Crystal Structures of Bis[(8′-(dimethylamino)naphth-1′-yl)dimethylsilyl] Ether and Bis[(8′-(dimethylamino)naphth-1′-yl)-1-silacyclobut-1-yl] Ether. Structural Evidence for the Enhanced Lewis Acidity of Silacyclobutane Derivatives

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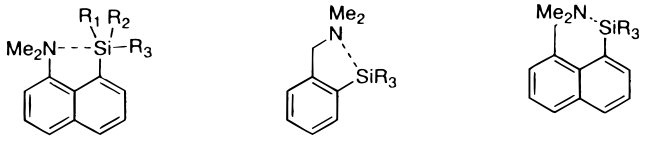
The X-ray structure of bis[(8′-(dimethylamino)naphth-1′-yl)-1-silacyclobut-1-yl] ether (**6**) provides structural evidence for enhanced Lewis aciditiy of the silicon in silacyclobutyl ring derivatives compared with that of the unstrained analogue **7**.

Introduction

Pentacoordinate (and higher coordinate) silicon has been the focus of much attention over the past decade, particularly in the studies of nucleophilic substitution at the silicon which can occur with retention or inversion of configuration depending on the nature of the nucleophile, the leaving group, and other groups attached to the silicon.[1] Studies on model systems such as **1**−**3** have

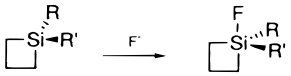


1 **2** **3**

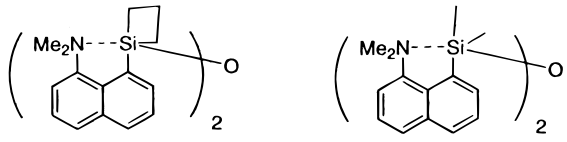
4; R_1 = OEt, R_2 = Me, R_3 = SiMePh2
5; R_1R_2,R_3 = F

provided a valuable insight into the structures and properties of these proposed intermediates. More recently, pentacoordinate silicon substituents have been investigated as alternatives to tetravalent tin substituents in organic synthesis: for example, the Stille cross-coupling reaction.[2,3] Some of these studies have involved the use of fluoroalkoxy-substituted silane[2] and trialkoxysilane substituents,[3] which can be readily converted to the hypercoordinate state by treatment with fluoride before subjection to the Stille coupling conditions. The silacyclobutanes have been shown to readily form hypercoordinate species in the presence of Lewis bases,[4] a property which has recently been exploited by Denmark et al.[5,6] The enhanced Lewis acidity of the silacyclobutanes is believed to arise from the relief of angle strain at the silicon in the trigonal-bipyramidal geometry (Scheme 1).

Scheme 1



In the [1-(dimethylamino)-8-naphthyl]silanes **1** the distance between the *peri* dimethylamino and silyl groups and also the geometry at the silicon (tetrahedral vs trigonal bipyramidal) are, as expected, very sensitive to the Lewis acidity of the silicon.[7] Thus, in the silane **4**[9] the N···Si distance is 2.969 Å, with the silicon showing only small distortions from tetrahedral geometry toward a trigonal bipyramid. By comparison the trifluorosilane **5** has a much shorter N···Si distance of 2.287 Å with an almost perfect trigonal-bipyramidal geometry at the Si.[10] On account of the demonstrated enhanced Lewis acidity of the silacyclobutane ring, and given that we had compounds in hand from other studies,[11] we were able to determine the structural effects which arise when a silacyclobutyl substituent is at the 8-position of 1-(dimethylamino)naphthalene. To this end, we determined the structure of the siloxycyclobutyl derivative **6**. The siloxy compound **6** was



6 **7**

(1) Corriu, R. J. *J. Organomet. Chem.* **1990**, *400*, 81.
(2) Hatanaka, Y.; Hiyama, T. *Synlett* **1991**, 845.
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(5) Denmark, S. E.; Griedal, B. D. *J. Org. Chem.* **1994**, *59*, 5136.
(6) Denmark, S. E.; Choi, J. Y. *J. Am. Chem. Soc.* **1999**, *121*, 5821.

