

Synthesis and Structural Characterization of Metalated 1,8-Bis(silylamino)naphthalene Derivatives

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Reaction of 1,8-C₁₀H₆{NHSiMe₃}₂ (**1**) with 2 molar equiv of butyllithium in toluene and subsequently added hmpa or tmeda as neutral coligands yields the lithium compounds [1,8-C₁₀H₆{N(Li-hmpa)SiMe₃}₂] (**2**) or [1,8-C₁₀H₆{N(Li)SiMe₃}₂(tmeda)_{1.5}]₂ (**3**), respectively which were both characterized by X-ray crystallography. Both compounds were obtained irrespective of the amide/coligand ratio in solution. Compound **3** is a dimeric complex containing two chelating and one bridging tmeda ligand. Lithiation of **1** in thf and reaction of the lithium amide with MgBr₂(Et₂O) gave the mixed-metal Li–Mg–amide [1,8-C₁₀H₆{NSiMe₃}₂Li(thf)MgBr(thf)] (**4**). A single-crystal X-ray structure analysis revealed that in the solid the MgBr units coordinate to neighboring lithium centers, leading to the aggregation of the molecules as polymeric chains.

Introduction

The amido function R₂N is readily incorporated in a great variety of highly charged polydentate ligands and thus enables a systematic ligand design in the coordination chemistry of the early transition elements. This has been an important underlying reason for the remarkable growth of this area in recent years.^{1–4} The availability of two substituent positions at the donor atom allows the integration of the anionic amido function into ligand systems of both podand and macrocyclic topology. This not only leads to a well-defined relative orientation of the ligating atoms but also opens up many possibilities of steric control. Moreover, amido functions may be combined with other donor functionalities with a different formal charge and chemical hardness, and more generally, a different thermodynamic and kinetic stability of their interactions with the metal center.³ In the latter case the strong metal–amide bonds form the anchoring elements of the polyfunctional ligands while the remaining donor functions may either influence the electronic properties of the central atom or mask coordination sites by virtue of their hemilabile nature. Led by these fundamental aspects of ligand design, it is the combination of the academic interest in amide chemistry and the prospect of the commercial exploitation of its results in catalysis that has provided the momentum for this development.

As part of our own investigations in amide chemistry, we studied the structural patterns that result from the fixed relative orientation of the amido functions in polydentate amido ligands.

These include simple bidentate amides^{5–7} and tripodal tridentate ligands^{8–15} as well as combinations of anionic amido with neutral donor functions.^{16,17} Particular rigidity of the donor arrangement is achieved if aromatic or condensed aromatic structures are employed as ligand backbones. These include the 1,2-diaminobenzene derivatives studied by Lappert,^{18,19} Boncella,^{20–27} and

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others.^{28–32} We recently began with a systematic investigation of the structural chemistry of main group metalated 1,8-diaminonaphthalenes,^{33,34} in particular, the silylated derivative 1,8-bis(trimethylsilylamino)naphthalene.^{35,36} This ligand has also been applied in the synthesis of amido titanium and zirconium complexes, which were shown to act as olefin polymerization catalysts.^{37–39}

In our investigation of this system we found that in particular the lithiated derivatives are isolated with varying degree of solvation if prepared in a donor solvent, which occasionally rendered their stoichiometric use as ligand transfer reagents difficult. In this paper we report the synthesis and structural characterization of several solvated metal derivatives.

Experimental Section

All manipulations were performed under an inert-gas atmosphere of dried argon in standard (Schlenk) glassware which was flame-dried with a Bunsen burner prior to use. Solvents were dried according to standard procedures and saturated with Ar. The deuterated solvents used for the NMR spectroscopic measurements were degassed by three successive “freeze–pump–thaw” cycles and dried over 4 Å molecular sieves.

