N,*N*-Dilithioarylamines as New Building Blocks in Amide Chemistry; the Structure of a Carbanion-Stabilized $[C_2N_5Li_{10}]^{2-}$ Cluster

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2-Biphenylamine reacts with (dimethylamino)trimethylstannane in a 2:1 molar ratio, undergoing transamination to the distannylamine **1a**. The extremely air and moisture sensitive (2-biphenyl)-*N*,*N*-dilithium amide **2a** is obtained by the stannazane cleavage reaction of **1a** with *n*BuLi in MeO*t*Bu. Compound **2a** is the first example of a highly reactive, doubly metallated amine that can be used as a precursor in inorganic synthesis under fairly mild conditions. For example, both lithium atoms can be substituted by boryl or silyl groups, which cannot be introduced using other routes. Amide **2a** crystallizes as a cluster containing five $RNLi_2$ units, and is unexpectedly stabilized by two methanide anions. When the methanide ions are included, the lattice of the central $C_2N_4Li_8$ unit represents a section of the antiisomorphic lattice of the CaF_2-type. DFT (B3LYP) calculations and population analysis (NBO) have been carried out to get further insights into the thermodynamics of several dilithioamines $(RNLi_2)_n$ (R = H, CH_3, Ph; n = 1–6).

Introduction

Lithium amides are of widespread importance as precursors in the synthesis of novel main group element-nitrogen compounds and as deprotonating agents.[1] Their synthesis from secondary amines and alkyllithium compounds,[1] as well as their structural features in solution and the solid state, have been documented in numerous examples.[2] In contrast, little information is available about synthetic routes to doubly lithiated primary amines and the molecular structures of these compounds. Apart from powder diffraction studies on $LiNH_2/Li_2NH$ in the early fifties,[3] only the complex structure of the dilithiated α-naphthylamine has been reported.[4] This metal amide crystallizes as a cyclo-oligomeric aggregate containing ten molecular units with intermolecular Li−N bridging bonds. Dilithiated species have been postulated as intermediates in the decomposition of metallated amines, although their existence has not yet been confirmed.[5]

Recently we reported the synthesis and structures of monometallated organostannylamides of the type $RN(SnMe_3)M$.[6] In this paper we want to describe the synthesis of the first example of a highly reactive dilithiated primary amine, its unexpected molecular structure and its promising use as a building block.

Results and Discussion

The dilithium organylamides **2** are obtained by stannazane cleavage reactions of the distannylamines **1** with lithium alkyls in a 1:2 molar ratio according to Equation (1) and (2) under kinetically controlled conditions in good yield.[7] The deprotonation reaction of primary amines with metal alkyls does not lead to dimetallated amides. These reactions are usually not straightforward and lead to a mixture of products owing to unintentional C−H bond-cleavage reactions.

$$R{-}NH_2 \xrightarrow[-\ 2\ Me_2NH]{+\ 2\ Me_3SnNMe_2} \underset{\mathbf{1}}{R{-}N(SnMe_3)_2} \tag{1}$$

$$R{-}N(SnMe_3)_2 \xrightarrow[-2\ Me_3SnR']{+\ 2\ R'Li} \underset{\mathbf{2}}{1/n\ [R{-}NLi_2]_n} \tag{2}$$

The distannazanes **1** can be obtained from the transamination of Me_3SnNR_2 (R = Me, Et) with primary amines [Equation (1)] according to well-known procedures.[8a,8b] The progress of the reaction [Equation (2)] can be monitored by ^1H and ^{119}Sn NMR spectroscopy by following the change of the signal intensity of the cleavage product tetraalkylstannane as well as of the signal of **1**.

The extremely air- and moisture-sensitive dilithium amides **2** can only be isolated as colorless powders when butyllithium is used as the metalating agent in a 1:1 mixture of hexane and diethyl ether. Monomeric species of **2** could

