# *Articles*

## Head-to-Head *versus* Head-to-Tail Dimerizations of Transient 2-[(Dimethylamino)phenyl]-1,1-bis(trimethylsilyl)silenes

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2-[2-(Dimethylamino)phenyl]-1,1-bis(trimethylsilyl)silene (**2**), generated by deprotonation and trimethylsilanolate elimination from [2-(dimethylamino)phenyl][tris(trimethylsilyl)silyl]-methanol (**1**), dimerizes in a head-to-tail mode with formation of an *E*/*Z* mixture of 2,4-bis[2-(dimethylamino)phenyl]-1,1,3,3-tetrakis(trimethylsilyl)-1,3-disilacyclobutane (**3**), while 2-methyl-2-[4-(dimethylamino)phenyl]-1,1-bis(trimethylsilyl)silene (**8**), prepared by treatment of [4-(dimethylamino)benzoyl]tris(trimethylsilyl)silane (**6**) with methyllithium, affords the head-to-head cyclodimer 3,4-dimethyl-3,4-bis[4-(dimethylamino)phenyl]-1,1,2,2-tetrakis(trimethylsilyl)-1,2-disilacyclobutane (**9**) in addition to the linear dimer 1-[1-(4-(dimethylamino)-phenyl)ethenyl]-2-[1-(4-(dimethylamino)phenyl)ethyl]-1,1,2,2-tetrakis(trimethylsilyl)disilane (**10**). 2-[2-((Dimethylamino)methyl)phenyl]-1,1-bis(trimethylsilyl)silene (**12**), prepared similarly by trimethylsilanolate elimination from [2-((dimethylamino)methyl)phenyl]tris-(trimethylsilyl)silylmethanol (**11**), gives under the same conditions [2-((dimethylamino)-methyl)benzyl](trimethylsiloxy)bis(trimethylsilyl)silane (**14**).

### Introduction

In the absence of scavenger reagents, sterically congested, transient silenes undergo rapid dimerization, in which, depending on the substitution pattern, head-to-tail as well as head-to-head reactions were observed.[1] 1,1-Bis(trimethylsilyl)silenes dimerize in a head-to-head mode, and as the result of a formal [2 + 2] cycloaddition, usually 1,2-disilacyclobutanes are obtained.[2−5] In the case of 2-aryl-1,1-bis(trimethylsilyl)silenes also products of a formal [2 + 4] reaction, i.e., tetrahydro-2,3-disilanaphthalenes, could be identified.[5] For silenes with "allylic" hydrogen atoms linear dimers also were isolated.[3,4a,5a,6]

In the course of our investigations on the synthesis of silenes by base-induced trimethylsilanolate elimination from (1-hydroxyalkyl)tris(trimethylsilyl)silanes according to a modified Peterson mechanism,[5] we were interested in forming structures which could be expected to result in an enhanced thermodynamic stability of the Si═C systems.[7] In this context we studied the generation and behavior of 2-[(dialkylamino)phenyl]silenes. $\pi$-Interactions, as shown in Scheme 1 for a 4-(dimethylamino)phenyl derivative, may contribute to stabilization of the unsaturated system and should also decrease the inherent polarity of the Si═C bond,[8] thus reducing the reactivity of the silene.

**Scheme 1**


### Results and Discussion

The deprotonation of [2-(dimethylamino)phenyl][tris-(trimethylsilyl)silyl]methanol (**1**) with methyllithium in ether gave in greater than 60% yield a mixture of the *E*/*Z* isomers of 2,4-bis[2-(dimethylamino)phenyl]-1,1,3,3-tetrakis(trimethylsilyl)-1,3-disilacyclobutane (**3**) (Scheme 2). The alcohol **1** was prepared according to a known procedure[5a] by the reaction of [tris(trimethylsilyl)silyl]-magnesium bromide with 2-(dimethylamino)benzalde-

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(2) Brook, A. G.; Baines, K. M. *Adv. Organomet. Chem.* **1986**, *25*, 26.

(3) Bravo-Zhivotovskii, D.; Brande, V.; Stanger, A.; Kapon, M.; Apeloig, Y. *Organometallics* **1992**, *11*, 2326.

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(7) Hoffmann, D.; Reinke, H.; Oehme, H. *J. Organomet. Chem.* **1996**, *526*, 185.

(8) Apeloig, Y.; Karni, M. *J. Am. Chem. Soc.* **1984**, *106*, 6676.