The ¹H, ¹³C, ⁷Li, ³¹P, and ²⁹Si NMR spectra were recorded on a Bruker AC 200 spectrometer equipped with a B-VT-2000 variable temperature unit (at 200.13, 50.32, 77.77, 81.03, and 39.76 MHz, respectively) or on a Bruker AMX 400 spectrometer (at 400.13, 100.61, and 161.98 MHz, respectively) with tetramethylsilane, H₃PO₄ (85%), or LiI/H₂O (1 M) as reference. The IR spectra were recorded on a Bruker IFS 25 FT-IR spectrometer.

Elemental analyses were carried out in the microanalytical laboratory of the Chemistry Department at Würzburg. The compound 1,8-bis(trimethylsilylamino)naphthalene (**1**) and the solvent-free lithium amide [1,8-C₁₀H₆{N(Li)SiMe₃}₂] were prepared as reported in the literature.^{33,35} All other chemicals used as starting materials were obtained commercially and used without further purification.

(1) Preparation of [1,8-C₁₀H₆{N(Li)hmpa}SiMe₃}₂] (2**).** To a stirred solution of 400 mg (1.27 mmol) of [1,8-C₁₀H₆{N(Li)SiMe₃}₂] in toluene (30 mL), 0.33 mL (1.90 mmol) of hmpa was added at room temperature. The mixture was stirred for another 1.5 h and centrifuged, and the colorless centrifugate was stored at –35 °C. Compound **2** was obtained as a colorless, highly crystalline solid (yield, 581 mg, 90%); mp, 180 °C. ¹H NMR (400.13 MHz, C₆D₆, 295 K): δ 0.64 (s, 18 H, Si(CH₃)₃), 2.09 (d, 36 H, ³J_{PH} = 9.4 Hz, OP(N(CH₃)₂)₃), 6.84 (dd, 2

H, ³J_{H^aH^b} = 7.6 Hz, ⁴J_{H^aH^c} = 1.2 Hz, H^a, C₁₀H₆), 7.16 (dd, 2 H, H^c, C₁₀H₆), 7.31 (t, 2 H, H^b, C₁₀H₆). ¹³C{¹H} NMR (100.61 MHz, C₆D₆, 295 K): δ 2.3 (Si(CH₃)₃), 36.3 (d, ²J_{PC} = 4.1 Hz, OP(N(CH₃)₂)₃), 113.7 (CH, C₁₀H₆), 113.8 (CH, C₁₀H₆), 126.4 (CH, C₁₀H₆), 127.9 (C, C₁₀H₆), 141.1 (C, C₁₀H₆), 159.0 (CN, C₁₀H₆). ³¹P{¹H} NMR (161.98 MHz, C₆D₆, 295 K): δ 25.3. ²⁹Si{¹H} NMR (39.76 MHz, C₆D₆, 295 K): δ –13.2. ⁷Li{¹H} NMR (77.77 MHz, C₆D₆, 295 K): δ –0.42. Anal. Calcd for C₂₈H₆₀Li₂N₈O₂P₂Si₂: C, 49.98; H, 8.99; N, 16.65. Found: C, 49.49; H, 9.24; N, 16.27.

(2) Preparation of [1,8-C₁₀H₆{N(Li)SiMe₃}₂(tmeda)_{1.5}] (3**).** To a stirred solution of 400 mg (1.27 mmol) of [1,8-C₁₀H₆{N(Li)SiMe₃}₂] in toluene (30 mL), 0.28 mL (1.90 mmol) of tmeda was added at room temperature. The mixture was stirred for another 1.5 h and centrifuged, and the orange centrifugate was stored at –35 °C. Compound **3** was obtained as a colorless, highly crystalline solid (yield, 313 mg, 46%); mp, 94 °C. ¹H NMR (400.13 MHz, C₆D₆, 295 K): δ 0.38 (s, 36 H, Si(CH₃)₃), 1.61 (s, 36 H, N(CH₃)₂), 1.68 (s, 12 H, N(CH₂)₂), 6.64 (dd, 4 H, ³J_{H^aH^b} = 7.6 Hz, ⁴J_{H^aH^c} = 1.2 Hz, H^a, C₁₀H₆), 7.14 (d, 4 H, H^c, C₁₀H₆), 7.20 (t, 4 H, H^b, C₁₀H₆). ¹³C{¹H} NMR (100.61 MHz, C₆D₆, 295 K): δ 3.3 (Si(CH₃)₃), 46.7 (N(CH₃)₂), 57.8 (N(CH₂)₂), 114.5 (CH, C₁₀H₆), 114.9 (CH, C₁₀H₆), 126.4 (CH, C₁₀H₆), 127.9 (C, C₁₀H₆), 140.9 (C, C₁₀H₆), 159.4 (CN, C₁₀H₆). ²⁹Si{¹H} NMR (39.76 MHz, C₆D₆, 295 K): δ –14.0. ⁷Li{¹H} NMR (77.77 MHz, C₆D₆, 295 K): δ –1.35. Anal. Calcd for C₂₅H₄₈Li₂N₅Si₂·2.5(C₆H₅CH₃): C, 70.99; H, 9.53; N, 9.74. Found: C, 70.42; H, 9.37; N, 9.89.

