rotation barriers in **9** and **10** has its basis in the less electropositive character of the silyl group in comparison to Li⁺.⁴⁰ This reduces the electron density on phosphorus in comparison to that in **5** and **6**, which in turn, weakens the P → B π-interaction. The rotation barrier found in **1** is also in harmony with these results. In **1**, it could be argued that the lower barrier results from the different steric effects of the H and the SiMe₃ groups. Nonetheless, it should be borne in mind that the crowding ability of SiMe₃ is not particularly high owing to the length of the P–Si bond. It is thus more probable that the differences between rotation barriers in **1** and **10** arise from the differences in electronegativity between H and Si.⁴⁰

A feature of the data in Tables I and III is the lack of a strict correlation between the B–P bond lengths and the rotation barriers, or even the pyramidicity, at phosphorus. The main reason for this is that X-ray structural data concerns the ground state only, whereas the rotation process involves both ground and transition states. Thus, **9** and **10**, which have shorter B–P bonds than that in **8**, have lower rotation barriers probably because of different excited-state structures. A further example of a lack of correlation concerns the different B–P distances found in the two Mes₂BP-(*t*-Bu)₂ molecules of **3** where the longer B–P distance is associated with the flatter P center.

The rotation barriers in Table III may also be compared with barriers in similar boron–nitrogen systems such as the amino-boranes.⁴,⁵,⁴⁴ A major difference between phosphinoboranes and aminoboranes is the much lower inversion barrier at nitrogen in comparison to phosphorus.³⁹,⁴⁵ Thus, the formation of a B–N π-bond is much less costly in energy terms than the formation of a B–P π-bond. In addition, the sizes of the B and N atoms suggest that π-overlap would be more efficient for this pair. On this basis, it might be expected that B–N π-bonds would be much stronger than those of B–P. In general, aminoboranes, R₂BNR′₂, have rotation barriers in the range 9–24 kcal mol⁻¹.⁴⁴ This range

of values is, of course, very similar to that found in this study. It may be concluded that B–P π-bonding is at least as strong as B–N π-bonding. This finding is in agreement with the theoretical data on phosphinoboranes⁹⁻¹¹,⁴² but also with calculations for the B–P analogues of borazines.⁴⁶,⁴⁷ The good π-donor characteristics of the –PR₂ group toward boron, implied by these results, are consistent with the lower electronegativity of phosphorus in comparison to nitrogen.⁴⁰ In fact, the electronegativities of B and P are very similar.⁴⁰ Thus, the B–P pair is not as polar as B–N, which suggests that B–P orbital overlap is quite effective. Also, the relative sizes of the B and P atoms are not as disparate as might be imagined, 0.85 vs 1.11 Å.²³

In conclusion, the results in this paper demonstrate that although higher inversion barriers at phosphorus (compared to those at nitrogen) may lead to differences in structures in the ground state, B–P π-bonding is quite strong and is comparable to that observed in B–N compounds. It may be anticipated that B–As π-bonding should also be quite substantial, and preliminary results have already indicated that it is almost as high as that seen between boron and phosphorus.⁴⁸

Supplementary Material Available: Table summarizing X-ray data collection and refinement, tables of atom coordinates, bond distances and angles, anisotropic thermal parameters, and hydrogen coordinates, and a table with full IR data for **1–3**, **5**, and **10** in the range 4000–200 cm⁻¹ (35 pages); tables of observed and calculated structure factors (108 pages). Ordering information is given on any current masthead page.

(44) (a) Barfield, P.; Lappert, M. F.; Lee, J. *Proc. Chem. Soc., London* **1961**, 421; *Trans. Faraday Soc.* **1968**, *64*, 2571. (b) Watanabe, H.; Totini, T.; Tori, K.; Nakagawa, T. *Proc. Colloq. AMPERE* **1965**, *13*, 374. (c) Dewar, A.; Rona, P. *J. Am. Chem. Soc.* **1969**, *91*, 2259. (d) Imbrey, P.; Jaeschke, A.; Friebolin, H. *Org. Magn. Reson.* **1970**, *2*, 271. (e) Neilson, R. H.; Wells, R. L. *Inorg. Chem.* **1977**, *16*, 7.

(45) (a) Andose, J. D.; Lehn, J. M.; Mislow, K.; Wagner, J. *J. Am. Chem. Soc.* **1970**, *92*, 4050. (b) Stackhouse, J.; Baechler, R. D.; Mislow, K. *Tetrahedron Lett.* **1971**, 3437, 3441. (c) Brois, S. J. *Trans. N.Y. Acad. Sci.* **1969**, *31*, 931. (d) Mislow, K. *Trans. N.Y. Acad. Sci.* **1973**, *34*, 227.

(46) Fink, W. H.; Richards, J. *J. Am. Chem. Soc.* **1991**, *113*, 3393.
(47) Power, P. P. *J. Organomet. Chem.* **1990**, *400*, 49.
(48) Dias, H. V. R.; Petrie, M. A.; Shoner, S. C.; Power, P. P. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1033.

Silaamidide Salts: Synthesis, Structure, and Reactions

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Abstract: Five silaamidides have been prepared and characterized: lithium *N,N′*-bis(2,4,6-tri-*tert*-butylphenyl)phenylsilaamidide (**2**), lithium *N,N′*-bis(2,4,6-tri-*tert*-butylphenyl)chlorosilaamidide (**5**), lithium *N,N′*-bis(2,4,6-tri-*tert*-butylphenyl)-*n*-butylsilaamidide (**6**), lithium *N,N′*-bis(2,4,6-tri-*tert*-butylphenyl)-*tert*-butylsilaamidide (**7**), and potassium *N,N′*-bis(2,4,6-tri-*tert*-butylphenyl)chlorosilaamidide (**8**). Reactions of silaamidides with alcohols, amines, hydrogen bromide, *n*-butyllithium, and benzaldehyde are described. The structure of **7**·(12-crown-4)(THF) was determined by X-ray analysis: crystals are orthorhombic, space group *Pna*2₁; *a* = 16.289 (7), *b* = 17.991 (8), *c* = 17.965 (8) Å; *V* = 5265 (4) Å³; *d*꜀ₐₗ꜀ₐ = 1.084 g/mL for *Z* = 4; *R* = 5.05%. The Si–N bond distances are 1.594 and 1.626 Å, and the Si and attached N, N, and C atoms are coplanar.

Introduction

The chemistry of multiply bonded silicon has become an active area of research, since the first isolation of such compounds in 1981.¹ Stable compounds are now known with Si=Si,² Si=C,³
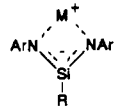
Si=N,⁴ and Si=P⁵ double bonds, and an allylic structure with a silicon atom in the central position, 1,3-diphospha-2-silaallyl

(1) West, R.; Fink, M. J.; Michl, J. *Science (Washington, D. C.)* **1981**, *214*, 1343.

(2) West, R. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1201.
(3) (a) Brook, A. G.; Abdesaken, F.; Gutekunst, B.; Gutekunst, G.; Kallury, R. K. *J. Chem. Soc., Chem. Commun.* **1981**, *191*. (b) Wiberg, N.; Wagner, G.; Müller, G. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 229.

anion **1**, was recently described.[6] We have previously reported the preparation of the first lithium silaamidide **2**,[7] a 1,3-diaza-2-silaallyl anion. In this paper, we describe the synthesis, reactions, and spectroscopic properties of several silaamidide anions, along with the crystal structure of one such compound, **7**·(12-crown-4)(THF).

Ar = 2,4,6-tri-tert-butylphenyl
R = tert-butyl

Results and Discussion

Synthesis. Our earlier communication reported the preparation of lithium phenylsilaamidide **2**·Et$_2$O, synthesized by reaction of (ArNH)$_2$SiPhCl (**3**, Ar = 2,4,6-tri-*tert*-butylphenyl) with 2 equiv of *t*-BuLi in Et$_2$O. Similarly, treatment of (ArNH)$_2$SiCl$_2$ (**4**) with 2 equiv of *t*-BuLi in Et$_2$O gave lithium chlorosilaamidide **5**·Et$_2$O (eq 1).

Treatment of dichlorosilane **4** with 3 equiv of *n*-BuLi or *t*-BuLi provided an alternative route to alkylsilaamidide salts **6**·Et$_2$O and **7**·Et$_2$O (eq 2). All the silaamidides are extremely moisture sensitive.

Silaamidides **2**·Et$_2$O and **6**·Et$_2$O lost ether when heated to 110–120 °C under vacuum (0.2 Torr) to give the unsolvated silaamidide salts **2** and **6**. Addition of ether returned **2** and **6** to their etherates. Addition of 12-crown-4 or 15-crown-5 ether to a benzene solution of **2**·Et$_2$O yielded yellow crystals of crown etherates of the phenylsilaamidide **2**·(12-crown-4)$_2$ and **2**·15-crown-5. Addition of 12-crown-4 or 15-crown-5 to **7**·Et$_2$O also led to crown etherates as colorless crystals **7**·(12-crown-4)$_2$ and **7**·15-crown-5.

The silaamidide salts are structurally related to the silanediimines Me$_3$MN=Si=NMMe$_3$ (M = C, Si), which have been isolated in hydrocarbon and argon matrices.[8] However, attempts to form a silanediimide (ArN=Si=NAr) from **5**·Et$_2$O by inducing elimination of LiCl were unsuccessful. Little change was observed after heating **5**·Et$_2$O several days in refluxing benzene. In an effort to facilitate the formation of a silanediimine, **4** was treated with a potassium base, KN(SiMe$_3$)$_2$, instead of an al-

(4) (a) Wiberg, N.; Schurz, K.; Fisher, G. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 1053. (b) Wiberg, N.; Schurz, K.; Reber, G.; Müller, G. *J. Chem. Soc., Chem. Commun.* **1986**, 591–592. (c) Klingebiel, U.; Hesse, M. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 649.

