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Structural Investigations into the β-Effect of Pentavalent Silicon

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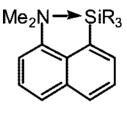
Ester and ether derivatives of 2-[(8-dimethylaminonaphthalen-1-yl)dimethylsilanyl]ethanol (**10a**) were prepared as part of a preliminary study to determine the β-effect of pentavalent silicon. The *p*-nitrobenzoate, 3,5-dinitrobenzoate, and *o*-nitrobenzoates ester derivatives **10e**−**10g**, which were characterized using X-ray crystallography, showed partial distortion of the silicon toward a trigonal bipyramidal geometry with the peri-nitrogen occupying one of the apical sites. The second apical site is occupied by a CH_3 substituent in **10e** and **10f**, while the CH_2CH_2OR substituent occupies the apical position in **10g**. The C−OR bond distances in these structures were lengthened compared to standard values, consistent with the presence of a strong $\sigma-\sigma^*$ interaction between the $\sigma_{\text{C-Si}}$ bonding orbital and the $\sigma^*_{\text{C-OR}}$ antibonding orbital.

Introduction

Hypercoordinate silicon compounds have generated much interest, particularly in the studies of nucleophilic substitution at 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.[1–4] Pentavalent silicon substituents have also been investigated as alternatives to tetravalent tin substituents in Stille cross-coupling reactions.[5,6]

Stable N→Si coordination complexes are generally characterized by the presence of a chelate ring having covalent bonds to silicon on one side and a dative N···Si bond on the other, the most widely studied of these being the silatranes.[7,8] In the dimethylaminonaphthalene derivative (**1**) the peri disposition between the nitrogen and silicon substituents places the donor nitrogen atom in close proximity to the silicon center and enhances the donor–acceptor interaction. This interaction is, however, also evident in structures (**2**) that are free from this geometrical constraint.[9]



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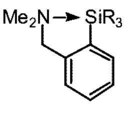

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The N···Si donor–acceptor distances in these complexes are significantly longer than normal single-bond lengths for the pair of atoms involved, but substantially shorter than the sum of van der Waals radii of nitrogen and silicon, which is 3.65Å.[10] In these molecules the tetrahedral arrangement of substituents around the silicon is distorted by the coordinated nitrogen that "caps" one of the tetrahedral faces, the degree of distortion being dependent on the length and hence strength of the N···Si interaction, with distances ranging from 2.5 to 3.0 Å determined from crystallographic data.[11–13] The strength of the N···Si bonding interaction can be also be inferred in solution from the ^{29}Si NMR chemical shift.[14–17] In molecules related to **1** the distance between the peri-dimethylamino and silyl groups and also the geometry at the silicon are very sensitive to the Lewis acidity of the silicon center.[18] Thus, in the weakly Lewis acidic silane **3** the N···Si distance is 2.969Å[19] with small distortions from tetrahedral toward a trigonal bipyramidal geometry at the silicon, with the peri-nitrogen and the −OEt substituent defining the apical positions. By comparison the more strongly Lewis acidic trifluorosilane **4** has an N···Si distance of 2.287 Å[20] (and 2.318 Å for the second molecule in the asymmetric unit) and a near idealized trigonal bipyramidal geometry at the silicon.

Our interest in pentavalent silicon complexes arises from our interest in the silicon β-effect, which describes the ability of a

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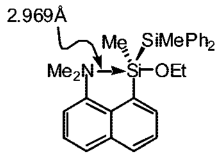

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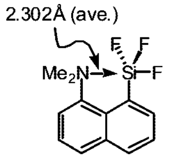

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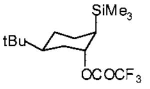
silicon substituent to stabilize positive charge at the β-position by hyperconjugation (Figure 1).

The β-effect of tetravalent silicon is nicely demonstrated by the solvolyses studies of Lambert and co-workers in which the trimethylsilyl- substituted trifluoroacetate **5** was shown to undergo unimolecular solvolysis at a rate 10^{12} times faster than cyclohexyl trifluoroacetate.[21] It was later shown that the silicon β-effect manifests in the ground-state structures of β-trimethylsilyl-substituted esters, as observable lengthening of the β C−O(ester) bond distance compared with silicon-free analogues. For example, the *p*-nitrobenzoate derivative **6** exhibits a C−OPNB distance of 1.487(2) Å, which is significantly longer than the silicon-free derivative **7** (1.473(2) Å).[22,23] The bond lengthening in **6** and other similarly substituted esters was rationalized as arising from a hyperconjugative-like $\sigma_{\text{C-Si}}-\sigma^*_{\text{C-O}}$ interaction, which is maximized in the antiperiplanar geometry. It has also been shown that the degree of bond lengthening of the β C−O distance is dependent on the σ-donor ability of the β-metal substituent. Thus β-trimethylgermyl and β-trimethylstannyl substituents have even larger bond-lengthening effects on C−O bond distances at the β-position.[23]



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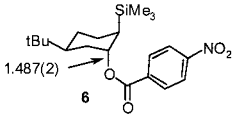

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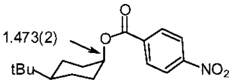

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The carbon−silicon bond is a strong σ-donor orbital, due to the fact that the C−Si bond is high energy and hence polarizable, and the electrons in the C−Si bond are polarized toward the carbon, resulting in effective overlap with an adjacent electron-deficient orbital.

