

Synthesis and characterization of substituted (aminomethyl)lithium compounds

The structures of $[\text{Li}_2(\text{CH}_2\text{NPh}_2)_2(\text{THF})_3]$ and $[\text{Li}_4(\text{CH}_2\text{NC}_5\text{H}_{10})_4(\text{THF})_2]$

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Abstract

(Aminomethyl)lithium compounds $\text{LiCH}_2\text{NRR}' \cdot x \text{ THF}$ ($\text{NRR}' = \text{NMe}_2$ (**1a**, $x = 0$), NPhMe (**1b**, $x = 2$), NPh_2 (**1c**, $x = 1 \dots 1.5$), NC_5H_{10} (**1d**, $x = 0$, NC_5H_{10} = piperidino), and NC_7H_{14} (**1e**, NC_7H_{14} = 2,6-dimethylpiperidino)) were prepared by the reaction of $\text{Bu}_3\text{SnCH}_2\text{NRR}'$ with BuLi . **1a–d** were isolated in solid state and characterized by NMR spectroscopy (^1H , ^{13}C , ^7Li). **1e** was obtained in solution and characterized via reaction with MeOH and with benzophenone to generate $\text{MeNC}_7\text{H}_{14}$ and $\text{Ph}_2\text{C}(\text{OH})\text{CH}_2\text{NC}_7\text{H}_{14}$, respectively. Recrystallization of **1c** and **1d** from *n*-hexane/THF gives $[\text{Li}_2(\text{CH}_2\text{NPh}_2)_2(\text{THF})_3]$ (**1c'**) and $[\text{Li}_4(\text{CH}_2\text{NC}_5\text{H}_{10})_4(\text{THF})_2]$ (**1d'**), respectively, whose structures (X-ray) were determined. The dimeric compound **1c'** forms a central planar four-membered Li_2C_2 ring. One lithium atom is four-coordinated to two methylene carbon atoms ($d(\text{Li}-\text{C}) = 2.246(9)$, $2.235(9)$ Å) and two oxygen atoms of THF. Unusually, the second lithium exhibits a nearly planar coordination sphere represented by two methylene carbon atoms ($d(\text{Li}-\text{C}) = 2.17(1)$ and $2.16(1)$ Å) and by the oxygen atom of the disordered THF molecule. **1d'** is a tetrameric species exhibiting a molecular C_2 symmetry. The lithium atoms are arranged in a distorted tetrahedron with methylene carbon atoms occupying each face of the tetrahedron. © 1997 Elsevier Science S.A.

Keywords: (Aminomethyl)lithium compounds; Crystal structures

1. Introduction

Functionalized methyllithium compounds of the type $[\text{LiCH}_2\text{YR}_n]$ ($\text{Y} = \text{N}, \text{S}, \text{P}, \text{Cl}, \dots$; $\text{R} = \text{alkyl}, \text{aryl}$) with a Lewis-basic heteroatomic center Y cover a wide range of reactivity and stability. Solid state structures are known for adducts with chelating N, N' -ligands. All of them are dimeric in which the heteroatom Y is either involved in the coordination of Li^+ (type **A**; e.g., $[\text{Li}_2(\text{CH}_2\text{SPh})_2(\text{TMEDA})_2]$ [1] ($\text{TMEDA} = N, N, iN', N'$ -tetramethylethylenediamine), $[\text{Li}_2(\text{CH}_2\text{PPh}_2)_2(\text{TMEDA})_2]$ [2,3], $[\text{Li}_2(\text{CH}_2\text{PMe}_2)_2(\text{TMEDA})_2]$ [4], $[\text{Li}_2(\text{CH}_2\text{PPhMe})_2(\text{TMEDA})_2]$ [4], $[\text{Li}_2(\text{CH}_2\text{PPhMe})_2$

(sparteine) $_2]$ [4] or not (type **B**; e.g., $[\text{Li}_2(\text{CH}_2\text{SMe})_2(\text{TMEDA})_2]$ [1]). To date, only three examples are known for solid state structures of $[\text{LiCH}_2\text{YR}_n]$ where Li^+ is not coordinated to a chelating N, N' -donor ligand: $[\{\text{Li}(\text{CH}_2\text{SMe})(\text{THF})\}_x]$ [5] and $[\{\text{Li}(\text{CH}_2\text{PPh}_2)(\text{THF})\}_x]$ [6] adopt polymeric structures with alternately arranged six-membered type **A** $\text{Li}_2\text{C}_2\text{Y}_2$ rings ($\text{Y} = \text{S}, \text{P}$) and four-membered type **B** Li_2C_2 rings, whereas $[\text{Li}_2(\text{CH}_2\text{SPh})_2(\text{THF})_4]$ [5] exhibits a dimeric structure.