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(8) Allen, F. H.; Bellard, S.; Brice, M. D.; Cartwright, B. A.; Doubleday, A.; Higgs, H.; Hummelink, T.; Hummelink-Peters, T.; Kennard, O.; Motherwell, W. D. S.; Rogers, J. R.; Watson, D. G. *Acta Crystallogr.* **1979**, *B35*, 2331.
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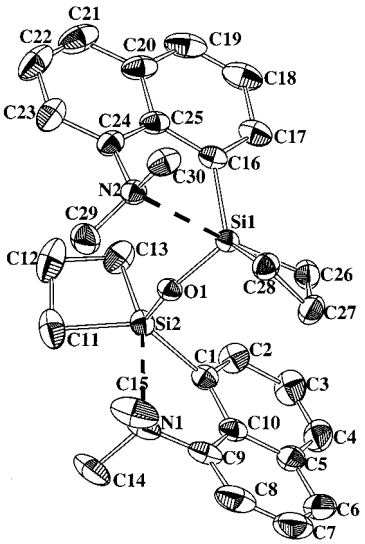
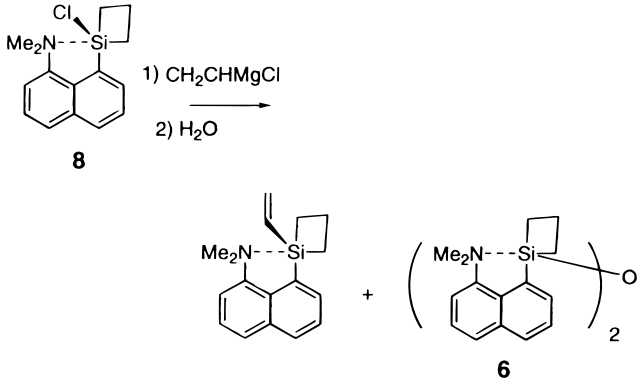
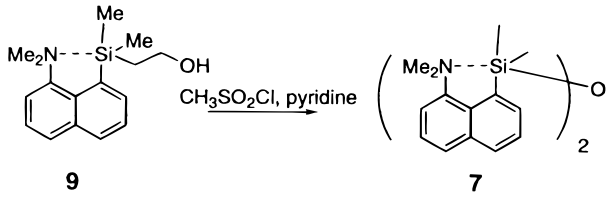


Figure 1. Thermal ellipsoid plot for compound **6**. Ellipsoids are at the 30% probability level.

Scheme 2



Scheme 3



obtained as a byproduct from the reaction of the chlorosilacyclobutane **8** with vinylmagnesium chloride followed by aqueous workup and is presumably a hydrolysis product from unreacted chlorosilane (Scheme 2). For comparison, we also determined the structure of the unstrained analogue **7**.

The siloxy dimer **7** was the only product isolated after treatment of the silylethanol derivative **9** with methanesulfonyl chloride in pyridine followed by aqueous workup (Scheme 3).

Molecular Structures

The X-ray structures of both **6** and **7** were determined at room temperature (unfortunately, both underwent destructive phase changes upon cooling). The structures of **6** and **7**, which are presented in Figures 1 and 2, respectively, depict 30% ellipsoids and were drawn

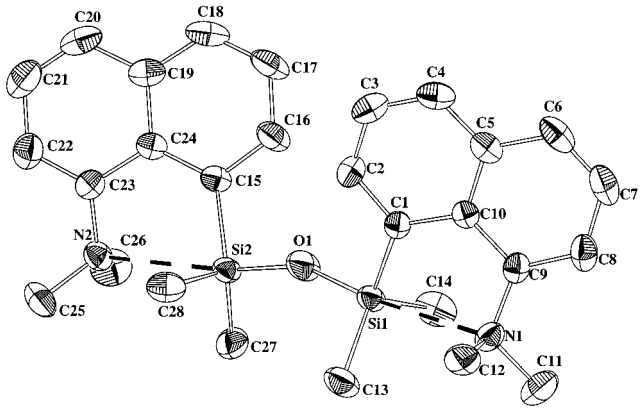


Figure 2. Thermal ellipsoid plot for compound **7**. Ellipsoids are at the 30% probability level.

