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Structures of [(Amino)phenylsilyl]lithiums and Related Compounds in Solution and in the Solid State

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Abstract: The solution structures of [bis(diethylamino)phenylsilyl]lithium (**1**), [(diethylamino)diphenylsilyl]lithium (**2**), and [(diethylamino)phenylmethylsilyl]lithium (**3**) were investigated by ^{13}C, ^{29}Si, ^{7}Li, and ^{15}N NMR spectroscopic experiments. The ^{29}Si−$^{7(6)}$Li coupling can be observed in each species at low temperature. The coupling patterns indicate that these three species exist as monomers in THF. Using a ^{15}N-enrichment technique, the ^{29}Si−^{15}N couplings in **1** and **2** are observed. Next, the solid-state structures of [(diphenylamino)diphenylsilyl]lithium ($(Ph_2N)Ph_2Si-X$; X = Li) (**4**) and its fluoro (X = F) (**16**), stannyl (X = $SnMe_3$) (**17**), and hydro (X = H) (**18**) derivatives were revealed by crystallographic studies as well as by solid-state ^{29}Si NMR experiments. In the solid state, **4** exists as a monomer solvated with three THF molecules arising from the reaction solvent. The electropositive substituent X, such as lithium, causes the elongation of the Si−C and Si−N bonds, reduction of the sum of the C−Si−N (or C) angles, and a downfield shift of the ^{29}Si resonances.

Introduction

Carbanion chemistry plays a central role in the field of organic chemistry:[1] A large number of carbanions have functional groups on the carbon center, including α-heteroatom-substituted carbanions (**A**).[2] In contrast, silyl anions have been much less extensively studied than carbanions.[3,4] Synthetically versatile silyl anions have long been limited to only several triorganosilyl anions such as Ph_3SiM,[5,6] Ph_2MeSiM,[6] $PhMe_2SiM$,[6] Me_3SiM,[7] and $(Me_3Si)_3SiM$,[8,9] where M stands for Li^+ and other alkaline metals. These species, especially (phenylsilyl)lithiums, have been studied using NMR spectroscopies from a structural viewpoint by Buncel and Edlund's group[10] and Olah's group.[11] As functionalized silyl anions of type **B**, $Cl_3Si^-NR_3H^+$,[12a−d] Cl_3SiLi,[12e] $(RO)_nMe_{3-n}SiNa$,[13] HPh_2SiLi,[14] and $H(Mes)_2SiLi$[15] have been reported. The first three are postulated active species generated in situ in the presence of quenching agents, and HPh_2SiLi is obtained in about 10% yield and tends to readily polymerize. Because of the low stability of these species, their structural analyses are quite limited. In the 1990s, new members of the functionalized silyllithiums, a (phosphinosilyl)lithium,[16]

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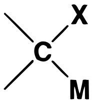
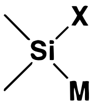
Chart 1



(**A**)



(**B**)

$(Et_2N)_2PhSiLi$ **1**

$(Et_2N)Ph_2SiLi$ **2**

$(Et_2N)MePhSiLi$ **3**

$(Ph_2N)Ph_2SiLi$ **4**

Ph_3SiLi **5**

$Ph_2MeSiLi$ **6**

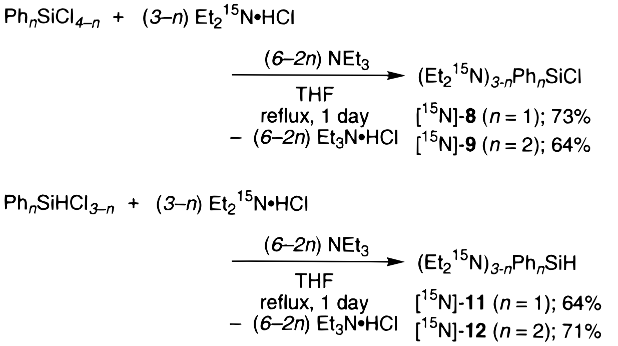
$PhMe_2SiLi$ **7**

a (bromosilyl)lithium,[17] lithium silenolates,[18] and lithium silacyclopentadienides,[19] have appeared. In 1992, we reported the preparation and reaction of the [(amino)phenylsilyl]lithiums **1**−**3** as the first stable and tractable functionalized silyl anions of type **B**.[20] These silyllithiums **1**−**3** undergo no significant decomposition for more than 3 days in THF at 0 °C, which makes it possible to observe the species in solution using NMR spectroscopies. We report here the ^{13}C, ^{29}Si, $^{7(6)}Li$, and ^{15}N NMR spectroscopic studies of [(diethylamino)phenylsilyl]lithiums (**1**−**3**), using ^6Li and ^{15}N-enrichment techniques. We also report the X-ray structure analysis of [(diphenylamino)diphenylsilyl]lithium (**4**).[21] The obtained data are discussed compared to those of the classical (triorganosilyl)lithiums, Ph_3SiLi (**5**), $Ph_2MeSiLi$ (**6**), and $PhMe_2SiLi$ (**7**), reported in the literature.[5,6] This report provides the first full details of the structural aspects of the heteroatom-substituted silyllithiums.

Results and Discussion

1. Structures in Solution. (a) Preparation of [(Diethylamino)phenylsilyl]lithiums 1−3 and Related Compounds 8−12.

Scheme 1



$$Ph_nSiCl_{4-n} + (3-n)\,Et_2{}^{15}N{\bullet}HCl \xrightarrow[\substack{\text{THF}\\ \text{reflux, 1 day}\\ -(6-2n)\,Et_3N\bullet HCl}]{(6-2n)\,NEt_3} (Et_2{}^{15}N)_{3-n}Ph_nSiCl \quad [^{15}N]\text{-}\mathbf{8}\ (n=1);\ 73\%,\ [^{15}N]\text{-}\mathbf{9}\ (n=2);\ 64\%$$

$$Ph_nSiHCl_{3-n} + (3-n)\,Et_2{}^{15}N{\bullet}HCl \xrightarrow[\substack{\text{THF}\\ \text{reflux, 1 day}\\ -(6-2n)\,Et_3N\bullet HCl}]{(6-2n)\,NEt_3} (Et_2{}^{15}N)_{3-n}Ph_nSiH \quad [^{15}N]\text{-}\mathbf{11}\ (n=1);\ 64\%,\ [^{15}N]\text{-}\mathbf{12}\ (n=2);\ 71\%$$

Table 1. ^{13}C Chemical Shifts of the (Aminosilyl)lithiums and Related Species in THF−THF-d_8[a]

	ipso	ortho	meta	para
$(Et_2N)_2PhSiLi$ (**1**)	160.0	134.9	126.6	123.2
$(Et_2N)Ph_2SiLi$ (**2**)	158.5	135.6	126.6	123.9
$(Et_2N)PhMeSiLi$ (**3**)	164.8	133.7	126.5	122.7
$(Et_2N)_2PhSiCl$ (**8**)	135.5	135.5	128.5	130.8
$(Et_2N)Ph_2SiCl$ (**9**)	134.3	135.6	128.7	131.2
$(Et_2N)PhMeSiCl$ (**10**)	135.7	134.8	128.6	130.9
$Ph_2MeSiLi$ (**6**)[b]	160.1	135.4	126.7	123.9
$Ph_2MeSiCl$ (**14**)[b]	134.4	134.0	128.1	130.5

[a] A 0.3 M THF−THF-d_8 solution with internal cyclohexane as reference (δ 27.7) at 273 K. [b] Reference 10a.

