

Reactions of Stable Silylenes with Organic Azides

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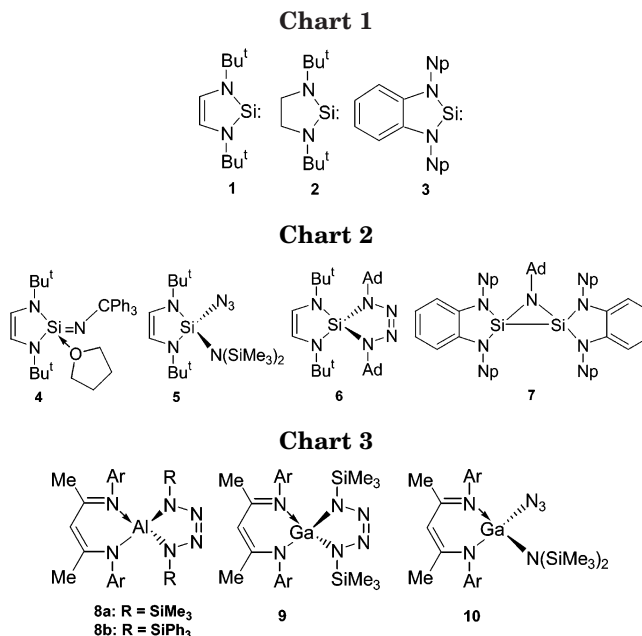
Summary: Reactions of *N*-heterocyclic stable silylenes **1** and **2** with various organic azides have been studied. Silylene **1** reacts with RN_3 ($R = \text{phenyl, } p\text{-tolyl, } Ph_3C, Ph_3Si$) to yield the spirocyclic silatetrazolines **11–14**. Silylene **2** reacts similarly to give derivatives **16–19**, except that with $R = p\text{-tolyl}$ a small amount of a μ^2 -azine-bridged tricyclic product **20** is also formed. The products are consistent with reactions proceeding through an unstable iminosilane intermediate. A definitive crystal structure for **2** is reported.

Introduction

Following the isolation of the thermally stable *N*-heterocyclic silylenes **1–3** in the mid 1990s (Chart 1),¹ several studies have examined their behavior toward a wide range of organic, inorganic, and organometallic substrates.² Among these, some reactions of **1** and **3** with organic azides have been reported.

The reactions of **1** with Ph_3CN_3 and Me_3SiN_3 in THF solution yielded the base-stabilized iminosilane **4** and the azidosilane **5**, respectively,³ both of which were structurally characterized (Chart 2). Silatetrazoline **6** was identified from the reaction of **1** with adamantyl azide (AdN_3).^{1b} A similar product was isolated from the equimolar reaction of **3** with AdN_3 , while the azadisilacyclopropane **7** was obtained from the 2:1 reaction,⁴ although neither of these species were crystallographically authenticated. Treatment of **3** with an equivalent of Me_3SiN_3 in THF yielded a base-stabilized azadisilacyclopropane derivative, while the use of 2 molar equiv of this azide produced an azidosilane.⁴

In related work, the reactions of various stable germylenes and stannylenes with organic azides have been examined,^{5,6} and the reaction of the *N*-heterocyclic carbene analogue of **1** with Me_3SiN_3 was recently reported.⁷ Roesky and co-workers observed that the



novel Al(I) compound $[HC(CMeNAr)_2]Al$ reacts with Me_3SiN_3 or Ph_3SiN_3 to give the corresponding tetrazolines **8** as the only products ($Ar = 2,6\text{-di-isopropylbenzene}$) (Chart 3).⁸ In contrast, the reaction of Me_3SiN_3 with the analogous Ga(I) species produced a mixture of the corresponding tetrazoline **9** and the isomeric azidogallane derivative **10** in an approximate 1:3 ratio.⁹

The chemistry of **2** has been investigated in less detail than that of **1** and **3**.² As the result of a delicate balance of steric and electronic factors, **2** exists in the solid state as a red, photo- and air-sensitive *Z*-diaminodisilyldisilene, with the colorless silylene predominant only in dilute solution.¹⁰ No reports have appeared concerning reactions of **2** with organic azides, and we were interested to see whether **2** might display different reactivity toward azides than **1** and **3**. We herein report the synthesis and X-ray crystallographic characterization of a range of new azide derivatives of **1** and **2**.