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not be detected in solution even when temperature-dependent NMR spectroscopy methods were applied. In most cases complex multiplet signals (^{7}Li or ^{13}C NMR) were detected, or the low concentration of compounds remaining in solution after cooling the reaction mixture did not allow the detection of nuclei with low natural abundance. This holds particularly for ^{15}N NMR studies, which are essential for the elucidation of structural features in solution. The signal pattern and the chemical shift of the nuclei measured (^{1}H, ^{7}Li, ^{13}C, ^{14}N) point to aggregation even in the presence of chelating amine ligands (pmdta, tmeda) for complexation of the lithium ions. These findings are in contrast to the properties of the respective precursors, the monolithium stannylamides.[6] Depending on the reaction conditions mono- or dinuclear units can be detected in solution, confirmed by their excellent resolved spin-spin coupling pattern of $^1J(^6\text{Li},^{15}\text{N})$ and $^2J(^6\text{Li},^{119}\text{Sn})$ and by an X-ray structure determination in the solid state. Although the predominant ionic character of the Li−N bond is indisputable, the values of the coupling constants mentioned above indicate a significant degree of covalency in that bond. Previous theoretical investigations of the hypothetical structure of the monomeric $HNLi_2$ [2d] suggested a considerable amount of p_π overlap in the Li−N bond, which has not been proved to be a good description.

The tendency of metal amides to form polynuclear aggregates should increase on going from mono- to dilithiated amides owing to the increase of electron density at the nitrogen center and the change of the ionic character in the Li−N bonds. To obtain an insight into the aggregation of dilithioamines, several species of the type $(RNLi_2)_n$ (R = H, CH_3, Ph; $n = 1-6$) have been studied by DFT (B3LYP)[9] calculations and population analysis (NBO).[10] These results are summarized in Table 1. They confirm that all the examined aggregation reactions are exothermic. For each substituent R attached to the nitrogen atom the calculated reaction enthalpy reveals the same trend. Starting with the dimer up to the hexamer, with R = H, the reaction enthalpy is smallest (largest stability) for the formation of the trimer (**C** in Figure 1).

The energy values of the exothermic oligomerization for different reactions decrease along the series $R = H > CH_3 > Ph$ (Table 1).[11] According to NBO analysis the Li−N bonds are highly polar with significant amounts of covalent bonding [e.g. in the trimer (**C**): only 90% of the σ(Li−N) orbital is localized at the N atom]. In general, the polarity of the Li−N bonds increases with growing cluster size. In all cluster units each nitrogen atom interacts with four lithium centers. The lithium atoms, however, show a strong interaction with one adjacent lithium center and two weak interactions with two additional lithium centers [e.g. **C**: $d(\text{Li}-\text{Li}) = 2.11$ Å vs. 2.63 Å]. The calculated covalent (atom-atom NLMO) bond orders for this type of Li···Li interaction lie in the range between 0.03 and 0.04. Consequently, edge-linked square pyramids, containing four lithium atoms in the square positions and a nitrogen in the apical position, represent the predominant structural element (**B**−**D** in Figure 1). It therefore becomes evident that there is a positively charged area perpendicular to the rings formed by linked pyramids (see **C** and **D**) which is suitable for the attack of Lewis bases. The title molecule **2a**, the *N*-arylated species 2-dilithioaminobiphenyl, represents the product of such a formal Lewis acid-base reaction.

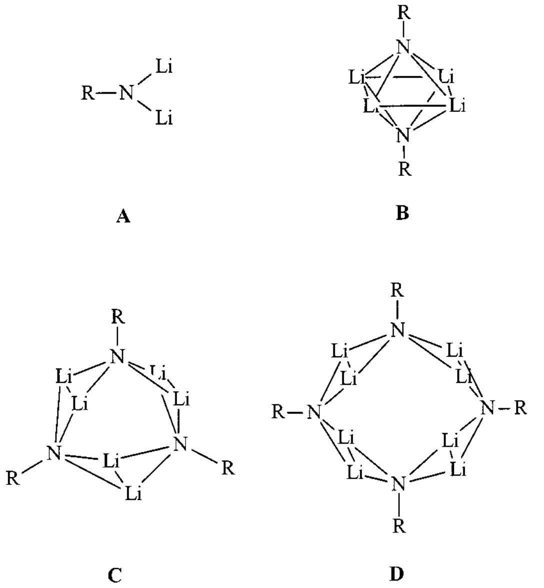


Figure 1. Schematic representation of di-, tetra-, hexa- and octanuclear Li clusters of the type ($[RNLi_2]_n$ for $n = 1-4$)