(3) Preparation of [1,8-C₁₀H₆{NSiMe₃}₂Li(thf)MgBr(thf)] (4**).** To a stirred solution of 1.00 g (3.31 mmol) of 1,8-C₁₀H₆{NHSiMe₃}₂ in thf (20 mL), 3.50 mL (7.00 mmol) of a 2.0 M solution of *n*-BuLi in cyclohexane was added at –40 °C. After the red solution was warmed to room temperature and stirred for 2 h, 1.30 g (4.97 mmol) of MgBr₂·(Et₂O) was added at –40 °C. While being stirred for another 18 h at room temperature, the mixture turned pale-green. The solvent was removed under reduced pressure, and the residue was extracted with a 1:1 mixture of toluene/CH₂Cl₂ (50 mL) and filtered. After the solvent was removed again under reduced pressure, and the brown residue was washed with cold *n*-pentane (20 mL). Compound **4** was obtained as a colorless, highly crystalline solid after recrystallization from *n*-pentane (20 mL) (yield, 1.23 g, 67%). ¹H NMR (200.13 MHz, C₆D₆, 295 K): δ 0.62 (s, 18 H, Si(CH₃)₃), 0.80 (m, 8 H, CH₂CH₂O), 3.03 (m, 8 H, CH₂CH₂O), 6.80–6.85 (m, 2 H, H^a, C₁₀H₆), 7.13–7.16 (m, 4 H, H^b + H^c, C₁₀H₆). ¹³C{¹H} NMR (50.32 MHz, C₆D₆, 295 K): δ 2.6 (Si(CH₃)₃), 24.8 (CH₂CH₂O), 68.7 (CH₂CH₂O), 115.9 (CH, C₁₀H₆), 117.8 (CH, C₁₀H₆), 125.0 (C, C₁₀H₆), 126.4 (CH, C₁₀H₆), 139.5 (C, C₁₀H₆), 154.5 (CN, C₁₀H₆). IR (benzene): 3038 w, 2942 vs, 2882 s, 2092 vw, 1550 vs sh, 1422 vs, 1369 s, 1278, 1251, 1064, 1044, 865, 840 vs, 763 cm^{–1}. Anal. Calcd for C₂₄H₄₀BrLiMgN₂O₂Si₂: C, 51.85; H, 7.25; N, 5.04. Found: C, 51.58; H, 7.14; N, 4.95.

(4) X-ray Crystallographic Study of 2–4. Data were collected using an Enraf-Nonius CAD4 diffractometer at a temperature of 193–(2) K (**2**) and 173(2) K (**3**) with oil-coated shock-cooled crystals^{40–42} mounted on the top of a glass pin under nitrogen. Data of **4** were collected using a Siemens P4 diffractometer at a temperature of 299–(2) K with an oil-coated crystal mounted in a Lindemann capillary under argon. Crystal data and experimental details for the crystals of **2–4** are given in Table 1. The data for the structures **2** and **3** were corrected for absorption using ψ -scans, and for **4** an empirical absorption correction was applied.⁴³ All structures were solved by direct methods (SHELXS-97) and refined on F² (SHELXL-97).^{44,45} There was some conformational disorder of both tmeda and one thf ligand in the crystal structures of **3** and **4**, respectively. In **3**, in addition to two ordered toluene solvent molecules, there was a half toluene molecule in the asymmetric unit, resulting from disorder across an inversion center. In the final cycle of the full-matrix least-squares refinement, anisotropic