The [(amino)phenylsilyl]lithiums **1**−**3** were prepared by the reactions of the (amino)phenylchlorosilanes **8**−**10** with ^7Li or ^6Li in THF, respectively.[20] The (amino)chlorosilanes **8**−**10** were prepared in the same manner as previously reported.[22] The ^{15}N-enriched species of the (amino)chlorosilanes [^{15}N]-**8** and [^{15}N]-**9** and the (amino)hydrosilanes [^{15}N]-**11** and [^{15}N]-**12** were prepared by the reactions of the corresponding dichlorophenylhydrosilane and chlorodiphenylhydrosilane, respectively, with ^{15}N-enriched diethylamine hydrogen chloride in the presence of triethylamine, as shown in Scheme 1.

(b) ^{13}C NMR Studies. Since the chemical shifts of the aromatic carbons are expected to be a probe for elucidation of the electronic structures of the silyllithiums,[10a,11] the ^{13}C NMR spectra of **1**−**3** were first examined. The data are listed in Table 1, which contains the data for $Ph_2MeSiLi$ (**6**) and the precursor chlorosilanes **8**−**10** and **14**, for comparison.

The aromatic carbons in **2** resonate at δ 158.5 (ipso), 135.6 (ortho), 126.6 (meta), and 123.9 (para) in THF at 273 K. The shift changes from the corresponding chlorosilane precursors **8**−**10**, $\Delta\delta$(SiLi − SiCl), are +24.2 (ipso), 0 (ortho), −2.1 (meta), and −7.3 (para) ppm (positive signs denote downfield shifts), as shown in Table 1 and illustrated in Figure 1. The (aminosilyl)lithiums **1** and **3** also show similar changes (Table 1)**:** $\Delta\delta$(SiLi − SiCl) for **1** are +24.5 (ipso), −0.6 (ortho), −1.9 (meta), and −7.6 (para) ppm, and $\Delta\delta$(SiLi − SiCl) for **3** are +29.1 (ipso), −1.1 (ortho), −2.1 (meta), and −8.2 (para) ppm. The changes from the chlorosilanes to the silyllithiums cause the ipso carbon to be strongly deshielded (24 to 29 ppm) and the para carbon to be shielded (7 to 8 ppm). The shift changes of the ortho and meta carbons are smaller (0 to 2 ppm). A similar charge distribution pattern has already been observed in the (triorganosilyl)lithiums, such as $Ph_2MeSiLi$ (**6**) in comparison with $Ph_2MeSiCl$ (**14**).[10a,11] Apparently, the charge distribution pattern in these (aminosilyl)lithiums is consistent with that of π-polarization and different from that of resonance. Thus the negative charge on the silicon atom is not delocalized onto the aromatic rings in **1**−**3** as well as in **6**.

(c) ^{29}Si NMR Studies. The ^{29}Si NMR spectra[23] of **1**−**3** and the corresponding chlorosilanes were examined and the data are summarized in Table 2 and are visualized in Figure 2, which also contain the reported data of the classical (phenylsilyl)lithiums **5**−**7** and the chlorosilanes **13**−**15**, for comparison.[10b,11]

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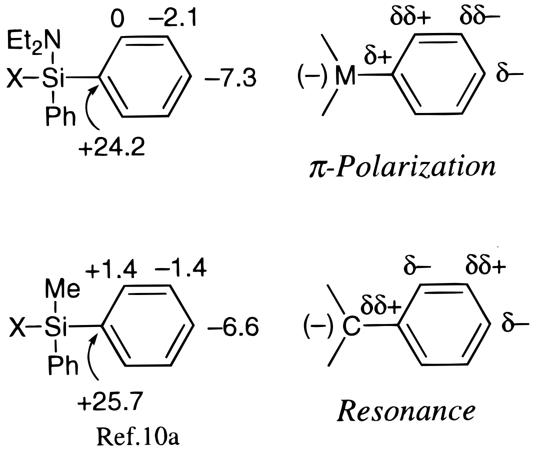


Figure 1. ^{13}C chemical shift changes $\Delta\delta$ from chlorosilanes (X = Cl) to the corresponding silyllithiums (X = Li). Also shown are schematic representations for the charge distribution on the benzene ring due to the π-polarization and resonance mechanism.

Table 2. ^{29}Si Chemical Shifts and ^{29}Si−^{7}Li and ^{29}Si−^{6}Li Coupling Constants of (Aminosilyl)lithiums and Related Species in THF[a]

	δ(273 K)[b]	^1J[^{29}Si−^{7}Li], Hz[c]	^1J[^{29}Si−^{6}Li], Hz[c,d]
$(Et_2N)_2PhSiLi$ (**1**)	27.9	q, 57 (173 K)	t, 22 (173 K)
$(Et_2N)Ph_2SiLi$ (**2**)	19.3	q, 48 (163 K)	t, 18 (173 K)[e]
$(Et_2N)PhMeSiLi$ (**3**)	14.4	q, 51 (163 K)	t, 20 (163 K)
Ph_3SiLi (**5**)[f]	−9.0		
$Ph_2MeSiLi$ (**6**)[f]	−20.6		t, 15 (158 K)
$PhMe_2SiLi$ (**7**)[f]	−27.8		t, 18 (173 K)
$(Et_2N)_2PhSiCl$ (**8**)	−18.8		
$(Et_2N)Ph_2SiCl$ (**9**)	−6.8		
$(Et_2N)PhMeSiCl$ (**10**)	2.3		
Ph_3SiCl (**13**)	1.7		
$Ph_2MeSiCl$ (**14**)[g]	10.0		
$PhMe_2SiCl$ (**15**)[g]	19.8		

[a] The spectra were recorded in an unlocked mode. [b] A 1.0 M THF solution with external Me_4Si as reference (δ 0.0). [c] A 0.3 M THF solution with internal Me_4Si as reference (δ 0.0). [d] ^{6}Li-enriched species were used. [e] MTHF solution. [f] Reference 10b, at 295 K. [g] Reference 11.

It is found that the (aminosilyl)lithiums in THF resonate in the relatively low field among the silyllithiums[3] reported so far: **1** at δ 27.9, **2** at δ 19.3, and **3** at δ 14.4.[24] There is a definite trend that the downfield shifts of the ^{29}Si NMR resonance of the silyllithiums are induced by the replacement of the methyl group by the phenyl group (e.g., from **7** to **6** to **5** and from **3** to **2**) and, in turn, by the replacement of the phenyl group by the amino group (e.g., from **6** to **3** and from **2** to **1**). This suggests that the amino group functions as a stronger electron-withdrawing group than the phenyl group in the silyllithiums.[26]

It is interesting to note that, in contrast to this, the ^{29}Si resonance of the chlorosilanes is shifted upfield as the number of the amino groups and the phenyl groups increases, as also shown in Figure 2. The origin of these tendencies remains to be clarified by further theoretical studies.

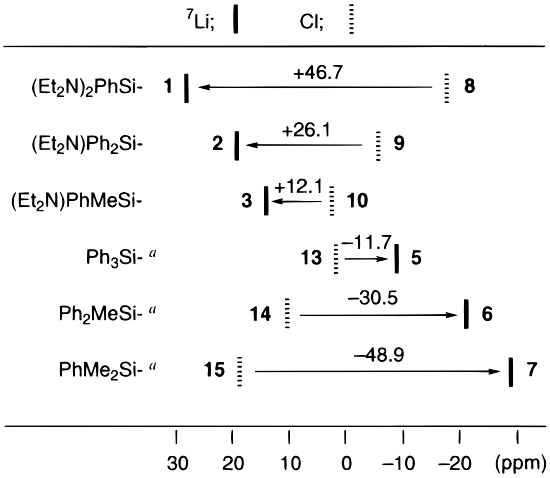
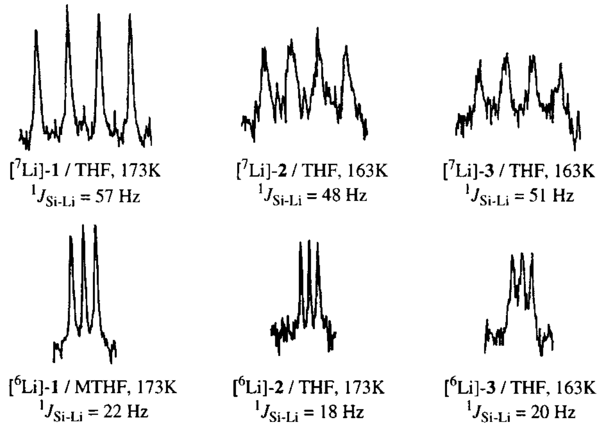


Figure 2. ^{29}Si chemical shift changes ($\Delta\delta$) from chlorosilanes to the corresponding silyllithiums. [a] Reference 10a.


