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Polylithiated Tetraaminosilanes: Synthesis and Characterization of $(Et_2O{\cdot}Li)_4[Si(Nnaph)_4]$ and X-ray Structure of $\{THF{\cdot}Li_3[Si(N^iPr)_3(NH^iPr)]\}_2$

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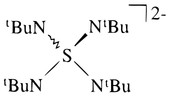
The treatment of $SiCl_4$ with 4 equiv of $Li_2(Nnaph)$ (naph = 1-naphthyl) in diethyl ether gives $(Et_2O{\cdot}Li)_4[Si(Nnaph)_4]$ (**4**), which, upon reaction with excess $^tBuNH_3Cl$ or MeO_3SCF_3, generates $Si[N(H)naph]_4$ (**5**) or $Si[N(Me)naph]_4$ (**6**), respectively. The centrosymmetric dimer $\{THF{\cdot}Li_3[Si(N^iPr)_3(NH^iPr)]\}_2$ (**7**), formed via trilithiation of $Si[N(H)^iPr]_4$ with *n*-butyllithium, consists of a bis-THF-solvated $Li_6(N^iPr)_6$ cyclic ladder bicapped by two Si−N(H)^{i}Pr units. Crystal data for **7**: $C_{32}H_{74}Li_6N_8O_2Si_2$, monoclinic, $P2_1/n$, $a = 10.661(7)$ Å, $b = 16.964(5)$ Å, $c = 12.405(4)$ Å, $\beta = 93.22(4)°$, $V = 2239.9(15)$ Å^3, and $Z = 2$.

Introduction

Current interests of our research group include the synthesis[1−5] and reaction chemistry[1,6] of the lithium derivatives of homoleptic polyimido anions containing p-block element centers. These anions, for example, $[Te(N^tBu)_3]^{2-}$ and $[C(N^tBu)_3]^{2-}$,[1,4] are isoelectronic with common oxo anions, for example, $[TeO_3]^{2-}$ and $[CO_3]^{2-}$, respectively. The tetrakisimido anions $[S(N^tBu)_4]^{2-}$ (**1**) and $[P(Nnaph)_4]^{3-}$ (**2**, naph = 1-naphthyl) were recently characterized as the highly solvated, spirocyclic monomers $[Li(THF)_4{}^+]_x[THF_2{\cdot}Li(\mu\text{-}NR)_2E(\mu\text{-}NR)_2Li{\cdot}THF_2]^{x-}$ (E = S, $x = 0$, R = ^{t}Bu; and E = P, $x = 1$, R = naph).[7,8] Generation of the related tetrakisimido tetraanion $[Si(NR)_4]^{4-}$ (**3**, R = alkyl or aryl), isoelectronic with the orthosilicate ion $[SiO_4]^{4-}$,[9] is therefore an intriguing possibility. Herein we report the preparation of the first tetraazasilicate ion **3** (R = naph) as the tetralithium derivative $(Et_2O{\cdot}Li)_4[Si(Nnaph)_4]$ (**4**) by treatment of silicon tetrachloride with 4 equiv of the dilithium imide $Li_2(Nnaph)$. The structural characterization of the dimer $\{THF{\cdot}Li_3[Si(N^iPr)_3(NH^iPr)]\}_2$ (**7**), formed via trilithiation of the tetraaminosilane $Si[N(H)^iPr]_4$ with *n*-butyllithium, is also described.



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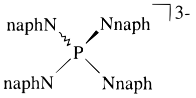

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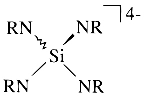

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Experimental Section

Reagents and General Procedures. Solvents were dried and distilled before use: diethyl ether, toluene, *n*-pentane, tetrahydrofuran, and *n*-hexane (Na/benzophenone). Li^{n}Bu (2.5 M solution in hexanes), H_2Nnaph (naph = 1-naphthyl), H_2N^tBu, $SiCl_4$, MeO_3SCF_3, and H_2N^i-Pr were used as received (Aldrich). $Li_2(Nnaph)$ was prepared via dilithiation of H_2Nnaph with Li^{n}Bu in diethyl ether[10] and was utilized in situ. $^tBuNH_3Cl$ was obtained by bubbling anhydrous HCl through a solution of H_2N^tBu in toluene. The compound $Si[N(H)^iPr]_4$ was prepared by the literature procedure.[11] The handling of air- and moisture-sensitive reagents was performed under an atmosphere of argon gas using Schlenk techniques or a glovebox.