(Aminomethyl)lithium compounds of the type $\text{LiCH}_2\text{NRR}'$ ($\text{R}, \text{R}' = \text{alkyl}, \text{aryl}$) were prepared for the first time in solution by Peterson via transmetalation reaction between $\text{Bu}_3\text{SnCH}_2\text{NRR}'$ and BuLi ($\text{NRR}' = \text{NMe}_2, \text{NPhMe}, \text{NPh}_2, \text{NC}_5\text{H}_{10}, \text{NC}_4\text{H}_8\text{O}$ ($\text{NC}_4\text{H}_8\text{O} = \text{morpholino}$)) [7,8]. Their isolation as very air sensitive and in part pyrophoric substances ($\text{NR}_2 = \text{NMe}_2$,

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NC_5H_{10} , NPh_2) was described by Ref. [9]. Very recently, the synthesis in solution by reductive cleavage of a carbon–sulphur bond in $\text{PhSCH}_2\text{NR}_2$ with lithium naphthalide was reported [10].

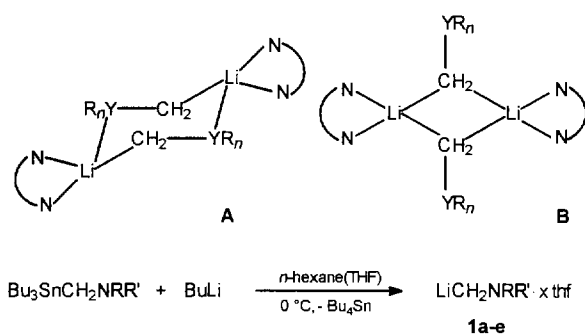
Until now, structures of (aminomethyl)lithium derivatives $\text{LiCH}_2\text{NRR}'$ were not described neither with chelating N,N' -ligands nor without them. Crystal structures of lithium compounds containing a $\text{Li}-\text{C}(sp^3)-\text{N}$ unit are known only for the benzyl derivatives ($[\text{Li}_2(\text{CHPh}(\text{NMe}_2))_2(\text{Et}_2\text{O})_2]$ and (1*S*)-1-(*N*-pivaloyl-*N*-methylamino)benzyl lithium · (-)-sparteine [11].

Here, we report on the synthesis and characterization of (aminomethyl)lithium compounds of the type $\text{LiCH}_2\text{NRR}'$ as well as on the structures of the diphenylamino [12] and the piperidino methyl derivatives.

2. Results and discussion

2.1. Synthesis and characterization of (aminomethyl)-lithium compounds

The (aminomethyl)lithium complexes **1** were prepared by reaction of BuLi ($\text{Bu} = n\text{-Bu}$) with the appropriate tributyltin derivative in *n*-hexane



	1a	1b	1c	1d	1e
NRR'	NMe ₂	NPhMe	NPh ₂	NC ₅ H ₁₀	NC ₇ H ₁₄
x	0	2	1.5	0	

The formation of **1b**, **1c** and **1e** required a small amount of THF as a polar aprotic solvent.

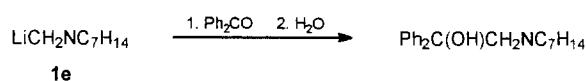
1b and **1c** crystallize as THF adducts. All compounds **1** are very sensitive toward oxygen and moisture. **1b** was isolated in solid state for the first time (yield: 46%) as light yellow microcrystals. At room temperature, **1b** is easily soluble in THF, diethyl ether and even in *n*-hexane. Compound **1e** with its sterically hindered nitrogen atom was obtained only in solution. Attempts to crystallize **1e** from a concentrated *n*-hexane solution failed. Recrystallization of **1c** and **1d** from *n*-

hexane/THF solutions gives $[\text{Li}_2(\text{CH}_2\text{NPh}_2)_2(\text{THF})_3]$ (**1c'**) and $[\text{Li}_4(\text{CH}_2\text{NC}_5\text{H}_{10})_4(\text{THF})_2]$ (**1d'**), respectively, whose solid state structures (X-ray) were determined.