Results and Discussion

a. Reaction of Silylene 1 with Azides. Previous studies on the reactivity of stable silylenes toward organic azides employed THF as solvent. Since our goal was to isolate a base-free iminosilane, the coordinating

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Scheme 1. Reaction of Silylene 1 with Azides

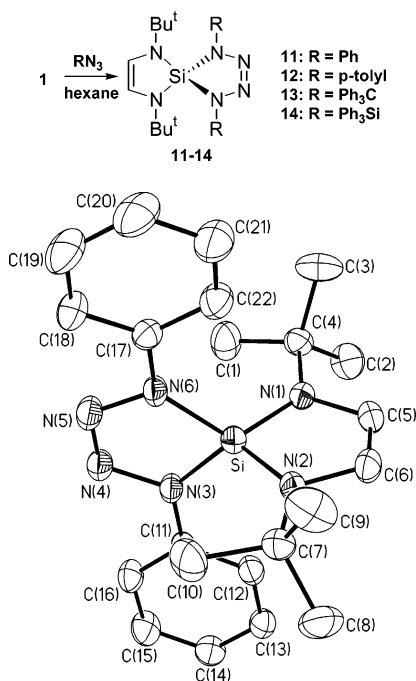


Figure 1. Thermal ellipsoid (40%) plot of **11** with H atoms omitted for clarity. Selected bond distances (Å): Si–N(1) 1.711(2), Si–N(2) 1.695(2), Si–N(3) 1.740(2), Si–N(6) 1.735(2), N(3)–N(4) 1.385(3), N(4)–N(5) 1.268(3), N(5)–N(6) 1.391(3). Selected bond angles (deg): N(1)–Si–N(2) 94.29(11), N(1)–Si–N(3) 119.08(11), N(1)–Si–N(6) 121.05(11), N(2)–Si–N(3) 119.83(11), N(2)–Si–N(6) 119.86(12), N(3)–Si–N(6) 85.53(11).

properties of THF (as evidenced by **4**) led us to select a noncoordinating solvent in which to study these reactions. Treatment of phenyl, *p*-tolyl, triphenylmethyl, or triphenylsilyl azide (**A–D**, respectively) with an equivalent of **1** in hexane solution at room temperature was accompanied by evolution of N₂ and yielded the white, air-stable solids **11–14** (Scheme 1). ¹H, ¹³C{¹H}, and ²⁹Si{¹H} NMR data indicated these compounds to be silatetrazolines. Formation of **11–14** is accompanied by a large shift to low frequency in the ²⁹Si NMR spectrum relative to the free silylene, from 78 ppm for **1** to ca. –53 ppm for **11–13** and –38.2 ppm for **14**.

A single-crystal X-ray diffraction study confirmed **11** to be a spirocyclic silatetrazoline, consisting of a central silicon atom coordinated to four separate nitrogen atoms (Figure 1). The SiN₄ core is comprised of two planar, orthogonal rings fused at the silicon atom.

The Si–N_(silylene) bond distances in **11** are slightly shorter than in free **1** (Si–N(1) 1.695(2) and Si–N(2) 1.711(2) vs 1.747(4) Å, respectively),¹¹ while the Si–N_(azo) distances are very similar to each other (Si–N(3) 1.740(2) and Si–N(6) 1.735(2) Å). The C₂N₂Si ring retains its planarity (torsion angles N(1)–Si–N(2)–C(6) –1.0(2)°, N(2)–Si–N(1)–C(5) 0.6(2)°). The N(3)–N(4) and N(5)–N(6) distances (1.385(3) and 1.391(3) Å) are typical of N–N single bonds, while the N(4)–N(5) distance is much shorter (1.268(3) Å), indicative of a N=N bond. The N–Si–N bond angles of the SiN₄ core are in the range 85.5–121.0° and thus