Instrumentation. ^{1}H NMR spectra were collected on a Bruker AM-200 spectrometer, and chemical shifts are reported relative to Me_4Si in $CDCl_3$. ^{7}Li and ^{29}Si NMR spectra were recorded on a Varian XL-200 instrument operating at 77.75 and 39.74 MHz, respectively; chemical shifts are reported relative to 1 M LiCl in D_2O and Me_4Si in $CDCl_3$, respectively. Elemental analyses were provided by the Analytical Services Laboratory of the Department of Chemistry, University of Calgary. Consistently low values for the carbon content of compounds **4**, **5**, and **7** are attributed to the formation of silicon carbide, as has been found for other tetra(alkylamino)silanes and related compounds.[11]

Preparation of $(Et_2O{\cdot}Li)_4[Si(Nnaph)_4]$ (4). Li^{n}Bu (10.00 mL, 25.0 mmol) was added slowly to a stirred solution of H_2Nnaph (1.79 g, 12.5 mmol) in diethyl ether (75 mL) cooled to 0 °C. After 1 h, a solution of $SiCl_4$ (0.36 mL, 3.13 mmol) in diethyl ether (25 mL) was added dropwise and the cooling bath was removed. The red reaction mixture was stirred for 24 h at 23 °C and subsequently filtered (reaction times of less than 24 h result in incomplete reaction). Removal of all volatiles in vacuo yielded yellow **4** (2.67 g, 2.91 mmol, 93%); mp 110 °C (dec). Anal. Calcd for $C_{56}H_{68}Li_4N_4O_4Si$: C, 73.35; H, 7.47; N, 6.11. Found: C, 71.94; H, 7.53; N, 5.91. ^{1}H NMR (in C_6D_6 at 23 °C): δ 8.67 (m, 1H), 7.80 (d, 1H), 7.56 (d, 1H), 7.38 (m, 2H), 7.09 (m, 1H), 6.91 (m, 1H), 2.67 [q, 4H, $(CH_3CH_2)_2O$], 0.58 [t, 6H, $(CH_3CH_2)_2O$]. ^{7}Li NMR (in C_6D_6 at 23 °C): δ −1.04 (s). ^{29}Si NMR (in C_6D_6 at 23 °C): δ −44.7 (s).

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Table 1. Crystallographic Data for **7**

formula	$C_{32}H_{74}Li_6N_8O_2Si_2$	Z	2
fw	700.80	temp, °C	−103.0
space group	$P2_1/n$ (No. 14)	λ, Å	0.710 69
a, Å	10.661(7)	d_{calcd}, g cm^{-3}	1.039
b, Å	16.964(5)	μ, cm^{-1}	1.13
c, Å	12.405(4)	R^a	0.061
β, deg	93.22(4)	$R_w{}^b$	0.061
V, Å^3	2239.9(15)		

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o{}^2]^{1/2}$.

Preparation of Si[N(H)naph]$_4$ (5). A solution of **4** (0.700 g, 0.763 mmol) in diethyl ether (25 mL) was added to a stirred white slurry of ^{t}BuNH$_3$Cl (0.500 g, 4.56 mmol) in diethyl ether (30 mL) at 23 °C. The pale-pink reaction mixture was stirred for 2 h and then filtered to remove LiCl and excess ^{t}BuNH$_3$Cl. Removal of all volatiles in vacuo and subsequent washing of the pink residue with *n*-pentane (2 × 20 mL) yielded, upon drying, white **5** (0.255 g, 0.427 mmol, 56%). Microcrystalline material was obtained from a diethyl ether solution (24 h at −20 °C); mp 159 °C. Anal. Calcd for $C_{40}H_{32}N_4Si$: C, 80.50; H, 5.40; N, 9.39. Found: C, 79.83; H, 5.28; N, 9.50. ^{1}H NMR (in C_6D_6 at 23 °C): δ 7.66 (m, 2H), 7.37 (d, 1H), 7.24 (m, 3H), 7.10 (d, 1H), 4.86 (s, 1H, N−H). ^{29}Si NMR (in C_6D_6 at 23 °C): δ −55.2 (s). IR (KBr, Nujol mull): 3305 (br) cm^{-1} [ν(N−H)]. EI-MS (70 eV): 596 (M$^+$, 32%).