As expected from the donor ability of the organo groups R ($\text{NMe}_2 > \text{NPhMe} > \text{NPh}_2$), the methylene proton shifts and coupling constants $^1J(\text{CH})$ for **1b** (2.10 ppm, 104.8 Hz) in benzene-*d*₆ lie in between the values found for **1a** (0.94 ppm, 102.9 Hz (THF-*d*₈)) and **1c** (2.59 ppm, 105.4 Hz (benzene-*d*₆)). The value for the methylene proton shift of **1b** depends greatly upon the polarity of the solvent: By using THF-*d*₈ instead of benzene-*d*₆, an upfield shift was noticed (1.67 vs. 2.10 ppm). The same effect was observed for the signal $\delta(^1\text{H})$ for $[\{\text{Li}(\mu_3\text{-Me})(\text{THF})_4\}]_4$ (-2.07 vs. -1.20 ppm) [14].

Deuterolysis of **1b** in benzene-*d*₆ gives monodeuterated DCH_2NPhMe (degree of deuteration: 80% (^1H NMR)). The results of NMR investigations and deuterolysis of **1b** confirm, that the phenyl ring is not lithiated as was discussed by Ref. [7].

Compound **1e** reacts with MeOH to generate $\text{MeNC}_7\text{H}_{14}$ (yield: 82%) and with benzophenone to form the corresponding alcohol (yield: 78%), which was characterized by NMR spectroscopy (^1H , ^{13}C), microanalysis, and MS.



2.2. Structures of compounds **1c'** and **1d'**

The ORTEP [14] representation of **1c'** and the solid state structure of **1d'** are shown in Figs. 1 and 2. Selected bond lengths and bond angles are listed in Table 1 for **1c'** and in Table 2 for **1d'**.

Compound **1c'** crystallizes as discrete dimers. The central planar four-membered Li_2C_2 ring is formed by μ -diphenylaminomethyl-1:2 $\kappa^2\text{C}$ ligands. One THF molecule is disordered. In **1c'**, the coordination of the two lithium atoms is quite different: Li1 is distorted tetrahedrally surrounded by two methylene carbon atoms (C1, C21) and two oxygen atoms of THF molecules (O1, O2). Neither the Li1–C bond lengths ($d(\text{Li1}-\text{C1}) = 2.246(9)$, $d(\text{Li1}-\text{C21}) = 2.235(9)$ Å) nor the Li1–O distances ($d(\text{Li1}-\text{O1}) = 1.988(7)$, $d(\text{Li1}-\text{O2}) = 1.975(8)$ Å) differ significantly. Li2 is nearly trigonal planar coordinated (sum of angles: 359.9°) by the two methylene carbon atoms and by the oxygen atom of the disordered THF molecule.

Due to the lower coordination number of Li2, the Li2–C bond lengths ($d(\text{Li2}-\text{C1}) = 2.17(1)$, $d(\text{Li2}-\text{C21}) = 2.16(1)$ Å) are significantly shorter than the Li1–C

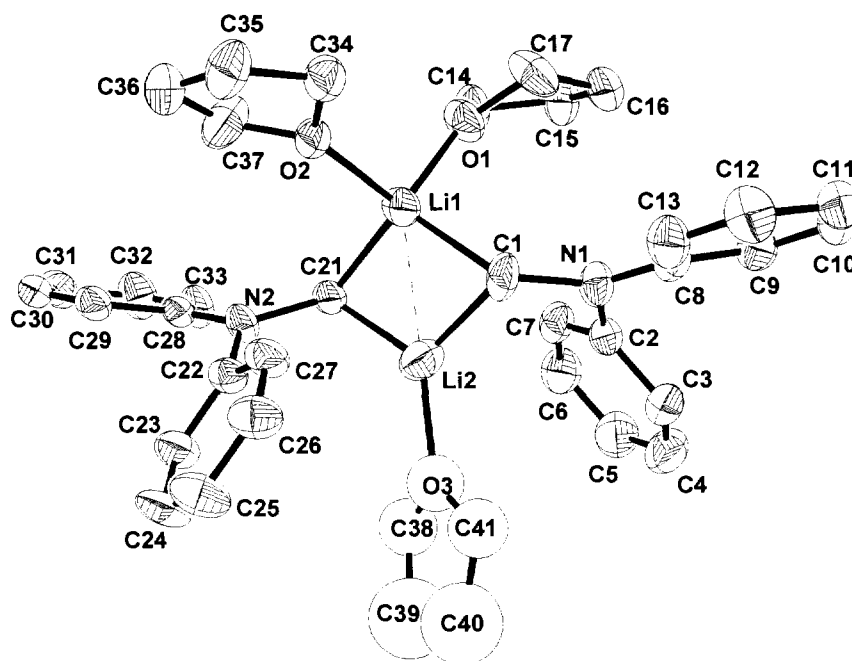


Fig. 1. ORTEP drawing of the structure of **1c'** (thermal ellipsoids at 50% probability). Hydrogen atoms are omitted for clarity.