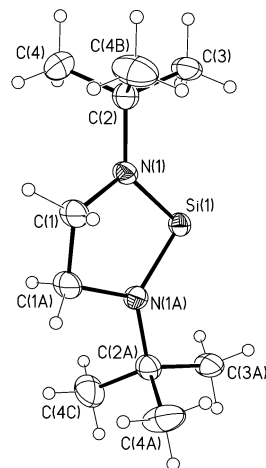


Figure 2. Thermal ellipsoid (40%) plot of **2**. Selected bond distances (Å): Si(1)–N(1) 1.719(3), N(1)–C(1) 1.489(6), N(1)–C(2) 1.468(5), C(1)–C(1A) 1.521(14). Selected bond angles (deg): N(1)–Si(1)–N(1A) 92.0(2), Si(1)–N(1)–C(1) 113.2(3), Si(1)–N(1)–C(2) 129.7(2).

significantly distorted from a regular tetrahedron. X-ray data were also obtained from small crystals of **14**. The quality of the data precludes detailed discussion of bond distances and angles but confirms **14** to be a silatetrazoline (see Supporting Information).

b. Crystal Structure of Silylene 2 and Its Reactions with Azides. Although first isolated and crystallographically characterized in 1996, initial (and subsequent) reports of **2** contained only selected bond data.^{1b} We now report the complete X-ray crystallographic data for the monomeric form of **2** (Figure 2). The molecule resides in two perpendicular crystallographic mirror planes and on a 2-fold axis formed at the intersection of these mirror planes. The two carbon atoms of the C₂N₂Si ring are equally disordered over a mirror plane.¹² The Si1–N1–C1–C1A–N1a heterocycle is in a twist conformation ³T₄, with the puckering amplitude *q*₂ of 0.289 Å and phase angle *φ*₂ of 90°. ¹³ The twisted conformation of **2** contrasts with the planarity of the C₂N₂Si ring of **1**, while the Si–N and N–C bond distances are similar to those observed for **1**. The packing diagram, shown in Figure 3, resembles that for **1** in the linear arrangement of the molecules.¹¹ There are no close intermolecular contacts.

Treatment of **2** with Me₃SiN₃ yielded a white, air-stable solid, which multinuclear NMR and single-crystal X-ray diffraction studies revealed to be an azidosilane. This species, **15**, is isostructural with **5** and has Si–N distances and N–Si–N angles very similar to this adduct (Figure 4).³

The reaction of **2** with azides **A–D** gave the silatetrazolines **16–19** (Scheme 2). **16**, **18**, and **19** were formed quantitatively (>98%) according to NMR spectroscopy and analytical data. The product from *p*-tolyl azide (**B**) consisted of two components, both of which were amenable to X-ray diffraction studies. The major product (ca. 95% by ¹H NMR) proved to be the silatetrazole **17**

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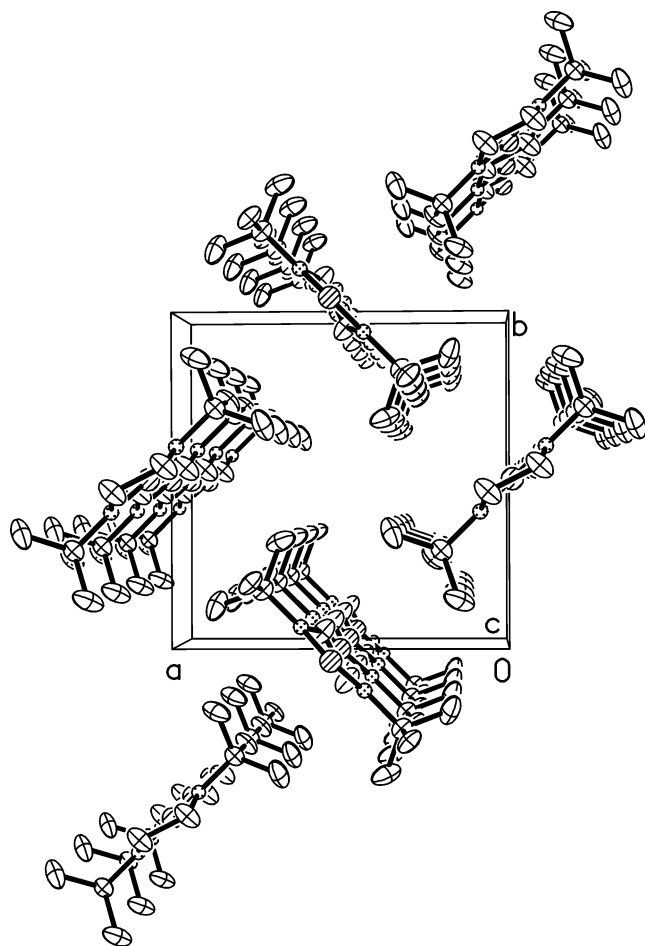