(5) Bickelhaupt, F.; Smit, C. *Organometallics* **1987**, *6*, 1156.

(6) Niecke, E.; Klein, E.; Nieger, M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 751.

(7) Underiner, G. E.; West, R. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 529.

(8) (a) Ziegler, S. S.; Welsh, K. M.; West, R.; Michl, J. *J. Am. Chem. Soc.* **1987**, *109*, 4392–4393. (b) Welsh, K. M.; Michl, J.; West, R. *J. Am. Chem. Soc.* **1988**, *110*, 6689–6696.

kyllithium reagent (eq 3). The product isolated was the potassium

chlorosilaamidide **8**, which also resisted loss of chloride ion (eq 3). Nor did changing the leaving group from Cl$^-$ to trifluoromethanesulfonate (TfO$^-$) lead to formation of silanediimine; treatment of (ArNH)$_2$Si(OTf)$_2$ (**10**), prepared by reaction of (ArNH)$_2$SiBr$_2$ (**9**) with AgOTf (eq 4), with *t*-BuLi gave no products that could be identified as a silanediimine either by direct observation by ^{29}Si NMR or by trapping reactions.

Addition Reactions. Lithium silaamidides **2**·Et$_2$O and **6**·Et$_2$O reacted with alcohols and amines to give products **11–17**, presumably by a stepwise process involving protonation at one nitrogen and addition across the double bond (eqs 5 and 6). Lithium

chlorosilaamidide **5**·Et$_2$O and potassium chlorosilaamidide **8** reacted with 2 equiv of alcohol or amine to give the double addition products **18–20** (eq 7).

Silaamidides **2**·Et$_2$O, **5**·Et$_2$O, **6**·Et$_2$O, and **8** reacted with HBr (as HBr·PPh$_3$ salt[9]) to give bromodiaminosilanes **21–23** (eq 8).

Treatment of **2**·Et$_2$O and **6**·Et$_2$O with *n*-BuLi resulted in addition across the silicon–nitrogen double bond, which then after protonation with water yielded aminosilanes **24** and **25** (eq 9).

(9) Hercouret, A.; LeCorre, M. *Synthesis* **1988**, 157.

Table I. [29]Si Shifts and IR Stretching Freqencies of Silaamidides

		$\delta^{a,b}$	ν (cm^{-1})^f
2	R = Ph, M = Li	+7.0	
2·Et$_2$O		+3.2	1303
2·(12-crown-4)$_2$		−36.3^d	
2·15-crown-5		−37.5^d	
5·Et$_2$O	R = Cl, M = Li	−35.4	1312
6	R = n-Bu, M = Li	+24.9^c	
6·Et$_2$O		+22.4	1295
7·Et$_2$O	R = t-Bu, M = Li	+20.6	1284
7·(12-crown-4)$_2$		−24.6^e	
7·15-crown-5		−23.8^d	
8	R = Cl, M = K	−54.2^d	

(structure above table: M$^+$ · ArN⟨···⟩NAr with Si–R)

^{a} Relative to TMS internal standard. ^{b}C$_6$D$_6$ unless otherwise noted. ^{c}In toluene-d_8. ^{d}In C$_6$D$_6$/THF. ^{e}In THF-d_8. ^{f}Nujol mull.

Silaamidide **6**·Et$_2$O reacted with benzaldehyde to give a [2+2] cycloaddition product; protonation with H$_2$O and recrystallization gave a stable 1-oxa-3-aza-2-silacyclobutane, **26** (eq 10). Only one diastereomer was isolated (a single ^{29}Si NMR resonance was observed). A similar cycloaddition has been reported for benzaldehyde and the silanimine (*tert*-butyl)$_2$Si=NSi(*tert*-butyl)$_3$.[10]

$$\text{(eq 10)}$$

6·Et$_2$O R = n-butyl
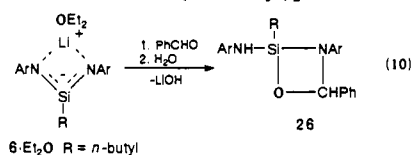
NMR Spectra. Silicon-29 chemical shift values for silaamidides are given in Table I. Lithium silaamidides **2** and **6** have ^{29}Si NMR shifts (in benzene-d_6) of +7.0 and +24.9 ppm, respectively. These values are shifted slightly upfield in the diethyl etherates **2**·Et$_2$O and **6**·Et$_2$O. The crown etherates **2**·(12-crown-4)$_2$, **2**·15-crown-5, **7**·(12-crown-4)$_2$, and **7**·15-crown-5 are sparingly soluble in benzene, and so were examined in THF-d_8 solution, where they exhibited chemical shifts from −23.8 to −37.5 ppm, indicating much greater shielding of the silicon nucleus. This is probably due to greater separation of the silaamidide anion and the lithium cation when the lithium cation is bound by the 12-crown-4 or 15-crown-5 ethers (see Figure 2). Evidently, the silicon atom is more shielded in an ion-separated compound, perhaps due to greater electron density in the allylic system. The chlorosilaamidides **5**·Et$_2$O and **8** also show a more shielded silicon atom (δ = −35.4 and −54.2 ppm).

The composition of the crown etherate salts may be altered in the THF solution. For example, one THF molecule might displace a 12-crown-4 molecule from the Li cation. (Actually, an X-ray analysis revealed that crystals of **7**·(12-crown-4)(THF) grew from a THF/hexane solution of **7**·(12-crown-4)$_2$.) All the silaamidide salts and their etherates exhibit only one set of resonances for the aryl groups in the ^{13}C and ^{1}H NMR spectra.

IR Spectra. The infrared spectra of **2**·Et$_2$O, **5**·Et$_2$O, **6**·Et$_2$O, and **7**·Et$_2$O were recorded. As shown in Table I, all four compounds exhibit an intense peak in the range of 1303–1284 cm^{-1} that we assign to the asymmetric stretching mode of the [N–Si–N]$^-$ system. As expected, these bands occur at lower energies than that reported for the Si=N stretching absorption of a silanimine, 1326 cm^{-1}.[11]

UV Spectra. In the UV spectrum of phenylchlorosilane **3** (in hexane), three bands are apparent at 224 nm (ϵ = 32 000), 242 nm (ϵ = 19 600), and 286 nm (ϵ = 1300), all arising from transitions associated with the aryl groups. Diaminodichlorosilane **4** exhibits two bands: 228 nm (ϵ = 13 500) and 284 nm (ϵ = 1100). Again, both bands are due to aryl groups. Figure 1 shows the UV spectra of **2**·Et$_2$O (in hexane), **2**·(12-crown-4)$_2$ (in THF), and
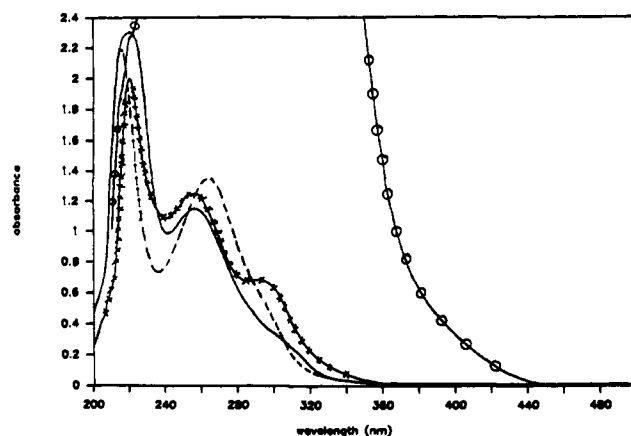

Figure 1. UV spectra of **2**·Et$_2$O, 4.75 × 10^{-5} M (X); **2**·(12-crown-4)$_2$, 5.02 × 10^{-5} M (—); **2**·(12-crown-4)$_2$, 8.91 × 10^{-4} M (○) and **6**·Et$_2$O, 4.86 × 10^{-5} M (- - -).
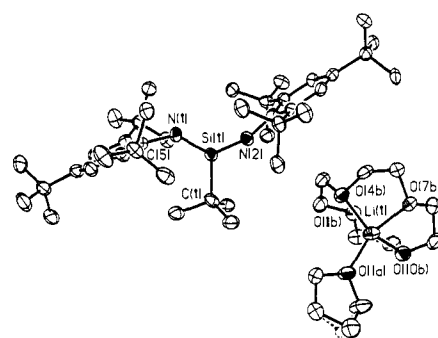

Figure 2. Thermal ellipsoid plot of **7**·(12-crown-4)(THF). Hydrogen atoms omitted for clarity.

6·Et$_2$O (in hexane). The UV spectrum of lithium phenylsilaamidide **2**·Et$_2$O shows a band at 256 nm (ϵ = 26 000) that we attribute to the π to π^* transition of the [NSiN]$^-$ system, in addition to bands at 220 nm (ϵ = 43 000) and 290 nm (ϵ = 14 000) associated with the aromatic rings. The spectrum of lithium n-butylsilaamidide **6**·Et$_2$O shows a new band at 264 nm (ϵ = 21 000) in addition to the aromatic bands at 216 nm (ϵ = 45 000) and 296 nm (ϵ = 9500). The n to π^* transitions of **2**·Et$_2$O and **6**·Et$_2$O were not observed, and may be buried under the 290- and 296-nm bands.