Preparation of Si[N(Me)naph]$_4$ (6). A solution of **4** (0.55 g, 0.60 mmol) in diethyl ether (20 mL) was added to a stirred solution of MeO$_3$SCF$_3$ (0.50 g, 3.0 mmol) in diethyl ether (20 mL) at 23 °C. The resulting white slurry was stirred for 2 h and then filtered to remove LiO$_3$SCF$_3$. Removal of all volatiles in vacuo and subsequent washing of the white residue with *n*-pentane (2 × 20 mL) yielded, upon drying, white **6** (0.19 g, 0.29 mmol, 48%). Microcrystalline material was obtained from a diethyl ether solution (24 h at −20 °C); mp 124−125 °C. Anal. Calcd for $C_{44}H_{40}N_4Si$: C, 80.94; H, 6.18; N, 8.58. Found: C, 80.61; H, 6.02; N, 8.77. ^{1}H NMR (in C_6D_6 at 23 °C): δ 7.68 (m, 2H), 7.59 (d, 1H), 7.35 (m, 3H), 6.91 (m, 1H), 2.60 (s, 3H, CH$_3$). ^{29}Si NMR (in C_6D_6 at 23 °C): δ −49.8 (s). EI-MS (70 eV): 652 (M$^+$, 17%).

Preparation of {THF·Li$_3$[Si(N^{i}Pr)$_3$(NH^{i}Pr)]}$_2$ (7). Li^{n}Bu (9.21 mL, 23.0 mmol) was added slowly to a stirred solution of Si[N(H)^{i}Pr]$_4$ (2.00 g, 7.68 mmol) in THF (60 mL) cooled to 0 °C. After 0.5 h the cooling bath was removed and the pale-yellow solution was stirred for a further 3 h at 23 °C. Removal of all volatiles in vacuo and subsequent washing of the white residue with *n*-pentane (30 mL) yielded, upon drying, white **7** (2.48 g, 3.54 mmol, 92%); mp 135 °C (dec). Anal. Calcd for $C_{32}H_{74}Li_6N_8O_2Si_2$: C, 54.84; H, 10.64; N, 15.99. Found: C, 53.63; H, 10.52; N, 16.14. ^{1}H NMR (in C_6D_6 at 23 °C): δ 3.89 [septet, 6H, (CH$_3$)$_2$C*H*, $^3J(^1H-^1H)$ = 6.1 Hz], 3.67 [m, 8H, O(C*H*$_2$)$_2$(CH$_2$)$_2$], 3.58 [m, 2H, (CH$_3$)$_2$C*H*], 1.45 [d, 12H, (C*H*$_3$)$_2$CH, $^3J(^1H-^1H)$ = 6.3 Hz], 1.38 [m, 8H, O(CH$_2$)$_2$(C*H*$_2$)$_2$], 1.33 [d, 36H, (C*H*$_3$)$_2$CH, $^3J(^1H-^1H)$ = 6.1 Hz], 0.78 [d, 2H, N−H, $^3J(^1H-^1H)$ = 9.9 Hz]. ^{7}Li NMR (in D$_8$-THF at 23 °C): δ 2.80, 1.05 (approximate relative intensities of 1:2, respectively). ^{29}Si NMR (in D$_8$-THF at 23 °C): δ −37.3 (s). IR (KBr, Nujol mull): 3176 (br) cm^{-1} [ν(N−H)].

X-ray Analyses. All measurements were made on a Rigaku AFC6S diffractometer. Crystallographic data are summarized in Table 1.