We were intrigued to determine the σ-donor ability of a C−Si bond where the silicon is pentavalent. The C−Si bonds in pentavalent silicon substituents should be even stronger σ-donors and therefore exhibit a stronger β-effect, particularly if the bond is at the apical position of the trigonal bipyramid defined by the silicon and its five substituents. Qualitative evidence exists that suggests that pentavalent silicon does indeed exert a stronger β-effect; for example the allyl siliconate **8** reacts readily with aldehydes via the β-silyl carbenium ion intermediate **9** (Scheme 1)[24] to give allyl transfer products. In contrast, reaction of simple allyltrialkylsilanes with aldehydes requires the presence of a Lewis acid catalyst,[25] suggesting that the intermediate carbenium ion **9** enjoys a higher degree of stabilization by the pentavalent β-silicon compared with a similar intermediate that is stabilized by a tetravalent β-silicon.

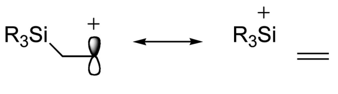
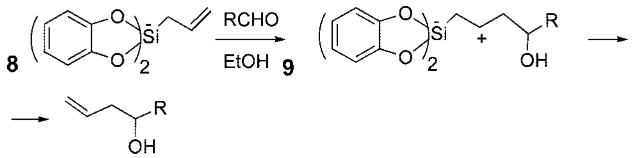


Figure 1. Schematic representation of β-silicon hyperconjugation.

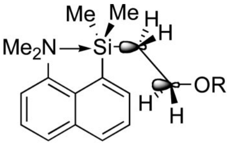
Scheme 1



Indirect evidence that a C−Si (pentavalent) bond has greater σ-donor ability than a C−Si (tetravalent) bond has also been provided from electrochemistry. Thus, the anodic oxidation potential for the removal of an electron from the C−Si bond in tetraalkylsilanes R_4Si (2.6 V vs Ag/Ag^+) was found to be significantly decreased in the presence of fluoride ion (2.3 V vs Ag/Ag^+). It was proposed that in the presence of fluoride ion it was the pentavalent species R_4SiF^- that was being oxidized.[26]

The suggestion that pentavalent silicon intermediates may well be involved in many silicon-directed reactions, which formally involve generation of positive charge β to tetracoordinate silicon substituents,[27] has made it important to quantify the β-effect of pentavalent silicon. Toward this end, we proposed to undertake a structural study of model compounds containing pentavalent silicon substituents with electron-deficient centers at the β-position.

We chose the model system **10**, where the peri interaction between the NMe_2 and silicon substituents forces the silicon center to become distorted toward a trigonal bipyramidal geometry.[1,2] We expected that the silicon to nitrogen interaction would strongly influence the strength of the σ−σ* interaction between the $Si-CH_2$ σ-bond and the CH_2-OR σ* antibonding orbital and vice versa.



10a; R = H
10b; R = 2,4-(NO_2)-C_6H_3
10c; R = 4-NO_2-C_6H_4
10d; R = 3-NO_2-C_6H_4CO
10e; R = 4-NO_2-C_6H_4CO
10f; R = 3,5-(NO_2)-C_6H_3CO
10g; R = 2-NO_2-C_6H_4CO
10h; R = 2,4-(NO_2)-C_6H_3CO

Results and Discussion: Synthesis

The alcohol precursor **10a** was prepared according to Scheme 2.[28] Thus, treatment of **11** with *n*-BuLi[16] followed by addition of chlorodimethylvinylsilane was followed by chromatographic purification from polymeric byproduct.[28] Reduction of the vinyl silane **12** with 9-BBN followed by oxidative workup gave the desired alcohol **10a**.

The alcohol **10a** was converted into the ester and ether derivatives **10b**−**10h** using standard techniques. The esters were

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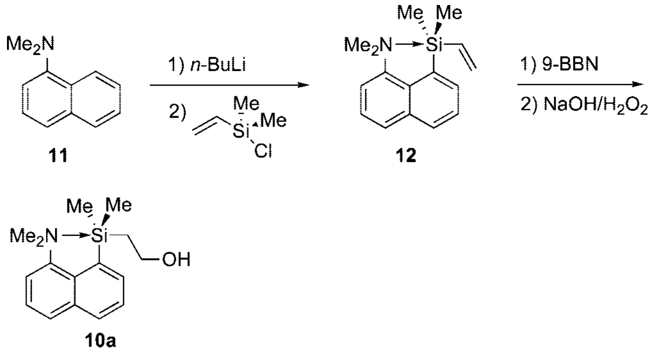
Scheme 2



prepared by treating the alcohols with appropriate acid chloride in the presence of anhydrous pyridine, while the aryl ethers were prepared by treating the sodium alkoxide derivative of **10a** with the appropriate fluorophenyl derivative. The derivatives of the model system were chosen to impart crystalline properties to the model substrates and to cover a wide range of reactivities.

