Crystal Transformation

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Pure α-Metallated Benzyllithium from a Single-Crystal-to-Single-Crystal Transition[**]

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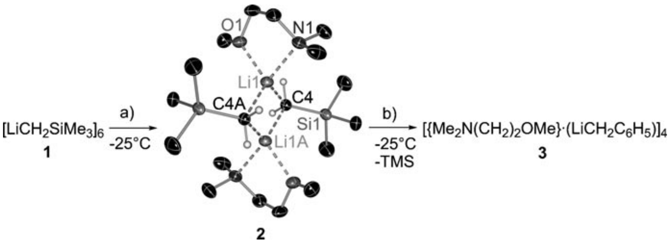
In memory of Gernot Boche

Understanding the chemical behavior of organolithium compounds is generally complicated by the presence of different oligomeric aggregates in the reaction medium.[1] The identification of their molecular structures is vital to deduce structure–reactivity relationships.[2] Herein, we report on the de-aggregation of the hexameric trimethylsilylmethyllithium **1**[3] and the subsequent deprotonation of toluene leading to pure crystalline benzyllithium in ligand-stabilized form. The related structures show new coordination patterns in organolithium chemistry. Solid-state structures of $[(\text{donor})\cdot\text{MCH}_2\text{Ph}]_n$, M = s-block metal, have been reported[4] and were studied theoretically.[5] Benzyllithium is an important industrial bulk material as, for example, a starting material for drug production and polymerization, but is difficult to produce in the required purity.[6] Ring (poly)metalation, preferentially in the *meta* and *para* position, occurs as a side reaction when toluene is treated with *n*BuLi/tmeda, as verified by quenching the products with dry ice.[7] Interestingly, we observed the formation of pure benzyllithium in a solution-mediated single-crystal-to-single-crystal transition from colorless to yellow crystals (Figure 1).

Figure 1. Microscope photograph of transforming crystals (colorless: reactive intermediate, yellow: benzyllithium compound).



Scheme 1. Reaction of parent trimethylsilylmethyllithium (**1**) via the reactive intermediate **2** to give **3**. a) −25 °C, 1 equiv $\text{Me}_2\text{N(CH}_2)_2\text{OMe}$, hexane, 2 equiv toluene; b) −25 °C. Anisotropic displacement parameters of **2** depicted at the 50% probability level (constrained hydrogen atoms are omitted for clarity). Selected bond lengths [pm] and angles [°] of **2**: Li1–O1 205.7(2), Li1–N1 215.2(2), Li1–C4 223.6(2), Si1–C4 182.49(11); Li1-C4-Li1A 66.16(8), C4-Li1-C4A 113.84(8).

By adding toluene to a solution of **1** in hexane and the ligand donor base $\text{Me}_2\text{N(CH}_2)_2\text{OMe}$ at −25 °C colorless crystals formed after several hours. After some days the colorless crystals disappeared in favor of yellow crystals. In the structure analysis the colorless crystals turned out to be the dimeric adduct $[\{\text{Me}_2\text{N(CH}_2)_2\text{OMe}\}\cdot(\text{LiCH}_2\text{SiMe}_3)]_2$ (**2**) in the monoclinic space group $P2_1/c$. The central structural motif is a planar Li_2C_2 rhombic four-membered ring (Scheme 1). ^{1}H-DOSY NMR experiments of **2** in [D$_8$]toluene gave diffusion coefficients of $\lg(D/\text{m}^2\text{s}^{-1}) = -9.01$ and −8.96 for the $\text{LiCH}_2\text{SiMe}_3$ and $\text{Me}_2\text{N(CH}_2)_2\text{OMe}$ signals, respectively. These values are in agreement with a dimeric structure in solution with most of the donor base coordinated (88%). This is futher supported by the diffusion coefficient of the free ligand in toluene $\lg(D/\text{m}^2\text{s}^{-1}) = -8.64$). This degree of binding is supported by the diffusion constant of the free ligand ($\log D/\text{m}^2\text{s}^{-1} = -8.64$) in solution.[8]

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Structure analysis shows the yellow crystals to be the tetrameric benzyllithium complex $[\{Me_2N(CH_2)_2OMe\}\cdot(LiCH_2C_6H_5)]_4$ (**3**) which crystallizes in the monoclinic space group *C2/c*. The central structural motif is a planar Li_4C_4 eight-membered ring with a crystallographic twofold rotation axis in the ring center and perpendicular to the Li_4C_4 plane. The four lithium atoms form a rectangle (Li···Li···Li av. 90.00°, Figure 2).