[^{7}Li]-**1** / THF, 173K $^1J_{\text{Si-Li}}$ = 57 Hz

[^{7}Li]-**2** / THF, 163K $^1J_{\text{Si-Li}}$ = 48 Hz

[^{7}Li]-**3** / THF, 163K $^1J_{\text{Si-Li}}$ = 51 Hz

[^{6}Li]-**1** / MTHF, 173K $^1J_{\text{Si-Li}}$ = 22 Hz

[^{6}Li]-**2** / THF, 173K $^1J_{\text{Si-Li}}$ = 18 Hz

[^{6}Li]-**3** / THF, 163K $^1J_{\text{Si-Li}}$ = 20 Hz

Figure 3. Low-temperature ^{29}Si NMR spectra of 0.3 M solutions of $(Et_2N)_2PhSiLi$ (**1**), $(Et_2N)Ph_2SiLi$ (**2**), and $(Et_2N)PhMeSiLi$ (**3**) in THF or MTHF.

The ^{29}Si−^{7}Li and ^{29}Si−^{6}Li scalar couplings[3,9d,10b] in **1**, **2**, and **3** were successfully observed in THF or 2-methyltetrahydrofuran (MTHF) at 173 or 163 K, as shown in Table 2 and Figure 3. In the natural abundant ^{7}Li derivatives, the ^{29}Si resonance resolves into a quartet with $^1J_{\text{Si−Li}}$ = 57 Hz for **1**, 48 Hz for **2**, and 51 Hz for **3**. In the ^{6}Li-enriched derivatives, the ^{29}Si resonance resolves into a triplet with $^1J_{\text{Si−Li}}$ = 22 Hz for **1**, 18 Hz for **2**, and 20 Hz for **3**. The splitting patterns clearly indicate that the silicon atom is coupled to one lithium atom. Thus, **1**, **2**, and **3** exist as monomers in the THF and MTHF solutions.

The amino group enlarges the ^{29}Si−^{6}Li coupling constant, and thus the diamino derivative **1** exhibits the largest coupling constant among **1**−**3**, as shown in Table 2. The electron-withdrawing amino group(s) may increase the p character of the silicon orbital in the Si−N bond(s) and, in turn, increase the s character of the silicon orbital in the Si−Li bond to enlarge the coupling constant of this bond. It is also noted that the diamino derivative **1** gave the better resolved signals than the monoamino derivatives **2** and **3**, especially in the ^{7}Li derivatives, as shown in Figure 3.

(d) ^{7}Li NMR Studies. The ^{7}Li NMR spectra[9c,10c] are expected to provide information on the Si−Li bond character of the (aminosilyl)lithiums. In THF, the natural abundant ^{7}Li derivatives **1**, **2**, and **3** resonate at δ 0.35, 0.49, and 0.37, respectively,

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(23) Reviews for ^{29}Si NMR spectroscopies: (a) Williams, E. A. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John-Wiley & Sons: Chichester, 1989; pp 511−554. (b) Takeuchi, Y.; Takayama, T. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; John-Wiley & Sons: Chichester, 1998; Vol. 2, pp 267−354.

(24) The ^{29}Si shift of **2** was reported uncorrectly in the original paper (ref 20a) and reinvestigated.

(25) There have been only two types of anionic silicon compounds in which the ^{29}Si NMR chemical shifts are lower than 20 ppm; e.g., (halosilyl)lithiums[12e,17] and alkali metal silacyclopentadienides.[19]

(26) For a study of the substituent effect on the ^{29}Si resonance, see; Ernst, C. R.; Spialter, L.; Buell, G. R.; Wilhite, D. L. *J. Am. Chem. Soc.* **1974**, *96*, 5375.

Table 3. ^{7}Li Chemical Shifts of Silylithiums in THF[a,b]

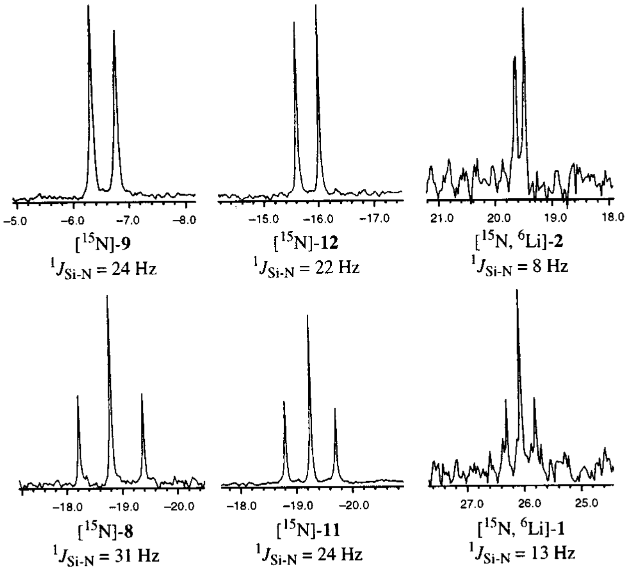
	δ
$(Et_2N)_2PhSiLi$ (**1**)	0.35
$(Et_2N)Ph_2SiLi$ (**2**)	0.49
$(Et_2N)PhMeSiLi$ (**3**)	0.37
$Ph_2MeSiLi$ (**6**)[c]	0.61

[a] The spectra were recorded in an unlocked mode. [b] A 0.3 M THF solution with external 0.3 M LiCl/MeOH as reference (δ 0.0) at 273 K. [c] Reference 10c.

Table 4. ^{15}N Chemical Shifts and ^{29}Si−^{15}N Coupling Constants of [^{15}N]-(Aminosilyl)lithiums and Related Species in THF−THF-d_8[a]

	δ	$^1J[^{29}Si-^{15}N]$, Hz[b]
$(Et_2N)_2PhSiLi$ (**1**)	48.6	13
$(Et_2N)Ph_2SiLi$ (**2**)	29.4	8
$(Et_2N)_2PhSiCl$ (**8**)	32.9	31
$(Et_2N)Ph_2SiCl$ (**6**)	35.2	24
$(Et_2N)_2PhSiH$ (**11**)	30.2	24
$(Et_2N)Ph_2SiH$ (**12**)	23.2	22

[a] A 0.3 M THF−THF-d_8 solution at 273 K with external [^{15}N]-aniline as reference (δ 52.0) (ref 37). [b] The couplings were observed in ^{29}Si NMR spectra at 273 K.



