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# Synthesis and Structure of the Tmeda Adduct of a Dibenzyl Lithiate Anion Containing Four-Coordinate Lithium

Ulrich Jürgen Bildmann and Gerhard Müller*

*Fachbereich Chemie, Universität Konstanz, Universitätsstrasse 10, 78464 Konstanz, Germany*

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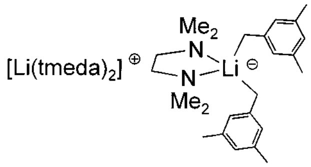
*Summary: Mesitylene may be lithiated almost quantitatively by Lin-Bu in a large excess of tmeda, resulting in the formation of the solvent-separated ion pairs* $[Li(tmeda)_2]^+[(tmeda)Li(CH_2C_6H_3\text{-}3,5\text{-}Me_2)_2]^-$ (**1**) *(tmeda = N,N,N′,N′-tetramethylethylenediamine), the anion of which is a lithiate containing lithium bound to two* $\eta^1$*-coordinated benzyl groups and one molecule of tmeda, resulting in the coordination number 4 at lithium in a distorted tetrahedral coordination geometry. Compound* **1** *is the first four-coordinate diorgano lithiate. Likewise, benzyl lithiates have no precedent in the rich structural chemistry of benzyllithium compounds.*

The formation of ate complexes[1] is rare in organolithium chemistry. The first example was $[Li(THF)_4]^+[Li\{C(SiMe_3)_3\}_2]^-$ (THF = tetrahydrofuran), which crystallizes as solvent-separated ion pairs, containing 2-fold linearly coordinated diorgano lithiate anions.[2] Some closely related complexes followed.[3] The only other examples are $[Na(tmeda)]_3[LiPh_4]$, the complex structure of which contains the triply negatively charged tetraphenyl lithiate $[LiPh_4]^{3-}$ core,[4] and the more recently discovered $\pi$-bonded lithocene sandwich anions,[5,6] such as $[PPh_4]^+[LiCp_2]^-$.[5] Four-coordinate lithiates with a coordination sphere at lithium comprised exclusively of nitrogen donor atoms have also been described.[7]

We have found that mesitylene may be lithiated almost quantitatively by Li*n*-Bu in a large excess of tmeda (see Experimental Section), resulting in the formation of the solvent-separated ion pairs $[Li(tmeda)_2]^+[(tmeda)Li(CH_2C_6H_3\text{-}3,5\text{-}Me_2)_2]^-$ (**1**), the anion of which is a lithiate containing lithium bound to two $\eta^1$-coordinated benzyl groups and one molecule of tmeda, resulting in the coordination number 4 at lithium. We are not aware of any other four-coordinate diorgano lithiates. Likewise, benzyl lithiates have no precedent in the rich structural chemistry of benzyllithium compounds.[8,9]



**1**

As the crystal structure of **1** shows (Figure 1), the lithium center Li1 in the anion is coordinated by the

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[*] To whom correspondence should be addressed. E-mail: gerhard.mueller@chemie.uni-konstanz.de. Fax: +(49) 7531 883140.

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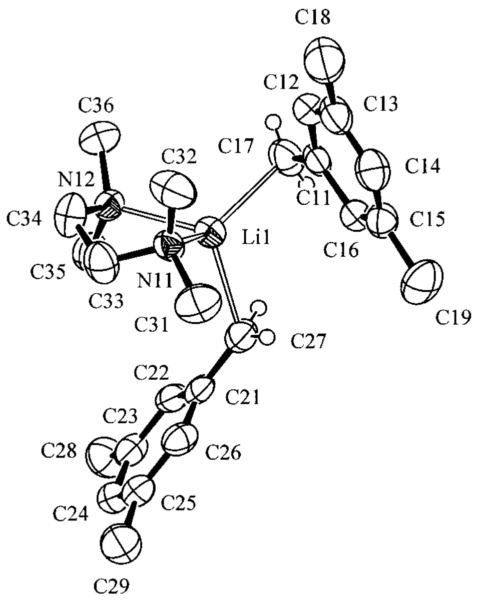

**Figure 1.** Molecular structure of the anion of **1** in the crystal and crystallographic numbering scheme used (ORTEP-III. Displacement ellipsoids at the 50% level. For clarity only the benzylic H atoms are drawn). Important distances (Å) and angles (deg): Li1−C17 = 2.257(7), Li1−C27 = 2.325(7), Li1−N11 = 2.161(6), Li1−N12 = 2.168(6), Li1···C11 = 2.637(6), Li1···C21 = 3.375(6); C17−Li1−C27 = 107.6(3), N11−Li1−N12 = 85.1(2), N11−Li1−C17 = 129.5(3), N11−Li1−C27 = 107.9(3), N12−Li1−C17 = 112.1(3), N12−Li1−C27 = 112.7(3), Li1−C17−C11 = 89.0(3), Li1−C27−C21 = 127.8(3). Cation: Li2−N21 = 2.116(6), Li2−N22 = 2.096(6), Li2−N31 = 2.122(6), Li2−N32 = 2.151(6); N21−Li2−N22 = 88.0(2), N31−Li2−N32 = 86.5(2), N21−Li2−N31 = 119.3(3), N21−Li2−N32 = 123.5(3), N22−Li2−N31 = 124.2(3), N22−Li2−N32 = 119.4(3).