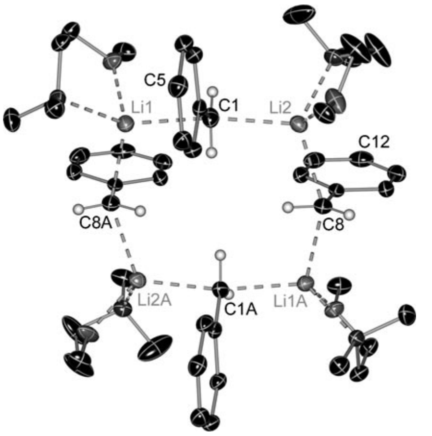

Figure 2. Molecular structure of **3** with anisotropic displacement parameters depicted at the 50% probability level (only C_α hydrogen atoms are shown for clarity). The atoms labeled "A" are symmetry equivalents generated by the twofold rotation axis perpendicular to the eight membered ring.

The bidentate $Me_2N(CH_2)_2OMe$ donor base molecules N,O-coordinate to the lithium metal vertices as chelating, not bridging ligands. There are no significant intermolecular contacts. The ring has two different benzyl groups, oriented alternately on either side of the ring (Figure 2). Hence each benzyl anion is coordinated to two lithium cations. The Li-C_α-Li angles are not the same for the two different types of benzyl moieties in **3** (see Figure 3 and Table 1). Each C_α carbon atom is in a distorted trigonal-bipyramidal geometry, which was predicted by calculations on $CH_3Li_2^+$ ions.[9]

To date only two comparable crystal structures of benzyl alkali-metal compounds with a motif of an eight-membered ring of alternating metal and carbon atoms have been reported, both containing tmeda ligands: $[Li_{1.67}Na_{2.33}(CH_2C_6H_5)_4\cdot(tmeda)_4]$[4e] and $[tmeda\cdot(NaCH_2C_6H_5)]_4$.[4i] The structure of **3** is even more remarkable as an octagonal ring structure complexed by a bidentate ligand is normally sterically forbidden in homometallic lithium tetramers.[4e]

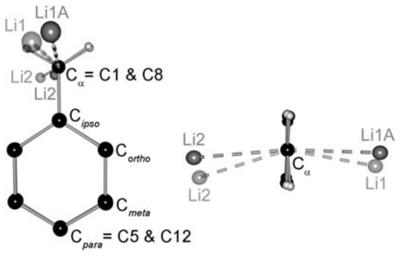

Figure 3. Superposition of the two different benzyllithium environments (left) and view along the C_α-C_{ipso} axis (right) in **3**.

Table 1: Structural parameters of **3** (see Figure 3); angles [°], distances in [pm].

Bent (transparent)		Straight (full)	
Li1-C1$_\alpha$-Li2	151.99(10)	Li1A-C8$_\alpha$-Li2	169.28(9)
Li1-C1	228.9(2)	Li1A-C8	231.4(2)
Li2-C1	231.5(2)	Li2-C8	230.9(2)
Li1-C1-C5	90	Li1A-C8-C12	94.7
Li2-C1-C5	92	Li2-C8-C12	93.8

To gain deeper insight into the formation of **3** an NMR reactivity study was performed (Figure 4). The spectra were measured every 24 h and show an increasing intensity of the signals of **3**. After 24 h the first signals of the *para* H-atoms of **3** can be detected and after 48 h the couplings to the *meta* H-atoms and the *ortho* H-atoms are fully resolved. ^{1}H-DOSY experiments indicate that the diffusion coefficients for the $LiCH_2Ph$ ($\log D/m^2s^{-1} = -9.04$) and $Me_2N(CH_2)_2OMe$ signals ($\log D/m^2s^{-1} = -8.98$) were found to be similar in the reaction solution; thus demonstrating that they are ligated to 90% in solution (see Supporting Information).

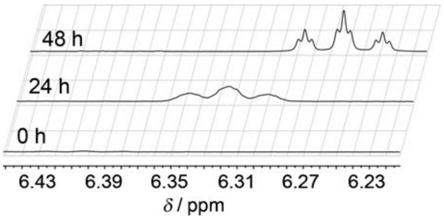

Figure 4. ^{1}H NMR spectra monitoring the transformation of complex **2** into **3** (*para*-H atom).