using the program ZORTEP.[12] Hydrogen atoms are omitted for clarity. Atomic coordinates for **6** and **7** are presented in the Supporting Information, while selected bond distances, angles, dihedral angles, and other relevant geometrical parameters are presented in Tables 1 and 2, respectively.

The N···Si distances in the siloxy dimer **7**, which are 2.849(4) and 2.851(4) Å, respectively, are well within the sum of the van der Waals radii[13] (3.65 Å) (Table 4) and compare well with those of other similarly substituted [(dimethylamino)naphthyl]silyl derivatives.[14] The geometries at both silicons show distortions toward a trigonal-bipyramidal geometry with the carbons C(1), C(14), and C(13) defining the basal plane at Si(1) and C(15), C(27), and C(28) defining the basal plane at Si(2) (mean C−Si(1)−C = 114.6°, C−Si(2)−C = 114.5°; the deviation of Si(1) from the plane defined by C(1), C(13), and C(14) is 0.441 Å, and that of Si(2) from the plane defined by C(15), C(27), and C(28) is 0.445 Å); the *peri* dimethylamino nitrogens N(1) and N(2) occupy one apical site at each silicon (as is enforced by the *peri* interaction), while O(1) occupies the second apical site (mean O(1)−Si(1)−C = 103.7°, O1−Si(2)−C = 103.9°), in accord with the greater apicophilicity of the siloxy oxygen over the methyl carbons.[1] Steric repulsion between the dimethylamino and silyl substituents is evident in both rings; thus, Si(1) twists from the mean plane of the naphthalene ring as defined by carbons C(1)−C(10) by 0.725 Å, N1 twists by 0.459 Å in the opposite sense (Table 4), and there are similar distortions evident in the second naphthalene sytem.

Examination of the structure of the siloxycyclobutyl dimer **6** reveals some interesting features. The N···Si distances, which are 2.614(2) and 2.621(2) Å, respectively, represent a decrease of 0.23 Å compared with the unconstrained disiloxy dimer **7**, suggesting a stronger interaction between the amino and silyl substituents. The silicon is more clearly distorted toward a trigonal-bipyramidal geometry, with C(1), C(11), and O(1) defining the basal plane at Si(1) (mean basal angle at Si(1) 117.9°) and C(1), C(11), and O(1) defining that at Si(2) (mean basal angle at Si(2) 117.6°; the deviation of Si(1) from the plane defined by C(1), C(11), and O(1) is 0.28

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Table 1. Selected Structural Parameters for Compound 6

Bond Distances (Å)			
Si(2)−O(1)	1.6361(12)	Si(1)−O(1)	1.6346(13)
Si(1)−C(1)	1.8769(19)	Si(1)−C(11)	1.878(2)
Si(1)−C(13)	1.895(2)	Si(2)−C(16)	1.883(2)
Si(2)−C(26)	1.891(2)	Si(2)−C(28)	1.872(2)
N(1)−C(9)	1.438(3)	N(1)−C(15)	1.470(3)
N(1)−C(14)	1.475(3)	N(2)−C(24)	1.435(3)
N(2)−C(29)	1.460(3)	N(2)−C(30)	1.471(2)
N(1)···Si(1)	2.614(2)	N(2)···Si(2)	2.621(2)