[^{15}N]-**9** $^1J_{Si-N}$ = 24 Hz

[^{15}N]-**12** $^1J_{Si-N}$ = 22 Hz

[^{15}N, ^{6}Li]-**2** $^1J_{Si-N}$ = 8 Hz

[^{15}N]-**8** $^1J_{Si-N}$ = 31 Hz

[^{15}N]-**11** $^1J_{Si-N}$ = 24 Hz

[^{15}N, ^{6}Li]-**1** $^1J_{Si-N}$ = 13 Hz

Figure 4. ^{29}Si NMR spectra of ^{15}N-enriched $(Et_2N)_2PhSiLi$ (**1**), $(Et_2N)Ph_2SiLi$ (**2**), $(Et_2N)_2PhSiCl$ (**8**), $(Et_2N)Ph_2SiCl$ (**9**), $(Et_2N)_2PhSiH$ (**11**), and $(Et_2N)Ph_2SiH$ (**12**) in THF-THF-d_8 at 273 K.

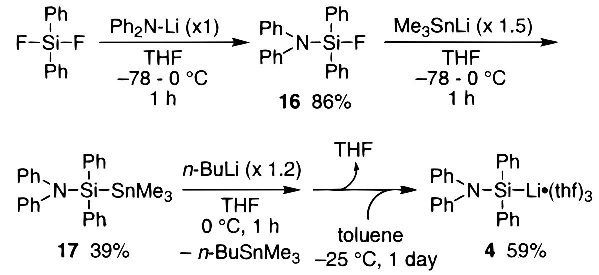
being shifted downfield relative to LiCl and close to **6** (δ 0.61), as shown in Table 3. Thus, the Si−Li bond in **1**−**3** in THF has some covalent character similar to that in the (phenylsilyl)lithiums.

(e) ^{15}N NMR Studies. The ^{15}N NMR spectra of **1** and **2** and the precursors **8** and **9** were investigated using the ^{15}N-enriched derivatives.[27] To get information on the Si−N bonding character, the ^{29}Si−^{15}N scalar couplings were also measured in the ^{29}Si NMR spectra using the ^{15}N-enriched derivatives.

In the ^{15}N NMR spectra, [^{15}N,^{6}Li]-**1** resonates at δ 48.6, the precursor [^{15}N]-**8** at δ 32.9, [^{15}N,^{6}Li]-**2** at δ 29.4, and the precursor [^{15}N]-**9** at δ 35.2, as shown in Table 4.

The ^{29}Si−^{15}N scalar couplings ($^1J_{Si-N}$)[27b] were observed in the ^{29}Si NMR spectra, as shown in Figure 4. It is noteworthy that the $^1J_{Si-N}$ values of the silyllithiums, 13 Hz for **1** and 8 Hz for **2**, are quite smaller than those of the chlorosilane precursors, 31 Hz for **8** and 24 Hz for **9**, and hydrosilanes, 24 Hz for **11** and 22 Hz for **12**. The decreased $^1J_{Si-N}$ values indicate an increase in the p character of the silicon orbital in the Si−N bond in **1** and **2** due to the connection to the electropositive lithium atom,[27] which agrees with the results obtained from the $^1J_{Si-Li}$ values mentioned above.

Scheme 2



2. Solid-State Structures. To obtain further information about the structures of the amino-substituted silicon compounds,[2828] we determined the crystal structures of [(diphenylamino)diphenylsilyl]lithium (**4**) and a series of (diphenylamino)diphenylsilyl derivatives $(Ph_2N)Ph_2Si-X$ **16** (X = F), **17** (X = $SnMe_3$), and **18** (X = H) by X-ray analysis.[21] The diphenylamino derivatives were used because they crystallize more readily than the diethylamino derivatives.[29] We also determined the solid-state CP/MAS ^{29}Si NMR spectra of the crystals of **4**, **16**, **17**, and **18**.

(a) Crystal Structures of 4 and the Related Compounds 16−18. The (aminosilyl)lithium **4** was prepared by a tin−lithium exchange reaction[20c] of the silylstannane **17** with *n*-BuLi in THF at 0 °C for 1 h as shown in Scheme 2. After removing the solvent, the resulting solid was recrystallized from toluene at −25 °C to give the pale-yellow crystals of **4** suitable for X-ray analysis in 59% yield.

The molecular structure of **4** is shown in Figure 5. Several structural features should be noted and discussed in comparison with those in $Ph_3SiLi(thf)_3$.[30] (1) The (aminosilyl)lithium **4** exists as a monomer with three THF molecules solvating the lithium atom. (2) The Si(1)−Li(1) bond (2.732(7) Å) is among the longest for the monomeric silyllithiums previously reported[28] (2.54−2.72 Å; 2.672(9) Å for $Ph_3SiLi(thf)_3$). (3) The Si(1)−N(1) bond (1.824(3) Å) is longer than the typical Si−N single bond (1.70−1.76 Å).[31] The Si(1)−C(1) (1.941(3) Å) and Si(1)−C(7) (1.923(3) Å) bonds are also elongated in comparison with the typical Si−C(sp^2) single bond (<1.86 Å).[31] These silicon−carbon bond lengths are quite similar to those in $Ph_3SiLi(thf)_3$ (1.923−1.947 Å). (4) The sum of the three angles around Si(1) of N(1)−Si(1)−C(1), N(1)−Si(1)−C(7), and C(1)−Si(1)−C(7) is 309.8°, being smaller than the ideal tetrahedral value (328°), but similar to the sum of the three angles of C−Si−C around the silicon atom in $Ph_3SiLi(thf)_3$ (304°). (5) The geometry around N(1) is planar; the sum of the three angles around N(1) is 360°. (6) The lone pair electrons on N(1) are almost orthogonal to the Si(1)−Li(1) bond, judging

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(27) (a) Kupce, E.; Liepins, E.; Pudova, O.; Lukevics, E. *J. Chem. Soc., Chem. Commun.* **1984**, 581. (b) Kupce, E.; Liepins, E.; Lukevics, E. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 568.

(28) A review of the solid-state structures of silyllithiums: Pauer, P.; Power, P. P. In *Lithium Chemistry*; Space, A.-M., Schleyer, P. v. R., Eds.; John-Wiley & Sons: New York, 1995; pp 295−392, and see also ref 3.

(29) Recently Strohmann et al. reported the crystal structure of $(Et_2N)_2PhSiLi(thf)_3$: Strohmann, C.; Ulbrich, O. In The 12th International Symposium on Organosilicon Chemistry, May, 1999, Sendai, Japan, Abstract P-81.

(30) Dias, H. V. R.; Olmstead, M. M.; Ruhlandt-Senge, K.; Power, P. P. *J. Organomet. Chem.* **1993**, *462*, 1.

(31) Sheldrick, W. S. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John-Wiley & Sons: Chichester, 1989; pp 227−304.

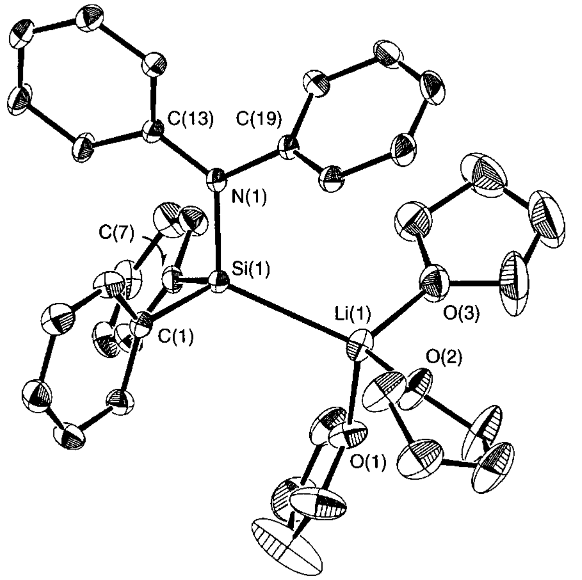

Figure 5. Crystal structure of **4**(thf)$_3$ with the 30% probability level. H atoms are omitted for clarity. Selected distances (Å) and angles (deg): Si(1)−Li(1) 2.732(7), Si(1)−N(1) 1.824(3), Si(1)−C(1) 1.923(3), Si(1)−C(7) 1.941(3), N(1)−C(13) 1.402(4), N(1)−C(19) 1.425(3), Li(1)−O(1) 1.979(8), Li(1)−O(2) 1.963(8), Li(1)−O(3) 1.941(8), Li(1)−Si(1)−N(1) 115.8(2), Li(1)−Si(1)−C(1) 123.2(2), Li(1)−Si(1)−C(7) 105.8(2), N(1)−Si(1)−C(1) 102.2(1), N(1)−Si(1)−C7 102.2(1), C(1)−Si(1)−C(7) 105.4(1), Si(1)−N(1)−C(13) 128.4(2), Si(1)−N(1)−C(19) 115.8(2), C(13)−N(1)−C(19) 115.8(2).