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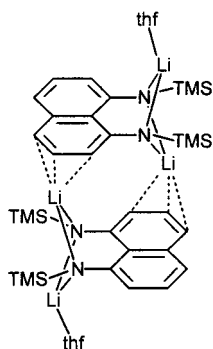
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Table 1. Crystal Data and Structure Refinement for 2–4^a

	2	3	4
empirical formula	C ₂₈ H ₆₀ Li ₂ N ₈ O ₂ P ₂ Si ₂	C _{42.50} H ₆₈ Li ₂ N ₅ Si ₂	C ₂₄ H ₄₀ BrLiMgN ₂ O ₂ Si ₂
fw	672.84	719.08	555.92
temp, K	193(2)	173(2)	299(2)
wavelength, Å	0.710 73	0.710 73	0.710 73
cryst syst	monoclinic	triclinic	monoclinic
space group	C2/c (No. 15)	P $\bar{1}$ (No. 2)	P2 ₁ /c (No. 14)
a, Å	18.983(2)	11.645(3)	11.6817(11)
b, Å	11.1727(13)	12.173(3)	11.7292(15)
c, Å	19.768(2)	15.959(4)	22.157(3)
α , deg		97.030(14)	
β , deg	110.603(5)	95.118(14)	94.625(7)
γ , deg		90.331(15)	
volume, Å ³	3924.5(8)	2235.8(9) Å ³	3026.0(6) Å ³
Z	4	2	4
D _{calcd} , g cm ⁻³	1.139	1.068	1.220
abs coeff, mm ⁻¹	0.206	0.112	1.479
final R indices [I > 2 σ (I)]	R ₁ = 0.0429 wR ₂ = 0.1054	R ₁ = 0.0709 wR ₂ = 0.1878	R ₁ = 0.0698 wR ₂ = 0.1291
R indices (all data)	R ₁ = 0.0579 wR ₂ = 0.1169	R ₁ = 0.1006 wR ₂ = 0.2114	R ₁ = 0.1735 wR ₂ = 0.1538

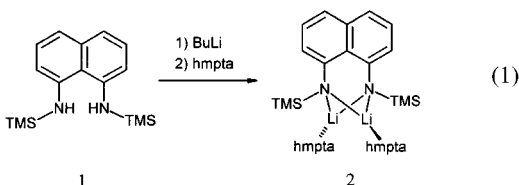
$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|, wR_2 = \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]^{1/2}, w^{-1} = [\sigma^2(F_o^2) + (aP)^2 + bP], P = [\max(F_o^2, 0) + 2(F_c^2)]/3.$$

Chart 1

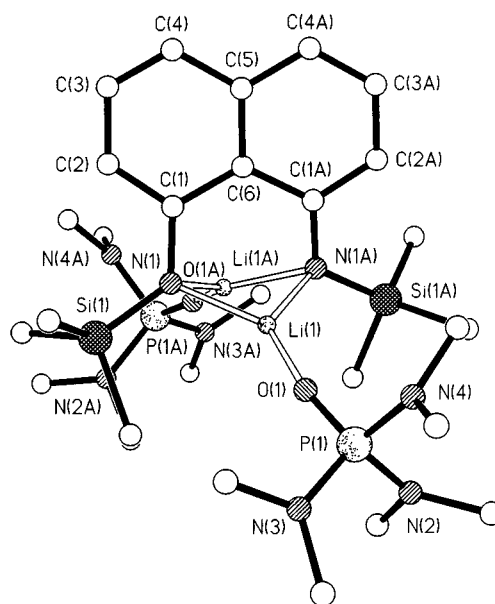
displacement parameters were assigned to all non-hydrogen atoms except for those of the disordered ligand components in 3 and 4 and the lithium atom in 4. Hydrogen atoms were included in idealized positions riding on the parent atoms and were assigned isotropic displacement parameters of 1.2U_{eq} (CH, CH₂) and 1.5U_{eq} (CH₃) of the parent atom.

