ for **8b** · Li$_3$ · Me$_2$O) is consistent with a 6-π-electron ring current in the five-membered ring.[17, 18]

Compounds **8a** · Li$_3$ · Et$_2$O and **8a** · Li$_3$ · 2Et$_2$O are the first with trianionic five-membered rings.[3] The absence of external π or n ligands at the η^5-π-coordinated lithium counterions in **8a** · Li$_3$ · Et$_2$O, as well as the highly negative charge, are responsible for the extremely short distances to the C$_3$B$_2$ ring.

Experimental Section

8a · Li$_3$ · 2Et$_2$O: A suspension of **9** (2.12 g, 3.8 mmol) and lithium powder (0.25 g, 45 mmol) in Et$_2$O (50 mL) is stirred until the ^{11}B NMR signal for **9** completely disappears (ca. 1 h). The volatile components are evaporated at 5×10^{-6} mbar, and the residue is then dissolved in pentane (50 mL). Excess lithium and LiCl are removed by filtration through a frit. After evaporation of the solvent **8a** · Li$_3$ · 2Et$_2$O (2.46 g, 95 %) remains as a powdery orange-red solid in spectroscopically pure form. Red cuboid crystals (1.41 g, 57 %; m.p. 183–185 °C (decomp.)) are obtained by crystallization at −30 °C from a solution of the raw product in toluene (40 mL). ^{1}H NMR (500 MHz, [D$_8$]toluene, 25 °C): $\delta = 6.65$ (s, *p*-H), 2.66 (br s, Et$_2$O), 2.56, 2.55 (s, duryl CH$_3$), 2.26 (s, C*H*(SiMe$_3$)$_2$), 2.18 (s, duryl CH$_3$), 2.03, 1.99 (s, ring CH$_3$), 0.60 (br s, Et$_2$O), 0.19 (s, SiCH$_3$); ^{11}B NMR (96 MHz, [D$_8$]toluene, 25 °C): $\delta = 15$ ($\nu_{1/2} = 190$ Hz); ^{7}Li NMR (156 MHz, [D$_8$]toluene, 25 °C): $\delta = -0.1$ (1 Li), −4.6 (2 Li); ^{13}C{^{11}B,^{1}H} NMR (125 MHz, [D$_8$]toluene, 25 °C): $\delta = 155.8$, 155.4 (s, *i*-C), 137.6, 137.5, 132.0, 131.9 (s, *o*-/*m*-C), 128.6, 128.5 (d, *p*-C), 116.2 (s, *C*CH), 104.1, 103.7 (each s, B*C*CH$_3$), 64.9 (t, Et$_2$O), 23.2, 23.0 (each q, *o*-CH$_3$), 21.6, 21.5 (each q, *m*-CH$_3$), 19.6 (d, *C*H(SiMe$_3$)$_2$), 19.1, 17.7 (each q, CH$_3$), 14.0 (q, Et$_2$O), 2.2 (q, Si*C*H$_3$).

8a · Li$_3$ · Et$_2$O: ^{7}Li NMR (156 MHz, [D$_8$]toluene, 25 °C): $\delta = 0.3$ (1 Li), −3.8 (2 Li); the rest of the NMR data exhibits only slight differences to that for **8a** · Li$_3$ · 2Et$_2$O.

9: At −110 °C, a 8 M solution of ethereal HCl (5 mL, 40 mmol) is added dropwise to **10** (7.18 g, 14.1 mmol) dissolved in Et$_2$O (150 mL). The mixture is warmed to −30 °C within 1 h. The volatile components are evaporated under high vacuum at −30 °C. The residue consists of **9** (7.03 g, 91 %), a white, powdery, spectroscopically pure solid; m.p. 148 °C. ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C): $\delta = 6.92$, 6.86 (s, *p*-H), 2.23, 2.21, 2.16, 2.08, 2.05 (s, duryl CH$_3$), 1.74 (s, Si$_2$CH), 1.66, 1.26 (s, CH$_3$), 0.36, 0.25 (s, SiMe$_3$); ^{11}B NMR (96 MHz, CDCl$_3$, 25 °C): $\delta = 70$ ($\nu_{1/2} = 2460$ Hz), 45 ($\nu_{1/2} = 2040$ Hz); ^{13}C NMR (75 MHz, CDCl$_3$, 25 °C): $\delta = 162.7$ (s, =C(C)), 157.9 (s, =C(B)), 144.0, 137.2 (br s, *i*-C), 135.1, 133.3, 133.2, 132.9, 132.1 (s, *o*-/*m*-C), 131.1, 131.0 (d, *p*-C), 64.7 (br s, CB$_2$), 25.9 (d, Si$_2$CH), 21.4, 19.7, 19.3, 19.1, 18.9, 18.1 (q, duryl CH$_3$), 18.0, 14.3 (q, CH$_3$), 2.8, 2.3 (q, SiMe$_3$).