The diffusion constants of **3** and **2** are similar, which indicates that **3** most likely is dimeric in toluene solution. This assumption is consistent with other NMR parameters. The $^1J_{H,C}$ coupling constants can be employed to determine the amount of delocalization at the benzyl anion. According to investigations of Boche et al. for a pyramidalized (sp^3) benzyl carbanion this coupling constant is expected to be 125 Hz, while the value expected for a planar (sp^2) CH_2 group is 167 Hz.[4a] The $^1J_{H,C}$ coupling of **3** in solution of 127 Hz indicates a far higher sp^3 character than in the tetrameric solid state. The $^1J_{H,C}$ coupling of monomeric **4** (see below, Figure 6, see also Ref. [4f]) is 134 Hz, indicating less sp^3 character than dimeric **3**.

Solid-state magic-angle spinning (MAS) NMR experiments were carried out on **3**. The sample was packed under argon atmosphere in a 4 mm MAS rotor. The ^{13}C NMR spectrum was recorded at a spinning frequency of 12.5 kHz, using high-power ^{1}H–^{13}C decoupling with a radio frequency amplitude of 90 kHz (Figure 5, for full spectrum see Supporting Information). As expected, this spectrum differs from the solution NMR spectrum, it shows twice the number of peaks

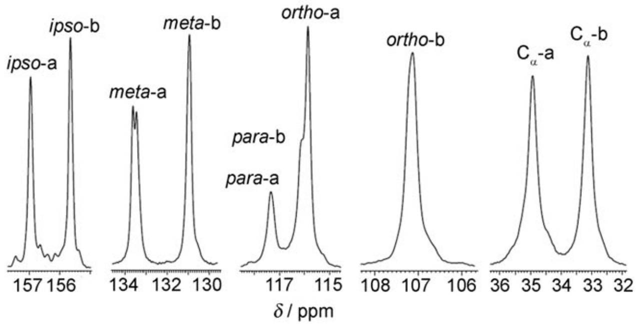

Figure 5. Solid-state ^{13}C NMR spectrum of **3** (only showing the region of the peaks for the benzylic carbon atoms), recorded on a 20 T wide-bore NMR spectrometer.

for the two independent benzylic carbanions in the asymmetric unit (indicated as a and b). A coupling between the C_α and ^{7}Li atoms could not be detected, but a line broadening is clear (line widths about 80 Hz). In comparison, the peaks for C_{ipso}-a and C_{ipso}-b show a line width of about 33 Hz.

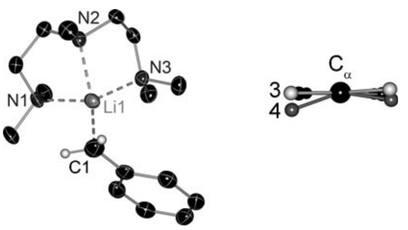

Figure 6. Left: Molecular structure of **4**. Anisotropic displacement parameters depicted at the 50% probability level (only C_α hydrogen atoms are shown for clarity). Selected bond lengths [pm]: Li1–N1 216.3(5), Li1–N2 209.9(5), Li1–N3 223.6(2), Li1–C1 211.4(5). Right: superposition of the benzyl anions with a view along the C_α-C_{ipso} axis of **3** and **4** showing the two different H-C_α-H arrangements.

Currently only three monomeric structures of benzyllithium are known: [(thf)·(tmeda)·($LiCH_2C_6H_5$)],[4a] [(Me$_3$-tacn)·($LiCH_2C_6H_5$)],[4b] and [(Me$_6$tren)·($LiCH_2C_6H_5$)].[4f] Herein we present the monomeric crystal structure of [(pmdeta)·($LiCH_2C_6H_5$)] (**4**) which crystallized from a solution of **1** containing pmdeta and toluene (Figure 6). In this case the crystallization of the intermediate stage was not observed in the presence of toluene, because of the intermediate's high reactivity to deprotonate toluene. By adding toluene to the reaction mixture an immediate reaction from colorless to yellow solution was observed within seconds. The crystal structure of the monomeric intermediate [(pmdeta)·($LiCH_2SiMe_3$)] (**5**) prepared in the absence of toluene was characterized before.[3b] Compound **5** converts instantly into **4** on addition of toluene. [(pmdeta)·($LiCH_2C_6H_5$)] (**4**) crystallizes in the monoclinic space group $P2_1/c$ with two independent molecules in the asymmetric unit (Figure 6). The angles between the Li–C_α bonds and the virtual lines between C_α and C_{para} are close to 90° (88.7° and 92.8°), documenting that the cation is located orthogonal above the C_α atom. The torsion angles involving the CH_2 hydrogen positions which are only slightly bent away from the lithium atom are 31.1° and 31.9°. With a tetrahedral environment at the C_α atom torsion angles of about 60° are expected.