Of all of the silaamidides, only the crown etherates **2**·(12-crown-4)$_2$ and **2**·15-crown-5 are colored. The UV/vis spectrum of **2**·(12-crown-4)$_2$ is similar to that of **2**·Et$_2$O, with a π to π^* band at 256 nm (ϵ = 25 000) and bands at 220 and 310 nm with ϵ = 40 000 and 14 000, respectively. At higher concentrations, however, it is apparent that the 310-nm band tails into the visible range to about 450 nm, perhaps due to an overlapping n to π^* transition. Previously reported values for π to π^* and n to π^* transitions of silanimines include 296 and 444 nm for Mes$_2$Si=NMes[12] and 272 and 474 nm for Mes$_2$Si=NSiMe$_3$,[13] both observed at 77 K in hydrocarbon matrices.

Crystal Structure of Lithium N,N'-**Bis(2,4,6-tri-*tert*-butylphenyl)-*tert*-butylsilaamidide (THF)(12-Crown-4) Etherate.** The thermal ellipsoid plot of **7**·(12-crown-4)(THF) is shown in Figure 2. The structure of **7**·(12-crown-4)(THF) consists of well-separated, noninteracting lithium cations [Li(12-crown-4)(THF)]$^+$ and N,N'-bis(2,4,6-tri-*tert*-butylphenyl)-*tert*-butylsilaamidide anions. In the anion, the silicon is tricoordinated to a carbon atom of the *tert*-butyl group and to two nitrogen atoms. The silicon-nitrogen bond distances in **7**, 1.594 and 1.626 Å, are intermediate between that reported for a silicon–nitrogen double bond, 1.568 Å,[4b] and the average Si–N single bond distance, 1.748 Å.[14]

(10) Wiberg, N.; Schurz, K.; Müller, G. J.; Riede, J. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 935.

(11) Wiberg, N.; Schurz, K. *Chem. Ber.* **1988**, *121*, 581.

(12) Ziegler, S. S.; West, R.; Michl, J. *Chem. Lett.* **1986**, 1025. (b) Ziegler, S. S.; Johnson, L.; West, R. *J. Organomet. Chem.* **1988**, *341*, 187.

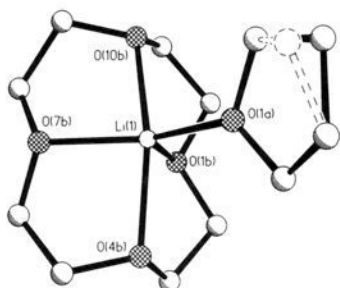(13) Sekiguchi, A.; Ando, W.; Honda, K. *Chem. Lett.* **1986**, 1029.

Figure 3. Molecular structure of the [Li(12-crown-4)(THF)]$^+$ cation of 7·(12-crown-4)(THF). Hydrogen atoms omitted for clarity.

Table II. Selected Bond Distances (Å) and Angles (deg) for 7·(12-crown-4)(THF)

Bond Distances			
Si(1)–C(1)	1.909 (6)	Si(1)–N(1)	1.626 (4)
Si(1)–N(2)	1.594 (4)	N(1)–C(5)	1.384 (7)
N(2)–C(23)	1.377 (6)	Li(1)–O(1b)	2.005 (10)
Li(1)–O(4b)	2.080 (10)	Li(1)–O(7b)	1.985 (11)
Li(1)–O(10b)	2.101 (11)	Li(1)–O(1a)	1.926 (10)

Bond Angles			
C(1)–Si(1)–N(1)	119.1 (2)	C(1)–Si(1)–N(2)	114.4 (2)
N(1)–Si(1)–N(2)	126.5 (2)	Si(1)–N(2)–C(23)	161.9 (4)
Si(1)–N(1)–C(5)	136.5 (4)	O(1b)–Li(1)–O(7b)	102.4 (4)
O(1b)–Li(1)–O(4b)	80.0 (4)	O(1b)–Li(1)–O(10b)	80.3 (4)
O(4b)–Li(1)–O(7b)	84.7 (4)	O(7b)–Li(1)–O(10b)	84.1 (4)
O(4b)–Li(1)–O(10b)	154.7 (5)		

However, the Si–N distances in **7** are significantly closer to the double bond than the single bond distance, consistent with considerable Si–N π bonding in the silaamidide anion.[15]

Another interesting structural feature of the anion is that the angle Si(1)–N(2)–C(23), 161.9°, is much larger than the angle Si(1)–N(1)–C(5), 136.5°. Corresponding to the larger angle at N(2) is the slightly smaller Si(1)–N(2) bond distance. It is possible that the larger angle at N(2) leads to greater p character for the lone pairs at N(2) and hence stronger π bonding between N$_2$ and Si.

The Si–C(1) bond distance in the anion is 1.909 Å, within the normal length for a silicon–carbon σ bond (1.87–1.91 Å).[16] The geometry around the silicon atom is planar (sum of angles 360°); similar planarity around the silicon atom is also found in other multiply bonded silicon compounds, e.g., silanimines[4b] and silaethenes.[17] The short Si–N bonds and the geometry around the silicon atom are consistent with the allylic anion structure for the silaamidide anion. The aromatic rings are almost perpendicular to the allylic N–Si–N π system; the dihedral angles between the planes of the aromatic rings and the C, Si, N, N plane are both 87°.

The structure of the cation, shown in Figure 3, is also of interest. The Li is pentacoordinated to the four oxygen atoms of the 12-crown-4 ether and to the oxygen of the THF, giving it a nearly square-pyramidal geometry. The distances between the lithium and the oxygens of the 12-crown-4 ether span the range 1.985–2.101 Å; the average distance is 2.04 Å, similar to the Li–O bond separation in another pentacoordinated lithium cation, dibenzo-14-crown-4-Li-SCN.[18] The distance between the Li cation

(14) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans 2* 1987, S1–S19.

(15) However, silicon–nitrogen single bond lengths are quite variable and can be decreased by negative charge on nitrogen, which may lead to increased p–σ^* back-bonding from nitrogen to silicon. This effect may cause some of the shortening in 7·(12-crown-4)(THF). The anion (Ph$_3$SiNSiPh$_3$)$^-$, isoelectronic with siloxanes, has an especially short Si–N distance of 1.63 Å. See: Bartlett, R. A.; Power, P. P. *J. Am. Chem. Soc.* 1987, *109*, 6509–6510.

(16) Bazant, V.; Chvalovsky, V.; Rathousky, J. *Organosilicon Compounds*; Academic Press: New York, 1965; p 179.

(17) Brook, A. G.; Nyburg, S. C.; Abdesaken, F.; Gutenkunst, B.; Gutenkunst, G.; Kallury, R. K. M. R.; Poon, Y. C.; Chang, Y. M.; Wong-Ng, W. *J. Am. Chem. Soc.* 1982, *104*, 5667.

(18) Shoham, G.; Lipscomb, W. N.; Olsher, U. *J. Chem. Soc., Chem. Commun.* 1983, 208–209.

and the oxygen of the THF molecule is 1.926 Å, significantly shorter than the average bond distance between the Li cation and the oxygens of the 12-crown-4 ether. As shown in Figure 3, one of the carbon atoms of the THF molecule is in a disordered position.

Other bond lengths and angles are given in Table II. Crystal data and experimental details for the structure determination of 7·(12-crown-4)(THF) are provided in Table III.

Experimental Section

^{1}H NMR were recorded on a Bruker WP-200 (200 MHz) instrument. ^{13}C and ^{29}Si NMR were determined on a Bruker AM-360 (90 and 72 MHz, respectively) unless otherwise noted. High-resolution mass spectra were measured on a MS80 Kratos instrument. FAB mass spectra were recorded on a MS50-TC Kratos instrument. Infrared spectra were performed on a Mattson Polaris FTIR spectrometer. UV–vis spectra were determined by using a Hewlett-Packard 8452A Diode Array spectrophotometer, in 1-cm quartz cells with teflon stoppers. All reactions were carried out under an atmosphere of nitrogen and in oven- or flame-dried glassware. Solvents were dried by distillation from Na or Na/K prior to use, and chlorosilanes and SiBr$_4$ were distilled from K$_2$CO$_3$. Elemental analyses were performed by Desert Analytics, Tuscon, AZ. The 2,4,6-tri-*tert*-butylnitrobenzene was synthesized from 1,3,5-tri-*tert*-butylbenzene (Aldrich Chemical Co.) via the synthesis described by Burgers et al.[19]

2,4,6-Tri-*tert*-butylaniline. To 250 mL of mercury in a 2-L three-neck flask equipped with a mechanical stirrer was slowly added 27.6 g (1.2 g-atom) of sodium in pieces under a flow of N$_2$, to make about a 0.9% by weight Na/Hg amalgam (*caution*, exothermic). After stirring, with cooling, for 8 h at room temperature, 1.3 L of MeOH was added to the flask, along with 2,4,6-tri-*tert*-butylnitrobenzene (68 g, 0.23 mol). After 15 min, an exothermic reaction was observed, after which the reaction was refluxed for 12 h. Methanol (~500 mL) was removed by distillation and 400 mL of H$_2$O added. The Hg° was collected by using a separatory funnel and may be reused for an amalgam. The aqueous mixture was extracted three times with Et$_2$O, and these washings were dried over MgSO$_4$. The solvent was removed by vacuum and the yellow residue recrystallized from MeOH to give the aniline: 52.2 g (87%); mp 146 °C (lit.[19] mp 147–148 °C); ^{1}H NMR (C$_6$D$_6$) δ 7.40 (s, 2 H, Ar H), 3.62 (s, 2 H, NH$_2$), 1.40 (s, 18 H, *o*-C(CH$_3$)$_3$), 1.39 (s, 9 H, *p*-C(CH$_3$)$_3$); IR (Nujol) 3518, 3443 (w), 1617 (w), 1363 (m), 1238 (m), 879 (w) cm^{-1}.