7. Crystals of {THF•Li$_3$[Si(N^{i}Pr)$_3$(NH^{i}Pr)]}$_2$ were obtained in 24 h from THF/*n*-hexane (1:1) at −30 °C. A colorless block crystal (0.65 mm × 0.60 mm × 0.55 mm) was coated with epoxy and mounted on a glass fiber. Cell constants and an orientation matrix were obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range $20.41 < 2\theta < 26.50°$. The systematic absences of $h0l$, $h = 2n - 1$ and $0k0$, $k = 2n$ uniquely determined the space group to be $P2_1/n$ (No. 14). Scans of $(1.10 + 0.34 \tan \theta)°$ were made at a speed of 4.0 deg/min^{-1} to a maximum 2θ value of 55.1°. Of a total of 5618 reflections collected, 5340 were independent (R_{int} = 0.059) and were used to refine 226 parameters, with 1351 reflections considered observed [$I > 3\sigma$]. The data were corrected for Lorentz and polarization effects. The structure was solved by and expanded using Fourier techniques.[12] All of the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included at geometrically idealized positions with C−H and N−H at 0.95 Å but were not refined. The maximum and minimum peaks on the final difference Fourier map correspond to 0.28 and −0.19 e$^-$/Å^3, respectively. Scattering factors were those of Cromer and Waber,[13] and allowance was made for anomalous dispersion.[14] All calculations were performed using teXsan.[15]

Results and Discussion

Preparation and Characterization of (Et$_2$O·Li)$_4$[Si(Nnaph)$_4$]. Synthetic routes to lithiated homoleptic polyimido anions of the p-block elements include (a) the use of secondary amido derivatives, for example, Sb(NMe$_2$)$_3$,[16] for transamination with primary lithium amides, (b) the reaction of chalcogen diimides[1,2,17] or carbodiimides[4] with primary lithium amides, and (c) the deprotonation of primary amido derivatives, for example, ^{t}BuN(H)P(μ-N^{t}Bu)$_2$PN(H)^{t}Bu[3,18] and Mes*N(H)P(NMes*)$_2$,[19] with organolithium reagents. The last route may result in the formation of incompletely lithiated products, for example, Li$_3$[Al$_2$(N^{t}Bu)$_3$(NH^{t}Bu)$_3$][5] and, in the present work, {THF•Li$_3$[Si(N^{i}Pr)$_3$(NH^{i}Pr)]}$_2$. Although the dilithiated primary amine Li$_2$(Nnaph) (naph = 1-naphthyl) is well-known,[10] this reagent has not been used for the synthesis of polyimido anions. In this work, the first ionic complex containing a tetrakisimidoorthosilicate tetraanion, [Si(NR)$_4$]$^{4-}$ (**3**), was prepared as the tetralithium etherate (Et$_2$O•Li)$_4$[Si(Nnaph)$_4$] (**4**) in 93% yield from the metathetical reaction of SiCl$_4$ with 4 equiv of Li$_2$(Nnaph) (Scheme 1).

Compound **4** is an extremely air- and moisture-sensitive amorphous yellow solid that decomposes above ca. 110 °C. Tetralithiation is indicated by the absence of a ν(N−H) vibration in the IR spectrum. The ^{1}H NMR spectrum of **4** in D$_6$-benzene reveals one naphthyl and one diethyl ether environment in a 1:1 stoichiometry. Thus, it can be concluded that each Li$^+$ ion is coordinated to one diethyl ether molecule. The CHN analyses for **4** are consistent with this conclusion. Consequently, an ion-separated structure [Figure 1a], similar to that found for the trilithium derivative of the isoelectronic [P(Nnaph)$_4$]$^{3-}$ trianion **2**,[8] can be ruled out. The ^{7}Li and ^{29}Si NMR spectra of **4** each exhibit single resonances at δ −1.04 and −44.7 ppm, respectively. Taken together, the NMR data indicate single environments for the naphthyl groups as well as for the Li(OEt$_2$)$^+$ ions. An aesthetically pleasing arrangement that is compatible with these observations involves a Si-centered Li$_4$N$_4$ cubane in which Li and N are four- and five-coordinate, respectively [Figure 1b]. This arrangement requires that each Li(OEt$_2$)$^+$ ion is coordinated