benzylic carbon atoms from the two 3,5-dimethylbenzyl ligands which enclose an almost ideal tetrahedral angle at lithium (107.6(3)°). A distorted tetrahedral coordination environment at Li1 is completed by the two nitrogen atoms of the co-ligand tmeda, the distortions from an ideal tetrahedron clearly resulting from the small bite angle of the bidentate tmeda. The bonding of the two benzyl ligands to lithium shows interesting peculiarities, as manifested by the Li1−C distances and the Li−CH$_2$−C$_{Ph}$ bond angles (Figure 1). In particular, the bond distances Li1−C17 and Li1−C27 are significantly different (2.257(7) and 2.325(7) Å). The corresponding bond angles at the benzylic carbon atoms are much smaller for the tighter bound benzyl anion (Li1−C17−C11 = 89.0(3)°), whereas Li1−C27−C21 (127.8(3)°) is even larger than the tetrahedral standard. As a consequence, C$_{ipso}$ of the tighter bound ligand is almost within bonding reach to lithium (Li1···C11 = 2.637(6) Å), whereas the other one is clearly nonbonded (Li1···C21 = 3.375(6) Å). Thus both benzyl ligands are only $\eta^1$-bound to lithium. The hapticity of lithium-bound benzyl anions has been found to be critically dependent on the state of aggregation, the overall connectivity pattern, and the conformation of the lithium benzyl.[8,9] An $\eta^2$-coordination of the benzylic C$_{benzyl}$−C$_{ipso}$ bond to lithium is most often observed, but higher and lower hapticities have also been found. This is especially true for simple benzyl anions which are unsubstituted at the benzylic α-carbon atom,[8a−c,f] but holds, grosso modo, also for carbon-[8d,e] and heteroatom-substituted benzyls.[9] Of particular importance is the overall coordination number at lithium, which in turn is crucially influenced by additional donor molecules present. In **1** the 4-fold coordination of lithium clearly leads to a reduced hapticity of the benzyl ligands, i.e., the $\eta^2$-coordination is less favorable and an $\eta^1$-coordination is preferred with one of the benzyl ligands still showing some inclination to $\eta^2$. An $\eta^1$-coordination to lithium has also been observed in [(tmeda)(THF)LiCH$_2$C$_6$H$_5$], in which the three other coordination sites at lithium are blocked by the good donor atoms oxygen and nitrogen.[8b] In this complex the Li−C bond distance is 2.210(5) Å and the angle Li−C−C at the benzylic carbon atom 94.6(2)°. In the crystal of **1** there is no apparent interaction between anion and cation. The cation [Li(tmeda)$_2$]$^+$ shows no significant differences from reference compounds.[3b−d,f,10]

In solution the structure of **1** seems to be maintained over a broad temperature range. At room temperature there are two signals in the $^7$Li NMR spectra, a sharp signal at 0.96 ppm and a very broad one at 1.63 ppm. We attribute the latter to the lithiate due to the lower anion symmetry.[3d] These and all other NMR signals (see Experimental Section) are not significantly altered upon cooling to −80 °C, thus proving that also the fluxionality of **1** is maintained in this temperature range.

Much theoretical, structural, and mechanistic information is now at hand with regard to the nature of the reacting species and the intermediates in reactions of lithium organyls.[11] The same is true for the effects of lithium salts upon organic reactions.[12,13] Lithium benzyls have not been used routinely for the deprotonation of other organic or inorganic molecules. As our results show, for their reactivity, especially in the presence of tmeda or similar co-ligands, intermediate lithiate species[1a] have also to be taken into account.

## Experimental Section

All experiments were carried out with rigorous exclusion of air and moisture under purified dry argon in standard Schlenk tube glassware. Solvents and tmeda (Aldrich) were dried under argon over sodium or sodium−potassium alloy and were freshly distilled prior to use.

**Instruments**. NMR spectra: JEOL JMN-GX-400, Bruker AMX-600. $^1$H NMR: internal C$_6$H$_6$ or external tetramethyl-

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silane, TMS, as standard. $^{13}C$ NMR: external tetramethylsilane, TMS. $^{7}Li$ NMR: external 70% LiBr in $D_2O$. Chemical shifts are in ppm with negative signs referring to high field. $^{1}H$ and $^{13}C$ chemical shifts are reported relative to TMS, while those of $^{7}Li$ are reported relative to the standard mentioned above. FT-IR spectra: Mattson Polaris. The elemental analysis was performed by the microanalytical laboratory of the University of Konstanz on a Heraeus CHN-O-Rapid instrument. The melting point was determined in a sealed capillary in a Büchi 530 apparatus and is uncorrected.