Results and Discussion: Molecular Structures

The esters **10e**, **10f**, and **10g** were the only derivatives that gave crystals of suitable quality for X-ray analysis. Thermal ellipsoid diagrams for **10e**–**10g** are presented in Figure 2, selected structural parameters are summarized in Table 1, and crystal data and structure refinement details are presented in Table 2. The N(1)···Si(1) distances for **10e**–**10g**, which are 2.938, 2.942, and 2.927 Å, respectively, are well within the sum of the van der Waals radii for N and Si (3.65Å).[18]

Steric repulsion between the NMe$_2$ and SiR$_3$ substituents in all three structures manifests in a twisting of the naphthalene ring from planarity with Si(1) lying above the plane defined by the fused aromatic rings and N(1) lying below the same plane. Thus, in **10e**–**10g**, Si(1) is above the plane by +0.64°, +0.63°, and +0.86° respectively, while N(1) is below the plane by −0.40°, −0.34°, and −0.41°, respectively. The peri interaction between the nitrogen and silicon substituents also leads to small but noticeable distortion of Si(1) toward the trigonal bipyramidal geometry, with discernible basal and apical substituents. The three structures adopt two fundamentally different arrangements of the substituents at the silicon; in **10e** and **10f** the basal plane is defined by the aromatic carbon, one methyl substituent, and the −CH$_2$CH$_2$OR substituent, with the apical positions occupied by a methyl group and the peri nitrogen. In contrast, in **10g**, the −CH$_2$CH$_2$OR substituent and the peri nitrogen occupy the apical positions. Another important difference in these structures arises from the conformation of the −CH$_2$CH$_2$OR substituent; in **10e** and **10g** this moiety adopts the antiperiplanar geometry, whereas in **10f** the −CH$_2$CH$_2$OR substituent is gauche. The gauche conformation of the −CH$_2$CH$_2$OR moiety in **10f** was unexpected, but examination of the crystal-packing diagram (Figure 3) suggests that it allows for a favorable packing arrangement, with π-stacking of the electron-deficient 3,5-dinitrobenzoate aromatic ring in between the relatively electron-rich naphthalene rings.

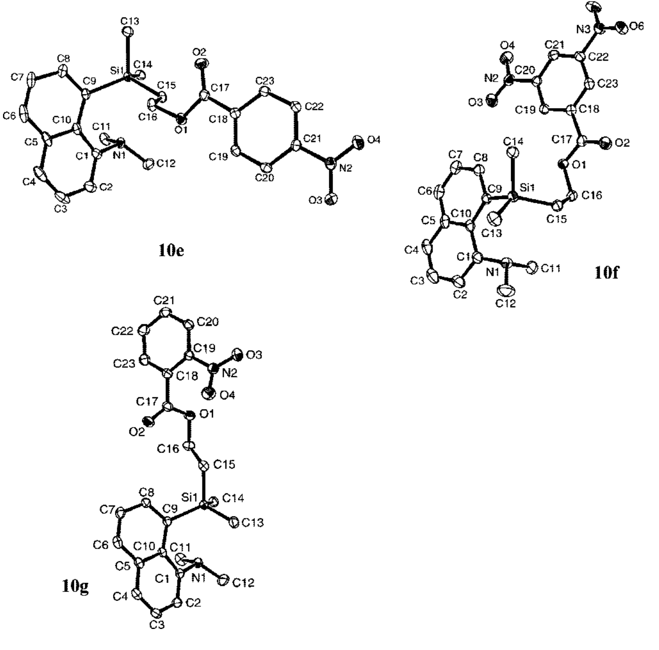


Figure 2. Molecular structures of esters **10e**–**10g**. Ellipsoids are at the 20% probability level.

Table 1. Selected Structural Parameters for 10e–10g

	10e	10f	10g
	Distances (Å)		
N1···Si	2.938(2)	2.942(2)	2.927(2)
Si–C9	1.917(2)	1.898(3)	1.904(2)
Si–C13	1.898(3)	1.867(3)	1.861(2)
Si–C14	1.879(3)	1.882(3)	1.865(2)
Si–C15	1.897(3)	1.891(3)	1.914(2)
C15–C16	1.506(4)	1.514(4)	1.498(3)
C16–O1	1.477(3)	1.468(3)	1.475(2)
	Angles (deg)		
N1···Si–C9	69.26	69.65	69.07
N1···Si–C13	173.28	76.21	82.13
N1···Si–C14	76.45	174.52	76.04
N1···Si–C15	81.49	81.82	173.95
C9–Si–C13	105.37(13)	112.55(14)	109.09(10)
C9–Si–C14	121.22(12)	105.95(12)	120.52(10)
C9–Si–C15	110.15(11)	118.05(11)	105.80(9)
C13–Si–C14	103.92(14)	103.10(16)	111.98(11)
C13–Si–C15	104.46(13)	111.99(14)	102.92(11)
C14–Si–C15	110.11(13)	103.39(13)	104.74(10)
Si–C15–C16–O1	195.4(2)	46.2(3)	−178.3(2)
mean C–Si–C (basal)	113.8	114.2	113.9
mean C(apical)–Si–C(basal)	104.6	104.1	105.4
mean N···Si–C(basal)	75.7	75.9	75.74

The apical Si–CH$_3$ bonds in **10e** and **10f** (mean 1.890 A) are significantly longer than the basal Si–CH$_3$ distances (mean 1.868 Å); furthermore the apical Si–CH$_2$ distance in **10g** (1.914 Å) is significantly longer than basal Si–CH$_2$ bonds in **10e** and **10f** (mean 1.894 Å). These structural effects are consistent with the expectation that apical bonds in pentavalent trigonal bipyramidal silicon are weaker and therefore longer than basal bonds. Lengthening of the Si(1)–C(15) bond length in **10g** can be rationalized as arising from donation of electron density from the peri nitrogen N(1) into the Si(1)–C(15) σ^* antibonding orbital (Figure 4).