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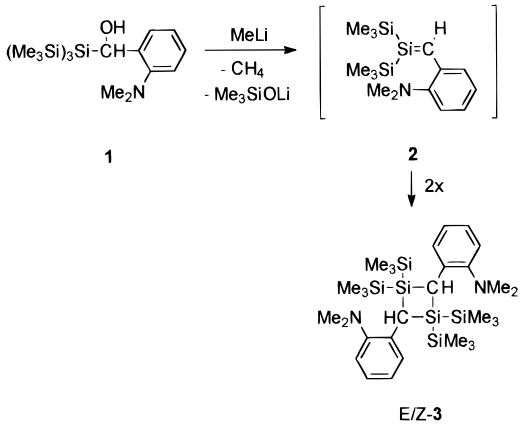
**Scheme 2**




hyde. *E*-**3** and *Z*-**3** were separated by column chromatography and were characterized by spectroscopy as well as by X-ray structural analyses. The results obtained confirm the proposed configuration of the aromatic substituents (Figures 1 and 2). The 1,3-disilacyclobutane ring in *E*-**3** is planar. *Z*-**3** is slightly folded; the torsional angle Si1−C1−Si4−C10 is 15.0°. Apart from slightly elongated ring Si−C distances, which are considered as being due to steric congestion, the bond parameters are in the expected region.

*E*-**3** and *Z*-**3** are the formal [2 + 2] head-to-tail dimers of 2-[2-(dimethylamino)phenyl]-1,1-bis(trimethylsilyl)-silene (**2**). This result is very surprising, since 1,1-bis-(trimethylsilyl)silenes, as mentioned in the introductory remarks, were found generally to undergo head-to-head dimerizations.

To confirm our assumption that the unusual behavior of **2** is due to the *o*-dimethylamino group of the aromatic substituent, we prepared 2-[4-(dimethylamino)phenyl]-1,1-bis(trimethylsilyl)silene (**5**) under the same conditions by deprotonation of [4-(dimethylamino)phenyl]-[tris(trimethylsilyl)silyl]methanol (**4**). But unfortunately, we obtained a very complex mixture of products containing large quantities of polymeric materials, and we did not succeed in isolating a definite compound. This is in agreement with our general experience that after generation of 2-aryl-2*H*-1,1-bis(trimethylsilyl)silenes a uniform product formation is observed only when at least one ortho position of the aromatic group is substituted. This, obviously, causes a certain selectivity with respect to cyclodimerization.

This problem could easily be avoided by a slight variation of the structure of **4** by synthesizing 2-methyl-2-[4-(dimethylamino)phenyl]-1,1-bis(trimethylsilyl)-silene (**8**). The influence of the 2-methyl group on the dimerization behavior of **8** can be neglected, since 1,1-bis(trimethylsilyl)silenes, independent of the substitution pattern at the silene carbon atom, were found to undergo head-to-head reactions.[2−5] The silene **8** was generated by the reaction of methyllithium with [4-(dimethylamino)benzoyl]tris(trimethylsilyl)silane (**6**) (Scheme 3). The lithium alkoxide **7**, formed by addition of MeLi at the carbonyl group of the acylsilane **6**, is unstable, and lithium trimethylsilanolate is eliminated *in situ* to give **8**. The generation of silenes by addition of an organolithium reagent to an acylpolysilane and subsequent silanolate elimination following the Peterson type mechanism is a known process and was used successfully by the groups of Ishikawa[4] and Apeloig.[3]

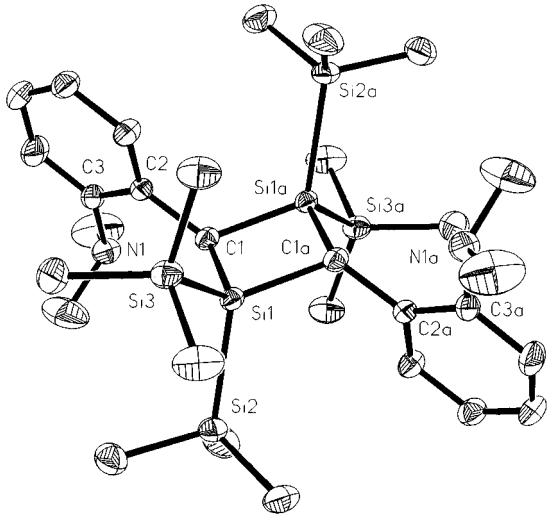



**Figure 1.** Molecular structure of *E*-**3** in the crystal (H atoms omitted). Selected bond lengths (Å) and angles (deg): Si1−C1, 1.925(3); Si1−Si2, 2.372(1); Si1−Si3, 2.365(1); Si1−Si1a, 2.682(2); C1−Si1−C1 91.8(1); Si1−C1−Si1, 88.2(1).