Bond Angles (deg)			
O(1)−Si(1)−C(1)	110.83(8)	O(1)−Si(1)−C(11)	112.89(10)
O(1)−Si(1)−C(13)	108.15(9)	O(1)−Si(2)−C(28)	112.48(8)
O(1)−Si(2)−C(16)	110.69(8)	O(1)−Si(2)−C(26)	108.64(8)
Si(1)−O(1)−Si(2)	139.19(8)	C(1)−Si(1)−C(13)	110.63(10)
C(11)−Si(1)−C(13)	77.29(13)	C(1)−Si(1)−C(11)	129.97(11)
C(16)−Si(2)−C(26)	111.51(10)	C(28)−Si(2)−C(16)	129.51(9)
C(28)−Si(2)−C(26)	77.75(10)	C(2)−C(1)−Si(1)	118.26(16)
C(10)−C(1)−Si(1)	122.69(15)	C(17)−C(16)−Si(2)	118.62(16)
C(25)−C(16)−Si(2)	122.66(15)	C(12)−C(13)−Si(1)	87.69(18)
C(12)−C(11)−Si(1)	87.45(16)	C(27)−C(26)−Si(2)	87.28(13)
C(27)−C(28)−Si(2)	87.82(16)	C(26)−C(27)−C(28)	99.41(17)
C(13)−C(12)−C(11)	100.4(2)	N(1)···Si(1)−C13	164.24(8)
N(2)···Si(2)−C26	168.28(8)	N(1)···Si(1)−C1	74.63(8)
N(2)···Si(2)−C16	74.10(8)	N(1)···Si(1)−C11	87.98(8)
N(2)···Si(2)−C28	87.41(8)	N(1)···Si(1)−O(1)	82.61(8)
N(2)···Si(2)−O(1)	81.70(8)		

Dihedral Angles (deg)	
Si(1)−C(1)−C(2)−C(3)	165.72(19)
Si(1)−C(1)−C(10)−C(9)	14.4(2)
Si(2)−C(16)−C(25)−C(24)	14.5(3)
C(7)−C(8)−C(9)−N(1)	175.2(2)
N(1)−C(9)−C(10)−C(1)	8.3(3)
N(2)−C(24)−C(25)−C(20)	−170.27(16)
Si(1)−C(11)−C(12)−C(13)	22.4(2)
Si(2)−C(16)−C(17)−C(18)	169.15(19)
Si(2)−C(16)−C(25)−C(20)	−164.19(15)
N(1)−C(9)−C(10)−C(5)	−174.18(17)
N(2)−C(24)−C(25)−C(16)	11.0(3)
C(22)−C(23)−C(24)−N(2)	173.3(2)

Deviations from Plane Defined by Ring 1 (C(1)−C(10)) (Å)	
Si(1)	0.496
N(1)	−0.181

Deviations from Plane Defined by Ring 2 (C(15)−C(24)) (Å)	
Si(2)	−0.496
N(2)	0.31

Å, while the deviation of Si(2) from the plane defined by C(16), C(28), and O(1) is 0.26 Å); the silacyclobutyl carbons C(13) and C(26) take up the apical positions (mean basal−Si(1)−C(13) = 98.7°, mean basal−Si(2)−C(26) = 99.3°). The preference of C(13) and C(26) for the apical position rather than the siloxy oxygen O(1) (compared with **7**, where the oxygen is apical) presumably reflects the inability of the trimethylene to span the basal positions. The relief of strain at the silicon resulting from this arrangement presumably compensates for the energy cost of placing carbon rather than oxygen in an apical position. The stronger interaction between the 1-dimethylamino substituents and the 8-silyl substituents in **6** over **7** is also evident in the smaller twisting of these substituents from the mean planes defined by the naphthalene ring carbons (Table 3). It is interesting to note that the two apical silacyclobutane C−Si bonds (mean 1.889 Å) are slightly longer than the corresponding basal silacyclobutane Si−C bonds (mean 1.875 Å); this lengthening possibly arises from some donation of electron density from the *peri* nitrogens into the Si−C σ^* orbital.