Kirby et al. have derived equations that relate C–OR bond distances for various types of saturated carbon atoms to the pK_a value of the parent acid ROH.[29] For primary R′CH$_2$–OR bond distances this is given as

$$r_{\text{C-O}}/\text{Å} = (1.458\text{–}2.02) \times 10^{-3}\ \mathrm{p}K_a(\text{ROH}) \quad R^2 = 0.995 \quad (1)$$

The observed CH$_2$–OR bond distances for **10e**–**10g** along with those predicted from eq 1 are presented in Table 3; for

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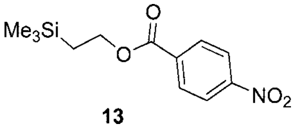
Table 2. Crystal Data and Structure Refinement Details for Compounds 10e−10g

	10e	**10f**	**10g**
empirical formula	$C_{23}H_{26}N_2O_4Si$	$C_{23}H_{24}N_3O_6Si$	$C_{23}H_{26}N_2O_4Si$
fw	422.55	466.54	422.55
temperature (K)	130(2)	200(2)	130(2)
radiation	Mo Kα	Cu Kα	Cu Kα
wavelength (Å)	0.71073	1.54180	1.54180
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	Pc	$P2_1/n$
unit cell dimens			
a (Å)	7.5985(11)	9.3410(10)	7.5840(10)
b (Å)	41.416(6)	10.4430(10)	13.923(2)
c (Å)	7.2772(11)	11.710(4)	20.265(3)
α (deg)	90	90	90
β (deg)	106.158(2)	99.72(2)	91.37(2)
γ (deg)	90	90	90
V (Å^3)	2199.7(6)	1125.9(4)	2139.2(5)
Z	4	2	4
D_c (Mg/m^3)	1.279	1.376	1.312
μ (mm$^{-1)}$	0.138	1.314	1.237
F(000)	900	490	896
cryst size (mm^3)	0.5 × 0.25 × 0.07	0.2 × 0.18 × 0.03	0.40 × 0.36 × 0.15
θ range (deg)	0.98−25.00	4.23−74.84	3.85−74.91
no. of reflns collected	21 104	2466	4516
indep	3866 [R_{int} = 0.0709]	2466 [R_{int} = 0.0000]	4237 [R_{int} = 0.0318]
obsd	3707	2339	3834
no. of data/restraint/params	3866/0/276	2466/2/399	4237/0/376
GOF on F^2	1.287	1.017	1.013
final R indices [$I > 2\theta(I)$]	R1 = 0. 0597, wR2 = 0.1490	R1 = 0.0314, wR2 = 0.0832	R1 = 0.0484, wR2 = 0.1272
R indices (all data)	R1 = 0.0618, wR2 = 0.1500	R1 = 0.0335, wR2 = 0.0851	R1 = 0.0532, wR2 = 0.1318
weighting scheme[a]			
A and B	A = 0.0388, B = 2.4686	A = 0.0643, B = 0.0559	A = 0.0644, B = 1.8358
largest diff peak/hole (e Å^{-3})	0.339 and −0.838	0.230 and −0.186	0.795 and −0.541

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

comparison purposes the structural data for **13**, which incorporates a tetravalent silicon substituent, are included.[30]



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In compounds **10e** and **10g**, which have an antiperiplanar Si−CH$_2$−CH$_2$−OR fragment, the observed C−OR bond distances are both significantly longer than those predicted from eq 1 for "normal" CH$_2$−OR bond distances, demonstrating the presence of strong σ−σ* interactions between the $\sigma_{C\text{-}Si}$ bonding orbital and the $\sigma^*_{C\text{-}O}$ antibonding orbital. In contrast compound **10f**, in which the Si−CH$_2$−CH$_2$−OR adopts the gauche conformation, the −OR bond distances is lengthened to a smaller extent, consistent with reduced overlap between the $\sigma_{C\text{-}Si}$ bonding orbital and the $\sigma^*_{C\text{-}O}$ antibonding orbital. Smaller, but systematic effects on the C15−C16 bond distance in these structures are also observed; in **10e** and **10g** the CH$_2$−CH$_2$ bond distance is shorter than **10f**, consistent with the expected CH$_2$−CH$_2$ bond strengthening effect of the σ−σ* interaction.

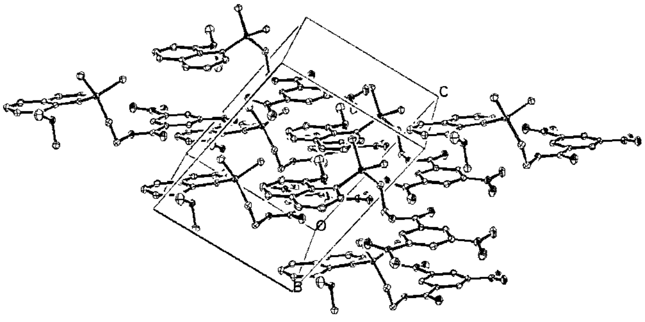

Figure 3. Partial packing diagram of **10f** showing the π-stacked arrangement of the naphthalene and dinitrobenzoate rings.