Bis[(2,4,6-tri-*tert*-butylphenyl)amino]phenylchlorosilane (3). Tri-*tert*-butylaniline (6.0 g, 23 mmol) in 120 mL of hexane was treated with

(19) Burgers, J.; Hoefnagel, M. A.; Verkade, P. E.; Visser, H.; Wepster, B. M. *Recl. Trav. Chim. Pays-Bas* 1985, *77*, 491–530.

n-BuLi (9.2 mL of a 2.5 M solution in hexane). The resulting white suspension was stirred for 1 h followed by 40 min of reflux, and then the reaction was cooled to room temperature and PhSiCl₃ (2.4 g, 12 mmol) was added by syringe. After refluxing for 48 h, the solution was filtered and the salts were washed several times with fresh hexane. All solvent was removed from the filtrate to give a sticky solid. Recrystallization from hexane yielded 5.30 g (67%) of colorless product: mp 156–7 °C; ¹H NMR (C₆D₆) δ 7.37 (s, 4 H, Ar H), 7.51–7.41, 6.98–6.92, (m, 5 H, phenyl H), 3.84 (s, 2 H, NH), 1.47 (s, 36 H, *o*-C(CH₃)₃), 1.30 (s, 18 H, *p*-C(CH₃)₃); ²⁹Si NMR (C₆D₆) δ −28.8; ¹³C NMR (C₆D₆) δ 147.9, 145.7, 137.1, 134.1 (*o/p*-aryl-C, SiC, CN), 136.4, 130.0, 127.3 (phenyl CH), 36.9 (*o*-C(CH₃)₃), 34.6 (*p*-C(CH₃)₃), 33.1 (*o*-C(CH₃)₃), 31.7 (*p*-C-(CH₃)₃); IR (Nujol) 3408 (w), 1597 (w), 1428 (s), 1364 (m), 1327 (br m), 1220 (m), 1112 (m), 917 (w), 887, 876 (m) cm⁻¹; MS, *m/e* 660 (M⁺, 25), 661 (M⁺ + 1, 13), 662 (M⁺ + 2, 12); HRMS (EI) for C₄₂H₆₅Cl-N₂Si, calcd 660.4605, found 660.4617. Anal. Calcd for C₄₂H₆₅ClN₂Si: C, 76.26; H, 9.90; N, 4.24; Cl, 5.36. Found C, 76.68; H, 9.97; N, 4.22; Cl, 5.21.

Bis[(2,4,6-tri-*tert*-butylphenyl)amino]dichlorosilane (4). 2,4,6-Tri-*tert*-butylaniline (20 g, 76.5 mmol) was dissolved in hexane (300 mL), and *n*-BuLi (30.6 mL of a 2.5 M solution in hexane, 76.5 mmol) was slowly added by syringe. The resulting white slurry was refluxed for 2 h. Silicon tetrachloride (6.50 g, 38.2 mmol) was slowly added by syringe, and the reaction was refluxed for 48 h. The salts were filtered off under nitrogen, and the solution was transferred to a separatory funnel and washed with H₂O and then with a saturated NaCl solution. The solution was dried with MgSO₄ and the solvent removed via rotary evaporation, leaving behind a brown oily solution. On cooling, crystals formed from the solution. The crystals were filtered and washed with cold hexane, yielding 4.7 g (20%) of the dichlorosilane: mp 189–191 °C; ¹H NMR (C₆D₆) δ 7.57 (s, 4 H, Ar H), 3.62 (s, 2 H, NH), 1.61 (s, 36 H, *o*-C-(CH₃)₃), 1.31 (s, 18 H, *p*-C(CH₃)₃); ¹³C NMR (C₆D₆) δ 148.9, 147.2 (*o/p*-C), 135.6 (CN), 123.5 (*m*-C), 37.0 (*o*-C(CH₃)₃), 34.7 (*p*-C(CH₃)₃), 33.1 (*o*-C(CH₃)₃), 31.6 (*p*-C(CH₃)₃); ²⁹Si NMR (C₆D₆) δ −38.6; MS *m/e* 620 (M⁺ + 2, 28), 618 (M⁺, 36); IR (Nujol) 3408 (w), 1598 (w), 1364 (m), 1314 (br m), 1220 (m), 1115 (m), 991 (br m), 877 (m) cm⁻¹; HRMS (EI) for C₃₆H₆₀Cl₂N₂Si, calcd 620.3871, found 620.3873. Anal. Calcd for C₃₆H₆₀Cl₂N₂Si: C, 69.74; H, 9.77; N, 4.52; Cl, 11.44. Found: C, 69.58; H, 9.89; N, 4.31; Cl, 11.32.

Lithium *N,N′*-Bis(2,4,6-tri-*tert*-butylphenyl)phenylsilaamidide Diethyl Etherate (2·Et₂O). Phenylchlorosilane 3 (2.00 g, 3.16 mmol) was dissolved in 10 mL of ether/50 of mL hexane and cooled to −78 °C, and *t*-BuLi was added (3.72 mL of a 1.7 M solution in hexane, 6.32 mmol). After 3–4 h, the solution was warmed to room temperature and stirred for 24 h. Salts were filtered under nitrogen, and the solvent was removed to give a colorless solid. Recrystallization from hexane gave 1.24 g (56%) of the lithium phenylsilaamidide etherate 2·Et₂O: ¹H NMR (C₆D₆) δ 7.67 (s, 4 H, Ar H), 7.32–6.65 (m, 5 H, phenyl H), 2.97 (q, *J* = 7 Hz, 4 H, OCH₂CH₃), 1.81 (s, 36 H, *o*-C(CH₃)₃), 1.45 (s, 18 H, *p*-C(CH₃)₃), 0.60 (t, *J* = 7 Hz, 6 H, OCH₂CH₃); ¹³C (C₆D₆) δ 149.9, 139.8, 138.6, 137.3, 131.6, 131.0, 128.5, 122.2 (aryl, phenyl-C), 64.9 (OCH₂CH₃), 37.1 (*o*-C(CH₃)₃, 34.7 (*p*-C(CH₃)₃), 32.6 (*o*-C(CH₃)₃), 32.2 (*p*-C-(CH₃)₃), 14.0 (OCH₂CH₃); ²⁹Si NMR (C₆D₆) δ +3.2; ⁷Li NMR (0.03 M LiCl/MeOH–C₆D₆ external reference (ext ref)) +2.10; IR (Nujol) 1458 (sh, s), 1420 (s), 1350 (m), 1303 (s), 1290 (sh, m), 1242 (w), 1110 (w), 1062 (w), 877 (w) cm⁻¹; MS, *m/e* 704 (M⁺, not obsd), 624 (M⁺ − Et₂O − Li + H, 29) 546 (M⁺ − Et₂O − Li − Ph, 100). HRMS (EI) for C₄₂H₆₄N₂Si (M⁺ − Et₂O − Li + H), calcd 624.4839, found 624.4857. Anal. Calcd for C₄₆H₇₃LiN₂OSi: C, 78.34; H, 10.45; N, 3.97. Found: C, 78.03; H, 10.71; N, 3.83.

Lithium *N,N′*-Bis(2,4,6-tri-*tert*-butylphenyl)chlorosilaamidide Diethyl Etherate (5·Et₂O). Dichlorosilane 4 (2.50 g, 4.04 mmol) in 40 mL of a 1:1 mixture of hexane and ether in a 100-mL round-bottom Schlenk flask at −78 °C was treated with *t*-BuLi (4.7 mL of a 1.7 M solution in hexane, 8.0 mmol). After 3–4 h, the reaction was allowed to warm to room temperature and stirred for 24 h. Salts were filtered off in a drybox, and the solution was concentrated and cooled to give the colorless silaamidide ethyl etherate: 1.31 g (49%); ¹H NMR (C₆D₆) δ 7.59 (s, 4 H, Ar H), 2.84 (q, *J* = 7.3, 4 H, OCH₂CH₃), 1.80 (s, 36 H, *o*-C(CH₃)₃), 1.38 (s, 18 H, *p*-C(CH₃)₃), 0.51 (t, *J* = 7.3, 6 H, OCH₂CH₃); ¹³C NMR (C₆D₆) δ 146.0, 141.5, 140.2 (*o/p*-C, CN), 122.2 (*m*-C), 62.5 (OCH₂CH₃), 36.9 (*o*-C(CH₃)₃), 34.7 (*p*-C(CH₃)₃), 32.5 (*o*-C(CH₃)₃), 32.0 (*p*-C(CH₃)₃), 14.0 (OCH₂CH₃); ²⁹Si NMR (C₆D₆) δ −35.4; ⁷Li NMR (0.03 M LiCl/MeOH–C₆D₆ ext ref) δ −1.67; IR (Nujol) 1458 (sh, s), 1420 (s), 1354 (m), 1312 (s), 1308 (sh, m), 1242 (m), 1123 (w), 1096 (w), 1066 (w), 879 (w), 789 (w) cm⁻¹; MS, *m/e* 663 (M⁺, not obsd), 620 (M⁺ − LiCl, 2), 546 (M⁺ − LiCl − Et₂O, 40); HRMS (EI) for C₄₀H₆₈N₂SiO (M⁺ − LiCl), calcd 620.5101, found 620.5129.