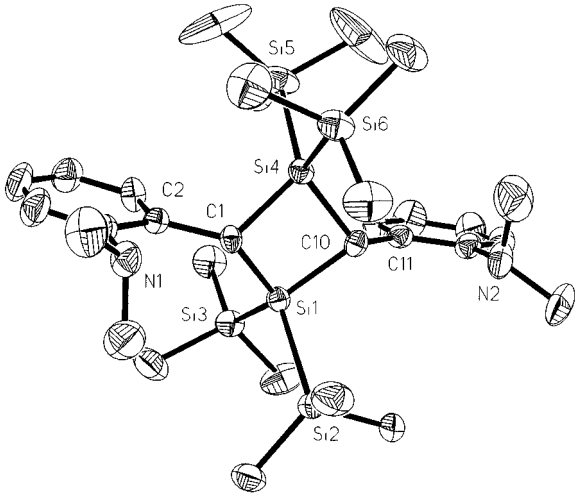
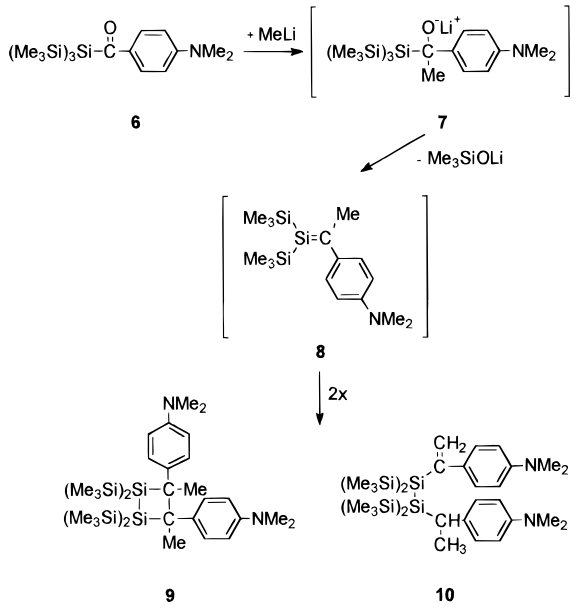



**Figure 2.** Molecular structure of *Z*-**3** in the crystal (H atoms omitted). Selected bond lengths (Å) and angles (deg): Si1−C1, 1.907(7); Si1−C10, 1.923(8); Si1−Si2, 2.375(3); Si1−Si3, 2.369(3); Si4−C1, 1.922(7); Si4−C10, 1.934(7); Si4−Si5, 2.359(3); Si4−Si6, 2.362(3); Si1−Si4, 2.689(2); C1−Si1−C10, 89.6(3); C1−Si4−C10, 88.8(3); Si1−C1−Si4, 89.2(3); Si1−C10−Si4 88.4(3).

As expected, **8** immediately dimerizes, and two products could be isolated from the reaction mixture: (*E*)-3,4-dimethyl-3,4-bis[4-(dimethylamino)phenyl]-1,1,2,2-tetrakis(trimethylsilyl)-1,2-disilacyclobutane (**9**; 15%) and 1-[1-(4-(dimethylamino)phenyl)ethenyl]-2-[1-(4-(dimethylamino)phenyl)ethyl]-1,1,2,2-tetrakis(trimethylsilyl)disilane (**10**; 61%). The structure elucidation of **9** and **10** was performed by NMR and MS studies and for **9** also by an X-ray structural analysis (Figure 3). Due to steric strain in **9** the Si−C as well as the C−C bonds are slightly elongated, but the values agree with those of similarly substituted 1,2-disilacyclobutane systems.[2−5] The ring is folded, the torsional angle Si1−C1−C1a−Si1a being 26.9°.

Both **9** and **10** are products of a head-to-head dimerization of the transient silene **8**. Assuming the reaction of **8** to give **9** and **10** follows the same mechanism as discovered by Brook et al. for the dimerization of silenes

**Scheme 3**




of similar structure, the conversion of **8** should proceed through radical intermediates.[6a,9] After Si−Si bond formation, the resulting 1,4-diradical dimerizes to give 1,2-disilacyclobutane **9**, or, after hydrogen transfer according to the known reaction pattern, the linear dimer **10** is formed.

These results indicate that the regiospecifity of the silene dimerization is heavily influenced by electronic effects (the steric effect of the dimethylamino groups in **2** and **8** is very likely of minor significance) and can be reversed by suitable substituents. In both cases the stabilization of the silene system by conjugation as shown in Scheme 1 appears not to be very effective, since **2** as well as **8** proved to be extremely reactive. Whereas silene **8** follows the usual dimerization pattern of 1,1-bis(trimethylsilyl)silenes, the structure of the product obtained in the dimerization of **2** indicates a complete change in the dimerization mechanism, which obviously is caused by the *o*-(dimethylamino)phenyl substituent. The reason for this unexpected behavior is not clear. An effective intramolecular donor−acceptor interaction between the dialkylamino group and the silene silicon atom in **2**, which actually is expected to reduce the positive charge on silicon but to enhance the negative charge at the silene carbon atom, thus facilitating a head-to-tail dimerization, is rather unlikely for steric reasons. Probably the head-to-tail dimerization of **2** is achieved by an intermolecular donor-acceptor interaction, the *o*-dimethylamino group acting as some kind of an anchor. Its interaction with the electrophilic silene silicon atom of a neighboring molecule and the attack of the activated nucleophilic silene carbon atom at the Si=C group of the first silene molecule possibly initiate a head-to-tail dimerization through a cyclic seven-membered transition state. Experiments to explore this idea are in progress.