distances. The distances $d(\text{Li2}-\text{C7}) = 2.712(9)$ and $d(\text{Li2}-\text{C27}) = 2.71(1)$ Å may indicate only weak interactions. Neglecting these interactions, Li2 exhibits the unusual coordination number three. The addition of a

further THF molecule to give the coordination number four might be prevented because of steric reasons.

The nearly planar NC_3 units (sum of angles: 357.6° (N1), 359.0° (N2)) indicate an sp^2 hybridization of

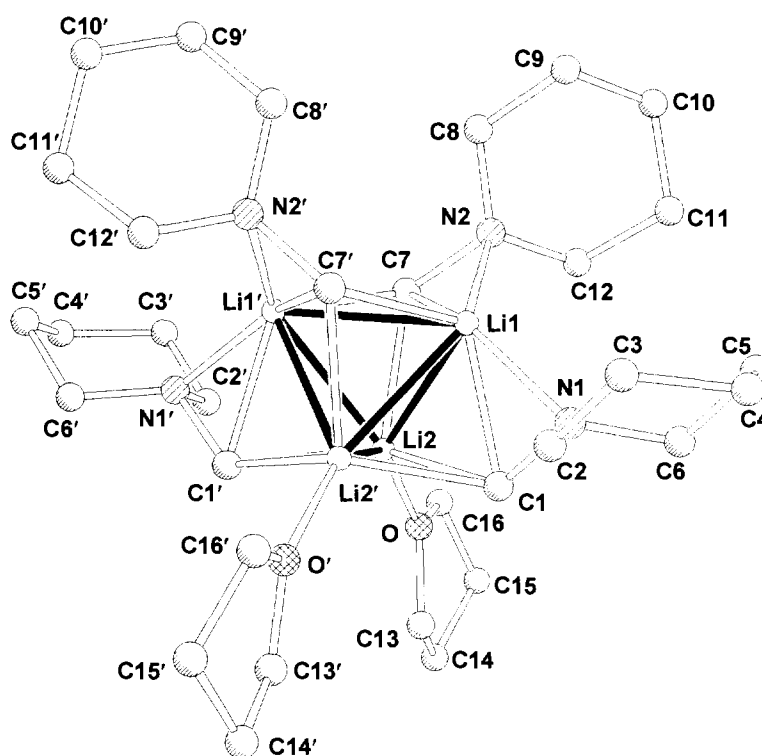


Fig. 2. Molecular structure of **1d'**. Hydrogen atoms are omitted for clarity.

Table 1
Selected distances (Å) and angles (°) for [Li₂(CH₂NPh₂)₂(THF)₃] (1c')

Li1–Li2	2.42(1)	Li1–C1	2.246(9)
Li1–C21	2.235(9)	Li2–C1	2.17(1)
Li2–C21	2.16(1)	Li1–O1	1.988(7)
Li1–O2	1.975(8)	Li2–O3	1.935
Li2–C7	2.712(9)	Li2–C27	2.71(1)
C1–N1	1.497(6)	N1–C2	1.434(6)
N1–C8	1.392(6)	C21–N2	1.486(5)
N2–C22	1.424(5)	N2–C28	1.409(6)
Li1–C1–Li2	66.4(3)	Li1–C21–Li2	66.7(3)
C1–Li2–C21	116.4(4)	C1–Li1–C21	110.5(3)
C1–Li1–O1	106.6(3)	O1–Li1–O2	104.3(3)
O2–Li1–C21	106.8(3)	C1–Li1–O2	112.4(4)
C21–Li1–O1	116.2(4)	C21–Li2–O3	124.0(4)
C1–Li2–O3	119.5(5)	C1–N1–C2	114.7(3)
C2–N1–C8	120.5(4)	C1–N1–C8	122.4(4)
C21–N2–C22	116.9(3)	C22–N2–C28	119.8(3)
C21–N2–C28	122.3(3)		