The CH$_2$−O bond distance in the *p*-nitrobenzoate ester **10e** (1.477(3) Å) is longer than that observed in trimethylsilylethyl *p*-nitrobenzoate (**13**), which is 1.468(2) Å, suggesting that the Si−CH$_2$ bond in the partially pentavalent silicon substituent in **10e** is a stronger σ-donor than the tetracoordinate trimethylsilyl substituent.

Conclusions

The low-temperature X-ray structures of **10e**−**10g** show clear distortion of the silicon from tetrahedral toward trigonal bipyramidal geometry. Structural effects consistent with strong σ−σ* interactions between the pentavalent C−Si bond and the $\sigma^*_{C\text{-}OR}$ antibonding orbital in the β-position are clearly present in those structures having an antiperiplanar Si−CH$_2$CH$_2$−OR

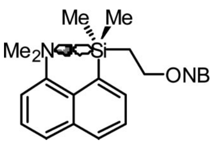

Figure 4. Orbital interaction between N(1) nonbonded electrons and the Si(1)−C(15) σ* antibonding orbital for **10g**.

Table 3. Observed and Calculated CH$_2$−OR Bond Distances for 10e−10g and 13

compound	pK_a (ROH)	observed (CH$_2$−OR)	predicted (CH$_2$−OR)[a]	Δ (Å)
10e	3.43	1.477(3)	1.451	0.027
10f	2.85	1.468(2)	1.452	0.016
10g	2.17	1.475(2)	1.453	0.022
13	3.43	1.468(2)	1.451	0.017

[a] Calculated from eq 1.

moiety. Thus significant lengthening of the C−OR bond distance is observed in **10e** and **10g**, and effects on the CH_2-CH_2 distance are smaller and barely significant. The strength of the $\sigma_{\text{C-Si}}-\sigma^*_{\text{C-O}}$ interaction for these pentavalent silicon substituents appears to be stronger than the corresponding interaction involving tetravalent silicon, in agreement with qualitative observations on the relative reactivities of molecules containing tetravalent[25] and pentavalent[24] silicon substituents.

Experimental Section

General Considerations. All fine chemicals were used as received from Aldrich Chemical Co. Inc. Anhydrous pyridine was distilled from calcium hydride and stored over 4 Å molecular sieves. Anhydrous tetrahydrofuran (THF) and anhydrous diethyl ether (Et_2O) were distilled from sodium benzophenone ketyl and sodium metal under a nitrogen atmosphere and distilled immediately prior to use. *tert*-Butyllithium was standardized according to literature procedure.[35] Petroleum ether (petrol) refers to the fraction boiling at 40–60 °C. Where necessary, all air- and moisture-sensitive reactions were performed in flame-dried glassware under a nitrogen atmosphere, which was purified by passage over activated 4 Å molecular sieves and BASF R3-11 copper catalyst. Flash column chromatography was carried out using Merck silica gel 60 (230–400 mesh ASTM). Analytical thin-layer chromatography (TLC) was carried out using aluminum-backed 2 mm thick Merck silica gel 60 GF254. Compounds were visualized under UV365 nm light or iodine. Melting points (mp) were determined on single crystals using a Reichert-Jung hot stage melting point apparatus and are uncorrected. Nuclear magnetic resonance (NMR) spectra for ^1H, ^{13}C, and ^{29}Si nuclei were recorded using a Varian Unity 300 NMR spectrometer operating at 300, 75.5, and 59.58 MHz, respectively. All NMR spectra were obtained in deuterochloroform solutions ($CDCl_3$) at ambient temperature with residual chloroform as internal reference, unless otherwise stated. Proton-decoupled ^{13}C NMR chemical shifts were referenced on the center peak of $CDCl_3$ (δ 77.0 ppm). Proton-decoupled ^{29}Si was externally referenced to tetramethylsilane (δ 0 ppm).

Crystallography. Data for structure **10e** were collected on a Bruker SMART Apex CCD detector using Mo Kα radiation (graphite crystal monochromator $\lambda = 0.71073$). Data were reduced using the program SAINT.[31] **10f** and **10g** were collected on an Enraf-Nonius CAD-4 diffractometer using Mo Kα radiation ($\lambda = 0.71069$ Å, graphite monochromator) or Ni-filtered Cu Kα radiation ($\lambda = 1.5418$ Å) at 130.0(1) K. The crystals were mounted on a glass fiber usually using low-temperature silicone oil and were then flash frozen by placing directly on a goniometer head under a stream of nitrogen gas at 130 K. The temperature was controlled using an Oxford Cryostream cooling device. The data were corrected for Lorentz and polarization effects[32] for absorption where appropriate (ABSORB)[33] and extinction[34] where appropriate. Structures were solved by direct methods (SHELXS-86)[34] and were refined on F^2 (SHELXL-97).[35] All non-hydrogen atoms were refined anisotropically, while the treatment of hydrogen atoms depended on the data/reflection ratio. In some structures hydrogen atoms were refined isotropically without restraint, while in others they were constrained. Thermal ellipsoids plots were generated using the program ORTEP-3.[36] All programs were implemented within the suite WINGX.[37]