Table 2. Selected Structural Parameters for Compound 7

Bond Distances (Å)			
Si(1)−O(1)	1.634(3)	Si(2)−O(1)	1.635(3)
Si(1)−C(1)	1.901(4)	Si(1)−C(13)	1.852(4)
Si(1)−C(14)	1.862(5)	Si(2)−C(15)	1.900(4)
Si(2)−C(27)	1.854(4)	Si(2)−C(28)	1.845(4)
N(1)−C(9)	1.432(5)	N(1)−C(11)	1.471(6)
N(1)−C(12)	1.484(5)	N(2)−C(23)	1.420(5)
N(2)−C(26)	1.467(5)	N(2)−C(25)	1.476(6)
N(1)···Si(1)	2.849(4)	N(2)···Si(2)	2.851(4)

Bond Angles (deg)			
O(1)−Si(1)−C(13)	104.9(2)	O(1)−Si(1)−C(14)	104.7(2)
O(1)−Si(1)−C(1)	101.36(16)	O(1)−Si(2)−C(28)	105.5(2)
O(1)−Si(2)−C(27)	104.90(19)	O(1)−Si(2)−C(15)	101.14(16)
Si(1)−O(1)−Si(2)	153.9(2)	C(2)−C(1)−Si(1)	117.3(3)
C(10)−C(1)−Si(1)	124.2(2)	C(16)−C(15)−Si(2)	116.7(3)
C(24)−C(15)−Si(2)	124.8(3)	C(8)−C(9)−N(1)	124.1(3)
C(10)−C(9)−N(1)	115.4(3)	C(22)−C(23)−N(2)	123.3(4)
N(2)−C(23)−C(24)	116.6(3)		
C(13)−Si(1)−C(14)	112.5(2)	C(13)−Si(1)−C(1)	121.2(2)
C(14)−Si(1)−C(1)	110.12(18)	C(28)−Si(2)−C(27)	112.6(2)
C(28)−Si(2)−C(15)	111.0(2)	C(27)−Si(2)−C(15)	119.9(2)
N(1)···Si(1)−O(1)	171.2(2)	N(2)...Si(2)−O(1)	170.9(2)
N(1)···Si(1)−C(1)	69.9(2)	N(1)···Si(1)−C(13)	79.8(2)
N(1)···Si(1)−C(14)	79.892)	N(2)···Si(2)−C(15)	69.8(2)
N(2)···Si(2)−C(27)	79.5(2)	N(2)···Si(2)−C(28)	79.7(2)

Dihedral Angles (deg)	
Si(1)−C(1)−C(2)−C(3)	−165.7(4)
Si(1)−C(1)−C(10)−C(5)	157.7(3)
Si(2)−C(15)−C(24)−C(23)	−22.4(5)
C(7)−C(8)−C(9)−N(1)	−170.8(4)
N(1)−C(9)−C(10)−C(5)	165.4(3)
N(2)−C(23)−C(24)−C(15)	−12.4(5)
Si(1)−C(1)−C(10)−C(9)	−19.8(5)
Si(2)−C(15)−C(16)−C(17)	−164.5(4)
Si(2)−C(15)−C(24)−C(19)	156.9(3)
N(1)−C(9)−C(10)−C(1)	−17.1(5)
C(21)−C(22)−C(23)−N(2)	−173.7(4)
N(2)−C(23)−C(24)−C(19)	168.2(3)

Deviations from Plane Defined by Ring 1 (C(1)−C(10)) (Å)	
Si(1)	−0.725
N(1)	0.459

Deviations from Plane Defined by Ring 2 (C(15)−C(24)) (Å)	
Si(2)	0.731
N(2)	−0.367