nitrogen. It is apparent from the interplanar angles $\text{N1C}_3/\text{Li}_2\text{C}_2 = 65.8^\circ$ and $\text{N2C}_3/\text{Li}_2\text{C}_2 = 63.6^\circ$ that π interactions between the lone pair of the nitrogen atoms and the methylene carbon atoms (C1, C14) do not play a significant role. However, the Li–N distances in the bent $\text{Li}_2\text{C}_2\text{N}_2$ unit (3.02–3.29 Å) are shorter than in a (hypothetical) planar one. If one considers these contacts as important at all (sum of van der Waals-radii $r(\text{Li}) + r(\text{N}) = 3.28$ Å [15]), than in the bent $\text{Li}_2\text{C}_2\text{N}_2$ arrangement, the strongly electropositive Li^+ centers occupy positions of higher electron densities.

Compound **1d'** is a tetrameric species exhibiting a molecular C_2 symmetry. The lithium atoms are ar-

Table 2
Selected distances (Å) and angles (°) for [Li₄(CH₂NC₅H₁₀)₄(THF)₂] (1d')^a

Li1–Li1'	2.72(3)	Li1–Li2	2.59(2)
Li1–Li2'	2.52(2)	Li2–Li2'	2.29(3)
Li2–C7	2.28(2)	Li1–C1	2.20(2)
Li1–C7	2.32(2)	Li1–C7'	2.24(2)
Li2–C1	2.26(2)	Li2'–C1	2.21(2)
Li1'–C7	2.24(2)	Li2–C1'	2.21(2)
Li1–N2	2.06(2)	Li1–N1	2.04(2)
Li2–O	1.99(2)	C7–N2	1.52(1)
C1–N1	1.52(1)		
Li2–Li1–Li1'	56.4(6)	Li2'–Li1–Li2	53.2(8)
Li2'–Li1–Li1'	59.2(6)	Li1'–Li2–Li1	64.4(9)
Li1–C1–N1	63.7(7)	Li2–C1–N1	134.2(9)
Li2'–C1–N1	106.7(8)	Li1–C7–N2	60.8(6)
Li2–C7–N2	121.9(9)	Li1'–C7–N2	118.4(9)
Li1–N2–C7	79.3(7)	Li1–N2–C12	111.5(8)
C7–N2–C8	113.4(10)	C8–N2–C12	107.2(9)
C7–N2–C12	110.1(9)	Li1–N2–C8	131.5(9)
Li1–N1–C1	74.5(8)	Li1–N1–C6	131.6(9)
C1–N1–C6	112.9(9)	C6–N1–C2	109.6(8)
C1–N1–C2	109.1(9)	Li1–N1–C2	112.3(8)

^a Symmetry transformation used to generate equivalent atoms: $-x + 1, y, -z + 3/2$.

ranged in a distorted tetrahedron whose faces are capped by the methylene carbon atoms. Due to Li–N interactions, the ligands exhibit a μ_3 -piperidinomethyl- $1\kappa\text{N}$, 1:2:3 $\kappa^3\text{C}$ coordination. Two of the lithium centers (Li1, Li1') exhibit the C.N. = 8 ($3 \times \text{Li}$, $3 \times \text{C}$, $2 \times \text{N}$). The other ones (Li2, Li2') are seven coordinated by three lithium, three methylene carbons and one oxygen (THF). The Li2–Li2' distance (2.29(3) Å) is considerably shorter than the Li1–Li1' distance (2.72(3) Å). The distances between Li1 (Li1') and Li2 (Li2') are in between 2.59(2) and 2.52(2) Å. All Li–Li distances in **1d'** are in a range of values found in other lithium organyls with Li_4 tetrahedrons, e.g., in $[(\text{LiMe})_4]$ (2.68(5) Å) [16], $[(\text{LiEt})_4]$ (2.4477(7)–2.5997(8) Å) [17], $[(\text{Li}'\text{Bu})_4]$ (2.383(9)–2.431(8) Å) [18], and in $[\{\text{LiPh}(\text{Et}_2\text{O})\}_4]$ (2.505(8)–2.707(6) Å) [19].