Results and Discussion

We recently reported the synthesis of the thf-solvated lithium amides [1,8-C₁₀H₆{N(Li)SiMe₃}₂](thf)_n (n = 1–4), which can be obtained by variation of the reaction conditions.^{33,34} Of these the monosolvated derivative adopts an unusual dimeric structure, the most characteristic feature of which are the intermolecular arene–lithium contacts (Chart 1).³³ Reaction of 1,8-C₁₀H₆{NHSiMe₃}₂ (1) with 2 molar equiv of butyllithium in toluene and subsequent addition of 2–4 equiv of hmpa yielded the disolvated lithium compound [1,8-C₁₀H₆{N(Li-hmpa)SiMe₃}₂] (2) irrespective of the stoichiometry:



While its formulation was based on the analytical and ¹H, ¹³C, ²⁹Si, ³¹P, and ⁷Li NMR spectroscopic data, its highly crystalline nature allowed its structural characterization by X-ray crystal-

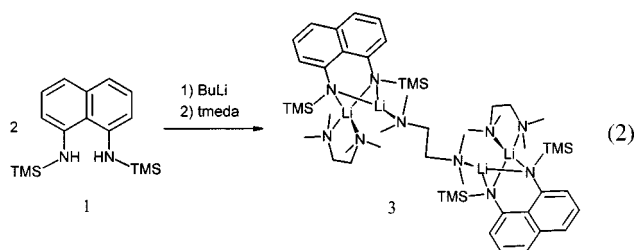
**Figure 1.** Molecular structure of compound 2. The principal bond lengths and interbond angles are listed in Table 2.**Table 2.** Selected Bond Lengths (Å) and Interbond Angles (deg) of 2

Bond Lengths			
Li(1)–N(1)	1.995(4)	N(1)–Si(1)	1.7068(17)
Li(1)–N(1A)	1.992(4)	N(1)–C(1)	1.380(3)
Li(1)–O(1)	1.801(4)	P(1)–O(1)	1.4772(16)
Bond Angles			
Li(1)–N(1)–Li(1A)	80.51(18)	O(1)–Li(1)–N(1A)	130.6(2)
N(1)–Li(1)–N(1A)	89.82(16)	O(1)–Li(1)–N(1)	139.6(2)
P(1)–O(1)–Li(1)	167.67(16)	C(1)–N(1)–Li(1)	109.17(17)
		C(1)–N(1)–Li(1A)	95.34(17)

lography. The molecular structure of 2 is displayed in Figure 1, while the principal bond lengths and interbond angles are listed in Table 2. The molecular structure of 2 has crystallographic C₂ symmetry about the C(5)–C(6) vector. It displays the expected Li₂N₂–ring system, the detailed geometry of which is entirely dictated by the structure of the ligand backbone. The amido functions being tied into the naphthalene framework enforces a nonplanar configuration of the four-membered amidolithium ring, the angle between the two Li(1)–N(1)–Li(1A)

planes being $44.64(14)^\circ$ and the sum of the inner ring angles, $\angle[\text{Li}(1)-\text{N}(1)-\text{Li}(1\text{A})]$ and $\angle[\text{N}(1)-\text{Li}(1)-\text{N}(1\text{A})]$, thus being 340.7° . The Li–N distances are equal within experimental error [$d\{\text{Li}(1)-\text{N}(1)\} = 1.995(4)$, $d\{\text{Li}(1)-\text{N}(1\text{A})\} = 1.992(4)$ Å] and lie in the range previously determined for lithium–nitrogen bonds.^{46,47} The hmpa ligands are almost linearly coordinated to the metal center, $\angle[\text{P}(1)-\text{O}(1)-\text{Li}(1)] = 167.67(16)^\circ$ with a typical oxygen–lithium distance of $1.801(4)$ Å.^{48–51} The bis(silylamido)naphthalene framework is not strictly planar; the two symmetry-related silyl groups are displaced out of the plane defined by the aromatic ring system in opposite directions [torsion angle $[\text{Si}(1)-\text{N}(1)-\text{C}(1)-\text{C}(2)] = 17.4(3)^\circ$], thus reducing repulsion between the two lone electron pairs of the amido nitrogen atoms.