Figure 3. Packing diagram of **2** viewed along the crystallographic *c* axis.

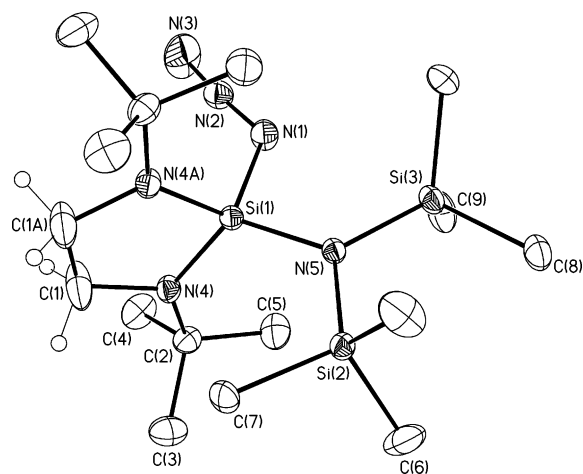
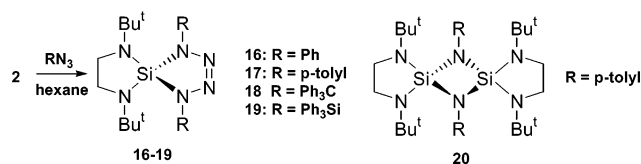


Figure 4. Thermal ellipsoid (40%) plot of **15**. Selected bond distances (Å): Si(1)–N(1) 1.773(2), Si(1)–N(4) 1.7132(17), Si(1)–N(5) 1.720(3), N(1)–N(2) 1.215(4), N(2)–N(3) 1.128(4). Selected bond angles (deg): N(1)–Si(1)–N(4) 111.90(8), N(1)–Si(1)–N(5) 99.35(11), N(4)–Si(1)–N(5) 119.73(7), N(1)–N(2)–N(3) 175.2(3).

($^{29}\text{Si}\{^1\text{H}\}$ NMR: δ –54.4 ppm, cf. 118.9 ppm for free **2**), while the minor product was the unusual μ^2 -azine-bridged dimer **20** ($^{29}\text{Si}\{^1\text{H}\}$ NMR: δ –55.7 ppm) (Figure 5).

The molecular structure of **17** strongly resembles that of **11**, with very similar Si–N distances and N–Si–N angles (see Supporting Information). Both Si–N(silylene)

Scheme 2. Reaction of Silylene **2** with Azides



bonds and the N(1)–C(1) and C(1)–C(2) bonds are shorter by ≤ 0.04 Å in **17** than in free **2** (1.719(3), 1.489(6), and 1.531(14) Å, respectively). The minor product, **20**, is a dimer consisting of two molecules of **2** linked by two μ^2 -*p*-tolyl azine units, with both phenyl groups tilted out of the plane of the bridge; this represents a new structural motif for silylene-azide adducts (Figure 5). The Si–N(azine) distances are in the range 1.742(2)–1.757(2) Å. The Si(1)–Si(2) separation distance is 2.596(1) Å.