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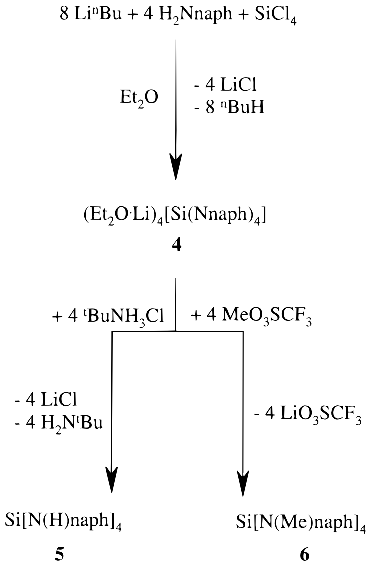
Scheme 1



to *three* naphN^{2-} ligands of the $[\text{Si(Nnaph)}_4]^{4-}$ ions. By contrast, half of the Na$^+$ ions in the related oxo system[20] Na_4SiO_4 are associated in a chelating fashion with only *two* O^{2-} ligands of the tetrahedral $[\text{SiO}_4]^{4-}$ ions. In the absence of solvation or bulky NR groups, these Na$^+$ ions are further linked in a monodentate fashion to three neighboring $[\text{SiO}_4]^{4-}$ units to give a 3D network. Thus, these Na$^+$ ions are five-coordinate, whereas the remaining Na$^+$ ions are four-coordinate.[21]

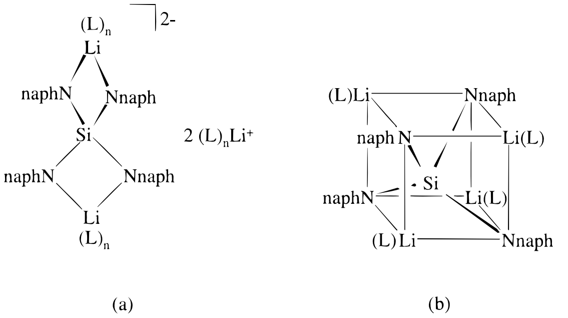


Figure 1. Possible structures for **4**: (a) $[\text{Li(L)}_n{}^+]_2[(\text{L})_n\cdot\text{Li}(\mu\text{-Nnaph})_2\text{Si}(\mu\text{-Nnaph})_2\text{Li}\cdot(\text{L})_n]^{2-}$; (b) $(\text{L}\cdot\text{Li})_4[\text{Si(Nnaph)}_4]$ (L = OEt$_2$).

Unfortunately, numerous attempts to obtain X-ray quality crystals of **4** were unsuccessful. However, the tetralithiated derivative **4** was further characterized by the preparation of Si[N(H)naph]_4 (**5**) and Si[N(Me)naph]_4 (**6**) in ca. 50% yields from the reactions of **4** with excess *tert*-butylammonium chloride and methyl triflate, respectively (Scheme 1). These derivatives were characterized by CHN analyses, IR spectra, ^{1}H, ^{13}C, and ^{29}Si NMR spectra, and the observation of parent ions in their mass spectra.

Preparation and X-ray Structure of $\{\text{THF}\cdot\text{Li}_3[\text{Si(N}^i\text{Pr)}_3(\text{NH}^i\text{Pr})]\}_2$. Attempts to generate **3** via deprotonation of a tetraaminosilane, Si[N(H)R]_4, resulted in incomplete lithiation. For example, the reaction of $\text{Si[N(H)}^i\text{Pr]}_4$ with 4 equiv of *n*-butyllithium in THF gave the dimeric trisimido/amido complex $\{\text{THF}\cdot\text{Li}_3[\text{Si(N}^i\text{Pr)}_3(\text{NH}^i\text{Pr})]\}_2$ (**7**). The presence of the N(H)^{i}Pr groups is readily evident in the IR spectrum [ν(N−H) 3176 cm^{-1}]. The yield of **7** is optimized when only three equiv of *n*-butyllithium are utilized:

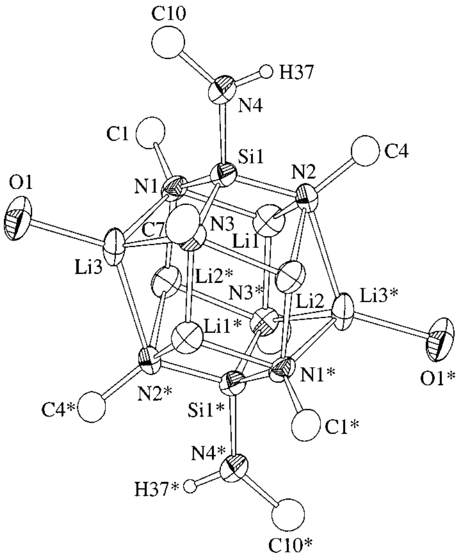
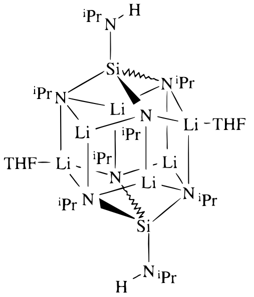


Figure 2. Molecular structure of $\{\text{THF}\cdot\text{Li}_3[\text{Si(N}^i\text{Pr)}_3(\text{NH}^i\text{Pr})]\}_2$ (**7**). For clarity, only the α-carbon atoms of the ^{i}Pr groups and the oxygen atoms of the THF molecules are shown. Displacement ellipsoids are plotted at the 35% probability level. Starred atoms are related by the symmetry transformation: $-x + 1$, $-y$, $-z + 1$.

$$3\text{Li}^n\text{Bu} + \text{Si[N(H)}^i\text{Pr]}_4 \rightarrow \tfrac{1}{2}\{\text{THF}\cdot\text{Li}_3[\text{Si(N}^i\text{Pr)}_3(\text{NH}^i\text{Pr})]\}_2 + 3\,{}^n\text{BuH} \quad (1)$$



7

To our knowledge **4** and **7** are the only known examples of tetra- and trilithiated tetraaminosilanes, respectively; the dilithiated species $\{\text{Li}_2[\text{Si(NMe)}_2(\text{NH}^t\text{Bu})_2]\}_4$ was reported previously.[22] The tetralithiated cyclodisilazane $(\text{N}^t\text{Bu})_6\text{Si}_2\text{Li}_4$ has also been prepared.[23]

X-ray structure analysis revealed a C_{2h}-symmetric 14-atom ($\text{Li}_6\text{Si}_2\text{N}_6$) ternary cluster for **7**, which can be viewed as a bis-THF-solvated $\text{Li}_6(\text{N}^i\text{Pr})_6$ cyclic ladder bicapped by two Si−N(H)^{i}Pr units (Figure 2). Selected bond distances and bond angles are listed in Table 2. Similar 14-atom clusters are observed for the homoleptic trisimido antimony(III) species $\{\text{L}\cdot\text{Li}_3[\text{Sb(NR)}_3]\}_2$ (R = CH$_2$CH$_2$Ph, L = THF; R = Cy, L = HNMe$_2$; R = 2,4-dmp, L = THF; and R = ^{t}Bu, unsolvated) in which Sb atoms bicap the Li_6N_6 ladders.[16] The cluster **7** is also isostructural, as well as isoelectronic, with the unsolvated dimers $\{\text{Li}_3[\text{RSi(N}^t\text{Bu)}_3]\}_2$ (R = Ph[24] and Me[24]) and $\{\text{Li}_3[\text{RSi-}$

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Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for {THF·$Li_3[Si(N^iPr)_3(NH^iPr)]\}_2$ (**7**)

Si(1)−N(1)	1.729(5)	N(2)−Li(1)	1.974(13)
Si(1)−N(2)	1.728(5)	N(2)−Li(2)	1.962(13)
Si(1)−N(3)	1.745(6)	N(2)−Li(3*)	2.457(13)
Si(1)−N(4)	1.739(6)	N(3)−C(7)	1.467(8)
N(1)−C(1)	1.451(8)	N(3)−Li(1*)	2.003(13)
N(1)−Li(1)	2.087(13)	N(3)−Li(2)	2.095(13)
N(1)−Li(2*)	2.001(13)	N(3)−Li(3)	2.043(13)
N(1)−Li(3)	2.005(13)	N(4)−C(10)	1.428(9)
N(2)−C(4)	1.457(9)	Li(3)−O(1)	2.007(13)