It should be pointed out that there is no strict steric reason that would prevent further coordination of hmpa molecules to the lithium centers as is observed for the thf adducts mentioned above. That there is some steric flexibility is nicely illustrated by the reaction product isolated upon addition of the bidentate tertiary diamine tmeda to the lithium amide of **1** generated in toluene:



Irrespective of the stoichiometry chosen, the only product crystallizing from the solutions thus obtained is the tmeda solvate containing 1.5 molecules of the bidentate donor ligand per formula unit of $[\text{1,8-C}_{10}\text{H}_6\{\text{N}(\text{Li})\text{SiMe}_3\}_2(\text{tmeda})_{1.5}]$ (**3**). The molecular structure of compound **3** was established by a single-crystal X-ray structure analysis and is depicted in Figure 2. The principal bond lengths and interbond angles are given in Table 3.

The molecular structure in the solid is a dimer of $[\text{1,8-C}_{10}\text{H}_6\{\text{N}(\text{Li})\text{SiMe}_3\}_2(\text{tmeda})]$ units that are linked by a bridging tmeda ligand. The two halves of the molecule are related by a crystallographic center of symmetry that is located at the midpoint of the $\text{C}(42)-\text{C}(42\text{A})$ vector. Whereas one of the lithium atoms, Li(1), in each diamido unit is coordinated by a tmeda ligand in a chelating fashion, rendering this metal center four-coordinate, the second lithium center, Li(2), is three-coordinate because of the monodentate binding of the bridging tmeda molecule. The difference in coordination number and thus steric crowding around the two metal centers is reflected in the Li–N distances. For Li(1) the amido–N–Li distances of $d\{\text{Li}(1)-\text{N}(1)\} = 2.099(7)$ and $d\{\text{Li}(1)-\text{N}(2)\} = 2.100(8)$ Å are significantly longer than for Li(2) [$d\{\text{Li}(2)-\text{N}(1)\} = 1.956(8)$ and $d\{\text{Li}(2)-\text{N}(2)\} = 1.969(8)$ Å]. The same applies

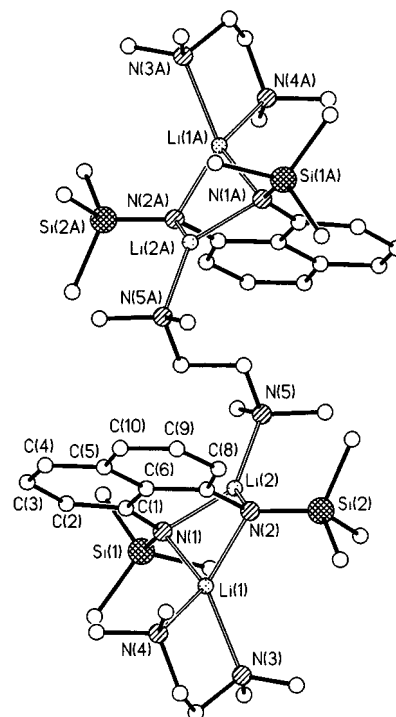


Figure 2. Molecular structure of the dimeric lithium amide **3**. The principal bond lengths and interbond angles are listed in Table 3.