In this context the dimerization behavior of 2-[2-((dimethylamino)methyl)phenyl]-1,1-bis(trimethylsilyl)-silene (**12**) is of particular interest. The mentioned restrictions of an effective intramolecular interaction in

(9) Brook, A. G.; Baines, K. M. *Adv. Organomet. Chem.* **1986**, *25*, 26.

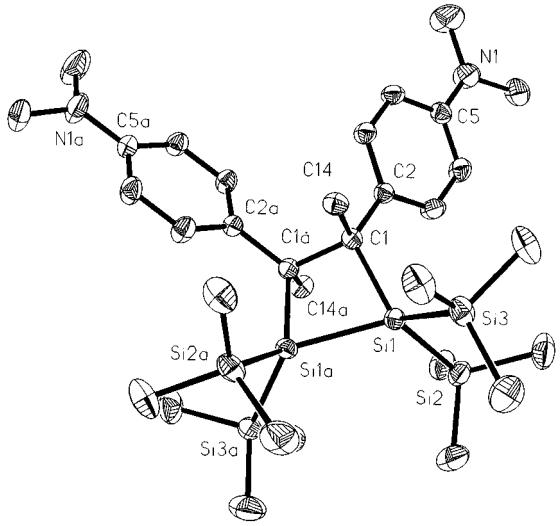
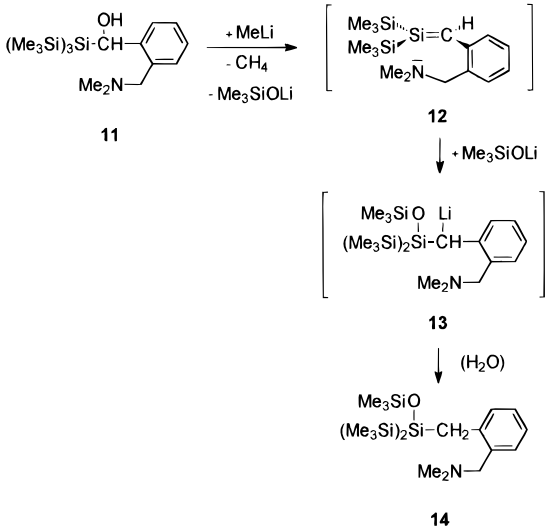



**Figure 3.** Molecular structure of **9** in the crystal (H atoms omitted). Selected bond lengths (Å) and angles (deg): C1−C1a, 1.627(5); C1−Si1, 1.969(3); Si1−Si1a, 2.365(2); C1−C2, 1.529(3); C1−C14, 1.545(3); Si1−Si2, 2.3872(11); Si1−Si3, 2.3736(11); C1−C1a−Si1a, 98.13(8); C1−Si1−Si1a, 77.36(8); C2−C1−C14, 108.7(2); Si2−Si1−Si3, 103.32(4).

**Scheme 4**




**2** do not apply to **12**, and a considerable stabilization of the silene by an intramolecular interaction of the dimethylamino group and the silene silicon atom can be expected. **12** is obtained in the usual manner by deprotonation of [2-((dimethylamino)methyl)phenyl]-[tris(trimethylsilyl)silyl]methanol (**11**) with methyllithium in ether. However, the compound isolated by column chromatography from the complex product mixture and identified by its NMR and MS data is neither a head-to-head nor a head-to-tail cycloadduct of the unstable silene **12** but rather, is 2-[2-((dimethylamino)methyl)phenyl]-1,1,1,3,3,3-hexamethyl-2-(trimethylsiloxy)trisilane (**14**) (Scheme 4). The formation of **14** is easily understood as the result of the readdition of the lithium trimethylsilanolate, generated according to the modified Peterson mechanism, at the Si=C bond of the silene **12**. Protonation of the carbanionic intermediate **13** during the aqueous workup gives the trisilane **14**.

The formation of readdition products in the course of the modified Peterson reaction was observed several

times, particularly in the case of sterically highly congested silenes,[4b,10] and is considered to be an indication of a moderate stability of the respective silene in solution. Due to the kinetic stabilization, the dimerization of these silenes becomes a comparatively slow reaction, making the silanolate addition the dominant process.

Whereas **2** rapidly dimerizes to give the 1,3-disilacyclobutane **3**, **12** obviously is stabilized, as we think, by an intramolecular donor-acceptor interaction between the dialkylamino group and the silene silicon atom. Interactions of labile silenes with donor molecules such as amines, halides, THF, etc. are known and lead to significant stabilization of these Si=C systems with respect to dimerization.[11] In the case of **12**, the steric situation allows a strong intramolecular interaction between the nitrogen lone pair and the silene silicon atom, forming a six-membered cyclic structure. **12** is not sufficiently stable to permit isolation, but the dimerization tendency is decreased and the lithium silanolate, present in the solution, adds to give **14**. On the other hand, the donor−acceptor interaction in **2** is less effective and the cyclization reaction described above dominates.