The X-ray structure determination of **2a** revealed an overall composition of $(C_{12}H_9NLi_2)_5 \cdot 2LiCH_3 \cdot 5OEt_2$ with a central $Li_8N_4C_2$ unit (Figure 2).[12] This structural feature is nicely in agreement with our theoretical prediction that the formation of oligomeric species (trimers and tetramers, respectively) is energetically preferred to the formation of monomeric or polymeric entities. Large *R* values are obtained due to the disorder of ether molecules in the crystal and the insufficient reflection properties of such a light atom cluster compound.[13] A detailed discussion of bond lengths and bond angles must therefore be carried out with care. However, the topological framework and the peculiar-

Table 1. Reaction enthalpies [B3LYP/6-31G(d,p); kcal mol^{-1}] for the successive aggregation of $n(RNLi_2) \rightarrow (RNLi_2)_n$

Reaction type[9]	**A** + **A** → **B**	**B** + **A** → **C**	**C** + **A** → **D**	**D** + **A** → **E**	**E** + **A** → **F**
R = H	−61.9	−91.1	−76.3	−68.9	−63.9
R = CH_3	−54.3	−82.5	−68.5	−	−
R = Ph	−40.9	−74.9	−	−	−

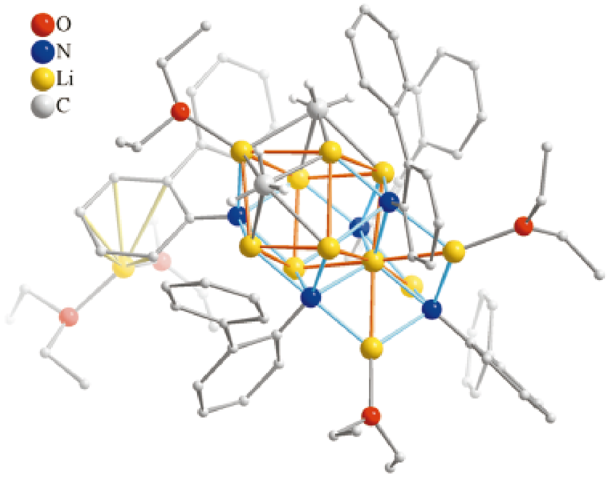


Figure 2. Molecular structure of [(2-Biphenyl-$NLi_2)_5$·2MeLi·5Et_2O] **2a**; the hydrogen atoms attached to the aryl groups are omitted for clarity, and the size of the carbon atoms of the aryl groups has been decreased.

ities of the cluster structure could be determined unambiguously. We should stress here that the results of the X-ray structure determination have been reproduced by the investigation of different single crystals deriving from several experiments. The most striking structural feature is the peculiar stabilization of the central Li_8N_4 aggregate (Figure 3) by the introduction of two methanide ions, each of them coordinating to four lithium centers. The eight lithium ions occupy the corners of a cube. The four organyl nitrogen and the two methanide anions compensate the positive charge of the cube by occupying the apical positions of six square pyramids. The six squares of the pyramids composed of lithium atoms form a cube as shown in Figure 3b. The two reactive sites in the tetrameric aggregate **D** are no longer available for further attack of the Biph-NLi_2 moiety, which would lead to the formation of larger aggregates, because of the introduction of the two methanide ions. However, the large biphenyl group of the amide center cannot prevent one additional $BiphNLi_2$ species from attaching itself to the periphery of the polyhedron stabilized by a lithium ion originally belonging to one of the methanide groups. Consequently the coordination number of three nitrogen centers of the polyhedron is extended to six. The Li cation of the second methanide ion is attached to a peripheral phenyl group of the biphenyl substituent by an η^6 π-interaction and additionally coordinates to two ether molecules. The lithium centers are three- and four-coordinate. The fourth position is predominantly occupied by an η^2 π-coordination with the aryl ligands (not shown in Figure 2)

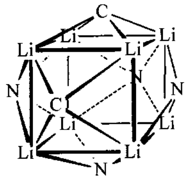


Figure 3. Central entity of the molecular structure of **2a** [without substituents R at the nitrogen atoms, the fifth $RNLi_2$ unit and the coordinating ether molecules]