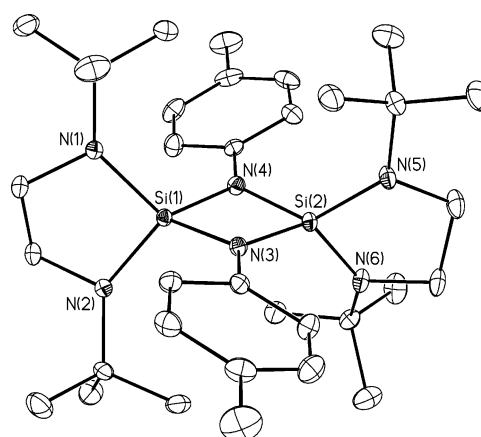
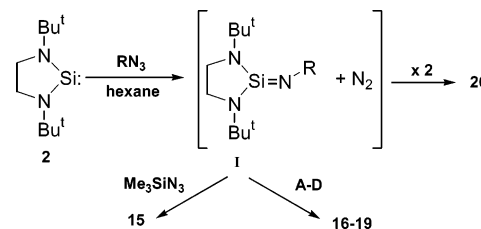


Figure 5. Thermal ellipsoid (40%) plot of **20** with H atoms omitted for clarity. Selected bond distances (Å): Si(1)–N(1) 1.730(2), Si(1)–N(2) 1.714(2), Si(1)–N(3) 1.743(2), Si(1)–N(4) 1.754(2), Si(2)–N(3) 1.757(2), Si(2)–N(4) 1.742(2), Si(2)–N(5) 1.728(2), Si(2)–N(6) 1.716(2). Selected bond angles (deg): N(1)–Si(1)–N(2) 94.80(10), N(1)–Si(1)–N(3) 130.48(10), N(1)–Si(1)–N(4) 111.97(10), N(2)–Si(1)–N(3) 112.86(10), N(2)–Si(1)–N(4) 126.97(10), Si(1)–N(3)–Si(2) 95.79(10), Si(1)–N(4)–Si(2) 95.95(10), N(5)–Si(2)–N(6) 94.74(10), N(5)–Si(2)–N(3) 111.94(10), N(5)–Si(2)–N(4) 130.73(11), N(6)–Si(2)–N(3) 126.86(11), N(6)–Si(2)–N(4) 112.86(10).

It is likely that formation of adducts **11**–**20** proceeds via an intermediate iminosilane **I** (shown for **2**) followed by reaction with a further azide molecule to yield the [2+3] cycloadducts **11**–**14** and **16**–**19** or the oxidative product **15** (Scheme 3). A similar route has been

Scheme 3. Proposed Pathway for Reaction of **2** with Azides



proposed for the formation of silatetazolines from the reaction of $\text{Me}_2\text{Si}(\text{Br})\text{CBr}(\text{SiMe}_3)_2$ with $^t\text{BuMeSiN}_3$ and

$n\text{BuLi}^{14}$ and for the reactions of **3** with Me_3SiN_3 and AdN_3 .⁴ Under the reaction conditions, we did not observe the formation of an azidodisilacyclopropane derivative akin to **7**, which would involve addition of a silylene to the Si=N bond of **I** as proposed by Gehrhus et al.⁴

Although the putative base-free iminosilane **I** was not observed directly,¹⁵ the molecular structure of **20** suggests its fleeting existence in solution, with the combination of two such units resulting in the observed product. Addition of a further molecule of RN_3 to **I** is evidently a more facile process than dimerization, however, since **20** was only isolated as a side product in very low yield. **I** is a plausible intermediate since reaction of **1** with Ph_3CN_3 in THF yielded the base-stabilized iminosilane **4**,³ although repeating the reaction in hexane resulted only in the silatetrazoline **12**. No reaction was observed between the germanium analogue of **1** and Ph_3CN_3 or Me_3SiN_3 in hexane at room temperature.