**$[Li(tmeda)_2]^+[(tmeda)Li(CH_2C_6H_3\text{-}3,5\text{-}Me_2)_2]^-$ (1).** To 1.2 g (10 mmol) of mesitylene dissolved in 20 mL of a 1:1 mixture of hexane/tmeda was added an equimolar amount of a 2.5 M solution of Li*n*-Bu in hexane (4 mL) at −78 °C. The clear yellow solution was left standing overnight and allowed to warm to room temperature, whereupon a color change to red occurred. Very slow cooling of the red solution to −30 °C over a period of 48 h yielded extremely air-sensitive deep red crystals suitable for X-ray structure determination. Yield: 2.9 g (4.83 mmol, 96%). Mp: 58−62 °C. Anal. Calcd for $C_{36}H_{70}Li_2N_6$ (600.86): C, 71.96; H, 11.74; N, 13.99. Found: C, 70.71; H, 10.64; N, 12.97. $^{1}H$ NMR (250 MHz, $C_6D_6$, RT): $\delta$ 6.22 (s, *o*-H), 5.75 (s, *p*-H), 2.48 (s, $PhCH_2$), 2.18 (s, $NCH_2$), 2.15 (s, $PhCH_3$), 1.91 (s, $NCH_3$). $^{13}C$ NMR (152 MHz, $C_6D_6$, RT): $\delta$ 156.5 (*ipso*-C), 138.7 (*m*-C), 112.6 (*o*-C), 108.6 (*p*-C), 57.2 ($NCH_2$), 45.4 ($NCH_3$), 38.8 ($PhCH_2$), 22.2 ($PhCH_3$). $^{7}Li$ NMR (155 MHz, toluene-$d_8$, RT): $\delta$ 0.96 (s, sharp), 1.63 (s, very broad). IR (Nujol, $CsF_2$, cm$^{-1}$): 1580 s (C=C), 1317 m ($\delta CH_3$), 1290 w, 1262 w, 1159 w, 1131 w, 1099 m, 1035 s, 970 m, 949 w, 791 m, 691 w, 588 w, 526 m.

**Structure Analysis**.[14] Intensity data of compound **1** were collected on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å). The structure was solved by direct methods. In the refinement all non-H atoms were refined with anisotropic displacement parameters except the carbon atoms of one of the tmeda molecules in the cation, which were treated in a split atom model (0.6/0.4) due to disorder. Most of the H atoms could be located, in particular the benzylic ones. The remainder (at some of the methyl groups and at the disordered molecule tmeda) were calculated at idealized geometrical positions. All H atoms were included as fixed-atom contributions into structure factor calculations. The N−C bonds of the disordered molecule tmeda were restrained to the same bond length. Programs used: SHELXS-97 (structure solution),[15] SHELXL-97 (structure refinement),[15] PLATON (molecular geometry),[16] ORTEP-III (molecular drawings).[17]

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**Supporting Information Available:** Tables of crystal data, atomic coordinates, anisotropic displacement parameters, hydrogen atom coordinates, and bond lengths and angles for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[14] Crystal structure data: $C_{36}H_{70}Li_2N_6$, $M_r = 600.86$, orthorhombic, space group $P2_12_12_1$ (No. 19), $a = 8.800(1)$, $b = 14.309(2)$, $c = 31.968(5)$ Å, $V = 4026(1)$ Å$^3$, $Z = 4$, $\rho_{calcd} = 0.992$ g cm$^{-3}$, $\mu$(Mo Kα) = 0.58 cm$^{-1}$, $F(000) = 1336$, $T = 188(2)$ K. $\omega$ scans, $\Delta\omega = 0.8°$, $(\sin\theta/\lambda)_{max} = 0.594$ Å$^{-1}$, *hkl* range: +10, +16, +37 and Friedel opposites. Of a total of 7977 measured reflections, 7054 were unique ($R_{int} = 0.017$) and 5026 were “observed” with $I > 2\sigma(I)$. Refinement of 485 parameters was done on $F^2$ of all unique reflections leading to $R(F)/R_w(F^2) = 0.064/0.189$, GoF = 1.02, $w = 1/[\sigma^2(F_o^2) + (0.1016P)^2 + 1.3226P)]$, $P = [\max(F_o^2, 0) + 2\ F_c^2]/3$, $x$(Flack) = 0(3). $\Delta\rho_{fin}$ (max./min.) = 0.34/−0.25 e Å$^{-3}$.

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