When the methanide ions are included, the arrangement of the atoms in the central cluster unit represents a section of the antiisomorphic lattice of the CaF_2-type (Figure 3).[14] The positions of the fluoride ions at the corners of the cube are occupied by the lithium ions and the calcium positions above the centers of the edges of the cube are filled with $(R\text{-}N)^{2-}$ and CH_3^- ions. The same arrangement of atoms is found in the lattice of Li_2O. The bond lengths in the cluster **2a** are summarized in Table 2. With the reservations mentioned above they can be compared to the interatomic distances of already known lithium amides and alkyllithium compounds to see if there is a small or large deviation from normal values. The Li−N bond lengths of 1.942(5)−2.149(6) Å are in the range of the values determined by ab initio calculations of the mono lithiated $(LiNH_2)_4$ [$d_{(LiN)}$: 1.99−2.06 Å].[2b] The structural features of the latter are similar to the cluster of $(MeLi)_4$, where the positions of the methyl groups are occupied by the amino groups instead. In general the Li−N distances are significantly shorter in **2a**, probably due to the change of the electron density at the doubly metallated nitrogen atom. The Li−C bond lengths of 2.156(6)−2.445(7) Å of the methyl carbanions are similar to the values determined for tetrameric MeLi {$d_{(LiC)}$: 2.36 Å[15] and 2.236 Å according to recent ab initio studies[2b]}. Moreover, the Li−Li distances of 2.329(7)−2.611(7) Å are in good agreement with the values of 2.420 Å calculated by ab initio studies of $(MeLi)_4$.[15] Finally, the sufficient agreement of the bond lengths in **2a** with those in similar compounds confirms the topology of this unusual cluster.

Table 2. Range of selected bond lengths [Å] of the cluster **2a**

Li−N	1.942(5)−2.149(6)	Li−Li	2.329(7)−2.611(7)
Li−O	1.921(6)−1.992(6)	Li−CH_3	2.156(6)−2.445(7)
Li···$C_{biphenyl}$	2.291(6)−2.786(6)		

The origin of MeLi, which was not used as the metalating agent, can be explained indirectly by the presence of the alkyl stannanes Me_2SnBu_2 and $SnMe_4$. This points to exchange reactions according to Equation (3) followed by the Sn−N cleavage reaction of **1a** according to Equation (4).

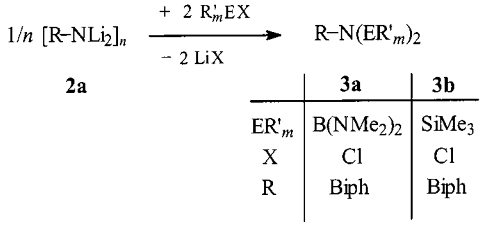
$$Me_3SnBu + LiBu \rightleftharpoons Me_2SnBu_2 + LiMe \tag{3}$$

$$R{-}N(SnMe_3)_2 + LiMe \longrightarrow R{-}N(SnMe_3)Li + SnMe_4 \tag{4}$$

However, it was not possible to detect MeLi in the cooled reaction mixture by means of ^{1}H and ^{13}C NMR spectroscopy, probably due to the Sn−N cleavage reactions proceeding very rapidly under these conditions. The equilibrium in Equation (3) was proved by reaction of Me_3SnBu with BuLi in a 1:1 molar ratio at −20 °C. The ^{1}H and ^{119}Sn NMR spectra showed that only ca. 30% of the products were formed under these conditions.[7]

The similarities in the lattices of **2a** and Li_2O may indicate that the Li−N bond is predominantly ionic in character despite a significant amount of covalent bonding as confirmed by our DFT studies. Additionally, Li−Li interactions may stabilize the cluster **2a**.

Astonishingly, the cluster compound **2a** is easily split into reactive cluster fragments, which makes it an ideal precursor for the formation of new element-nitrogen compounds. A convenient method of using the dilithium amide in solution even at low temperatures (−40 °C to −50 °C) is the reaction of **2a** with element halides according to Equation (5). A crucial condition for this procedure is the formation of the cluster compound in methyl *tert*-butyl ether (mtbe) as solvent and with methyllithium in ether as reagent.