In conclusion, we present the quantitative synthesis of tetrameric benzyllithium [{$Me_2N(CH_2)_2OMe$}·($LiCH_2C_6H_5$)]$_4$ from dimeric [{$Me_2N(CH_2)_2OMe$}·($LiCH_2SiMe_3$)]$_2$ monitored by ^{1}H NMR experiments. Employing monomeric [(pmdeta)·($LiCH_2SiMe_3$)] immediately gives [(pmdeta)·($LiCH_2C_6H_5$)]. Hence a straightforward access to commercially interesting pure crystalline benzyllithium is provided. We currently explore this route to other aliphatic systems difficult to metalate otherwise.

Experimental Section

2–4: 1.5 equivalents of the donor bases $Me_2N(CH_2)_2OMe$ (for **2** and **3**) or pmdeta (for **4**) were added to trimethylsilylmethyllithium in hexane at −25 °C under inert atmosphere. Toluene was added for the crystallization of **3** and **4**. The crystallization was carried out in the freezer. Yields of first crystalline batch under non-optimized conditions: 48 (**2**), 54 (**3**), 69 (**4**).

2: ^{1}H NMR (500 MHz, $C_6D_5CD_3$, 25 °C): $\delta = -2.12$ (s, 4H, CH_2Li), 0.29 (s, 18H, $Si(CH_3)_3$), 2.02 (s, 12H, NCH_3), 2.05–2.11 (m, 4H, CH_2), 2.91 (t, 4H, CH_2), 3.13 ppm (s, 6H, OCH_3); ^{7}Li NMR (117 MHz, $C_6D_5CD_3$, 25 °C): $\delta = 1.16$ ppm (s, CH_2Li), ^{13}C NMR (126 MHz, $C_6D_5CD_3$, 25 °C): $\delta = -6.3$ (CH_2Li), 6.1 ($Si(CH_3)_3$), 45.5 (NCH_3), 58.1 (CH_2), 59.0 (OCH_3), 69.0 ppm (OCH_2); ^{29}Si NMR (99 MHz, $C_6D_5CD_3$, 25 °C): $\delta = -0.70$ ppm (s). Elemental analysis (%) calcd for $C_{18}H_{48}Li_2N_2\ O_2Si_2$: C 54.78, H 12.26, N 7.10; found: C 54.31, H 12.14, N 7.32.

3: ^{1}H NMR (300 MHz, $C_6D_5CD_3$, 25 °C): $\delta = 1.69$ (s, 2H, CH_2Li), 2.04 (s, 6H, $N(CH_3)_2$), 2.10 (m, 2H, CH_2N), 3.15 (s, 3H, OCH_3), 6.28 (m, 1H, *para*-H), 6.68 (m, 2H, *ortho*-H), 6.84 ppm (m, 2H, *meta*-H); ^{7}Li NMR (194 MHz, $C_6D_5CD_3$, 25 °C): $\delta = 1.07$ (s, CH_2Li), ^{13}C NMR (75 MHz, $C_6D_5CD_3$, 25 °C): $\delta = 31.7$ (CH_2Li), 45.4 (CH_3N), 58.3 (CH_2N), 59.0 (OCH_3), 69.7 (OCH_2), 109.6 (*ortho*-C), 119.4 (*para*-C), 128.5 (*meta*-C), 155.9 ppm (*ipso*-C). Elemental analysis (%) calcd for $C_{48}H_{80}Li_4N_4\ O_4$: C 71.62, H 10.02, N 6.96; found: C 70.86, H 9.87, N 7.10.