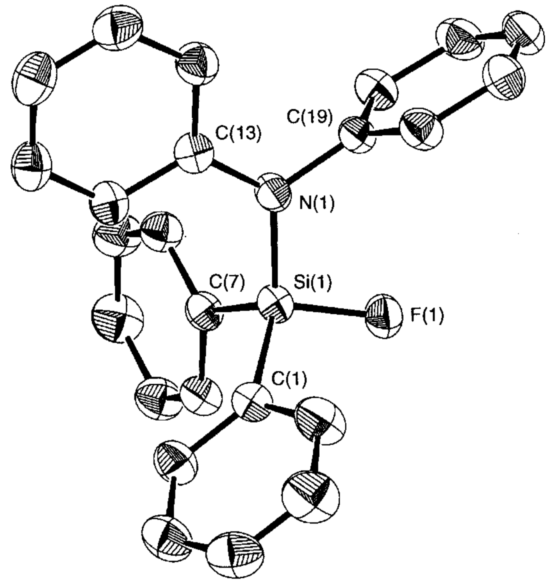

Figure 6. Crystal structure of **16** with the 30% probability level. H atoms are omitted for clarity. Selected distances (Å) and angles (deg): Si(1)−F(1) 1.594(2), Si(1)−N(1) 1.728(2), Si(1)−C(1) 1.844(3), Si(1)−C(7) 1.851(3), N(1)−C(13) 1.417(3), N(1)−C(19) 1.450(3), F(1)−Si(1)−N(1) 102.90(9), F(1)−Si(1)−C(1) 104.8(1), F(1)−Si(1)−C(7) 107.18(10), N(1)−Si(1)−C(1) 114.3(1), N(1)−Si(1)−C(7) 113.0(1), C(1)−Si(1)−C(7) 113.4(1), Si(1)−N(1)−C(13) 124.8(2), Si(1)−N(1)−C(19) 117.5(2), C(13)−N(1)−C(19) 117.7(2).

from the dihedral angles of Li(1)−Si(1)−N(1)−C(13) (−9.3°) and Li(1)−Si(1)−N(1)−C(19) (173.2°). This conformation minimizes the electrostatic repulsion between the lone pair electrons on N(1) and the anionic electrons on Si(1). Thus, the similarity of the parameters in **4** to those in Ph$_3$SiLi(thf)$_3$ (comments 3 and 4) indicates that the amino group has essentially no significant influence on the structure.

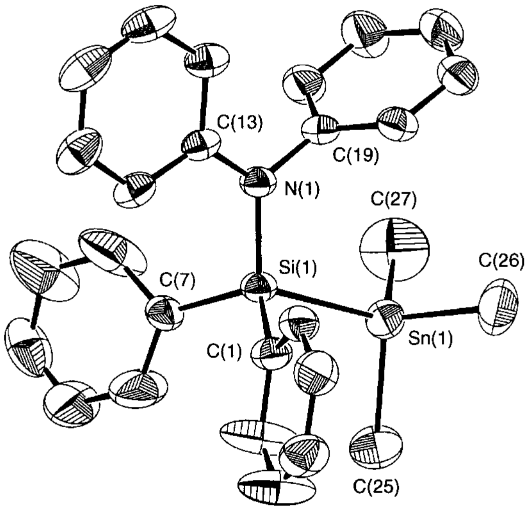

Figure 7. Crystal structure of **17** with the 30% probability level. H atoms are omitted for clarity. Selected distances (Å) and angles (deg): Si(1)−Sn(1) 2.562(1), Si(1)−N(1) 1.755(4), Si(1)−C(1) 1.887(5), Si(1)−C(7) 1.879(5), N(1)−C(13) 1.398(6), N(1)−C(19) 1.447(6), Sn(1)−C(25) 2.151(8), Sn(1)−C(26) 2.150(8), Sn(1)−C(27) 2.126(10), Sn(1)−Si(1)−N(1) 110.7(1), Sn(1)−Si(1)−C(1) 104.9(2), Sn(1)−Si(1)−C(7) 108.2(2), N(1)−Si(1)−C(1) 109.5(2), N(1)−Si(1)−C(7) 110.7(2), C(1)−Si(1)−C(7) 112.7(2), Si(1)−N(1)−C(13) 125.6(3), Si(1)−N(1)−C(19) 116.7(3), C(13)−N(1)−C(19) 117.6(4).

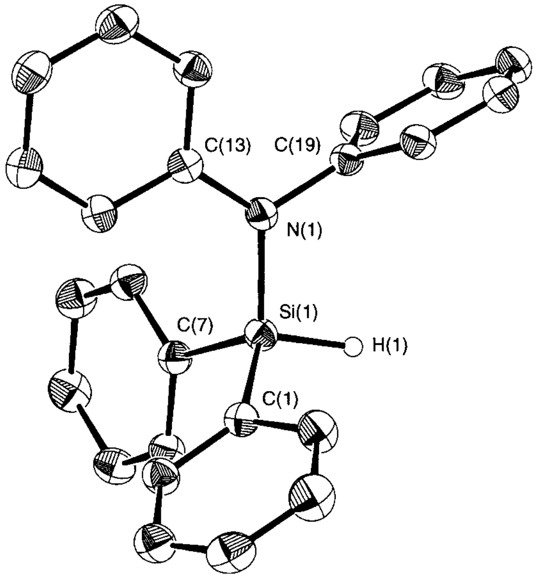

Figure 8. Crystal structure of **18** with the 30% probability level. H atoms except for H(1) on Si(1) are omitted for clarity. Selected distances (Å) and angles (deg): Si(1)−H(1) 1.38(2), Si(1)−N(1) 1.745(2), Si(1)−C(1) 1.858(2), Si(1)−C(7) 1.867(2), N(1)−C(13) 1.411(3), N(1)−C(19) 1.448(3), H(1)−Si(1)−N(1) 102.2(10), H(1)−Si(1)−C(1) 108.5(10), H(1)−Si(1)−C(7) 108.1(10), N(1)−Si(1)−C(1) 113.46(10), N(1)−Si(1)−C(7) 112.46(10), C(1)−Si(1)−C(7) 111.5(1), Si(1)−N(1)−C(13) 125.7(2), Si(1)−N(1)−C(19) 115.9(1), C(13)−N(1)−C(19) 118.4(2).

The crystal structures of **16**, **17**, and **18** were also determined as shown in Figures 6, 7, and 8, respectively. Crystal data are shown in Tables 5 and 6. The selected bond lengths and angles of **4**, **16**, **17**, and **18** ((Ph$_2$N)Ph$_2$Si−X; X = Li, F, SnMe$_3$, and H) are listed in Table 7. The Si−N bond length and the Si−C bond lengths increase in the order of X = F < H < SnMe$_3$ < Li, as the electronegativity decreases.[32] Thus, **4** has the longest Si−N bond among the four compounds. In the same order, the sum of the C−Si−N(or C) angles decreases.