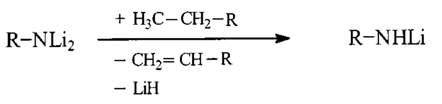


$$1/n\,[\text{R–NLi}_2]_n \xrightarrow[-\,2\,\text{LiX}]{+\,2\,\text{R}'_m\text{EX}} \text{R–N(ER}'_m)_2 \qquad (5)$$

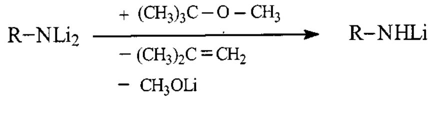
2a

	3a	**3b**
ER'$_m$	B(NMe$_2$)$_2$	SiMe$_3$
X	Cl	Cl
R	Biph	Biph

Using this technique diborylamines (**3a**) or disilylamines (**3b**) are accessible under mild conditions [Equation (5)]. These compounds are not easily synthesized by existing techniques and, to the best of our knowledge, routes including Si−N or Sn−N cleavage reactions do not yield satisfactory results.[7] The application of the synthetic potential of **2a** is not restricted to the examples described in this paper, it is also suitable for a variety of element halides as well as organyl groups R (e.g. R = *t*Bu, Me_3Si, Me_3Sn, C_6H_5, 2,6-*i*$Pr_2C_6H_3$, etc.). The extreme reactivity of the $R\text{-}N^{2-}$ group is revealed by the existence of protonation reactions [Equation (6) and (7)] upon allowing the reaction mixture to warm to ambient temperature.[7]



$$\text{R–NLi}_2 \xrightarrow[\substack{-\,\text{CH}_2{=}\text{CH–R}\\ -\,\text{LiH}}]{+\,\text{H}_3\text{C–CH}_2\text{–R}} \text{R–NHLi} \qquad (6)$$



$$\text{R–NLi}_2 \xrightarrow[\substack{-\,(\text{CH}_3)_2\text{C}{=}\text{CH}_2\\ -\,\text{CH}_3\text{OLi}}]{+\,(\text{CH}_3)_3\text{C–O–CH}_3} \text{R–NHLi} \qquad (7)$$

Experimental Section

General Remarks: Due to the moisture sensitivity of the compounds, some extremely so, all experiments and manipulations were carried out under argon purified by passage through a BTS catalyst. Reactions were performed by using standard Schlenk techniques and using dried, thoroughly deoxygenated solvents. The starting materials 2-aminobiphenyl, Me_3SiCl (all Aldrich) were used after redestillation. Me_3SnNMe_2[19] was prepared according to a literature procedure from Me_2NLi and Me_3SnCl. However, the yield could be improved by separation of surplus Me_2NLi before the addition of the exact stochiometric amount of Me_3SnCl. (2-Biphenyl)N$(SnMe_3)_2$[8c] and $(Me_2N)_2BCl$,[20] were prepared according to literature procedures. NMR spectra were recorded with Jeol GSX270 and Jeol EX400 spectrometers. A Perkin-Elmer Paragon 1000 PC spectrophotometer was used to record the IR spectra; solid substances were examined as Nujol mulls between KBr plates (vs: very strong, s: strong, m: medium, w: weak, vw: very weak, sh. shoulder).

(2-Biphenyl)dilithium amide (2a): A 1.1 mL portion of a solution of 2-biphenyl-N$(SnMe_3)_2$ (1.5 g, 3 mmol) dissolved in Et_2O (20 mL) was treated dropwise at −50 °C with *n*BuLi (3.75 mL, 1.6 M in hexane) diluted with 10 mL of hexane, resulting in a yellow solution. An orange solid precipitated from the solution, which redissolved (complete at −20 °C) upon allowing the reaction mixture to slowly warm to 0 °C. After removal of a sample for NMR investigations [$\delta^{7}Li$ = 3.5 (broad); $\delta^{119}Sn$ = 0.2 ($BuSnMe_3$), 2.6 ($SnMe_4$); signal ratio 100:12], the orange solution was cooled to −20 °C again, concentrated to a volume of ca 1.5 mL, diluted with 10 mL of Et_2O and stored at −78 °C for a fortnight. Some of the orange single crystals obtained by this procedure and suitable for X-ray structure analysis were isolated from the cooled solution. After separation of the solid from the solution, the crystalline material was dried in vacuo (10 °C/10^{-3} Torr). The residual yellow powder (0.31 g, 57%; m.p. > 280 °C, decomp.), which burns upon contact with air or moisture, changed color to dark brown when attempting to isolate a sample for elemental analysis, even under an argon atmosphere, hence the reported data are fairly inaccurate (ca. 12.5% too low). ^{1}H NMR (C_6D_6): δ = −1.31 [s, $(CH_3Li)_n$], 0.83 [t, $^{3}J_{H,H}$ = 7.0 Hz, $(CH_3CH_2)_2O$], 2.98 [q, $^{3}J_{H,H}$ = 7.0 Hz, $(CH_3CH_2)_2O$], 6.5−7.8 (unresolved m, aryl-*H*). ^{7}Li NMR (C_6D_6): δ = −4.9, −0.9 (very broad, signal ratio 11:100). ^{13}C NMR (C_6D_6): δ = −4.6 [s, $(CH_3Li)_n$], 14.9 [$(CH_3CH_2)_2O$], 65.2 [$(CH_3CH_2)_2O$], 120.7−155.8 (ca. 20 signals, aryl area, diphenyl groups). IR (nujol): $\tilde{\nu}$ =3048 cm^{-1} w, 3034 w, 2972 m, 2929 m, 2871 m, 1573 s, 1443 s, 1411 vs, 1309 s, 1293 s, 1249 s, 1184 m, 1093 m, 987 m, 840 m, 762 m, 738 m, 600 m, 532 m, 497 m. $C_{12}H_9NLi_2$ (181.1): calcd. C 79.59, H 5.01, N 7.73; found C 69.57, H 4.34, N 6.66.