The methylene carbon atoms are placed at 1.70(1) Å (C1) and 1.71(1) Å (C2) above the Li_3 -planes. The Li–C bond lengths in **1d'** (2.20(2)–2.32(2) Å) are in line with the distances found in $[(\text{LiMe})_4]$ (2.31(5) Å) [16], $[(\text{LiEt})_4]$ (2.2007(6)–2.4082(6) Å) [17], and $[\{\text{LiPh}(\text{Et}_2\text{O})\}_4]$ (2.277(5)–2.348(5) Å) [19].

Due to the coordination of nitrogen to Li1 only, small Li–C–N angles ($\text{Li1–C1–N1} = 63.7(7)^\circ$; $\text{Li1–C7–N2} = 60.8(6)^\circ$) were observed in **1d'**. There are no significant differences within the Li–N ($d(\text{Li1–N1}) = 2.04(2)$ Å; $d(\text{Li1–N2}) = 2.06(2)$ Å) and C–N bond lengths ($d(\text{C1–N1}) = d(\text{C7–N2}) = 1.52(1)$ Å).

The bond length $d(\text{Li2–O}) = 1.99(2)$ Å is equivalent within the 3σ -limit with values found in $[\{\text{Li}(\mu_3\text{-Bu})(\text{THF})\}_4] \cdot \text{C}_6\text{H}_{14}$ (1.95(2)–2.00(2) Å; $\text{C}_6\text{H}_{14} = n$ -hexane) [20] and in $[\{\text{Li}(\mu_3\text{-Me})(\text{THF})\}_4]$ (1.96(1) Å) [13].

3. Experimental

All reactions and manipulations were carried out under purified argon using standard Schlenk techniques. *n*-Hexane, THF-*d*₈, and benzene-*d*₆ were dried with LiAlH_4 . Diethyl ether and THF were distilled from sodium benzophenone ketyl. NMR spectra were recorded on Varian Gemini 300 or Varian Unity 500 NMR spectrometers using the protio impurities and the ¹³C resonances of the deuterated solvents as references for ¹H and ¹³C NMR spectroscopy, respectively. The chemical shifts $\delta(^7\text{Li})$ are reported relative to a solution of LiCl in THF-*d*₈ (external). GC-MS investigations were carried out on HP 5890 Series II/HP 5972 (Hewlett Packard). Mass spectra (EI, 70 eV) were obtained by using an AMD 402 instrument. The lithium contents were determined by AES (PU 7000, Unicam). A 15% solution of BuLi in hexane was obtained from Merck. $\text{MeNCH}_2\text{NC}_7\text{H}_{14}$ was prepared according to Ref. [21]. The tin compounds $\text{Bu}_3\text{SnCH}_2\text{NR}_2$ ($\text{NR}_2 = \text{NMe}_2, \text{NPhMe}, \text{NPh}_2, \text{NC}_5\text{H}_{10}, \text{NC}_7\text{H}_{14}$) were synthesized according to published procedures [7,8].

3.1. Synthesis of $\text{LiCH}_2\text{NMe}_2$ (**1a**), $\text{LiCH}_2\text{NPh}_2 \cdot 1,5$ THF (**1c**) and $\text{LiCH}_2\text{NC}_5\text{H}_{10}$ (**1d**)

1a, **1c** and **1d** were prepared according to Ref. [9].

1a: ^1H NMR (300.07 MHz, THF- d_8): $\delta = 0.94$ (s, 2H, CH_2), 2.15 ppm (s, 6H, CH_3). ^{13}C NMR (75.46 MHz, THF- d_8 , coupled spectrum): $\delta = 53.9$ (q, $^1J(\text{CH}) = 130.6$ Hz, CH_3), 57.0 ppm (t, $^1J(\text{CH}) = 102.9$ Hz, CH_2). ^7Li NMR (194.27 MHz, THF- d_8): $\delta = 0.80$ ppm (s).

1c: ^1H NMR (300.07 MHz, benzene- d_6): $\delta = 1.44$ (m, THF), 2.59 (s, 2H, CH_2), 3.46 (t, THF), 6.50–7.40 ppm (m, 10H, phenyl). ^{13}C NMR (75.46 MHz, benzene- d_6 , coupled spectrum): $\delta = 25.8$ (t, THF), 46.1 (t, $^1J(\text{CH}) = 105.4$ Hz, CH_2), 68.1 (t, THF), 118.9 (d, $^1J(\text{CH}) = 159.2$ Hz, C_o), 121.2 (d, $^1J(\text{CH}) = 155.2$ Hz, C_p), 129.1 (d, $^1J(\text{CH}) = 156.2$ Hz, C_m), 155.4 ppm (s, C_i). ^7Li NMR (194.27 MHz, THF- d_8): $\delta = 0.68$ ppm (s).