In summary, we have demonstrated that the saturated silylene **2** shows similar reactivity toward organic azides as its unsaturated counterparts **1** and **3**. Although a base-free iminosilane was not isolated, the molecular structure of **20** provides evidence for the role of such a species in the formation of **11**–**19** in noncoordinating solvents. The isolation of silatetrazolines rather than the target iminosilanes exemplifies the high reactivity of the latter species. It appears that for stable silylenes an iminosilane can be isolated only from a donor-solvent such as THF, in which the reactive intermediate is stabilized by base coordination to the silicon atom, as observed for **4**.³

Experimental Section

Silylenes **1**^{1a} and **2**¹⁶ and aryl azides¹⁷ were prepared by literature procedures, except Ph_3CN_3 and Ph_3SiN_3 , which were obtained commercially (Frinton Laboratories and Aldrich, respectively) and used as received. Me_3SiN_3 was also obtained from Aldrich. All reactions and manipulations were conducted under a dry dinitrogen atmosphere using standard Schlenk techniques, and all solvents were distilled from appropriate drying agents and degassed immediately prior to use. ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra were recorded in C_6D_6 solutions at room temperature on a Varian UNITY-500 spectrometer operating at 500 MHz for ^1H , 125.75 MHz for ^{13}C , and 99.38 MHz for ^{29}Si . Chemical shifts are reported in ppm using SiMe_4 as an internal standard. All compounds were synthesized by the same procedure, detailed below for **11**.

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11. To a solution of phenyl azide (0.055 g, 0.46 mmol) in hexane (5 mL) was added a solution of **1** (0.09 g, 0.46 mmol) in hexane (10 mL), and the mixture stirred at room temperature for 3 h. Concentration of the solvent in vacuo followed by storage at -20°C produced a colorless crystalline solid. Yield: 76 mg, 87%. ^1H NMR: 7.57 (d, 4H); 7.14 (t, 4H); 6.86 (t, 2H); 5.78 (s, 2H) 0.97 (s, 18H). $^{13}\text{C}\{^1\text{H}\}$ NMR: 142.5; 129.6; 123.3; 116.6; 110.1; 52.2; 29.9. $^{29}\text{Si}\{^1\text{H}\}$ NMR: -53.5 (s) ppm. Anal. Calcd for $\text{C}_{22}\text{H}_{30}\text{N}_6\text{Si}$: C, 64.99; H, 7.44; N, 20.67. Found: C, 64.67; H, 7.92; N, 20.62.

12. Yield: 95 mg, 88%. ^1H NMR: 7.51 (d, 4H); 6.95 (d, 4H) 5.81 (s, 2H); 2.04 (s, 6H) 1.01 (s, 18H). $^{13}\text{C}\{^1\text{H}\}$ NMR: 140.3; 130.2; 123.2; 116.6; 110.1; 52.3; 29.9. $^{29}\text{Si}\{^1\text{H}\}$ NMR: -53.4 (s) ppm. Anal. Calcd for $\text{C}_{24}\text{H}_{34}\text{N}_6\text{Si}$: C, 66.32; H, 7.88; N, 19.33. Found: C, 66.01; H, 8.02; N, 19.54.

13. Yield: 151 mg, 80%. ^1H NMR: 7.76–7.66 (m, 12H); 7.16–7.12 (m, 18H); 5.88 (s, 2H); 0.89 (s, 18H). $^{13}\text{C}\{^1\text{H}\}$ NMR: 147.6; 142.8; 131.2; 130.8; 127.6; 125.33; 109.6; 51.6; 29.7. $^{29}\text{Si}\{^1\text{H}\}$ NMR: -53.8 ppm. Anal. Calcd for $\text{C}_{48}\text{H}_{50}\text{N}_6\text{Si}$: C, 78.00; H, 6.82; N, 11.37. Found: C, 77.95; H, 6.76; N, 11.31.

14. Yield: 153 mg, 78%. ^1H NMR: 7.81–7.75 (m, 12H); 7.15–7.12 (m, 18H); 5.46 (s, 2H); 0.76 (s, 18H). $^{13}\text{C}\{^1\text{H}\}$ NMR: 136.8; 134.3; 130.1; 128.2; 109.6; 52.0; 30.1. $^{29}\text{Si}\{^1\text{H}\}$ NMR: -38.2 (s, SiN); -13.5 (s, SiPh_3) ppm. Anal. Calcd for $\text{C}_{46}\text{H}_{50}\text{N}_6\text{Si}_3$: C, 71.64; H, 6.53; N, 10.92. Found: C, 71.59; H, 6.48; N, 11.04.