Bis[bis(dimethylamino)boryl](2-biphenyl)amine (3a): BuLi (3.1 mL, 1.6 M in hexane) was added dropwise at −55 °C to a stirred solution of 2-biphenyl-N$(SnMe_3)_2$ (**1a**; 1.1 g, 2.5 mmol) in mtbe (25 mL). The suspension turned to an orange solution at −30 °C. After stirring for 2 h at −30 °C, $(Me_2N)_2BCl$ (0.7 mL, 5 mmol), dissolved in hexane (12 mL), was added. After allowing the yellow suspension to warm to ambient temp. and stirring for a further 48 h the colorless solid was filtered off (G4-frit). [NMR spectroscopic data of the filtrate: $\delta^{11}B$ = 24.0, 28.6 (br, 2-Biph-N$[B(NMe_2)_2]_2$ **3a**); $\delta^{119}Sn$ = −3.6 (Bu_2SnMe_2), 0.2 ($BuSnMe_3$), 2.3 ($SnMe_4$), signal ratio: 24:100:24]. After removal of all volatile components in vacuo (40 °C/10^{-3} Torr), **3a** (0.66 g, 72%, bp. 87 °C/10^{-5} Torr) could be isolated as a yellow oil. ^{1}H NMR (C_6D_6): δ = 2.45 [broad, 24 H, $(Me_2N)_2$], 6.77 (m, 1 H, 3-H), 6.95 (m, 1 H, 5-H), 7.09−7.28 (m, 5 H, 2′- 6′-H), 7.49 (m, 2 H, 4-H/6-H). ^{11}B NMR (C_6D_6): δ = 29.1. ^{13}C NMR (C_6D_6): δ = 39.4 [broad, (*Me*$_2$N)$_2$], 121.2 (C3), 126.3 (C5), 127.2 (C1), 128.3 (C2′, C6′), 128.7 (C3′, C5′), 129.0 (C6), 132.2 (C4), 135.1 (C4′), 142.4 (C1′), 148.5 (C2). IR (nujol): $\tilde{\nu}$ = 3073 cm^{-1} w, 2992 m, 2896 s, 2791 m, 1580 w, 1510 s, 1388 s, 1349 s, 1246 m, 1224 s, 1136 m, 1122 m, 1064 m, 1028 m, 862 s, 744 m, 702 m. $C_{20}H_{32}B_2N_5$ (365.1): calcd. C 65.79, H 9.11, N 19.18; found C 63.69, H 8.94, N 18.18. MS: *m*/*z* = 365 [M$^+$].