## Experimental Section

All reactions involving organometallic reagents were performed under purified argon. NMR spectra were recorded with a Bruker AC 250 or a Bruker ARX 300 spectrometer using tetramethylsilane as internal standard. IR spectra were measured with a Nicolet 205 FT-IR spectrometer, and mass spectra were recorded with an Intectra AMD 402 instrument applying chemical ionization with isobutane as the reactant gas. $(Me_3Si)_3SiLi\cdot 3THF$ is prepared as reported in the literature.[12]

**Preparation of 1.** According to the procedure described,[5a] 24 mmol of $(Me_3Si)_3SiMgBr$ (from 11.0 g (24 mmol) of $(Me_3Si)_3SiLi\cdot 3THF$ and an equimolar quantity of $MgBr_2$) and 1.19 g (8 mmol) of 2-(dimethylamino)benzaldehyde in ether gave 2.09 g (66 %) of **1**; mp 58 °C (acetonitrile). IR (Nujol): 3533, 3445 $cm^{-1}$ (OH). $^1H$ NMR (benzene-$d_6$): $\delta$ 0.31 (s, $SiCH_3$, 27 H), 2.40 (s, $NCH_3$, 6 H), 2.78 (br. s, OH, 1 H), 5.70 (s, OCH, 1 H), 6.82−7.54 (m, Ar H, 4H). $^{13}C$ NMR ($CDCl_3$): $\delta_C$ 1.5 ($SiCH_3$), 45.6 ($NCH_3$), 65.4 (COH), 119.8, 124.0, 127.0, 129.5 (arom CH), 140.9, 150.7 (arom quat C). $^{29}Si$ NMR ($CDCl_3$): $\delta_{Si}$ −12.7 ($SiCH_3$), −68.2 ($SiSiCH_3$). MS (CI, isobutane; $m/z$ (%)): 397 (8) [$M^+$], 382 (9) [$M^+ - CH_3$], 324 (17) [$M^+ - Si(CH_3)_3$], 150 (100) [$M^+ - Si(SiMe_3)_3$]. Anal. Calcd for $C_{18}H_{29}NOSi_4$ (397.86): C, 54.34; H, 9.88; N, 3.52. Found: C, 54.42; H, 9.89; N, 3.71.

**Reaction of 1 with Methyllithium.** At −78 ° C an equimolar quantity of ethereal MeLi solution was added to a solution of 0.5 g (1.3 mmol) of **1** in 30 mL of ether. The mixture was stirred for 1 h at −78 °C with subsequent warming for 3 h at room temperature. After addition of aqueous $NH_4Cl$, the organic phase was separated, the aqueous layer was extracted with ether, and the collected extracts were dried and evaporated. The crystalline residue was washed with acetone and filtered to give 0.24 g (63%) of *E*/*Z*-**3**, containing *E*-**3** and *Z*-**3** in a ratio of 1:2 ($^1H$ NMR). Repeated recrystallization from n-hexane afforded pure *Z*-**3**. The residue obtained by evaporation of the mother liquor was purified by chromatography (silica gel/heptane) to give pure *E*-**3**.

*Z*-**3**: mp 206 °C dec. $^1H$ NMR (benzene-$d_6$): $\delta$ 0.21, 0.34 (2s, $SiCH_3$, 2 × 18 H), 2.56 (s, $NCH_3$, 12 H), 3.80 (s, CH, 2 H), 6.93−7.84 (m, Ar H, 8 H). $^{13}C$ NMR (benzene-$d_6$): $\delta_C$ −0.1, 1.6 ($SiCH_3$), 10.3 (CH), 45.4 ($NCH_3$), 119.9, 123.3, 124.2, 131.9 (arom CH), 140.3, 151.6 (arom quat C). $^{29}Si$ NMR (benzene-$d_6$): $\delta_{Si}$ −14.4, −13.9 ($SiCH_3$), −5.9 ($SiSiCH_3$). MS (70 eV; $m/z$ (%)): 614 (45) [$M^+$], 599 (12) [$M^+ - CH_3$], 541 (100) [$M^+ - Si(CH_3)_3$], 307 (50) [$\mathbf{2}^+$], 234 (40) [$\mathbf{2}^+$-$CH_3$]. Exact mass: cald for $C_{30}H_{58}N_2Si_6$ 614.3286, found 614.3250.