Table 3. Selected Bond Lengths (Å) and Interbond Angles (deg) of **3**

Bond Lengths			
Li(1)–N(1)	2.099(7)	Li(2)–N(1)	1.956(8)
Li(1)–N(2)	2.100(8)	Li(2)–N(2)	1.969(8)
Li(1)–N(3)	2.305(8)	Li(2)–N(5)	2.147(8)
Li(1)–N(4)	2.216(8)	N(1)–Si(1)	1.705(3)
Bond Angles			
Li(1)–N(1)–Li(2)	84.2(3)	Li(1)–N(2)–Li(2)	83.9(3)
N(1)–Li(1)–N(2)	84.0(3)	N(1)–Li(2)–N(2)	91.4(3)
N(1)–Li(1)–N(3)	126.9(4)	N(1)–Li(2)–N(5)	131.5(4)
N(3)–Li(1)–N(4)	82.1(3)	C(1)–N(1)–Li(1)	95.3(3)
		C(1)–N(1)–Li(2)	108.3(3)

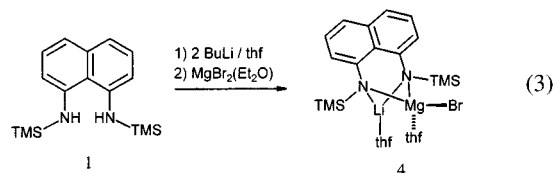
for the amino–N–Li distances involving the tmeda ligands, the corresponding bond lengths for the chelating ligand being $d\{\text{Li}(1)-\text{N}(3)\} = 2.305(8)$ and $d\{\text{Li}(1)-\text{N}(4)\} = 2.216(8)$ Å in comparison to $d\{\text{Li}(2)-\text{N}(5)\} = 2.147(8)$ Å found for the bridging ligand. The metric parameters lie in the usual range found for lithium amides^{46,47} and Li–tmeda complexes.⁵² In contrast to the structure of the hmpa-solvated compound **2**, the silylamido groups in **3** are only slightly displaced from the plane of the aromatic ring system and in the same direction [torsion angles $[\text{Si}(1)-\text{N}(1)-\text{C}(1)-\text{C}(2)] = 4.9^\circ$ and $[\text{Si}(2)-\text{N}(2)-\text{C}(7)-\text{C}(8)] = -3.7^\circ$].

The chelating tmeda ligand has found many applications in the coordination chemistry of the alkali metals^{53–72} and has been

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found to adopt both bidentate and bridging coordination modes as found in **3**. There are several examples of bridging Li–tmeda–Li units, most notably in solvated alkyl lithium reagents.^{73–77} However, we are aware of only a single amido–Li structure for which such a unit was found, namely, the compound [(iPr₂N–Li)₄(tmeda)₃] reported by Collum and co-workers.⁷⁸



Reaction of amine **1** lithiated in thf with MgBr₂(Et₂O) gave the mixed Mg–Li amide [1,8-C₁₀H₆{NSiMe₃}₂Li(thf)MgBr(thf)] (**4**) (eq 3). Even in the presence of an excess of the magnesium bromide etherate only the mixed-metal amide could be isolated from the thf solutions. The spectroscopic and analytical data, while indicating the organic components, did not allow an unambiguous formulation of the compound. This was achieved by an X-ray diffraction study, which established the structure of the compound. Its asymmetric unit is displayed in Figure 3, while the principal bond lengths and angles are listed in Table 4.

The molecular structure shown in Figure 3a is similar to those of the lithium amides discussed above in that the anionic donor functions in the bidentate amido ligand are bridged by the metal fragments arranged outside the plane of the aromatic ligand framework. The MgBr fragment is bound to the two amido N atoms and is additionally coordinated by a thf molecule, leading to a distorted tetrahedral coordination sphere. The lithium atom on the other side of the molecule is coordinated by one thf ligand. This does not lead to a planar coordination at the lithium