Bis(trimethylsilyl)(2-biphenyl)amine (3b): BuLi (4.19 mL, 1.6 molar in hexane) was added dropwise at −55 °C to a stirred solution of the distannylamine **1a** (1.66 g, 3.35 mmol) dissolved in mtbe (25 mL) at the same temperature. After 1 h stirring at −10 °C the orange colored solution was cooled to −30 °C. Me_3SiCl (0.84 mL, 6.7 mmol) dissolved in hexane (12 mL) was then added dropwise and the solution was allowed to attain ambient temp. within 2 h. After additional stirring for 12 h the solid components were separated by filtration (0.35 g, 120% according to LiCl, G4-frit). The volatile compounds of the filtrate were removed in vacuo (30 °C/10^{-2} Torr) and **3b** (0.7 g, 67%, 80 °C/10^{-3} Torr, solidifying after 12 h) was obtained by distillation as a colorless liquid from the residual viscous, brown oil. ^{1}H NMR (400 MHz, C_6D_6): δ = 0.08 (s, 18 H, *Me*$_3$Si), 6.81 (m, 1 H, 3-H), 6.96 (m, 1 H, 5-H), 7.11−7.24 (m, 5 H, 2′-H/6′-H), 7.36−7.49 (m, 2 H, 4-H/6-H) ^{13}C NMR: δ = −0.01 (s, *Me*$_3$Si), 115.7 (C3), 118.3 (C5), 127.3 (C1), 128.0 (C2′, C6′), 128.8 (C3′, C5′), 129.2 (C6), 129.7 (C4), 130.6 (C4′), 131.1 (C1′), 144.8 (C2). ^{29}Si NMR: δ = 5.9. $C_{18}H_{27}N_1Si_2$ (313.6): calcd. C 68.94, H 8.68, N 4.47; found C 68.32, H 8.43, N 4.21. MS: *m*/*z* = 313 [M$^+$].

Computational Methods: The structural and vibrational data of several lithium-nitrogen clusters $(RNLi_2)_n$ (R = H, CH_3, Ph; *n* = 1−6; for CH_3 and Ph *n* = 1−4) were calculated by using the hybrid density functional theory (B3LYP) with the program package Gaussian 98.[9] For all elements a standard 6-31G(d,p) basis set was used. The computations were carried out at the DFT level using the hybrid method B3LYP which includes a mixture of Hartree−Fock exchange with hybrid DFT exchange correlations. Becke's three parameter functional where the non-local correlation is provided by the LYP expression (Lee, Yang, Parr correlation functional) was used as implemented in Gaussian 98. An NBO population analysis was carried out to investigate the bonding in these species.[10]

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[11] The calculated reaction enthalpies refer to the following reactions: monomer (**A**) + monomer (**A**) dimer (**B**), dimer (**B**) + monomer (**A**) trimer (**C**), trimer (**C**) + monomer (**A**) tetramer (**D**), tetramer (**D**) + monomer (**A**) pentamer **E**, etc.

[12] *X-ray structure determination:* Single crystals (0.10 × 0.10 × 0.10 mm), mounted on a glass fiber at −30 °C coated with oxygen-free perfluoropolyether oil. Crystal data were determined and intensity data recorded at −90 °C with a Siemens/Bruker P4 diffractometer (Mo-K_α radiation, λ = 0.71063 Å, graphite monochromator, $d_{\text{detektor-crystal}} \approx$ 50 mm, CCD-area detector with Siemens LT2-device). Data reduction was performed with SAINT,[16] absorption correction with SADABS.[17] Structure solution was performed by direct methods (SHELXTL system)[18] and final refinement by using the SHELXL-97[16] program. The H-atoms of the methyl anions were localized by difference Fourier-synthesis. Crystal data: *a* = 14.332(4) Å, *b* = 46.98(2) Å, *c* = 13.387 Å, α = 90°, β = 96.05(1)°, γ = 90°, *V* = 8963(4) Å^3; monoclinic, space group $P2_1/c$, *Z* = 4, 2θ range for data collection: 13.62−50.06°, 14385 independent, 8710 observed reflections [$F > 4\sigma(F)$], R_{int} = 0.0730, *R*1 = 0.1016, *wR*^{2} = 0.2290. CCDC-141383 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving. html [or from the Cambridge Crystallographic Data Centre, 12, Union Road,

Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

[13] Cluster compounds with such a composition of elements frequently show a drastic decrease in the number of reflections at larger decline angles Θ when small crystals (edge length < 0.1 mm) of low quality are measured. As a consequence the standard deviations of atom distances and bond angles increase, as do the conventional *R* value and the weighted *R* value, wR_2. Even exposures of 40 s/frame (ΔΦ and Δω = 0.3°) only result in a slight improvement of the data.

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