*E*-**3**: sublimation beginning at 250 °C. $^1H$ NMR (benzene-$d_6$): $\delta$ 0.25 (s, $SiCH_3$, 36 H), 2.50 (s, $NCH_3$, 12 H), 4.10 (s, CH, 2 H), 6.85−7.80 (m, Ar H, 8 H). $^{13}C$ NMR (benzene-$d_6$): $\delta_C$ 0.0 ($SiCH_3$), 8.3 (CH), 44.7 ($NCH_3$), 119.3, 123.0, 123.3, 130.4 (arom CH), 140.5, 150.8 (arom quat C). $^{29}Si$ NMR (benzene-$d_6$): $\delta_{Si}$ −14.2 ($SiCH_3$), −8.3 ($SiSiCH_3$). MS (70 eV; $m/z$ (%)): 615 (100) [$M^+ + 1$], 495 (45) [$M^+ - Me_2NC_6H_4$]. Anal. Calcd for $C_{30}H_{58}N_2Si_6$ (615.30): C, 58.56; H, 9.50; N, 4.55. Found: C, 58.22; H, 9.56; N, 4.61.

**Preparation of 4.** Applying the procedure given for the preparation of **1**, 11.0 g (24 mmol) of $(Me_3Si)_3SiLi\cdot 3THF$ and 1.19 g (8 mmol) of 4-(dimethylamino)benzaldehyde gave 2.07 g (65%) of **4**, mp 75 °C (acetonitrile). IR (Nujol): 3570, 3295 $cm^{-1}$ (OH). $^1H$ NMR ($CDCl_3$): $\delta$ 0.14 (s, $SiCH_3$, 27H), 1.49 (d, $^3J$ = 3.4 Hz, OH, 1H), 2.91 (s, $NCH_3$, 6H), 4.91 (d, $^3J$ = 3.3 Hz, OCH, 1H), 6.69 (d, $^3J$ = 8.7 Hz, Ar H, 2H), 7.14 (d, $^3J$ = 8.7 Hz, Ar H, 2H). $^{13}C$ NMR (benzene-$d_6$): $\delta_C$ 1.8 ($SiCH_3$), 40.4 ($NCH_3$), 69.2 (COH), 112.8, 127.1 (arom CH), 135.8, 149.8 (arom quat C). $^{29}Si$ NMR (benzene-$d_6$): $\delta_{Si}$ −13.2 ($SiCH_3$), −69.4 ($SiSiCH_3$). MS (70 eV; $m/z$ (%)): 397 (7) [$M^+$], 324 (3) [$M^+ - Si(CH_3)_3$], 150 (100) [$M^+ - Si(SiMe_3)_3$]. Anal. Calcd for $C_{18}H_{39}NOSi_4$ (397.86): C, 54.34; H, 9.88; N, 3.52. Found: C, 54.31; H, 9.75; N, 3.76.

**Preparation of 6.** At room temperature, 5.0 g (10.6 mmol) of $(Me_3Si)_3SiLi\cdot 3THF$, dissolved in THF, was added to a stirred solution of 2.05 g (10.6 mmol) of ethyl 4-(dimethylamino)-benzoate. After 2 h, water was added and the mixture was extracted with ether. The dried ethereal solution was evaporated and the residue purified by column chromatography (silica gel, heptane/ethyl acetate 20/1). The product was recrystallized from methanol: yellow crystals; yield 1.8 g (43%); mp 86−88 °C. IR (Nujol): 1611 $cm^{-1}$ (CO). $^1H$ NMR (benzene-$d_6$): $\delta$ 0.41 (s, $SiCH_3$, 27 H), 2.32 (s, $NCH_3$, 6 H), 6.41 (d, $^3J$ = 8.85 Hz, Ar H, 2 H), 8.02 (d, $^3J$ = 9.15 Hz, Ar H, 2H). $^{13}C$ NMR (benzene-$d_6$): $\delta_C$ 1.9 ($SiCH_3$), 39.4 ($NCH_3$), 110.6, 130.7 (arom CH), 134.2, 153.4 (arom quat C), 220.9 (CO). $^{29}Si$ NMR (benzene-$d_6$): $\delta_{Si}$ −75.0 ($SiSiCH_3$), −11.9 ($SiCH_3$). MS ($m/z$ (%)): 395 (10) [$M^+$], 380 (100) [$M^+ - CH_3$], 148 (52) [$M^+ - Si(SiMe_3)_3$]. Anal. Calcd for $C_{18}H_{37}NOSi_4$ (395.84): C, 54.62; H, 9.42; N, 3.54. Found: C, 54.49; H, 9.27; N, 3.70.

**Reaction of 6 with Methyllithium.** An equimolar quantity of MeLi was added to an ethereal solution of 1.0 g (2.5 mmol) of **6** at −78 °C. The stirred solution was warmed to room temperature and stirring was continued for a further 3 h. Subsequently, water was added and the organic layer was separated, dried over $MgSO_4$, and evaporated. Treatment of the residue with heptane gave colorless crystals of **9** (0.13 g, 15%). The filtrate was again evaporated, and **10** was separated by column chromatography (silica gel, heptane/ethyl acetate 20/1) as a colorless oil, which gradually crystallized. Yield: 0.5 g (61%).