Lithium *N,N′*-Bis(2,4,6-tri-*tert*-butylphenyl)-*n*-butylsilaamidide Diethyl Etherate (6·Et₂O). Dichlorosilane 4 (1.00 g, 1.61 mmol) was dis-

solved in 30 mL of ether and the solution cooled to −78 °C, and then treated with *n*-BuLi (3.2 mL of a 1.5 M solution in hexane, 4.8 mmol). After 3 h, the reaction was allowed to warm to room temperature, whereupon salts precipitated immediately. After stirring for an additional 24 h, the salts were filtered off under N₂ in a drybox, and ether was removed to give a colorless solid. Recrystallization from hexane gave 800 mg (73%) of colorless 6·Et₂O: mp 188–190 °C dec; ¹H NMR (C₆D₆) δ 7.57 (s, 2 H, Ar H), 2.93 (q, *J* = 7.3 Hz, 4 H, OCH₂CH₃), 1.80 (s, 36 H, *o*-C(CH₃)₃), 1.41 (s, 18 H, *p*-C(CH₃)₃), 0.85–0.51 (m, 9 H, butyl), 0.59 (t, *J* = 7.3, 6 H, OCH₂CH₃); ¹³C NMR (C₆D₆) δ 149.3, 138.9, 138.3 (CN, *o/p*-C), 121.9 (*m*-C), 65.1 (OCH₂CH₃), 36.9 (*o*-C-(CH₃)₃), 34.6 (*p*-C(CH₃)₃), 32.5 (*o*-C(CH₃)₃), 32.2 (*p*-C(CH₃)₃), 25.9, 24.8, 19.2, 14.3, 13.4 (butyl, OCH₂CH₃); ²⁹Si NMR (C₆D₆) δ +22.4; ⁷Li NMR (0.03 M LiCl/MeOH–C₆D₆ ext ref) δ +2.03; IR (Nujol) 1598 (w), 1460 (sh, s), 1418 (s), 1348 (m), 1295 (br s), 1290 (sh, m), 1241 (m), 1121 (m), 1052 (m), 878 (w), 797 (w), 780 (w) cm⁻¹; MS, *m/e* 684 (M⁺, no obsd), 546 (M⁺ − Li − Et₂O − C₄H₉ + 1, 18). Anal. Calcd for C₄₄H₇₇LiN₂OSi: C, 77.13; H, 11.33; N, 4.09; Li, 1.01. Found: C, 76.99; H, 11.41; N, 4.13; Li, 0.87.

Lithium *N,N′*-Bis(2,4,6-tri-*tert*-butylphenyl)-*tert*-butylsilaamidide Diethyl Etherate (7·Et₂O). To the dichlorosilane 4 (0.50 g, 0.81 mmol) in 20 mL of ether/10 mL of hexane at −78 °C was added *t*-BuLi (2.4 mmol, 1.4 mL of a 1.7 M solution in pentane) via syringe. After 2.5 h, the reaction was allowed to warm slowly to room temperature, whereupon salts began to form, and stirred for 20 h. The salts were filtered in a drybox, and upon concentration of the filtrate, the colorless product precipitated. Recrystallization from hexane gave 262 mg (47%) of 7·Et₂O: ¹H NMR (C₆D₆) δ 7.49 (s, 4 H, Ar H), 3.05 (q, *J* = 7.6 Hz, 4 H, OCH₂CH₃), 1.78 (s, 36 H, *o*-*tert*-butyl), 1.42 (s, 18 H, *p*-*tert*-butyl), 0.94 (s, 9 H, SiC(CH₃)₃), 0.64 (t, *J* = 7.6 Hz, 6 H, OCH₂CH₃); ¹³C NMR (C₆D₆) δ 150.2, 139.0, 137.9 (CN, *o/p*-C), 121.8 (*m*-C), 64.3 (OCH₂CH₃), 37.2 (*o*-C(CH₃)₃), 34.5 (*p*-C(CH₃)₃), 33.0 (*o*-C(CH₃)₃), 32.4 (SiC(CH₃)₃), 32.1 (*p*-C(CH₃)₃), 29.5 (SiC(CH₃)₃), 13.9 (OCH₂C-H₃); IR (Nujol) 1462 (s), 1417 (m), 1284 (br s), 1120 (w), 1058 (w), 878 (w), 792 (w) cm⁻¹; ²⁹Si NMR (C₆D₆) δ +20.6. Anal. Calcd for C₄₄H₇₇LiN₂OSi: C, 77.13; H, 11.33; N, 4.09. Found: C, 77.25; H, 11.49; N, 4.08.

Lithium *N,N′*-Bis(2,4,6-tri-*tert*-butylphenyl)phenylsilaamidide (2). Phenylsilaamidide diethyl etherate 2·Et₂O (1.00 g, 5.06 mmol) was placed in a 100-mL round-bottom Schlenk flask and heated in an oil bath at 120 °C under vacuum for 10 h. Recrystallization from benzene gave 630 mg (66%) of 2: mp 249 °C dec; ¹H NMR (C₆D₆) δ 7.65 (s, 4 H, Ar H), 6.79–6.53 (m, 5 H, phenyl H), 1.70 (s, 36 H, *o*-*tert*-butyl), 1.46 (s, 18 H, *p*-*tert*-butyl); ¹³C NMR (C₆D₆) δ 149.6, 140.0, 138.9, 137.1, 131.7, 130.6, 128.6, 122.2 (aryl, phenyl-C), 37.0 (*o*-C(CH₃)₃), 34.7 (*p*-C(CH₃)₃), 32.9 (*o*-C(CH₃)₃), 32.2 (*p*-C(CH₃)₃); ²⁹Si NMR (C₆D₆) δ +7.0; ⁷Li (0.03 M LiCl/MeOH–C₆D₆ ext ref) δ −0.10; MS, *m/e* 630 (M⁺, not obsd), 624 (M⁺ − Li + 1, 45). HRMS (EI) for C₄₂H₆₄N₂Si (M⁺ − Li + H), calcd 624.4839, found 624.4846.

Lithium *N,N′*-Bis(2,4,6-tri-*tert*-butylphenyl)-*n*-butylsilaamidide (6). Ether-free butylsilaamidide 6 was prepared from 6·Et₂O (900 mg, 1.31 mmol) by the same method as 2. Recrystallization from benzene gave the silaamidide as colorless crystals: 608 mg (76%); mp 235–240 °C dec; ¹H NMR (C₆D₆) δ 7.53 (s, 2 H, Ar H), 1.68 (s, 36 H, *o*-C(CH₃)₃), 1.41 (s, 18 H, *p*-C(CH₃)₃); ¹³C NMR (C₆D₆) δ 149.0, 139.9, 138.5 (*o/p*-C, CN), 121.8 (*m*-C), 36.8 (*o*-C(CH₃)₃), 34.6 (*p*-C(CH₃)₃), 32.7 (*o*-C-(CH₃)₃), 32.1 (*p*-C(CH₃)₃), 25.7, 24.6, 18.9, 13.3 (butyl); ²⁹Si NMR (toluene-*d₈*) δ +24.9; ⁷Li NMR (0.03 M LiCl/MeOH–C₆D₆ ext ref) δ −0.07; MS, *m/e* 604 (M⁺ − Li + H, 27), 546 (M⁺ − Li − butyl + H, 39). HRMS (EI) for C₄₀H₆₈N₂Si (M⁺ − Li + H), calcd 604.5151, found 604.5157. Anal. Calcd for C₄₀H₆₇LiN₂Si: C, 78.63; H, 11.05; N, 4.59; Li, 1.14. Found: C, 78.46; H, 11.41; N, 4.51; Li, 0.81.

Lithium *N,N′*-Bis(2,4,6-tri-*tert*-butylphenyl)phenylsilaamidide Bis-(12-crown-4) Etherate [2·(12-Crown-4)₂] and 15-Crown-5 Etherate (2·15-Crown-5) and Lithium *N,N′*-Bis(2,4,6-tri-*tert*-butylphenyl)-*tert*-butylsilaamidide Bis(12-crown-4) Etherate [7·(12-Crown-4)₂] and 15-Crown-5 Etherate (7·15-Crown-5). To a solution of silaamidide in benzene was added dropwise 2.5 equiv of 12-crown-4 or 1.5 equiv of 15-crown-5 ether. For 2·12-crown-4 and 2·15-crown-5, the solution immediately became bright yellow, and upon concentration of the solution, fine needles of product precipitated. Recrystallization from benzene gave crystals of the etherate.

Data for 2·(12-crown-4)₂: 52%; mp 206–8 °C; ¹H NMR (THF-*d₈*) δ 7.43–6.87 (m, 5 H, phenyl), 7.06 (s, 4 H, Ar H), 3.61 (s, 32 H, crown ether), 1.55 (s, 36 H, *o*-*tert*-butyl), 1.29 (s, 18 H, *p*-*tert*-butyl); ¹³C NMR (THF-*d₈*) δ 151.7, 139.2, 137.1, 136.7, 131.7, 128.8, 127.1 (CN, *o/p*-C, phenyl), 121.1 (*m*-C), 70.2 (OCH₂), 37.2 (*o*-C(CH₃)₃), 33.3 (*p*-C-(CH₃)₃), 32.7 (*o*-C(CH₃)₃), 32.2 (*p*-C(CH₃)₃); ²⁹Si NMR (C₆D₆/THF) δ −36.3. HRMS (EI) for C₄₂H₆₄N₂Si (M⁺ − 2(12-crown-4) − Li + H), calcd 624.4839, found 624.4953.

Data for 2·15-crown-5: 63%; ^{1}H NMR (THF-d_8) δ 7.32–6.72 (m, 5 H, phenyl), 7.06 (s, 4 H, Ar H), 3.50 (s, 20 H, crown ether), 1.54 (s, 36 H, *o-tert*-butyl), 1.29 (s, 18 H, *p-tert*-butyl); ^{29}Si NMR (C$_6$D$_6$/THF) δ −37.5.

Data for 7·(12-crown-4)$_2$: 61%; ^{1}H NMR (THF-d_8) δ 6.93 (s, 4 H, Ar H), 3.59 (s, 32 H, crown ether), 1.56 (s, 36 H, *o-tert*-butyl), 1.23 (s, 18 H, *p-tert*-butyl), 1.23 (s, 9 H, SiC(CH$_3$)$_3$); ^{29}Si NMR (THF-d_8) δ −24.6.