Synthesis. [8-(Dimethylvinylsilanyl)naphthalen-1-yl]dimethylamine (11). To a cooled (−78 °C) solution of *N*,*N*-dimethyl-1-naphthylamine **10** (2.50 g, 0.0146 mol) in anhydrous Et_2O (20 mL) was added *tert*-butyllithium in hexane (2.4 M, 8.1 mL, 0.022 mol). The reaction was stirred at room temperature for 24 h (during which time a yellow precipitate of 1-lithio-8-dimethylaminonaphthalene etherate formed). This suspension was then chilled (0 °C) before chlorodimethylvinylsilane (1.85 g, 0.0146 mol) was added to the yellow suspension and then stirred at room temperature for a further 24 h. The resulting mixture was filtered and the solvent removed *in vacuo* to give a viscous yellow oil. This was then taken up in CH_2Cl_2 and washed with aqueous HCl solution (0.25 M) several times, 10% aqueous $NaHCO_3$ solution, and water, dried ($MgSO_4$), filtered, and concentrated *in vacuo* to give a viscous oil, which was purified by column chromatography (petrol, $R_f = 0.30$) to afford **12** as a pale yellow viscous oil (1.85 g, 19%). ^1H NMR: δ 0.34 (6H, s), 2.53 (6H, s), 5.64 (1H, dd, $J = 20.4$, 3.7 Hz), 5.90 (1H, dd, $J = 14.70$, 3.7 Hz), 6.41 (1H, dd, $J = 20.4$, 14.70 Hz), 7.27 (1H, d, $J = 7.2$ Hz), 7.40 (2H, m), 7.59 (1H, d, $J = 8.1$ Hz), 7.78 (1H, d, $J = 8.1$ Hz), 7.83 (1H, d, $J = 6.6$ Hz). ^{13}C NMR: δ 0.32, 47.44, 116.33, 125.14, 125.18, 125.52, 128.32, 129.50, 134.42, 134.54, 134.81, 136.35, 142.60, 153.21. ^{29}Si NMR: δ −15.62. HRMS (ESI): calcd for $C_{16}H_{22}NSi^+$ $[M + H]^+$ 256.1522, found 256.1518.

2-[(8-Dimethylaminonaphthalen-1-yl)dimethylsilanyl]ethanol (10a). To a solution of dimethylaminonaphthylvinylsilane **12** (3.89 mg, 15.2 mmol) in anhydrous THF (60 mL) was added dropwise 9-BBN in THF (0.5 M, 61 mL, 30.5 mmol). The reaction was stirred at room temperature overnight, then poured into water and stirred for a further 30 min. Then aqueous NaOH (40 mL, 3 M) was added in one portion, followed by dropwise addition of H_2O_2 (40 mL, 30%) to the chilled (0 °C) solution. The resulting mixture was then stirred until it reached room temperature, and the resulting mixture was extracted with Et_2O. The combined organic extracts were washed with saturated aqueous NaCl solution and water, dried ($MgSO_4$), filtered, and concentrated *in vacuo* to afford a pungent viscous yellow oil, which was then purified by column chromatography (CH_2Cl_2/Et_2O, $R_f = 0.46$) followed by distillation (140 °C/15 mmHg) to give **8a** as a yellow oil (3.51 g, 84%). ^1H NMR: δ 0.35 (6H, s), 1.27 (2H, t, $J = 8.6$ Hz), 1.42 (1H, bs), 2.61 (6H, s), 3.64 (2H, t, $J = 8.6$ Hz), 7.31 (1H, m), 7.43 (2H, m), 7.62 (1H, m), 7.79 (2H, m). ^{13}C NMR: δ 0.68, 23.08, 47.22, 60.73, 116.19, 125.01, 125.24, 125.55, 129.55, 134.36, 134.84, 135.82, 153.04, 155.51. ^{29}Si NMR: δ −9.36. HRMS (ESI): calcd for $C_{16}H_{23}NNaOSi^+$ $[M + Na]^+$ 296.1447, found 296.1451.

(8-{[2-(2,4-Dinitrophenoxy)ethyl]dimethylsilanyl}naphthalen-1-yl)dimethylamine (10b). To a suspension of KH (100 mg, 0.5 mmol) in anhydrous THF (10 mL) was added a solution of alcohol **12** (100 mg, 0.37 mmol) in anhydrous THF (10 mL). The resulting solution was stirred at room temperature for 1 h, then cooled (−78 °C) before a solution of 1-fluoro-2,4-dinitrobenzene (75 mg, 0.4 mmol) in anhydrous THF (10 mL) was added. The reaction was then stirred at room temperature for 24 h, then diluted with water. The resulting mixture was then extracted with Et_2O. The combined organic extracts were washed with water, dried ($MgSO_4$), filtered, and concentrated *in vacuo* to afford **10b** as a yellow oil (11.3 mg, 7%). ^1H NMR: δ 0.46 (6H, s), 1.54 (2H, t, $J = 8.7$ Hz), 2.62 (6H, s), 4.12 (2H, t, $J = 8.7$ Hz), 6.72 (1H, d, $J = 9.9$ Hz), 7.33 (1H, m), 7.44 (2H, m), 7.63 (1H, m), 7.81 (2H, m), 8.19 (1H, d, $J = 6.9$ Hz), 8.68 (1H, d, $J = 3$ Hz). ^{13}C NMR: δ 0.78, 18.35, 30.33, 47.20, 67.22, 114.36, 116.25, 125.30, 125.450, 125.76, 125.79, 129.86, 133.58, 134.39, 134.86, 136.00, 141.08, 152.94, 164.23. ^{29}Si NMR: δ −9.14.