Variable-Temperature ^{13}C NMR Studies of 6 and 7

To investigate the solution structures of **6** and **7**, the ^{13}C NMR spectra were measured in CD_2Cl_2 at various temperatures ranging from room temperature down to −90 °C. In the ^{13}C NMR spectrum of the siloxy dimer **7** at room temperature in the aliphatic region a single signal at δ 47.7 ppm arising from the four N−CH_3 carbons and a single signal at 3.64 from the four Si−CH_3 carbons was observed; these signals remained sharp down to −95 °C, and the chemical shift values did not vary significantly. The equivalence of the four N−CH_3's and the four Si−CH_3's and the lack of dynamic behavior of **7** suggests that the siloxy dimer adopts the same conformation in solution as in the crystal. Barriers to pseudorotation at silicon in compounds similar to **7** are generally of the order of 8−12 kcal/mol.[1] If there was any substantial population of the alternative configuration of **7** with a methyl rather than oxygen at the apical position, then coalescence of signals would be expected at ca. −60 to −70 °C. In contrast to the behavior of **7**, the ^{13}C NMR spectrum of the silacyclobutyl dimer does change upon cooling (Figure 3). At room

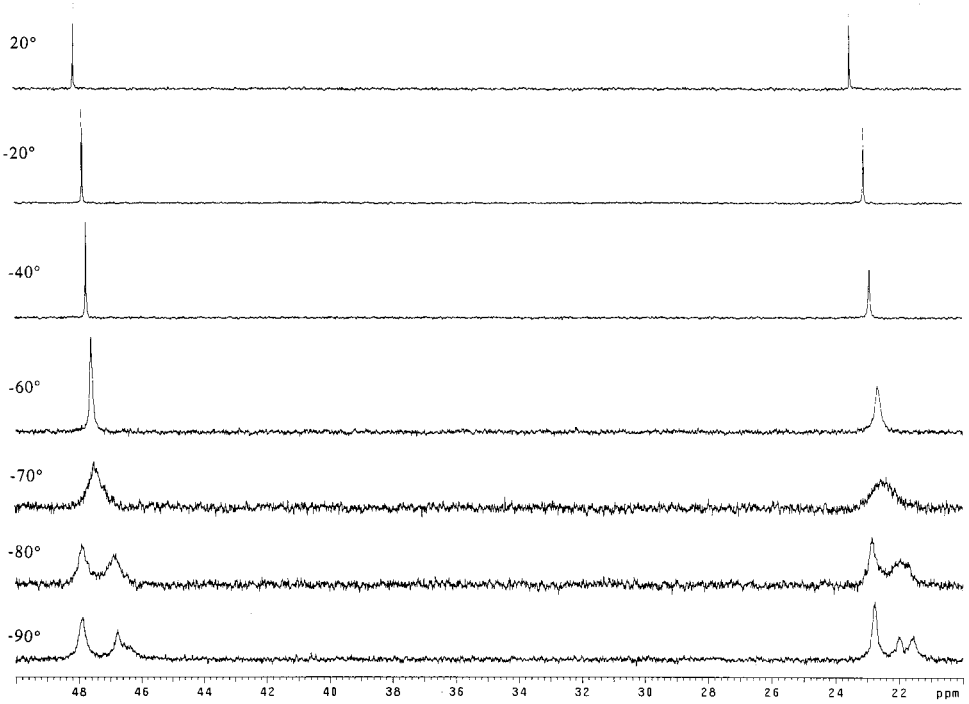
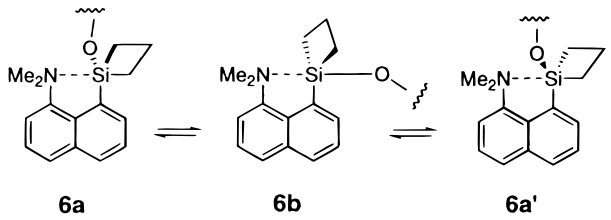


Figure 3. Variable-temperature ^{13}C NMR of compound **6** in CD_2Cl_2 (temperatures are given in °C).