Data for 7·15-crown-5: 72%; ^{1}H NMR (THF-d_8) δ 6.97 (s, 4 H, Ar H), 3.59 (s, 20 H, crown ether), 1.61 (s, 36 H, *o-tert*-butyl), 1.27 (s, 18 H, *p-tert*-butyl), 1.01 (s, 9 H, SiC(CH$_3$)$_3$); ^{29}Si NMR (C$_6$D$_6$/THF) δ −23.8.

Potassium *N,N′*-Bis(2,4,6-tri-*tert*-butylphenyl)chlorosilaamidide (8). To a solution of **4** (2.00 g, 3.23 mmol) in 30 mL of benzene was added KN(SiMe$_3$)$_2$ (12.8 mL of a 0.5 M solution in toluene, 6.4 mmol). After 24 h, the resulting white slurry was filtered under N$_2$ in a drybox, giving 1.97 g of a white powder, a mixture of the silaamidide and KCl: ^{1}H NMR (THF-d_8/C$_6$D$_6$) δ 7.39 (s, 4 H, Ar H), 1.56 (s, 36 H, *o-tert*-butyl), 1.27 (s, 18 H, *p-tert*-butyl); ^{29}Si NMR (C$_6$D$_6$/THF) δ −54.2.

Bis[(2,4,6-tri-*tert*-butylphenyl)amino]dibromosilane (9). 2,4,6-Tri-*tert*-butylaniline (5.0 g, 19.2 mmol) was dissolved in hexane (150 mL), and *n*-BuLi (7.7 mL of a 2.5 M solution in hexane, 19.2 mmol) was slowly added by syringe. The resulting white slurry was refluxed for 2 h. Silicon tetrabromide (3.35 g, 9.6 mmol) was slowly added by syringe, and the reaction was refluxed for 22 h, after which the salts were filtered off under nitrogen and the solvent was removed to give a white solid. Recrystallization from hexane gave 3.47 g (51%) of colorless dibromide: mp 168–180 °C; ^{1}H NMR (C$_6$D$_6$) δ 7.52 (s, 4 H, Ar H), 4.01 (s, 2 H, NH), 1.62 (s, 36 H, *o*-C(CH$_3$)$_3$), 1.31 (s, 18 H, *p*-C(CH$_3$)$_3$); ^{13}C NMR (C$_6$D$_6$) δ 149.0, 147.3, 135.4 (*o/p*-C,CN), 123.5 (*m*-C), 37.1 (*o*-C-(CH$_3$)$_3$), 34.8 (*p*-C(CH$_3$)$_3$), 33.3 (*o*-C(CH$_3$)$_3$), 31.6 (*p*-C(CH$_3$)$_3$); ^{29}Si NMR (C$_6$D$_6$) δ −48.6; MS, *m/e* 706 (M$^+$, 22), 707 (M$^+$ + 1, 13), 708 (M$^+$ + 2, 49), 709 (M$^+$ + 3, 22), 710 (M$^+$ + 4, 30); HRMS (EI) for C$_{36}$H$_{60}$Br$_2$N$_2$Si (M$^+$), calcd 706.2893, found 706.2855. Anal. Calcd for C$_{36}$H$_{60}$Br$_2$N$_2$Si: C, 61.00; H, 8.53; N, 3.95; Br, 22.55. Found: C, 60.61; H, 8.75; N, 4.24; Br, 22.78.

Bis[(2,4,6-tri-*tert*-butylphenyl)amino]bis(trifluoromethanesulfonato)-silane (10). Dibromosilane **9** (4.2 g, 5.9 mmol) was dissolved in 150 mL of benzene in a darkened 250-mL round-bottomed three-neck flask with silver triflate (8.7 g, excess), and the reaction was refluxed for 4 days. Solvent was then removed in vacuum and replaced with 300 mL of hexane, and all salts were filtered off and rinsed several times with fresh hexane under N$_2$ to give a purple solution from which 1.2 g (26%) of the colorless ditriflate **10** crystallized upon cooling: mp 221–228 °C; ^{1}H NMR δ 7.38 (s, 4 H, Ar H), 4.48 (s, 2 H, NH), 1.38 (br s, 36 H, *o*-C(CH$_3$)$_3$), 1.27 (s, 18 H, *p*-C(CH$_3$)$_3$); ^{13}C NMR (C$_6$D$_6$) 148.5, 147.8, 130.7 (*o/p*-C,CN), 124.4 (*m*-C), 118.7 (q, *J* = 319.2 Hz, CF$_3$), 37.1 (*o*-C(CH$_3$)$_3$), 34.7 (*p*-C(CH$_3$)$_3$), 33.3 (*o*-C(CH$_3$)$_3$), 31.4 (*p*-C(CH$_3$)$_3$); ^{29}Si NMR (C$_6$D$_6$) δ −75.8; MS, *m/e* 846 (M$^+$, 40); HRMS (EI) for C$_{38}$H$_{60}$N$_2$O$_6$F$_6$S$_2$Si (M$^+$), calcd 846.3566, found 846.3568. Anal. Calcd for C$_{38}$H$_{60}$N$_2$O$_6$F$_6$S$_2$Si: C, 53.87; H, 7.13; N, 3.31; F, 13.46; S, 7.57. Found: C, 53.35; H, 7.23; N, 3.22; F, 13.31; S, 7.58.

Reaction of Alcohols, H$_2$O, and Amines with 2·Et$_2$O, 5·Et$_2$O, 6·Et$_2$O and 8. To an ether solution of lithium silaamidide, or benzene slurry of **8**, was added excess amine or alcohol. Solution was complete in minutes. Precipitates were filtered off, and ether was removed by vacuum. All addition products were purified by recrystallization from hexane.

Data for bis[(2,4,6-tri-*tert*-butylphenyl)amino]phenylhydroxysilane (11): 64%; mp 190 °C dec; ^{1}H NMR (C$_6$D$_6$) δ 7.41 (s, 4 H, Ar H), 3.78 (s, 2 H, NH), 2.41 (s, 1 H, OH), 1.51 (s, 36 H, *o*-C(CH$_3$)$_3$), 1.32 (s, 18 H, *p*-C(CH$_3$)$_3$); MS, *m/e* 642 (M$^+$, 15); HRMS (EI) for C$_{42}$H$_{66}$N$_2$OSi (M$^+$), calcd 642.4944, found 642.4940. Anal. Calcd for C$_{42}$H$_{66}$N$_2$OSi: C, 78.44; H, 10.34; N, 4.36. Found: C, 79.02; H, 10.67; N, 4.01.

Data for bis[(2,4,6-tri-*tert*-butylphenyl)amino]phenyl-*tert*-butoxysilane (12): 68%; mp 226–7 °C; ^{1}H NMR (C$_6$D$_6$) δ 7.48–6.98 (m, 5 H, phenyl), 7.35 (s, 4 H, Ar H), 3.74 (s, 2 H, NH), 1.57 (s, 36 H, *o*-C(CH$_3$)$_3$), 1.34 (s, 18 H, *p*-C(CH$_3$)$_3$), 1.12 (s, 9 H, OC(CH$_3$)$_3$); ^{29}Si NMR (C$_6$D$_6$) δ −54.6; MS, *m/e* 699 (M$^+$, 3), 438 (M$^+$ − NHAr, 19); HRMS (EI) for C$_{46}$H$_{74}$N$_2$OSi (M$^+$), calcd 698.5570, found 698.5572.

Data for bis[(2,4,6-*tert*-butylphenyl)amino]-*n*-butylmethoxysilane (13): 70%; mp 140–143 °C; ^{1}H NMR (C$_6$D$_6$) δ 7.46 (s, 4 H, Ar H), 3.42 (s, 2 H, NH), 2.82 (s, 3 H, OCH$_3$), 1.64 (s, 36 H, *o-tert*-butyl), 1.35 (s, 18 H, *p-tert*-butyl), 1.16–0.72 (m, 9 H, C$_4$H$_9$); ^{13}C NMR (C$_6$D$_6$) δ 147.3, 144.7, 139.1 (CN, *o/p*-C), 122.9 (*m*-C), 50.0 (OCH$_3$), 36.9 (*o*-C-(CH$_3$)$_3$), 34.6 (*p*-C(CH$_3$)$_3$), 33.0 (*o*-C(CH$_3$)$_3$), 31.8 (*p*-C(CH$_3$)$_3$), 27.0, 25.5, 14.9, 13.6 (butyl); MS, *m/e* 636 (M$^+$, 7), 320 (M$^+$ − NHAr − OMe + 1, 100); HRMS (EI) for C$_{41}$H$_{72}$N$_2$OSi (M$^+$), calcd 636.5414, found 636.5395. Anal. Calcd for C$_{41}$H$_{72}$N$_2$OSi: C, 77.29; H, 11.39; N, 4.40. Found: C, 77.27; H, 11.34; N, 4.40.

Data for bis[(2,4,6-tri-*tert*-butylphenyl)amino]-*n*-butylisopropoxysilane (14): 65%; mp 235–237 °C; ^{1}H NMR (C$_6$D$_6$) δ 7.44 (s, 4 H, Ar H), 3.49 (sept, *J* = 4 Hz, 1 H, CHMe$_2$), 3.39 (s, 2 H, NH), 1.65 (s, 36 H, *o-tert*-butyl), 1.36 (s, 18 H, *p-tert*-butyl), 0.86 (d, *J* = 6.4 Hz, 6 H, CH(CH$_3$)$_3$), 1.08–0.68 (m, 9 H, C$_4$H$_9$); ^{13}C NMR δ 147.3, 144.5, 139.4 (CN, *o/p*-C), 122.8 (*m*-C), 66.25 (OCH(CH$_3$)$_2$), 36.9 (*o*-C(CH$_3$)$_3$), 34.6 (*p*-C(CH$_3$)$_3$), 33.1 (*o*-C(CH$_3$)$_3$), 31.8 (*p*-C(CH$_3$)$_3$), 33.0 (OCH(CH$_3$)$_2$), 27.2, 25.4, 16.5, 13.3 (C-butyl); MS, *m/e* 664 (M$^+$, 18), 348 (M$^+$ − NHAr − C$_4$H$_9$ + 1, 100); HRMS (EI) for C$_{43}$H$_{76}$N$_2$OSi (M$^+$), calcd 664.5727, found 664.5745.