(8-{Dimethyl-[2-(4-nitrophenoxy)ethyl]silanyl}naphthalen-1-yl)dimethylamine (10c). To a suspension of NaH (100 mg, 4.8 mmol) in anhydrous THF (10 mL) was added a solution of alcohol

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(31) *Siemens 1999, SMART, SAINT, SADABS*; Siemens Analytical X-ray Instruments Inc.: Madison, WI.

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12 (95 mg, 0.34 mmol) in anhydrous THF (10 mL). The resulting solution was stirred at room temperature for 1 h, then cooled (−78 °C) before a solution of 1-fluoro-4-nitrobenzene (53 mg, 0.38 mmol) in anhydrous THF (10 mL) was added. The reaction was then stirred at room temperature for 24 h, then diluted with water. The resulting mixture was then extracted with Et_2O. The combined organic extracts were washed with water, dried ($MgSO_4$), filtered, and concentrated *in vacuo* to afford a yellow oil, which was then purified by chromatography (petrol/Et_2O, $R_f = 0.30$) to give **10c** as a yellow oil (46.6 mg, 34%). ^{1}H NMR: δ 0.42 (6H, s), 1.45 (2H, t, $J = 8.4$ Hz), 2.61 (6H, s), 3.97 (2H, t, $J = 8.4$ Hz), 6.70 (2H, d, $J = 9.3$ Hz), 7.31 (1H, m), 7.44 (2H, m), 7.62 (1H, m), 7.81 (2H, m), 8.10 (2H, d, $J = 9$ Hz). ^{13}C NMR: δ 0.79, 18.31, 30.30, 47.24, 67.25, 114.33, 116.30, 125.11, 125.40, 125.71, 125.78, 129.82, 133.63, 134.33, 134.89, 135.91, 141.01, 152.91, 164.04. ^{29}Si NMR: δ −9.05. HRMS (ESI): calcd for $C_{22}H_{26}N_2NaO_3Si^+$ $[M + Na]^+$ 417.1610, found 417.1614.

2-[(8-Dimethylaminonaphthalen-1-yl)dimethylsilanyl]ethyl 3-nitrobenzoate (10d). A solution of the alcohol **10a** (106 mg, 0.38 mmol) in pyridine (2 mL) was stirred for 30 min and treated with 3-nitrobenzoyl chloride (108 mg, 0.58 mmol); the reaction was stirred for 24 h. After subsequent workup the product **10d** was afforded as a yellow oil, which was triturated from pentane, then recrystallized from pentane to give a yellow solid (144 mg, 88%). ^{1}H NMR: δ 0.43 (6H, s), 1.47 (2H, t, $J = 8.7$ Hz), 2.64 (6H, s), 4.40 (2H, t, $J = 8.7$ Hz), 7.32 (1H, d, $J = 7.5$ Hz), 7.43 (2H, m), 7.58 (2H, m), 7.78 (1H, d, $J = 8.1$ Hz), 7.84 (1H, d, $J = 6.6$ Hz), 8.23 (1H, d, $J = 7.8$ Hz), 8.37 (1H, d, $J = 8.4$ Hz), 8.78 (1H, s). ^{13}C NMR: δ 0.65, 18.54, 47.30, 65.11, 116.33, 123.40, 125.08, 125.33, 125.64, 126.97, 129.36, 129.74, 132.47, 133.58, 134.32, 134.87, 135.09, 135.89, 148.19, 152.91, 164.47. ^{29}Si NMR: δ −9.36. HRMS (ESI): calcd for $C_{23}H_{27}N_2O_4Si^+$ $[M + H]^+$ 423.1740, found 423.1729.

2-[(8-Dimethylaminonaphthalen-1-yl)dimethylsilanyl]ethyl 4-nitrobenzoate (10e). To a solution of alcohol **10a** (1 g, 3.6 mmol) in pyridine (10 mL) was added 4-nitrobenzoyl chloride (1 g, 5.5 mmol). The reaction was then stirred for 24 h. After subsequent workup the product **10e** was afforded as a yellow oil (1.46 g, 94%), which was triturated from pentane and then recrystallized from pentane to give pale brown plates, mp 102–103 °C. ^{1}H NMR: δ 0.42 (6H, s), 1.45 (2H, t, $J = 8.5$ Hz), 2.63 (6H, s), 4.39 (2H, t, $J = 8.4$ Hz), 7.32 (1H, d, $J = 7.2$ Hz), 7.43 (2H, m), 7.61 (1H, d, $J = 8.1$ Hz), 7.82 (2H, m), 8.05 (2H, d, $J = 9$ Hz), 8.23 (2H, d, $J = 8.7$ Hz). ^{13}C NMR: δ 0.67, 18.45, 47.33, 65.14, 116.36, 123.34, 125.11, 125.38, 125.69, 129.79, 130.51, 133.63, 134.33, 134.88, 135.90, 136.09, 150.30, 152.91, 164.73. ^{29}Si NMR: δ −9.28. HRMS (ESI): calcd for $C_{23}H_{26}N_2NaO_4Si^+$ $[M + Na]^+$ 445.1560, found 445.1559.