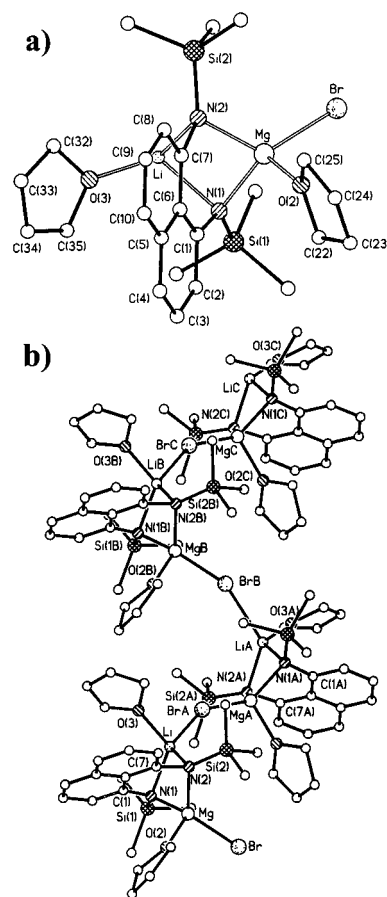


Figure 3. (a) Molecular structure of the monomeric unit of [1,8-C₁₀H₆{NSiMe₃}₂Li(thf)MgBr(thf)] (**4**). The principal bond lengths and angles are listed in Table 4. (b) Part of the helical polymeric structure of **4** observed in the solid state.

Table 4. Selected Bond Lengths (Å) and Interbond Angles (deg) of **4**

Bond Lengths			
Li–N(1)	2.107(12)	Mg–N(1)	2.031(6)
Li–N(2)	2.108(12)	Mg–N(2)	2.047(6)
Li–O(3)	1.934(14)	Mg–O(2)	2.042(7)
Li–Br(A)	2.717(14)	Mg–Br	2.469(3)
Bond Angles			
Li–N(1)–Mg	88.7(4)	N(1)–Li–Br(A)	125.4(5)
N(1)–Li–N(2)	83.8(6)	N(1)–Li–O(3)	117.7(6)
N(1)–Mg–N(2)	87.3(3)	N(1)–Mg–O(2)	106.8(3)
N(1)–Mg–Br	127.7(2)	O(2)–Mg–Br	100.1(2)
Mg–Br–Li(Z)	150.3(3)	O(3)–Li–Br(A)	89.4(6)

center but to tetrahedral coordination, the fourth site at the lithium center being occupied by the bromide ligand of a neighboring molecule, related to the first by a crystallographic 2₁ screw axis. This results in the crystal being composed of helical polymeric chains running parallel to the *b* axis (Figure 3b). The second lithium–bromine distance of *d*{Li–BrA} = 2.717(14) Å is rather longer than the interatomic Li–Br distances normally found in saltlike structures,^{74,79–85} but

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relatively long Li \cdots Br distances have been reported for bridging bromide ligands.^{86–88} We note that there is one previous report in the literature by Eaborn, Smith, and co-workers of the structural characterization of an Mg–Br \cdots Li bridge.⁸⁵

Again, in the structure of **4** the bis(silylamido)naphthalene framework is not exactly planar, the two silicon atoms lying out of the plane of the aromatic rings [deviations Si(1) of 0.126 Å and Si(2) of 0.186 Å, Si–N–C–C torsion angles of 7.7° and –7.7°] in a direction away from the bromide ligand. This minimizes repulsion between the hydrogen atoms on the trimethylsilyl groups and the bromine atom [Br \cdots H(43a) = 2.93 Å and Br \cdots H(52a) = 2.93 Å].

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Conclusions

The 1,8-diaminonaphthalene derivatives described in this study are of interest as ligands in the coordination chemistry of the early transition elements. In addition, an interesting structural chemistry of their groups 1 and 2 amido complexes as well as the thallium(I) analogues is beginning to emerge. The presence of donor solvents or coligands leads to well-defined finite and infinite structural arrays that may be readily characterized.

In this study, the structural patterns observed for the lithium amides of this ligand system have been extended and includes a group 1/group 2 mixed-metal species. Current and future studies in this laboratory are aimed at the extension of the group 2 chemistry of this system.

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Supporting Information Available: X-ray crystallographic files, in CIF format, for the structures of **2–4**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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