**9**: mp 220−222 °C. $^1H$ NMR (benzene-$d_6$): $\delta$ 0.37, 0.60 (2s, $SiCH_3$, 2 × 18H), 1.95 (s, ring $CH_3$, 6H), 2.56 (s, $N(CH_3)_2$, 12H), 6.70 (d, $^3J$ = 8.85 Hz, Ar H, 4H), 7.31 (d, $^3J$ = 8.85 Hz, Ar H, 4H). $^{13}C$ NMR (benzene-$d_6$): $\delta_C$ 3.4, 3.5 ($SiCH_3$), 31.3 (ring $CH_3$), 40.3 ($NCH_3$), 53.1 (ring -C), 112.0, 131.0 (arom CH), 136.1, 148.9 (arom quat C). $^{29}Si$ NMR (benzene-$d_6$): $\delta_{Si}$ −39.6 ($SiSiCH_3$), −12.6, −12.2 ($SiCH_3$). MS ($m/z$ (%)): 642 (7) [$M^+$], 348 (10) [$(Me_3Si)_2Si{=}Si(SiMe_3)_2^+$], 148 (100) [$MeCHArNMe_2^+$]. Anal. Calcd for $C_{32}H_{62}N_2Si_6$ (643.37): C, 59.74; H, 9.71; N, 4.35. Found: C, 59.60; H, 9.58; N, 4.46.

**10**: mp 95−97 °C. $^1H$ NMR (benzene-$d_6$): $\delta$ 0.21, 0.53 (2s, $SiCH_3$, 2 × 9H), 0.42 (s, $SiCH_3$, 18H), 1.27 (d, $^3J$ = 7.63 Hz,

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**Table 1. Crystallographic Data for *E*-3, *Z*-3, and 9**

| | *E*-3 | *Z*-3 | **9** |
|---|---|---|---|
| crystal system | monoclinic | monoclinic | monoclinic |
| space group | $P2_1/n$ | $Cc$ | $C2/c$ |
| $a$, Å | 11.377(2) | 23.165(3) | 14.095(2) |
| $b$, Å | 11.396(2) | 22.896(3) | 13.066(2) |
| $c$, Å | 14.865(3) | 17.856(3) | 22.544(3) |
| $\beta$, deg | 96.82(1) | 123.08(1) | 97.36(1) |
| $V$, Å$^3$ | 1913.6(6) | 7936(2) | 4118(1) |
| $Z$ | 2 | 8 | 4 |
| cryst color | colorless | colorless | colorless |
| cryst size, mm | 0.3 × 0.3 × 0.3 | 0.5 × 0.4 × 0.3 | 0.4 × 0.4 × 0.4 |
| fw | 615.32 | 615.32 | 643.38 |
| $\rho_{calcd}$, g cm$^{-3}$ | 1.068 | 1.030 | 1.038 |
| $\mu$, cm$^{-1}$ (Mo K$\alpha$) | 2.38 | 2.30 | 2.24 |
| $F(000)$ | 672 | 2688 | 1408 |
| $T$, K | 200 | 293 | 293 |
| $\theta$ range, deg | 2.14−24.31 | 1.78−24.35 | 1.82−24.36 |
| no. of rflns | 5562 | 11752 | 6004 |
| no. of unique rflns | 3070 | 6466 | 3288 |
| no. of obsd reflections ($I > 2\sigma(I)$) | 2174 | 3162 | 2087 |
| no. of params | 173 | 686 | 181 |
| wR2 (all data) | 0.121 | 0.080 | 0.120 |
| $R$ value ($I > 2\sigma(I)$) | 0.043 | 0.042 | 0.045 |

HC$CH_3$, 3H), 2.53, 2.56 (2s, $NCH_3$, 2 × 6H), 3.21 (q, $^3J$ = 7.63 Hz, $HCCH_3$, 1H), 5.96, 5.97 (2d, $^2J$ = 18.9 Hz, $CCH_2$, 2 × 1H), 6.65, 6.66 (2d, $^3J$ = 8.85 Hz, Ar H, 2 × 2 H), 7.33, 7.37 (2d, $^3J$ = 8.83 Hz, Ar H, 2 × 2H). $^{13}$C NMR (benzene-$d_6$): $\delta_C$ 3.0, 3.1, 3.2, 4.4 ($SiCH_3$), 24.1, 27.5 (H$CCH_3$ and HC$CH_3$), 40.3, 40.6 ($NCH_3$), 112.3, 113.3, 128.7, 129.0 (arom CH), 130.7 (C$CH_2$), 136.5, 136.7, 149.0, 149.8, 150.4 (arom quat C and $CCH_2$). $^{29}$Si NMR (benzene-$d_6$): $\delta_{Si}$ −68.5, −55.9 ($Si$SiCH$_3$), −12.8, −12.1, −12.0, −11.7 ($SiCH_3$). MS ($m/z$ (%)): 642 (6) [M$^+$], 627 (2) [M$^+$ − $CH_3$], 494 (20) [M$^+$ − $CH_3$CHArNMe$_2$], 148 (100) [$CH_3$CHArNMe$_2^+$]. Anal. Calcd for $C_{32}H_{62}N_2Si_6$ (643.37): C, 59.74; H, 9.71; N, 4.35. Found: C, 59.78; H, 9.61; N, 4.43.