2-[(8-Dimethylaminonaphthalen-1-yl)dimethylsilanyl]ethyl 3,5-dinitrobenzoate (10f). A solution of alcohol **10a** (1 g, 3.68 mmol) in pyridine (10 mL) was treated with 3,5-dinitrobenzoyl chloride (1.7 g, 7.3 mmol), and the reaction was stirred for 48 h. After subsequent workup the product **10f** was afforded as a yellow-orange oil (1.34 g, 77%), which was triturated from pentane and then recrystallized from MeOH to give yellow plates, mp 115–117 °C. ^{1}H NMR: δ 0.45 (6H, s), 1.50 (2H, t, $J = 8.4$ Hz), 2.63 (6H, s), 4.45 (2H, t, $J = 8.4$ Hz), 7.31 (1H, d, $J = 7.2$ Hz), 7.39 (2H, m), 7.51 (1H, d, $J = 7.8$ Hz), 7.70 (1H, d, $J = 8.1$ Hz), 7.83 (1H, d, $J = 6.6$ Hz), 8.97 (2H, m), 9.17 (1H, m). ^{13}C NMR: δ 0.74, 18.53, 47.35, 66.21, 116.42, 121.92, 125.07, 125.25, 125.69, 129.20, 129.70, 133.35, 134.22, 134.78, 135.87, 148.45, 152.86, 162.34. ^{29}Si NMR: δ −9.41. HRMS (ESI): calcd for $C_{23}H_{25}N_3NaO_6Si^+$ $[M + Na]^+$ 490.1410, found 490.1418.

2-[(8-Dimethylaminonaphthalen-1-yl)dimethylsilanyl]ethyl 2-nitrobenzoate (10g). A solution of alcohol **10a** (233 mg, 0.85 mmol) in pyridine (2 mL) was stirred for 30 min and treated with 2-nitrobenzoyl chloride (237 mg, 1.2 mmol). The reaction was stirred for 24 h. After subsequent workup the product **10g** was afforded as a yellow-orange oil (328 mg, 91%), which was triturated from pentane and then recrystallized from MeOH to give yellow rods, mp 90–92 °C. ^{1}H NMR: δ 0.39 (6H, s), 1.44 (2H, t, $J = 8.9$ Hz), 2.62 (6H, s), 4.37 (2H, t, $J = 8.9$ Hz), 7.32 (2H, m), 7.43 (2H, m), 7.62 (3H, m), 7.83 (3H, m). ^{13}C NMR: δ 0.55, 18.02, 47.26, 65.88, 116.32, 125.71, 125.06, 125.28, 125.63, 128.11, 129.72, 131.35, 132.67, 133.52, 134.31, 134.83, 135.89, 148.18, 152.94, 165.41. ^{29}Si NMR: δ −9.49. HRMS (ESI): calcd for $C_{23}H_{26}N_2NaO_4Si^+$ $[M + Na]^+$ 445.1560, found 445.1557.

2-[(8-Dimethylaminonaphthalen-1-yl)dimethylsilanyl]ethyl 2,4-dinitrobenzoate (10h). A solution of alcohol **10a** (1 g, 3.7 mmol) in pyridine (10 mL) was treated with 2,4-dinitrobenzoyl chloride (1.3 g, 5.6 mmol), and the reaction was stirred for 18 h. After subsequent workup the product **10h** was afforded as a viscous orange oil (1.63 g, 93%), which was triturated from pentane and then recrystallized from MeOH to give pale yellow plates, mp 109–110 °C. ^{1}H NMR: δ 0.40 (6H, s), 1.45 (2H, t, $J = 8.85$ Hz), 2.63 (6H, s), 4.40 (2H, t, $J = 8.85$ Hz), 7.32 (1H, d, $J = 7.2$ Hz), 7.43 (2H, t, $J = 7.6$ Hz), 7.60 (1H, d, $J = 7.8$ Hz), 7.80 (2H, d, $J = 7.5$ Hz), 8.45 (2H, dd, $J = 8.4, 2.1$ Hz), 8.74 (1H, m). ^{13}C NMR: δ 0.54, 18.01, 47.24, 66.90, 116.37, 119.37, 125.04, 125.26, 125.67, 127.26, 129.74, 131.06, 133.24, 133.38, 134.22, 134.74, 135.84, 148.60, 152.83, 163.62. ^{29}Si NMR: δ −9.36. HRMS (ESI): calcd for $C_{23}H_{25}N_3NaO_6Si^+$ $[M + Na]^+$ 490.1410, found 490.1411.

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Supporting Information Available: Crystallographic information files for **10e**, **10f**, and **10g**. This material is available free of charge via the Internet at http://pubs.acs.org. All atomic coordinates, bond lengths and angles, and thermal parameters have also been deposited at the Cambridge Crystallographic Data Centre (CCDC) and have been assigned the CCDC codes 000000–000000, respectively.

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