1d: ^1H NMR (300.07 MHz, THF- d_8): $\delta = 0.98$ (s, 2H, CH_2), 1.29–2.23 ppm (m, 10H, ring). ^{13}C NMR (125.71 MHz, THF- d_8 , coupled spectrum): $\delta = 25.1$ (t, $^1J(\text{CH}) = 124.7$ Hz, $\text{C}3_{\text{ring}}$), 28.4 (t, $^1J(\text{CH}) = 124.7$ Hz, $\text{C}2_{\text{ring}}$), 55.3 (t, $^1J(\text{CH}) = 103.7$ Hz, CH_2), 63.1 ppm (t, $^1J(\text{CH}) = 131.6$ Hz, $\text{C}1_{\text{ring}}$). ^7Li NMR (194.27 MHz, THF- d_8): $\delta = 1.08$ ppm (s).

3.2. Synthesis of $\text{LiCH}_2\text{NPhMe} \cdot 2$ THF (**1b**)

To a stirred solution of $\text{Bu}_3\text{SnCH}_2\text{NPhMe}$ (1.6 g, 4.0 mmol) in *n*-hexane (15 ml) and THF (2 ml), an equimolar amount of a solution of BuLi in *n*-hexane (0°C) was added. Stirring was continued for 20 min at

room temperature. Upon cooling to -78°C , a light yellow precipitate was formed, which was filtered off (-78°C). **1b** was recrystallized from *n*-hexane/THF and dried using flowing argon. Yield: 0.5 g (46%). **1b** was stored at -30°C .

1b: ^1H NMR (499.88 MHz, benzene- d_6): $\delta = 1.34$ (m, THF), 2.10 (s, 2H, CH_2), 3.16 (s, 3H, CH_3), 3.58 (t, THF), 6.98–7.82 ppm (m, 5H, phenyl). ^{13}C NMR (75.46 MHz, benzene- d_6 , coupled spectrum): $\delta = 25.7$ (t, THF), 46.4 (q, $^1J(\text{CH}) = 133.6$ Hz, CH_3), 47.4 (t, $^1J(\text{CH}) = 104.8$ Hz, CH_2), 67.9 (t, THF), 113.6 (d, $^1J(\text{CH}) = 152.5$ Hz, C_p), 113.9 (d, $^1J(\text{CH}) = 155.8$ Hz, C_o), 128.8 (d, $^1J(\text{CH}) = 152.5$ Hz, C_m), 156.4 ppm (s, C_i). ^7Li NMR (194.27 MHz, THF- d_8): $\delta = 1.22$ ppm (s).

3.3. Synthesis of $\text{LiCH}_2\text{NC}_7\text{H}_{14}$ (**1e**)

To a stirred solution of $\text{Bu}_3\text{SnCH}_2\text{NC}_7\text{H}_{14}$ (0.83 g, 2.0 mmol) in *n*-hexane (2 ml) and THF (1 ml), an equimolar amount of a solution of BuLi in *n*-hexane (0°C) was added rapidly. The light yellow solution of **1e** was stirred for 30 min at room temperature and stored at -78°C .

3.4. Reaction of **1e** with methanol

To a stirred solution of **1e** (2.0 mmol, prepared as described above), methanol (2 ml) was added rapidly at -78°C . The solution was warmed to room temperature. After removing the volatile products at 100°C in vacuo, the residue (Bu_4Sn) was characterized by ^{13}C NMR spectroscopy. In the distillate, $\text{MeNC}_7\text{H}_{14}$ was determined by GC analysis (Yield: 82%).