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[7] Crystal structure determinations: **8a**·Li_3·2Et_2O: measurements were made with a red block-shaped crystal ($0.7 \times 0.6 \times 0.4$ mm^3) on a Stoe IPDS diffractometer at −80 °C using $Mo_{K\alpha}$ radiation. $C_{40}H_{71}B_2Li_3O_2$. Si_2, orthorhombic, space group $P2_12_12_1$, $Z = 4$, $a = 1485.8(1)$, $b = 1620.0(1)$, $c = 1819.2(1)$ pm, $V = 4378.8(5) \times 10^{-30}$ m^3, $\rho_{calcd} = 1.035$ g cm^{-3}; a total of 21536 reflections were recorded in the range $1.45° < \theta < 24.2°$, resulting in 6846 independent reflections from which 3646 with $F_o > 4\sigma(F_o)$ were observed. All 6846 independent reflections were used for the subsequent calculations; no absorption correction was applied ($\mu = 1.1$ cm^{-1}). The structure was solved by direct methods and refined against F_o^2 with full matrix. Disorder appearing in difference Fourier syntheses were taken into account by refining split positions for the following atoms: 1) the two trimethylsilyl groups (C9, C10, C11 and C12, C13, C14) as well as C7 with site occupations of 50%; 2) the Et_2O molecule coordinated to Li1 (C42, C43) with occupations of 63(2) and 37(2)%. Non-hydrogen atoms were refined using anisotropic displacement factors. Hydrogen atoms were kept on calculated positions, and 1.2 or 1.5 times (CH_3) the equivalent isotropic *U* values of the corresponding C atom were used as displacement factors. An indicated inversion twinning could not be verified significantly. The refinement converged at $wR_2 = 0.1060$ for all reflections, corresponding to a conventional $R = 0.0435$ for the observed reflections. **8a**·Li_3·Et_2O: measurements were made with a red block-shaped crystal ($0.7 \times 0.4 \times 0.3$ mm^3) on a Stoe IPDS diffractometer at −80 °C using $Mo_{K\alpha}$ radiation. $C_{36}H_{61}B_2Li_3OSi_2$, orthorhombic, space group *Pnma*, $Z = 4$, $a = 1390.3(1)$, $b = 1590.6(1)$, $c = 1766.9(1)$ pm, $V = 3907.2(5) \times 10^{-30}$ m^3, $\rho_{calcd} = 1.033$ g cm^{-3}; a total of 24794 reflections were recorded in the range $2.26° < \theta < 25.94°$, resulting in 3909 independent reflections from which 2194 with $F_o < 4\sigma(F_o)$ were observed. All 3909 independent reflections were used for the subsequent calculations; no absorption correction was applied ($\mu = 1.15$ cm^{-1}). The solution and refinement procedure was the same as above, but the hydrogen atoms at C7–C9 were refined. The Et_2O molecule proved to be disordered over at least four positions. A residual $wR_2 = 0.1390$ was obtained for all reflections, corresponding to a conventional $R = 0.0517$ for the observed reflections. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-119471 (**8a**·Li_3·2Et_2O) and CCDC-119470 (**8a**·Li_3·Et_2O). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[16] The appearance of different signals in the NMR spectra at 25 °C for the boron atoms and their substituents, as well as for the boron-bound C atoms of the five-membered ring and the methyl groups attached to them, can be explained by hindered rotation of the bis(trimethylsilyl)methyl group. The rotational barrier was determined to be $\Delta G^{\neq} = 18.5$ kcal mol^{-1}. A rotational barrier of similar magnitude (18.8 kcal mol^{-1}) was deduced for 1,1,2,2 tetrakis(trimethylsilyl)ethane: S. Brownstein, J. Dunogues, D. Lindsay, K. U. Ingold, *J. Am. Chem. Soc.* **1977**, *99*, 2073.

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[18] We have no explanation at present for the discrepancy between the experimental (−0.1 ppm) and the computed NMR chemical shift (3.2 ppm) of the third lithium ion in the ring plane.

Ramberg–Bäcklund Approaches to the Synthesis of C-Linked Disaccharides**

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C-Disaccharides have attracted considerable interest,[1] particularly in view of their hydrolytic stability and potential enzyme inhibitory properties. Since the first synthesis of a carba-disaccharide by Sinaÿ and Rouzaud in 1983,[2] a number of synthetic methodologies have been developed for the preparation of this class of compounds.[1–3] Recent work in our laboratory has focussed on the use of the Ramberg–Bäcklund rearrangement[4] of *S*-glycoside dioxides as the key step in the formation of di-, tri-, and tetra-substituted *exo*-glycals,[5a] which are useful intermediates for the preparation of more elaborate C-glycosides.[5b,c] Scheme 1a illustrates this approach with a glucose-derived sulfone: The Meyers variant[6] of the Ramberg–Bäcklund rearrangement is used to convert the sulfone directly into the corresponding *exo*-glycal without competing 1,2-glycal formation. We have now applied this methodology to the construction of C-linked disaccharides from readily prepared S-linked precursors. The general

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