Data for bis[(2,4,6-tri-*tert*-butylphenyl)amino]-*n*-butyl-*tert*-butoxy-silane (15): 60%; mp 242–5 °C; ^{1}H NMR (C$_6$D$_6$) δ 7.37 (s, 4 H, Ar H), 3.30 (s, 2 H, NH), 1.56 (s, 36 H, *o-tert*-butyl), 1.31 (s, 18 H, *p-tert*-butyl), 1.00 (s, 9 H, *O-tert*-Bu), 0.80–0.74 (m, 9 H, C$_4$H$_9$); ^{13}C NMR (C$_6$D$_6$) δ 147.1, 144.1 (*o/p*-C), 139.4 (CN), 122.9 (*m*-C), 73.9 (OC(CH$_3$)$_3$), 37.0 (*o*-C(CH$_3$)$_3$), 34.5 (*p*-C(CH$_3$)$_3$), 33.3 (*o*-C(CH$_3$)$_3$), 31.9 (OC(CH$_3$)$_3$), 31.8 (*p*-C(CH$_3$)$_3$), 27.2, 25.2, 19.4, 13.6 (butyl-C); MS, *m/e* 679 (M$^+$, 3), 362 (M$^+$ − NHAr − C$_4$H$_9$ + 1, 100); HRMS (EI) for C$_{44}$H$_{78}$N$_2$OSi (M$^+$), calcd 678.5883, found 678.5910. Anal. Calcd for C$_{44}$H$_{78}$N$_2$OSi: C, 77.81; H, 11.57; N, 4.13. Found: C, 77.82; H, 11.79; N, 4.36.

Data for bis[(2,4,6-tri-*tert*-butylphenyl)amino]-*n*-butyl(*n*-butyl-amino)silane (16): 68%; mp 207–8 °C; ^{1}H NMR (CDCl$_3$) δ 7.27 (s, 4 H, Ar H), 3.17 (s, 2 H, NH), 2.10 (t, *J* = 4 Hz, NHCH$_2$), 1.51 (s, 36 H, *o-tert*-butyl), 1.30 (s, 18 H, *p-tert*-butyl), 0.91–0.55 (mult, 9 H, C$_4$H$_9$); ^{13}C NMR (C$_6$D$_6$) δ 146.4, 144.0 (*o/p*-C), 140.5 (CN), 122.8 (*m*-C), 41.5 (NHCH$_2$), 36.9 (*o*-C(CH$_3$)$_3$), 34.6 (*p*-C(CH$_3$)$_3$), 33.0 (*o*-C(CH$_3$)$_3$), 31.9 (*p*-C(CH$_3$)$_3$), 35.8, 27.3, 26.4, 20.2, 15.6, 14.2, 13.8 (butyl-C).

Data for bis[(2,4,6-tri-*tert*-butylphenyl)amino]-*n*-butyl(phenyl-amino)silane (17): 72%; ^{1}H NMR (C$_6$D$_6$) δ 7.38 (s, 4 H, Ar H), 7.10–6.29 (m, 5 H, phenyl), 3.77 (s, 1 H, PhNH), 3.55 (s, 2 H, ArNH), 1.58 (s, 36 H, *o-tert*-butyl), 1.32 (s, 18 H, *p-tert*-butyl), 1.27–0.80 (m, 9 H, C$_4$H$_9$); ^{13}C NMR (C$_6$D$_6$) δ 146.4, 145.6, 144.3, 138.9, 128.9, 123.1, 118.7, 117.8 (Ar, phenyl-C), 37.0 (*o*-C(CH$_3$)$_3$), 34.5 (*p*-C(CH$_3$)$_3$), 33.2 (*o*-C(CH$_3$)$_3$), 31.9 (*p*-C(CH$_3$)$_3$), 26.9, 25.8, 16.3, 13.5 (butyl-C); ^{29}Si NMR (C$_6$D$_6$) δ −29.4; MS, *m/e* 697 (M$^+$, 4), 437 (M$^+$ − ArNH, 38), 381 (M$^+$ − ArNH − C$_4$H$_9$ + 1, 100); HRMS (EI) for C$_{46}$H$_{75}$N$_3$Si (M$^+$), calcd 697.5730, found 697.5764.

Data for bis[(2,4,6-tri-*tert*-butylphenyl)amino]di-*tert*-butoxysilane (18): 60%; ^{1}H NMR δ (C$_6$D$_6$) 7.40 (br AB q, 4 H, Ar H), 3.21 (s, 2 H, NH), 1.70 (br s, 36 H, *o-tert*-butyl), 1.43 (br s, 18 H, *p-tert*-butyl), 1.37 (br s, 18 H, *O-tert*-Bu); ^{13}C NMR δ 147.7, 147.2, 143.9, 138.6 (CN, *o/p*-C), 124.0, 122.1 (*m*-C), 74.2 (OC(CH$_3$)$_3$), 37.7, 36.6, 34.5, 34.1, 33.1, 32.2, 31.8 (OC(CH$_3$)$_3$, *o/p-tert*-butyl); MS, *m/e* 695 (M$^+$, 4), 639 (M$^+$ − C$_4$H$_9$, 12), 378 (M$^+$ − C$_4$H$_9$ − NHAr, 100); HRMS (EI) for C$_{44}$H$_{78}$N$_2$O$_2$Si (M$^+$), calcd 694.5832, found 694.5834. Anal. Calcd for C$_{44}$H$_{78}$N$_2$O$_2$Si: C, 76.02; H, 11.31; N, 4.03. Found: C, 76.30; H, 11.14; N, 3.82.

Data for bis[(2,4,6-tri-*tert*-butylphenyl)amino]dianilinosilane (19): 83%; mp 256–7 °C; ^{1}H NMR (C$_6$D$_6$) δ 7.46 (s, 4 H, Ar H), 6.91–6.53 (m, 10 H, phenyl), 3.91 (s, 2 H, NH), 3.80 (s, 2 H, NH), 1.52 (s, 36 H, *o-tert*-butyl), 1.35 (s, 18 H, *p-tert*-butyl); ^{13}C NMR (C$_6$D$_6$) δ 147.6, 145.3, 145.0, 137.9 (SiC, *o/p*-C, NC), 128.8, 123.5, 119.3, 118.7 (PhCH, *m*-CH), 37.4 (*o*-C(CH$_3$)$_3$), 34.6 (*p*-C(CH$_3$)$_3$), 33.4 (*o*-C(CH$_3$)$_3$), 31.7 (*p*-C(CH$_3$)$_3$); ^{29}Si (C$_6$D$_6$) δ −59.5; MS, *m/e* 732 (M$^+$, 9); HRMS (EI) for C$_{48}$H$_{72}$N$_4$Si, calcd 732.5526, found 732.5539. Anal. Calcd for C$_{48}$H$_{72}$N$_4$Si: C, 78.63; H, 9.90; N, 7.65. Found: C, 78.97; H, 9.78; N, 7.66.

Data for bis[(2,4,6-tri-*tert*-butylphenyl)amino]bis(*n*-butylamino)silane (20): 49%; mp 197–199 °C; ^{1}H NMR (C$_6$D$_6$) δ 7.48 (s, 4 H, Ar H), 3.14 (s, 2 H, NHAr), 2.67 (q, *J* = 6.9, 4 H, NHC*H*$_2$), 1.65 (s, 36 H, *o-tert*-butyl), 1.38 (s, 18 H, *p-tert*-butyl), 1.18–0.96 (m, 14 H, (CH$_2$)$_2$CH$_3$), 0.50 (t, *J* = 6.9, 2 H, NHC*H*$_2$); ^{13}C NMR (C$_6$D$_6$, 125 MHz) δ 147.3, 144.3, 140.0, (*o/p*-C, NC), 123.1 (*m*-CH), 42.0 (−NH-CH$_2$−), 37.0 (*o*-C(CH$_3$)$_3$), 36.3 (−NHCH$_2$CH$_2$−), 34.6 (*p*-C(CH$_3$)$_3$), 33.2 (*o*-C(CH$_3$)$_3$), 31.9 (*p*-C(CH$_3$)$_3$), 20.0 (−CH$_2$CH$_3$), 14.2 (−CH$_2$C-H$_3$); MS, *m/e* 693 (M$^+$, 0.5), 432 (M$^+$ − NHAr, 85); HRMS (EI) for C$_{44}$H$_{80}$N$_4$Si (M$^+$), calcd 692.6152, found 692.6209. Anal. Calcd for C$_{44}$H$_{80}$N$_4$Si: C, 76.23; H, 11.63; N, 8.08. Found: C, 76.27; H, 11.90; N, 8.13.

Reaction of 2·Et$_2$O, 5·Et$_2$O, 6·Et$_2$O, and 8 with HBr·PPh$_3$. To an ether solution of silaamidide, or a benzene slurry of **8**, was added 2.2 equiv of HBr·PPh$_3$, and the mixture was then stirred for 20 h. After filtration, PPh$_3$ was removed by Kugelrohr distillation under vacuum (0.2 Torr) at 110 °C for 6 h. Recrystallization from hexane gave the colorless di-aminobromosilanes.