Scheme 4



temperature a single signal was observed for the four N−CH_3 carbons (48.04 ppm) the four Si−CH_2 (23.47 ppm) carbons, and the two $CH_2CH_2CH_2$ (14.81 ppm) carbons. Upon cooling the N−CH_3 carbons broaden and coalesce at ca. −80 °C, and at −90 °C they gave rise to three resonances: 47.85 ppm (sharp) and 46.75 ppm (broad, two overlapping signals). The Si−CH_2 carbons broadened and coalesced at a similar temperature, giving rise to three signals at 22.74, 22.0, 21.52 ppm (approximate ratios 2:1:1), and the $CH_2CH_2CH_2$ carbons remained as a single absorption (13.97 ppm). We believe that this dynamic behavior is consistent with **6** existing in solution as a mixture of the conformations **6a**, **6b**, and **6a′**, which equilibrate (presumable by turnstile rotation at the Si) (Scheme 4) with a barrier of ca. 9.3 kcal/mol.

^{29}Si NMR Studies of 6 and 7

The ^{29}Si NMR spectra of **6** and **7** revealed single absorptions at δ −14.16 and −11.78 ppm, respectively (relative to TMS) at room temperature (18 °C). The ^{29}Si chemical shift of **6** appears to be slightly deshielded relative to **7**; however, when the ^{29}Si data for **6** and **7** are compared, allowance must be made for the effect of incorporating the silicon into a four-membered ring in **6**. This has been reported to be deshielding by as much as ca. 18 ppm,[15] therefore suggesting that the ^{29}Si NMR shift for **6** is in fact substantially shielded, presumably due to the strong *peri* interaction with the dimethylamino substituent.

Experimental Section

General Considerations. Diffraction data were recorded on an Enraf-Nonius CAD4f diffractometer operating in the $\theta/2\theta$ scan. Crystal data and structure refinement details for **6** and **7** are presented in Table 3. Unit cell dimensions were corrected for any θ zero errors by centering reflections at both positive and negative θ angles. The data were corrected for Lorentz and polarization effects (Process_data)[16] and for absorption (SHELX76).[17] Structures were solved by direct methods (SHELXS-86)[18] and were refined on F^2 (SHELXL-97).[19] ^{13}C NMR spectra were recorded on a Varian Unity Plus 400 system.

Preparation of Compound 6. To a solution of the chlorosilane **8** (1.28 g, 4.6 mmol) in anhydrous diethyl ether (10 mL) was added vinylmagnesium bromide as a 1 M solution in THF (5.1 mL, 5.1 mmol). The resulting mixture was stirred at room temperature for 3 h. The mixture was quenched with water (5 drops), and then more water (20 mL) was added and the mixture stirred for 15 min. This mixture was extracted with ether (3 × 20 mL), and the combined extracts were washed with water (3 × 30 mL), dried ($MgSO_4$), and evaporated to a thick yellow oil (0.8 g, 64%). Upon separation of 0.8 g of the yellow oil using silica flash chromatography, the desired vinyl-substituted silane (Scheme 2) was isolated (0.32

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Table 3. Crystal Data and Structure Refinement Details for 6 and 7

	6	**7**
empirical formula	$C_{30}H_{36}N_2OSi_2$	$C_{28}H_{36}N_2OSi_2$
fw	496.79	472.77
temp (K)	293(2)	293(2)
wavelength (Å)	1.541 80	0.710 69
cryst syst	orthorhombic	orthorhombic
space group	*Pbcn*	$Pca2_1$
unit cell dimens		
a (Å)	31.7348(9)	16.071(2)
b (Å)	8.0482(5)	13.4900(10)
c (Å)	21.4631(3)	12.6256(6)
V (Å^3)	5481.8(4)	2737.2(4)
Z	8	4
calcd density (Mg/m^3)	1.204	1.147
abs coeff (mm^{-1})	1.359	0.151
abs cor	Gaussian	not applied
max, min transmissn	0.85, 0.62	
F(000)	2128	1016
cryst size (mm^3)	0.5 × 0.25 × 0.12	0.5 × 0.2 × 0.15
θ range for data collecn (deg)	2.78−74.91	2.53−27.47
index ranges	$0 \le h \le 38$	$0 \le h \le 20$
	$0 \le k \le 9$	$-17 \le k \le 0$
	$0 \le l \le 26$	$0 \le l \le 16$
no. of rflns collected	5607	3281
no. of indep rflns	5607 (R(int) = 0.0000)	3281
no. of obsd rflns ($I > 2\sigma(I)$)	4505	2435
completeness to θ = 74.91° (%)	99.5	99.9
no. of data/restraints/params	5607/0/317	3281/1/299
goodness of fit on F^2	1.020	1.024
final R indices ($I > 2\sigma(I)$)	R1 = 0.0431, wR2 = 0.1117	R1 = 0.0444, wR2 = 0.1069
R indices (all data)	R1 = 0.0568, wR2 = 0.1212	R1 = 0.0689, wR2 = 0.1209
weighting scheme		
A and B for w^a	A = 0.0573, B = 1.83	A = 0.0596, B = 0.54
abs structure param	n/a	0.20(18)
extinction coeff	0.00032(8)	0.0010(8)
largest diff peak and hole (e Å^{-3})	0.251 and −0.222	0.172 and −0.175