4: ^{1}H NMR (300 MHz, $C_6D_5CD_3$, 25 °C): $\delta = 1.96$ (s, 2H, CH_2Li), 2.25 (s, 12H, $N(CH_3)_2$), 2.36 (s, 8H, CH_2N), 6.08 (m, 1H, *para*-H), 6.56 (m, 2H, *ortho*-H), 6.91 ppm (m, 2H, *meta*-H); ^{7}Li NMR (194 MHz, $C_6D_5CD_3$, 25 °C): $\delta = 1.20$ ppm (s, CH_2Li), ^{13}C NMR (75 MHz, $C_6D_5CD_3$, 25 °C): $\delta = 36.2$ (CH_2Li), 44.1 (CH_3N), 45.8 (CH_3N), 54.3 (CH_2N), 57.7 (CH_2N), 105.9 (*ortho*-C), 117.0 (*para*-C), 128.5 (*meta*-C), 160.3 ppm (*ipso*-C); elemental analysis (%) calcd for $C_{16}H_{30}LiN_3$: C 70.28, H 11.14, N 15.48; found: C 69.98, H 12.03, N 16.57.

Single-crystal structural analysis: The single crystals were mounted in inert oil under protective atmosphere by applying special cryo application techniques.[10] The X-Ray data sets **2**, **3**, **4** were collected at 100(2) K on an INCOATEC microfocus source[11] with mirror-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) and equipped with a Bruker Smart Apex II detector. The structures were solved by direct methods with SHELXS and refined by full-matrix least squares on F^2 for all data with SHELXL.[12] Non-hydrogen atoms were refined with anisotropic displacement parameters. H atoms in non-disordered C_α-positions were located in the difference Fourier map and refined isotropically, all other H atoms were placed in calculated positions and refined using a riding-model.

2: $Li_2C_{18}H_{48}N_2O_2Si_2$, $M_r = 394.64\ \mathrm{g\,mol^{-1}}$, monoclinic, space group $P2_1/c$, $a = 7.6190(7)$, $b = 18.5142(16)$, $c = 9.8057(9)$ Å, $\beta = 100.5560(10)°$, $V = 1359.8(2)\ \mathrm{nm^3}$, $Z = 2$, $\mu(Mo_{K\alpha}) = 0.142\ \mathrm{mm^{-1}}$, $T = 100(2)$ K, 26481 reflections measured, 3113 unique reflections, $R_{int} = 0.0292$, 132 parameters refined, $R1(\text{all data}) = 0.0366$, $R1[I>2\sigma(I)] =$

0.0332, w$R2$(all data) = 0.0893, w$R2[I>2\sigma(I)]$ = 0.0869, GOF = 1.085, largest diff. peak and hole 0.325 and −0.184 e Å^{-3}.

3: $Li_4C_{48}H_{80}N_4O_4$, M_r = 804.92 g mol^{-1}, monoclinic, space group $C2/c$, a = 2429.0(5), b = 889.00(18), c = 2452.9(5) pm, β = 111.23(3)°, V = 4.9355(17) nm^3, Z = 4, $\mu(Mo_{K\alpha})$ = 0.066 mm^{-1}, T = 100(2) K, 64798 reflections measured, 6888 unique reflections, R_{int} = 0.0346, 342 parameters refined, 175 restraints, $R1$(all data) = 0.0577, $R1[I>2\sigma(I)]$ = 0.0452, w$R2$(all data) = 0.1281, w$R2[I>2\sigma(I)]$ = 0.1190, GOF = 1.058, largest diff. peak and hole 0.410 and −0.385 e Å^{-3}.

4: $LiC_{16}H_{30}N_3$, M_r = 271.37 g mol^{-1}, monoclinic, space group $P2_1/c$, a = 1538.8(10), b = 1337.9(8), c = 1706.8(11) Å, β = 93.381(11)°, V = 3.51(1) nm^3, Z = 8, $\mu(Mo_{K\alpha})$ = 0.060 mm^{-1}, T = 100(2) K, 31672 reflections measured, 4068 unique reflections, R_{int} = 0.0826, 387 parameters refined, $R1$(all data) = 0.0682, $R1[I>2\sigma(I)]$ = 0.0500, w$R2$(all data) = 0.1298, w$R2[I>2\sigma(I)]$ = 0.1198, GOF = 1.078, largest diff. peak and hole 0.270 and −0.208 e Å^{-3}.

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