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[32] Emsley, J. In *The Elements*, 2nd ed.; Clarendon Press: Oxford, 1992.

Table 5. Crystal Data for **4** and **18**

	4	**18**
chemical formula	$C_{36}H_{44}LiNO_3Si$	$C_{24}H_{21}NSi$
formula weight	573.78	351.52
crystal size (mm)	0.30 × 0.20 × 0.20	0.60 × 0.50 × 0.50
crystal system	monoclinic	monoclinic
space group	$P2_1$ (No. 4)	$P2_1/n$ (No. 14)
a (Å)	10.6091(3)	9.4557(5)
b (Å)	16.4474(7)	20.739(1)
c (Å)	10.6701(4)	10.0569(6)
α (deg)		
β (deg)	116.877(2)	103.887(3)
γ (deg)		
V (Å^3)	1660.7100	1914.5200
Z	2	4
D(calcd) (g/cm^3)	1.147	1.219
F_{000}	616.00	744.00
μ (cm^{-1})	1.05	1.29
radiation	Mo Kα	Mo Kα
diffractometer	Rigaku RAXIS-IV	Rigaku RAXIS-IV
temp (K)	203	203
$2\theta_{max}$	55.4	55.3
no. of reflns collcd	3536	4236
no. of obsd reflns $I > 3\sigma(I)$	3213	3165
no. of variables	379	320
R (%)	5.6	6.2
R_w (%)	8.0	9.1
max peak, e$^-$/Å^3	0.36	0.39
min peak, e$^-$/Å^3	−0.32	−0.50
goodness of fit	1.21	1.15

Table 6. Crystal Data for **16** and **17**

	16	**17**
chemical formula	$C_{24}H_{20}NFSi$	$C_{27}H_{29}NSiSn$
formula weight	369.51	514.31
crystal size (mm)	0.30 × 0.30 × 0.20	0.30 × 0.30 × 0.30
crystal system	monoclinic	triclinic
space group	$P2_1/n$ (No.14)	P1 (No. 2)
a (Å)	9.562(3)	10.413(2)
b (Å)	20.869(3)	12.8154(7)
c (Å)	10.136(2)	9.740(2)
α (deg)	97.081(10)	
β (deg)	104.42(2)	92.01(2)
γ (deg)	86.315(8)	
V (Å^3)	1959.0(7)	1286.7(3)
Z	4	2
D(calcd) (g/cm^3)	1.253	1.327
F_{000}	776.00	524.00
μ (cm^{-1})	11.87	84.35
radiation	Cu Kα	Cu Kα
diffractometer	Rigaku AFC7R	Rigaku AFC7R
temp (K)	293	293
scan mode	$\omega-2\theta$	$\omega-2\theta$
$2\theta_{max}$	120.1	120.1
no. of reflns collcd	3221	4060
no. of reflns unique	3025	3818
no. of obsd reflns $I > 3\sigma(I)$	2345	3380
no. of variables	325	272
R (%)	4.3	4.2
R_w (%)	5.8	7.0
max peak, e$^-$/Å^3	0.32	0.52
min peak, e$^-$/Å^3	−0.29	−0.46
goodness of fit	1.84	1.55

Table 7. Selected Structural Parameters in **4**, **16**, **17**, and **18**

	$(Ph_2N)Ph_2Si$-X, X =			
	Li(thf)$_3$ (**4**)	SnMe$_3$ (**17**)	H (**18**)	F (**16**)
electronegativity^a	0.97	1.72	2.20	4.10
Si-X (Å)	2.732(7)	2.562(1)	1.38(2)	1.594(2)
Si−N (Å)	1.824(3)	1.755(4)	1.745(2)	1.728(2)
Si−C (Å)	1.923(3)	1.887(5)	1.858(2)	1.844(3)
	1.941(3)	1.879(5)	1.867(2)	1.851(3)
N−Si−X (deg)	115.8(2)	110.7(1)	102.2(10)	102.90(9)
C−Si−X (deg)	123.2(2)	104.9(2)	108.5(10)	104.8(1)
	105.8(2)	108.2(2)	108.1(10)	107.2(1)
ΣC−Si−N (C) (deg)	309.8	332.9	337.4	340.7
^{29}Si Shift (THF) (δ)	10.6	−3.7	−16.4	−23.4
^{29}Si Shift (solid) (δ)	11.1	−3.4	−14.1	−22.4

[a] Reference 32.

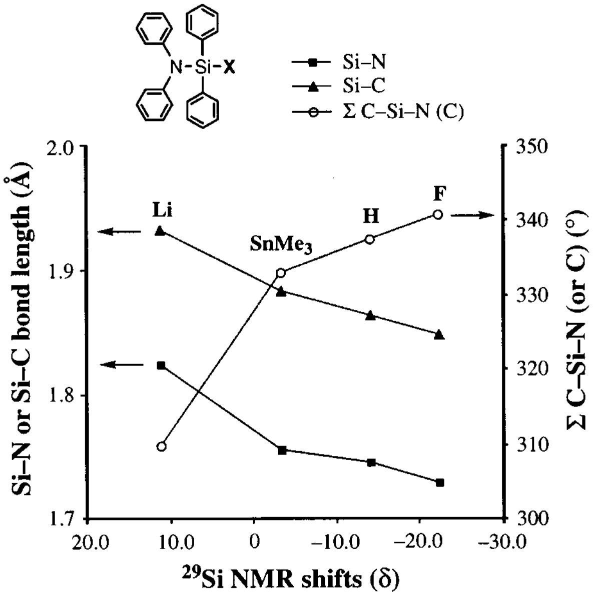

Figure 9. Plot of the Si−N or Si−C (average) bond length and the sum of the C−Si−N (or C) angles vs ^{29}Si NMR shifts in the solid state. Dependence on the X group (X = Li, $SnMe_3$, H, and F).

The electropositive substituents X, such as lithium, enhance the s-character of the silicon orbital in the Si−X bond and, in turn, enhance the p-character of the silicon orbital in the Si−N and the Si−C bonds, resulting in the elongation of the Si−N and Si−C bonds and the reduction of the sum of the C−Si−N (or C) angles. This is consistent with Bent's rule[33] and might be similar to the argument for the structures of carbenoids.[2h,i] This may also indicate that the Si−Li bond has a considerable covalent character, through which the whole structure is electronically influenced by the lithium.

To discuss the correlation between the solid-state structures and the ^{29}Si shifts, the solid-state CP/MAS ^{29}Si NMR were measured. As a result, they are almost consistent with those observed in solution, as shown in Table 7. The ^{29}Si shifts in the solid state are plotted for the Si−N (or C) bond lengths and the sum of the C−Si−N (or C), as shown in Figure 9. It is clear that the electropositive substituents cause a downfield shift in the ^{29}Si resonance, and in the same order, the Si−N (or C) bonds lengthen and the sum of the C−Si−N (or C) angles decreases.

Conclusion

We have analyzed the structures of the amino-substituted silyllithium compounds in solution and in the solid state. (1) The (aminosilyl)lithiums solvated with THF exist as a monomer both in solution and in the solid state. (2) The silicon nucleus of the (aminosilyl)lithiums is deshielded by the amino group, resulting in the downfield shifts of the ^{29}Si NMR resonance. (3) However, the amino group has essentially no significant

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(33) (a) Bent, A. H. *J. Chem. Educ.* **1960**, *37*, 616. (b) Bent, A. H. *Chem. Rev.* **1961**, *61*, 275.

influence on the solid-state structure of the silyllithium, when compared with the classical Ph_3SiLi. (4) The electropositive substituent X causes a lengthening of the Si−C and Si−N bonds, a reduction of the sum of the C−Si−N (or C) angles, and a downfield shift of the ^{29}Si resonances.