[a] $w = 1/[\sigma^2(F_o^2) + (AP)^2 + BP]$, where $P = (F_o^2 + 2F_c^2)/3$.

g, 26%) along with the oxygen dimer **6** (0.17 g, 14%). Compound **6** was recrystallized from methanol, giving white blocks, mp 134−136 °C. ^{1}H NMR (δ; $CDCl_3$): 1.40 (2H, m); 1.63 (4H, m); 2.51 (12H, s); 7.29 (2H, d, J = 7.5 Hz); 7.49 (4H, m); 7.71 (2H, d, J = 8.1 Hz); 7.85 (2H, d J = 6.6 Hz); 7.89 (2H, d, J = 8.4 Hz). ^{13}C NMR (δ; $CDCl_3$): 14.35, 22.95, 47.59, 166.86, 125.314, 125.641, 125.86, 129.41, 133.91, 134.30, 134.82, 135.14, 152.37. ^{29}Si NMR ($CDCl_3$): −14.16 ppm (relative to tetramethylsilane). MS (m/z): [$M^+ - CH_3$], 481.2122; calcd for $C_{29}H_{33}N_2OSi_2$, 481.2131.

Preparation of Compound 7. To a solution of the silylethanol **9** (0.1 g, 0.37 mmol) in pyridine (2 mL) stirred at 0 °C was added methanesulfonyl chloride (0.05 mL, 0.65 mmol). The mixture was stirred at room temperature for 3 h and then quenched with water (5 drops); then more water (20 mL) was added and this mixture stirred for 15 min. The mixture was extracted with ether (3 × 20 mL), and the combined extracts were washed with aqueous copper sulfate (3 × 30 mL), water (3 × 20 mL), and aqueous sodium bicarbonate (3 × 20 mL), dried ($MgSO_4$), and evaporated down to a brown oil. Trituration with pentane gave a white solid. Recrystallization from ether gave **7** as colorless blocks, mp 150−153 °C (0.08 g, 45%). ^{1}H NMR (δ; $CDCl_3$): 0.478 (s, 12H); 2.627 (s, 12H); 7.36 (2H, d, J = 7.2 Hz); 7.47 (4H, m); 7.70 (2H, d, J = 7.8 Hz); 7.86 (2H, d, J = 8 Hz); 8.23 (2H, d, J = 6.9 Hz). ^{13}C NMR (δ; $CDCl_3$): 3.308, 47.415, 116.32, 125.253, 125.374, 125.400, 129.186, 134.768, 134.815, 136.497, 136.731, 153.183. ^{29}Si NMR ($CDCl_3$): −11.78 ppm (relative to tetramethylsilane). MS (m/z): [$M^{+\cdot}$] 472.2378; calcd for $C_{28}H_{36}N_2OSi_2$ 472.2366.

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Supporting Information Available: Tables giving X-ray crystal data for **6** and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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