15. Yield: 146 mg, 74%. ^1H NMR: 2.82 (m, 4H); 1.21 (s, 18H); 0.32 (d, 18H). $^{13}\text{C}\{^1\text{H}\}$ NMR: 51.4; 41.8; 29.9; 5.8; 5.3. $^{29}\text{Si}\{^1\text{H}\}$ NMR: -46.7 (SiN); 3.24, 2.08 (SiMe_3) ppm. Anal. Calcd for $\text{C}_{16}\text{H}_{40}\text{N}_6\text{Si}_3$: C, 47.95; H, 10.06; N, 20.96. Found: C, 48.01; H, 10.10; N, 20.93.

16. Yield: 177 mg, 86%. ^1H NMR: 7.54–7.50 (m, 4H); 7.18–7.13 (m, 4H); 6.89–6.87 (m, 2H); 2.96 (s, 4H); 0.94 (s, 18H). $^{13}\text{C}\{^1\text{H}\}$ NMR: 141.3; 129.4; 123.5; 115.7; 51.6; 41.2; 29.8. $^{29}\text{Si}\{^1\text{H}\}$ NMR: -53.5 ppm. Anal. Calcd for $\text{C}_{22}\text{H}_{32}\text{N}_6\text{Si}$: C, 64.67; H, 7.89; N, 20.57. Found: C, 64.60; H, 7.94; N, 20.59.

17. Yield: 183 mg, 83%. ^1H NMR: 7.53–7.50 (m, 4H); 7.18–7.15 (m, 4H); 6.91–6.87 (m, 2H); 2.97 (s, 4H); 2.05 (s, 6H); 0.94 (s, 18H). $^{13}\text{C}\{^1\text{H}\}$ NMR: 140.6; 130.1; 121.5; 117.0; 51.4; 41.2; 29.7; 20.8. $^{29}\text{Si}\{^1\text{H}\}$ NMR: -53.3 ppm. Anal. Calcd for $\text{C}_{24}\text{H}_{36}\text{N}_6\text{Si}$: C, 66.02; H, 8.31; N, 19.24. Found: C, 66.05; H, 8.26; N, 19.28.

18. Yield: 255 mg, 68%. ^1H NMR: 7.82–7.75 (m, 12H); 7.15–7.13 (m, 18H); 2.91 (s, 4H); 0.96 (s, 18H). $^{13}\text{C}\{^1\text{H}\}$ NMR: 149.7; 142.6; 131.2; 130.5; 126.6; 125.3; 51.9; 41.4; 29.3. $^{29}\text{Si}\{^1\text{H}\}$ NMR: -53.8 ppm. Anal. Calcd for $\text{C}_{48}\text{H}_{52}\text{N}_6\text{Si}$: C, 78.80; H, 7.07; N, 11.34. Found: C, 78.74; H, 7.13; N, 11.28.

19. Yield: 282 mg, 72%. ^1H NMR: 7.75–7.69 (m, 12H); 7.15–7.11 (m, 18H); 2.89 (s, 4H); 0.94 (s, 18H). $^{13}\text{C}\{^1\text{H}\}$ NMR: 142.5; 131.6; 130.6; 127.0; 125.5; 51.2; 41.5 29.9. $^{29}\text{Si}\{^1\text{H}\}$ NMR: -38.5 (SiN); -13.4 (SiPh_3). Anal. Calcd for $\text{C}_{46}\text{H}_{52}\text{N}_6\text{Si}_3$: C, 71.46; H, 6.78; N, 10.81. Found: C, 71.49; H, 6.72; N, 10.84.

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Supporting Information Available: X-ray experimental and structural data for **2**, **11**, **14**, **15**, **17**, and **20**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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