Experimental Section

General Remarks. ^1H (270 MHz), ^{13}C (67.94 MHz), ^{29}Si (53.67 MHz), ^7Li (105.01 MHz), and ^{15}N (27.38 MHz) NMR spectra were recorded on a JEOL EX-270 spectrometer and the ^1H (200 MHz) and ^{13}C (50.29 MHz) NMR spectra were recorded on a Varian VXR-200 spectrometer. The solid-state CP/MAS ^{29}Si (79.43 MHz) NMR spectra were recorded on a JEOL JNM-GX 400 spectrometer (GSX solid NMR System) at the NMR Laboratory of the Institute for Chemical Research, Kyoto University. Mass spectra were measured at 70 eV on a JEOL JMS-DX300 mass spectrometer. Melting points were measured with a Yanaco-MP-S3 apparatus. The elemental analyses were performed at the Microanalysis Division of the Institute for Chemical Research, Kyoto University. Analytical samples were purified by recrystallization.

Diphenyldichlorosilane, phenyltrichlorosilane, and phenylmethyldichlorosilane were kindly donated by the Shin-Etsu Chemical Co. Diphenylchlorosilane and phenyldichlorosilane were purchased from Shin-Etsu Chemical Co., Ltd. Trimethylchlorostannane was prepared by disproportionation between tetramethylstannane and dimethyldichlorostannane;[34] the latter was kindly donated from Nitto Kasei Co., Ltd. Diphenyldifluorosilane was prepared by the reaction of diphenyldichlorosilane with CuF_2.[35] Granular lithium was purchased from Chemetall Gesellshaft. The lithium dispersion (25 or 30 wt % in mineral oil) and lithium-6 metal (95 atom % ^6Li) were purchased from Aldrich. Diethylamine-^{15}N·HCl (99 atom % ^{15}N) was purchased from C/D/N Isotopes. Diethylamine and triethylamine were distilled from calcium hydride under a nitrogen atmosphere. Diphenylamine was purchased from Nacalai Tesque. Inc. and used without purification. *n*-BuLi in hexane was purchased from Wako Pure Chemical Industries. THF and 2-methyltetrahydrofuran (MTHF) were distilled from sodium/benzophenone ketyl or sodium/potassium alloy under a nitrogen atmosphere. THF-d_8 was distilled from $LiAlH_4$ under a nitrogen atmosphere. Toluene and toluene-d_8 were distilled from sodium under a nitrogen atmosphere. Hexane was distilled from sodium under a nitrogen atmosphere. All reactions were carried out under an inert atmosphere.

Preparation of Bis(diethylamino)phenylchlorosilane (8), (Diethylamino)diphenylchlorosilane (9), and (Diethylamino)phenylmethylchlorosilane (10). These (amino)chlorosilanes were prepared in the same manner as previously reported.[22]

Preparation of [^{15}N]-(Diethylamino)phenylchlorosilanes: A Typical Procedure for Preparation of [^{15}N]-8. To a solution of diethylamine-^{15}N·HCl (1.39 g, 12.6 mmol) and triethylamine (3.5 mL, 25 mmol) in THF (50 mL) was added a solution of phenyltrichlorosilane (0.96 mL, 6.0 mmol) in THF (1.0 mL) at room temperature. The reaction solution was refluxed for 1 day. After being cooled to room temperature, the solvent was removed. The residue was diluted with hexane (20 mL) and filtered and the filtrate was evaporated. The residue was subjected to bulb-to-bulb distillation (92−102 °C (bath temperature)/0.30 mmHg) to give [^{15}N]-**8** as a colorless liquid (1.26 g, 73% yield).

[^{15}N]-8. ^1H NMR (C_6D_6): δ 1.00 (dt, 12H, $J = 7.0$ and 2.2 Hz), 2.96 (dq, 8H, $J = 7.0$ and 3.5 Hz), 7.22−7.26 (m, 3H), 7.89−7.92 (m, 2H).

[^{15}N]-9. Yield 64%. Bp 104−114 °C/0.40 mmHg (bath temperature). ^1H NMR (C_6D_6): δ 0.96 (dt, 6H, $J = 7.0$ and 2.7 Hz), 2.90 (q, 4H, $J = 7.0$ Hz), 7.18−7.23 (m, 6H), 7.90−7.94 (m, 4H).

Preparation of [^{15}N]-(Diethylamino)phenylsilanes: A Typical Procedure for Preparation of [^{15}N]-11. To a solution of diethylamine-^{15}N·HCl (516 mg, 4.7 mmol) and triethylamine (1.3 mL, 9.3 mmol) in THF (11 mL) was added a solution of phenyldichlorosilane (0.32 mL, 2.2 mmol) in THF (1.0 mL) at room temperature. The reaction solution was refluxed for 1 day. After being cooled to room temperature, the solvent was removed. The residue was diluted with hexane (10 mL) and filtered, and the filtrate was evaporated. The residue was subjected to bulb-to-bulb distillation (85−115 °C (bath temperature)/0.30 mmHg) to give [^{15}N]-**11** as a colorless liquid (356 mg, 64% yield).

[^{15}N]-11. ^1H NMR (C_6D_6): δ 1.04 (dt, 12H, $J = 7.0$ and 2.4 Hz), 2.97 (q, 8H, $J = 7.0$ Hz), 5.23 (t, 1H, $J = 7.0$ Hz), 7.26−7.33 (m, 3H), 7.76−7.79 (m, 2H).

[^{15}N]-12. Yield 71%. Bp 125−155 °C (bath temperature)/0.70 mmHg. ^1H NMR (C_6D_6): δ 0.99 (dt, 6H, $J = 7.0$ and 2.5 Hz), 2.94 (q, 4H, $J = 7.0$ Hz), 5.65 (d, 1H, $J = 5.7$ Hz), 7.23−7.27 (m, 6H), 7.71−7.75 (m, 4H).

Preparation of [Bis(diethylamino)phenylsilyl]lithium (1), [(Diethylamino)diphenylsilyl]lithium (2), and [(Diethylamino)phenylmethylsilyl]lithium (3). These (aminosilyl)lithiums were prepared by the reaction of the corresponding (amino)chlorosilanes (**8**−**10**) with granular lithium, lithium dispersion, or lithium-6 metal in THF, THF-d_8, MTHF, or their mixed solvents using previously reported procedures.[20]

Preparation of (Diphenylamino)diphenylfluorosilane (16). To a solution of diphenylamine (8.46 g, 50.0 mmol) in THF (75 mL) was added *n*-BuLi in hexane (1.54 M, 34.1 mL, 52.5 mmol) at −78 °C over 30 min. The reaction mixture was stirred at −78 °C for 10 min and at 0 °C for 10 min. To the solution of lithium diphenylamide was added diphenyldifluorosilane (9.6 mL, 50 mmol) at −78 °C over 20 min. The reaction mixture was stirred at 0 °C for 20 min and then allowed to warm to room temperature. After 2 h, the solvent was removed. The residue was diluted with benzene (60 mL) and filtered. The filtrate was concentrated and the resulting solid was recrystallized from hexane to afford **16** as colorless crystals (15.8 g, 86% yield). Mp 105.0−106.0 °C. ^1H NMR (C_6D_6): δ 6.76−6.82 (m, 2H), 6.93−6.99 (m, 4H), 7.02−7.16 (m, 10H), 7.66−7.70 (m, 4H). ^{13}C NMR (THF-d_8): δ 124.08, 126.56, 128.57, 129.56, 131.32, 135.05, 135.78, 147.69. ^{29}Si NMR (THF-d_8): δ −23.4. MS: *m/e* 369 (M^+, 100), 201 (FPh_2Si^+, 86). Anal. Calcd for $C_{24}H_{20}NFSi$: C, 78.01, H, 5.46; N, 3.79. Found: C 78.20; H 5.51, N, 3.73.