Table 3
Crystal data and structure refinement for **1c'** and **1d'**

	1c'	1d'
Empirical formula	$\text{C}_{38}\text{H}_{48}\text{N}_2\text{O}_3\text{Li}_2$	$\text{C}_{32}\text{H}_{64}\text{N}_4\text{O}_2\text{Li}_4$
<i>T</i> (K)	165	200(2)
Crystal dimensions (mm)	0.20 × 0.20 × 0.30	0.30 × 0.30 × 0.15
λ (Å)	0.71069	0.71073
Crystal system	monoclinic	orthorhombic
Space group (No.)	$P2_1/c$ (Nr. 14)	$Pbcn$ (Nr. 60)
<i>a</i> , <i>b</i> , <i>c</i> (Å)	15.756(7), 10.458(13), 21.691(9)	17.105(3), 11.051(2), 19.759(4)
α , β , γ (°)	90.0, 101.23(4), 90.0	90.0, 90.0, 90.0
<i>V</i> (Å ³)	3506(4)	3735(1)
<i>Z</i>	4	4
D_{calcd} (g cm ⁻³)	1.127	1.004
μ (Mo K α) (mm ⁻¹)	0.07	0.06
Scan range (°)	$3 \leq 2\theta \leq 55$	$4 \leq 2\theta \leq 40$
Reflections collected	9964	2426
Independent reflections	6025	1751
Observed reflections ($F_o \geq 4\sigma(F)$)	3679	475
Parameters refined	393	202
<i>R</i>	0.0872	0.0897
R_w (<i>wR2</i>)	0.0823	(0.1370)
Larg. diff. peak and hole (e Å ⁻³)	0.71 and -0.43	0.160 and -0.179

3.5. Reaction of **1e** with benzophenone

To a stirred solution of **1e** (24.0 mmol, prepared as described above) in *n*-hexane (20 ml) and THF (10 ml), Ph₂CO (4.4 g, 24.0 mmol) was added rapidly. The mixture was stirred for 1 h at room temperature. After hydrolysis with water, the organic layer was separated, dried (Na₂SO₄), and concentrated in vacuo. The solid residue was recrystallized from THF/*n*-hexane to form colorless crystals of Ph₂C(OH)CH₂NC₇H₁₄ which were filtered off and dried in vacuo (m.p. 138–139°C). Yield: 5.8 g (78%). Anal. Calcd. for Ph₂C(OH)CH₂NC₇H₁₄: C, 81.51; H, 8.79; N, 4.53. Found: C, 81.38; H, 8.59; N, 4.38. ¹H NMR (199.97 MHz, CDCl₃): δ = 0.77 (d, 6H, CH₃), 1.22–1.63 (m, 6H, (CH₂)₃), 2.57–2.65 (m, 2H, NCH), 3.43 (s, 2H, CH₂N), 6.20 (s, 1H, OH), 7.12 (t, 2H, *p*), 7.26 (t, 4H, *m*), 7.57 ppm (d, 4H, *o*). ¹³C NMR (50.29 MHz, CDCl₃): δ = 20.0 (CH₂CH₂CH₂), 20.1 (CH₃), 31.9 (CHCH₂), 56.2 (NCH), 61.4 (CH₂N), 72.1 (COH), 125.4 (C_o), 126.0 (C_p), 127.9 (C_m), 149.5 ppm (C_i). MS: *m/z* (relative intensity, %) 308 (0.1) [M-1]⁺, 232 (3) [C₁₃H₉O]⁺, 165 (2) [C₁₃H₉]⁺, 152 (1) [C₁₂H₈]⁺, 126 (100) [CH₂NC₇H₁₄]⁺.

3.6. X-ray structure determination of **1c'** and **1d'**

Suitable crystals were obtained from *n*-hexane/THF solutions. X-ray measurements were performed on a Nicolet R3m/V (**1c'**) and a Stoe STADI 4 diffractometer (**1d'**). Crystal data and details of data collection are summarized in Table 3. The structures were solved by direct methods with SHELXS-86 [22], and refined using full-matrix least-squares procedures on *F* (SHELXTL-Plus [23] (**1c'**)), and on *F*² (SHELXL-93 [24] (**1d'**)), respectively.

For compound **1c'**, non-hydrogen atoms were refined with anisotropic thermal parameters except for the atoms of the disordered THF molecule. In the disordered molecule, the occupancies of the two positions were refined to 0.741(8) and 0.259(8). Except for methylene protons of the ligands, all other hydrogen atoms were included in the refinement using a rigid model.

Due to the very weak diffraction power of the single crystals of **1d'**, intensity data were collected only up to 2θ = 40°. For compound **1d'**, non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were geometrically positioned with fixed isotropic thermal parameters being 1.5 times the values of the equivalent isotropic thermal parameters of the carrier carbon atoms. Further details of the crystal structure

analyses can be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, citing the deposition numbers CSD-406762 (**1c'**) and CSD-406768 (**1d'**).

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