N(1)−Si(1)−N(2)	108.7(3)	Li(2)−N(2)−Li(3*)	64.0(6)
N(1)−Si(1)−N(3)	101.9(3)	Si(1)−N(3)−Li(1*)	123.8(5)
N(1)−Si(1)−N(4)	114.5(3)	Si(1)−N(3)−Li(2)	81.0(4)
N(2)−Si(1)−N(3)	106.8(3)	Si(1)−N(3)−Li(3)	85.2(4)
N(2)−Si(1)−N(4)	109.1(3)	Li(1*)−N(3)−Li(2)	69.6(5)
N(3)−Si(1)−N(4)	115.2(3)	Li(1*)−N(3)−Li(3)	74.8(5)
Si(1)−N(1)−Li(1)	80.3(4)	Li(2)−N(3)−Li(3)	124.5(5)
Si(1)−N(1)−Li(2*)	122.6(4)	Si(1)−N(4)−C(10)	132.7(5)
Si(1)−N(1)−Li(3)	86.8(4)	N(1)−Li(1)−N(2)	87.5(5)
Li(1)−N(1)−Li(2*)	69.8(5)	N(1)−Li(1)−N(3*)	108.7(6)
Li(1)−N(1)−Li(3)	124.3(6)	N(2)−Li(1)−N(3*)	114.7(6)
Li(2*)−N(1)−Li(3)	72.8(5)	N(1*)−Li(2)−N(2)	116.5(6)
Si(1)−N(2)−Li(1)	83.6(4)	N(1*)−Li(2)−N(3)	108.4(6)
Si(1)−N(2)−Li(2)	85.4(4)	N(2)−Li(2)−N(3)	86.8(5)
Si(1)−N(2)−Li(3*)	124.8(5)	N(1)−Li(3)−N(2*)	97.7(6)
Li(1)−N(2)−Li(2)	108.2(6)	N(1)−Li(3)−N(3)	83.6(5)
Li(1)−N(2)−Li(3*)	66.3(6)	N(2*)−Li(3)−N(3)	95.8(6)

$(NSiMe_3)_3]]\}_2$ (R = Ph, Me, ^{t}Bu,[25] and H[25]), formed via trilithiation of the corresponding triaminosilanes. With the exception of the N(2)−Li(3*) distance of 2.457(13) Å, the structural parameters for the $Li_6Si_2N_6$ clusters in these dimers encompass those for **7**, for example, d(Si−N) = 1.69−1.77 Å and d(N−Li) = 1.91−2.16 Å.[24,25] The long Li−N bonds are presumably a result of the higher coordination number (λ^4) of Li(3), due to solvation by one molecule of THF, compared to the three-coordinate Li(1) and Li(2) ions. The N−Si−N angles within the cluster of **7** [mean 105.8(3)°, range 101.9(3)−108.7(3)°] are narrower than those involving the exocyclic $N(H)^iPr$ group [N(4)−Si(1)−N(cluster): mean 112.9(3)°, range 109.1(3)−115.2(3)°], an indication of the structural rigidity of the Li_6N_6 cyclic ladder.

The inability to tetralithiate $Si[N(H)^iPr]_4$ with *n*-butyllithium is attributed to steric considerations. Formation of the Li_6N_6 ladder directs the ^{i}Pr substituents of the cluster-forming imido groups toward the exo cluster $N(H)^iPr$ groups, effectively encumbering nucleophilic attack by *n*-butyllithium. Attempts at deprotonation with other metallating agents were also unsuccessful. No reaction occurred when THF solutions of **7** were refluxed for 24 h with 2 equiv of LiMe, NaH, KH, or KCH_2Ph (in the presence of 18-crown-6) or with 1 equiv of $Mg^nBu^{sec}Bu$.

Conclusions

In summary, the dilithium imide Li_2(Nnaph) has been utilized as a source of $[Li(Nnaph)]^-$ to generate $(Et_2O{\cdot}Li)_4[Si(Nnaph)_4]$ with elimination of LiCl. This novel methodology may provide a general one-pot synthesis for lithiated homoleptic polyimido complexes of the form $Li_x[E(Nnaph)_x]$ (E = p-block element) from the corresponding halides. An investigation of the reactions of Li_2(Nnaph) with other main group halides is in progress.

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Supporting Information Available: X-ray crystallographic file, in CIF format, for complex **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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