[(Diphenylamino)diphenylsilyl]trimethylstannane (17). (Trimethylstannyl)lithium was prepared from trimethylstannyl chloride (5.09 g, 25.6 mmol) with granular lithium (67 mg, 97 mmol) in THF (24 mL).[36] The solution of (trimethylstannyl)lithium in THF was added to a solution of **16** (7.40 g, 20.1 mmol) in THF (20 mL) at −78 °C over 15 min. The reaction mixture was stirred at 0 °C for 30 min and at room temperature for 5 h. The reaction mixture was filtered and the filtrate was evaporated. The residue was dissolved in refluxing hexane (80 mL) and then filtered. The filtrate was concentrated to one-half the volume and cooled at 0 °C to yield **17** as colorless crystals (4.00 g, 39% yield). Mp 120.0−121.0 °C. ^1H NMR (C_6D_6): δ 0.050 (S, 9H, $^2J_{Sn-H} = 48$ Hz), 6.79−6.85 (m, 2H), 7.00−7.05 (m, 4H), 7.10−7.18 (m, 10H), 7.79−7.82 (m, 4H). ^{13}C NMR (THF-d_8): δ −10.14, 123.18, 125.35, 128.80, 129.81, 130.02, 135.58, 137.10, 149.56. ^{29}Si NMR (THF-d_8): δ −3.7. MS: *m/e* 515 (M^+, 4), 500 (M^+ − Me, 8), 365 (12), 350 ($(Ph_2N)Ph_2Si^+$, 100), 272 (35). Anal. Calcd for $C_{27}H_{29}NSiSn$: C, 63.05; H, 5.68; N, 2.72. Found: C, 63.10; H, 5.71; N, 2.70.

[(Diphenylamino)diphenylsilyl]lithium (4). To a solution of **17** (254 mg, 0.49 mmol) in THF (2.0 mL) was slowly added *n*-BuLi in hexane (1.60 M, 0.37 mL, 0.59 mmol) at 0 °C. The mixture was stirred at 0 °C for 1 h to give a pale-yellow solution of **4**. The solvent was removed under reduced pressure (ca. 20 mmHg) and the residual solid was dissolved in toluene (ca. 2.0 mL). The solution was cooled to −25 °C. After 1 day pale yellow crystals of **4**$(thf)_3$ (166 mg, 59% yield) were obtained, which were suitable for X-ray analysis: Mp (in a sealed tube) >91 °C dec. ^1H NMR (toluene-d_8): δ 1.29 (m, 12H, THF), 3.31 (m, 12H, THF), 6.72−6.78 (m, 2H), 7.04−7.15 (m, 6H), 7.25−7.36 (m, 8H), 7.91−7.94 (m, 4H). ^{13}C NMR (THF-d_8): δ 118.85, 124.27, 124.94, 126.79, 128.17, 134.71, 154.10, 154.64. ^{29}Si NMR (THF-d_8): δ 10.8. ^7Li NMR (THF-d_8): δ 0.073. ^7Li NMR (toluene-d_8): δ −0.15.

(Diphenylamino)diphenylsilane (18). To a solution of diphenylamine (1.71 g, 10.1 mmol) in THF (10 mL) was added *n*-BuLi in hexane (1.60 M, 6.3 mL, 10.1 mmol) at −78 °C over 3 min. The reaction mixture was stirred at −78 °C for 5 min and at 0 °C for 20

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min. To the lithium diphenylamide was added diphenylchlorosilane (2.0 mL, 10.1 mmol) at −78 °C over 5 min. The reaction mixture was stirred at −78 °C for 10 min and at 0 °C for 10 min, and then allowed to warm to room temperature. The solvent was removed and the residue was diluted with hexane (35 mL) and filtered. The filtrate was concentrated and the resulting solid was recrystallized from hexane to afford **18** as colorless crystals (2.03 g, 57% yield). Mp 137.0−138.0 °C. ^{1}H NMR (C_6D_6): δ 6.06 (s, 1H), 6.80−6.87 (m, 2H), 7.00−7.07 (m, 4H), 7.10−7.18 (m, 10H), 7.66−7.70 (m, 4H). ^{13}C NMR (THF-d_8): δ 117.95, 120.64, 128.43, 129.75, 130.85, 135.15, 135.38, 144.87. ^{29}Si NMR (THF-d_8): δ −16.4. MS: *m*/*e* 351 (M^+, 100), 273 (15), 183 (Ph_2HSi^+, 67), 167 (14). Anal. Calcd for $C_{24}H_{21}NSi$: C, 82.00; H, 6.02; N, 3.98. Found: C, 81.78; H, 6.04; N, 3.88.

NMR Experiments of (Aminosilyl)lithiums 1−3. The solution was prepared in a reaction flask and transferred to an NMR tube under an inert atmosphere. The solution in the nondeuterated solvent was directly subjected to the measurement, or combined with a small amount of the corresponding deuterated solvent for *d*-lock. The ^{13}C chemical shifts were referenced to internal cyclohexane (27.7 ppm). The ^{29}Si chemical shifts were referenced to external (at 273 K) or internal (at 173 and 163 K) tetramethylsilane (0 ppm). ^{29}Si NMR spectra were observed in an unlocked mode. Although the spectrometer was unlocked during the acquisition, the field was stable and no significant field shift was observed. The ^{7}Li chemical shifts were referenced to external 0.3 M LiCl/MeOH (0 ppm). The ^{15}N chemical shifts were referenced to external [^{15}N]-aniline (52.0 ppm).[37]

NMR Experiments of (Aminosilyl)lithium 4. The crystals were dissolved in THF-d_8 or toluene-d_8 under an inert atmosphere, and the solution was transferred to an NMR tube.

The Solid-State CP/MAS NMR. The ^{29}Si chemical shifts were referenced to external poly(dimethylsilylene) (−34.0 ppm).

X-ray Structure Determination for 4. A crystal of **4**(thf)$_3$ was mounted in a glass capillary and placed on the X-ray diffractometer in a cold nitrogen stream. All the measurements were made on a Rigaku RAXIS imaging plate area detector with graphite monochromated Mo Kα radiation. The structure was solved by direct methods[38] and expanded using Fourier techniques.[39] The non-hydrogen atoms were anisotropically refined. The hydrogen atoms were included but not refined.

X-ray Structure Determination for 18. A crystal of **18** was mounted under silicone oil and placed on the X-ray diffractometer in a cold nitrogen stream. All the measurements were made on a Rigaku RAXIS imaging plate area detector with graphite monochromated Mo Kα radiation. The structure was solved by direct methods[35] and expanded using Fourier techniques.[39] The non-hydrogen atoms were anisotropically refined. The hydrogen atoms were isotropically refined.

X-ray Structure Determination for 16. A crystal of **16** was mounted on a glass fiber with epoxy. All measurements were made on a Rigaku AFC7R diffractometer with graphite monochromated Cu Kα radiation. The structure was solved by heavy-atom Patterson methods[40] and expanded using Fourier techniques.[41] The non-hydrogen atoms were anisotropically refined. The hydrogen atoms were isotropically refined.

X-ray Structure Determination for 17. A crystal of **17** was mounted on a glass fiber with epoxy. All measurements were made on a Rigaku AFC7R diffractometer with graphite monochromated Cu Kα radiation. The structure was solved by heavy-atom Patterson methods[40] and expanded using Fourier techniques.[41] The non-hydrogen atoms were anisotropically refined. The hydrogen atoms were included but not refined.

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Supporting Information Available: A table of crystal data, structure solution and refinement, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for **4**, **16**, **17**, and **18** (PDF). An X-ray crystallographic file (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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