**Preparation of 11.** Using the general procedure described previously,[5a] the reaction of 7.3 g (16 mmol) of $(Me_3Si)_3$-SiLi·3THF, converted with an equimolar quantity of $MgBr_2$ to the silylmagnesium derivative, and 2.6 g (16 mmol) of 2-[(dimethylamino)methyl]benzaldehyde gave a product, which was purified by column chromatography (silica gel, heptane/ethyl acetate 5/1). Recrystallization from acetonitrile gave pure **11**: yield 3.2 g (49%), mp 59 °C. IR (Nujol): 3378 cm$^{-1}$ (OH). $^1$H NMR (benzene-$d_6$): $\delta$ 0.37 (s, $SiCH_3$, 27H), 1.85 (s, $NCH_3$, 6H), 2.94 (d, $^2J$ = 12.2 Hz, $NCH_2$, 1H), 3.64 (d, $^2J$ = 12.2 Hz, $NCH_2$, 1H), 5.75 (br s, OH, 1H), 6.91−7.04 (m, Ar H, 2H), 7.10−7.20 (m, Ar H, 1H), 7.61−7.64 (m, Ar H, 1H). $^{13}$C NMR ($CDCl_3$): $\delta_C$ 1.6 ($SiCH_3$), 44.7 ($NCH_3$), 63.7 ($NCH_2$), 66.2 (COH), 126.3, 127.8, 129.9, 131.1 (arom CH), 136.2, 145.9 (arom quat C). $^{29}$Si NMR ($CDCl_3$): $\delta_{Si}$ −12.6 ($SiCH_3$), −73.4 ($Si$SiCH$_3$). MS (70 eV; $m/z$ (%)): 411 (2) [M$^+$], 396 (5) [M$^+$ − $CH_3$], 164 (100) [M$^+$ − Si(SiMe$_3$)$_3$]. Anal. Calcd for $C_{19}H_{41}$-$NOSi_4$ (411.89): C, 55.41; H, 10.03; N, 3.40. Found: C, 55.55; H, 10.09; N, 3.58.

**Reaction of 11 with Methyllithium.** An equimolar quantity of MeLi was added to a stirred solution of 0.5 g (1.2 mmol) of **11** in 30 mL of ether at −78 °C. Stirring was continued for 1 h in the cold and 3 h at room temperature. After addition of aqueous $NH_4Cl$ the organic layer was separated and the aqueous phase extracted with ether. The collected extracts were dried over $MgSO_4$ and evaporated. Chromatographic separation of the residue (silica gel, heptane/ethyl acetate 10/1) gave 0.2 g (38%) of **14**. $^1$H NMR (benzene-$d_6$): $\delta$ 0.10 (s, $OSiCH_3$, 9H), 0.16 (s, $SiSiCH_3$, 18H), 2.17 (s, $NCH_3$, 6H), 2.81 (s, $PhCH_2$, 2H), 3.43 (s, $NCH_2$, 2H), 6.98−7.26 (m, arom CH, 4H). $^{13}$C NMR (benzene-$d_6$): $\delta_C$ −1.1 ($SiSiCH_3$), 2.2 ($OSiCH_3$), 23.6 ($PhCH_2$), 45.5 ($NCH_3$), 124.5, 127.4, 130.0, 131.0 (arom CH), 136.3, 140.9 (arom quat C). $^{29}$Si NMR (benzene-$d_6$): $\delta_{Si}$ −21.1 (OSi$Si$CH$_3$), −0.9 (O$Si$SiCH$_3$), 7.5 ($OSiCH_3$). MS (70 eV; $m/z$ (%)): 410 (1) [M$^+$ − 1], 396 (10) [M$^+$ − $CH_3$], 338 (100) [M$^+$ − ($SiCH_3$)$_3$]. Anal. Calcd for $C_{19}H_{41}NOSi_4$ (411.90): C, 55.41; H, 10.03; N, 3.40. Found: C, 55.18; H, 10.12; N, 3.50.

**X-ray Structure Determinations.** X-ray diffraction data were collected on a STOE-IPDS diffractometer using graphite-monochromated Mo K$\alpha$ radiation. The crystals were mounted in a cold nitrogen stream or sealed inside a capillary. The structures were solved by direct methods (SHELXS-86)[13] and refined by full-matrix least-squares techniques against $F^2$ (SHELXL-93).[14] XP (Siemens Analytical X-ray Instruments, Inc.) was used for structure representations.

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**Supporting Information Available:** Descriptions of the X-ray experimental details for *E*-**3**, *Z*-**3**, and **9**, including tables of crystal data, positional parameters, all bond distances and angles, and thermal parameters and figures giving additional views of the structures (29 pages). Ordering information is given on any current masthead page.

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