Data for bis[(2,4,6-tri-*tert*-butylphenyl)amino]phenylbromosilane (21): 71%; mp 160–160 °C; ^{1}H NMR (C$_6$D$_6$) δ 7.57–7.53, 6.98–6.95 (m, 5 H, phenyl H), 7.38 (s, 4 H, Ar H), 3.96 (s, 2 H, NH), 1.50 (s, 36 H,

Silaamidide Salts

J. Am. Chem. Soc., Vol. 113, No. 22, 1991 8443

o-C(CH$_3$)$_3$), 1.30 (s, 18 H, p-C(CH$_3$)$_3$); MS, m/e 704 (M$^+$, 24), 706 (M$^+$ + 2, 28); HRMS (EI) for C$_{42}$H$_{65}$BrN$_2$Si (M$^+$), calcd 704.4101, found 704.4035.

Data for bis[(2,4,6-tri-*tert*-butylphenyl)amino]bromochlorosilane (22): 47% from 5·Et$_2$O, 38% from 8; ^{1}H NMR (C$_6$D$_6$) δ 7.52 (s, 4 H, Ar H), 3.91 (s, 2 H, NH), 1.61 (s, 36 H, o-C(CH$_3$)$_3$), 1.31 (s, 18 H, p-C(CH$_3$)$_3$); MS, m/e 662 (M$^+$, 16), 664 (M$^+$ + 2, 22), 666 (M$^+$ + 4, 6); HRMS (EI) for C$_{36}$H$_{60}$BrClN$_2$Si (M$^+$), calcd 662.3398, found 662.3400.

Data for bis[(2,4,6-tri-*tert*-butylphenyl)amino]-*n*-butylbromosilane (23): 26%; ^{1}H NMR (C$_6$D$_6$) δ 7.45 (s, 4 H, Ar H), 3.68 (s, 2 H, NH), 1.59 (s, 36 H, o-C(CH$_3$)$_3$), 1.33 (s, 18 H, p-C(CH$_3$)$_3$), 0.65–1.20 (m, 9 H, butyl); MS, m/e 684 (M$^+$, 4), 686 (M$^+$ + 2, 5), 491 (M$^+$ – 2C$_4$H$_9$, 41); HRMS (EI) for C$_{40}$H$_{69}$BrN$_2$Si (M$^+$), calcd 684.4414, found 684.4455.

Addition of *n*-Butyllithium to 2·Et$_2$O and 6·Et$_2$O. To an ether solution of 2·Et$_2$O or 6·Et$_2$O was added 1 equiv of n-BuLi (1.5 M solution in hexane). After 16 h of stirring, a small amount of water was added dropwise to quench the reaction and the solvent was removed by vacuum and replaced with hexane. Filtration of salts and concentration and cooling gave the colorless diaminosilanes 24 and 25.

Data for bis[(2,4,6-tri-*tert*-butylphenyl)amino]-*n*-butylphenylsilane (24): 54%; mp 220–228 °C; ^{1}H NMR (C$_6$D$_6$, 125 MHz) δ 7.44–7.39, 7.02–6.98 (m, 5 H, phenyl), 7.30 (s, 4 H, Ar H), 3.68 (s, 2 H, NH), 1.55 (s, 36 H, o-*tert*-butyl), 1.34 (s, 18 H, p-*tert*-butyl), 1.26–0.80 (m, 9 H, C$_4$H$_9$); ^{13}C NMR (C$_6$D$_6$) δ 146.2, 144.0, 144.3, 138.5 (o/p-Ar C, Ph CSi, Ar CN), 136.7, 128.7, 127.0, 122.6 (Ph CH, m-Ar CH), 36.8 (o-C-(CH$_3$)$_3$), 34.5 (p-C(CH$_3$)$_3$), 33.1 (o-C(CH$_3$)$_3$), 31.9 (p-C(CH$_3$)$_3$), 27.5, 25.5, 16.3, 13.7 (butyl-C); MS, m/e 683 (M$^+$, 0.4), 624 (M$^+$ – C$_4$H$_{10}$, 6), 381 (M$^+$ – ArNH – C$_4$H$_9$ + 1, 100); HRMS (EI) for C$_{46}$H$_{74}$N$_2$Si (M$^+$), calcd 682.5621, found 682.5625. Anal. Calcd for C$_{46}$H$_{74}$N$_2$Si: C, 80.87; H, 10.92; N, 4.10. Found: C, 80.85; N, 11.14; H, 4.00.

Data for bis[(2,4,6-tri-*tert*-butylphenyl)amino]di-*n*-butylsilane (25): 88%; mp 238 °C; ^{1}H NMR (C$_6$D$_6$) δ 7.42 (s, 4 H, Ar H), 3.38 (s, 2 H, NH), 1.61 (s, 36 H, o-*tert*-butyl), 1.38 (s, 18 H, p-*tert*-butyl), 1.18–0.74 (m, 9 H, 2C$_4$H$_9$); ^{13}C NMR (C$_6$D$_6$) 146.5, 144.0, 140.5 (CN, o/p-C), 122.8 (m-C), 36.9 (o-C(CH$_3$)$_3$), 34.5 (p-C(CH$_3$)$_3$), 33.1 (o-C(CH$_3$)$_3$), 31.8 (p-C(CH$_3$)$_3$), 27.2, 25.9, 16.0, 13.7 (butyl); MS, m/e 662 (M$^+$, 0.4), 346 (M$^+$ – NHAr – butyl + 1, 40); HRMS (EI) for C$_{44}$H$_{78}$N$_2$Si (M$^+$), calcd 662.5934, found 662.5903. Anal. Calcd for C$_{44}$H$_{78}$N$_2$Si: C, 79.79; H, 11.79; N, 4.20. Found: C, 80.13; H, 12.16; N, 4.24.

Addition of Benzaldehyde to 6·Et$_2$O. To a solution of 6·Et$_2$O (0.51 g, 0.74 mmol) in 20 mL of ether was added benzaldehyde (0.075 mL, 0.078 g, 0.74 mmol) by syringe. After 1 h of stirring, H$_2$O (0.011 g, 0.74 mmol) was added. The solution was filtered and the solvent removed by vacuum to give a yellowish solid. Recrystallization in hexane gave 230 mg (44%) of colorless air-stable crystals of the cycloadduct 2-butyl-4-phenyl-2-[(2,4,6-tri-*tert*-butylphenyl)amino]-3-(2,4,6-tri-*tert*-butyl-phenyl)-1-oxa-3-aza-2-silacyclobutane (26): mp 166–172 °C; ^{1}H NMR (CDCl$_3$) δ 7.49–6.49 (mult, 9 H, Ar H, phenyl), 6.09 (s, 1 H, CHPh),

4.11 (s, 1 H, NH), 1.69 (s, 9 H, C(CH$_3$)$_3$), 1.61 (s, 9 H, C(CH$_3$)$_3$), 1.39 (s, 9 H, C(CH$_3$)$_3$), 1.35 (s, 9 H, C(CH$_3$)$_3$), 1.30 (s, 9 H, C(CH$_3$)$_3$), 0.93 (s, 9 H, C(CH$_3$)$_3$), 1.30–0.61 (m, 9 H, butyl); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 148.95, 148.87, 147.34, 147.09, 145.79, 145.51, 141.02, 138.40, 136.55 (aryl o/p-C, aryl CN, phenyl CCN), 127.15, 127.12, 125.75, 125.14, 122.86, 122.79, 122.05 (aryl m-C, phenyl CH), 92.55 (OCHN), 37.97, 37.08, 36.84, 34.54, 34.51 (C(CH$_3$)$_3$), 34.20, 33.50, 33.08, 32.78, 31.51, 31.48 (C(CH$_3$)$_3$), 26.26, 25.04, 16.53 (butyl CH$_2$), 13.19 (butyl CH$_3$); ^{29}Si NMR (C$_6$D$_6$) δ –18.07; MS (FAB), m/e 709 (M$^+$ – 1, 4), 654 (M$^+$ – *tert*-butyl + 1, 38), 604 (M$^+$ – PhCHO, 100). Anal. Calcd for C$_{47}$H$_{74}$N$_2$OSi: C, 79.37; H, 10.49; N, 3.94. Found: C, 79.26; H, 10.88; N, 3.88.

X-ray Structure Determination. Single crystals of 7·(12-crown-4)-(THF) for X-ray diffraction experiments were grown by layering of n-hexane over a THF solution of 7·(12-crown-4)$_2$. A single crystal was selected, coated with paratone-N, cut to a suitable size, and mounted on a thin glass fiber for X-ray analysis.

The X-ray crystallographic experiments were performed on a Siemens P3/F diffractometer equipped with a graphite-monochromated Cu Kα X-radiation source (λ = 1.541 78 Å) and a low-temperature device.

Unit cell parameters were determined by least-squares refinements based on 25 centered reflections. Three standard reflections were measured after every 100 reflections during the data collection. No significant decrease in the intensity of the standard reflections was observed during the data collection.

The structures were solved by direct methods using the SHELXTL PLUS program on a MicroVAX II, and refined by the full-matrix least-squares refinement method using the reflections with F_o > 4.0$\sigma(F)$. The non-hydrogen atoms (except disordered C4a, C4a') were refined with anisotropic thermal parameters, and the hydrogen atoms were placed in idealized positions and refined by using a riding model and isotropic thermal parameters. The refinement converged by using statistical weights to unweighted and weighted agreement factors of R = 5.05% and R_w = 5.73%.

Supplementary Material Available: Tables of crystallographic data, atomic coordinates and anisotropic thermal parameters, and bond lengths and angles for 7·(12-crown-4)(THF) and molecular structure of 7·(12-crown-4)(THF) (13 pages); listing of observed and calculated structure factor amplitudes for 7·(12-crown-4)-(THF) (14 pages). Ordering information is given on any current masthead page.