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Stable Silaimines with Three- and Four-Coordinate Silicon Atoms

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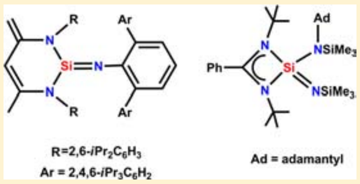
Supporting Information



ABSTRACT: The reactions of silylenes with organic azides are quite diverse, depending on the substituents of the silylene center and on the nature of the azide employed. Elusive silaimine with three-coordinate silicon atom $L^1SiN(2,6\text{-}Triip_2\text{-}C_6H_3)$ (**5**) {$L^1 = CH[(C{=}CH_2)(CMe)(2,6\text{-}iPr_2C_6H_3N)_2]$ and Triip = 2,4,6-triisopropylphenyl} was synthesized by treatment of the silylene L^1Si (**1**) with a sterically demanding 2,6-bis(2,4,6-triisopropylphenyl)phenyl azide ($2,6\text{-}Triip_2C_6H_3N_3$). The reaction of Lewis base-stabilized dichlorosilylene L^2SiCl_2 (**2**) {L^2 = 1,3-bis(2,6-$iPr_2C_6H_3$)imidazol-2-ylidene} with Ph_3SiN_3 afforded four-coordinate silaimine $L^2(Cl_2)SiNSiPh_3$ (**6**). Treatment of $2,6\text{-}Triip_2C_6H_3N_3$ with L^3SiCl (**3**) ($L^3 = PhC(NtBu)_2$) yielded silaimine $L^3(Cl)SiN(2,6\text{-}Triip_2\text{-}C_6H_3)$ (**7**) possessing a four-coordinate silicon atom. The reactions of $L^3SiN(SiMe_3)_2$ (**4**) with adamantyl and trimethylsilyl azide furnished silaimine compounds with a four-coordinate silicon atom $L^3(N(Ad)SiMe_3)\text{-}SiN(SiMe_3)$ (**8**) (Ad = adamantyl) and $L^3(N(SiMe_3)_2)SiN(SiMe_3)$ (**9**). Compound **8** was formed by migration of one of the $SiMe_3$ groups. Compounds **5**−**9** are stable under inert atmosphere and were characterized by elemental analysis, NMR spectroscopy, and single-crystal X-ray studies.

■ INTRODUCTION

Silylenes are the heavier analogues of carbenes, with the carbon atom replaced by a silicon atom.[1] Initially, these species were generated as short-lived reactive intermediates and studied by trapping experiments with other unsaturated substrates. The first stable silylene was isolated in 1994 by Denk et al.[2] as *N*-heterocyclic silylene (NHSi) using the same stabilization concept employed by Arduengo et al. to prepare the carbon analogue, *N*-heterocyclic carbene (NHC).[3] Since their first isolation, the stable silylenes emerged as versatile building blocks for novel silicon compounds, which were otherwise difficult to access using a conventional protocol. Remarkable advances in the reactivity studies of silylene compounds were made possible very recently due to the availability of these elusive species in high yield using very facile and safe methods.

The search for the formation of multiply bonded silicon compounds has attracted attention throughout the last decades and is still one of the most fascinating topics for silicon chemists. The availability of stable silylenes allows direct access to compounds with silicon−heteroatom (Si═X, X = O,[4] P,[5] S,[6] Se,[6a,b] Te,[6b] N[7]) multiple bonds. Key members of this class of compounds are silaimines ($R_2Si{=}NR'$, where R or R′ is alkyl or aryl group), which are considered highly reactive species due to the polarity of the $Si^{\delta+}-N^{\delta-}$ bond.[8] The first stable silaimines were isolated independently by Wiberg[9] and Klingebiel[10] in 1986 by thermal salt elimination through multistep reactions. However, direct methods for silaimine synthesis are limited, and silaimines with less bulky terminal groups are still scarce. A THF adduct of a silaimine was reported by West et al. by the reaction of a NHSi with sterically hindered Ph_3CN_3.[7] However, most of the reactions of NHSis including well-known L^1Si (**1**) ($L^1 = CH\{(C{=}CH_2)(CMe)(2,6\text{-}iPr_2C_6H_3N)_2\}$[11] with less bulky organic azides resulted in the formation of either azidosilane or silatetrazolines.[1a,12] In almost all of these reactions involvement of initial formation of an unstable silaimine as an intermediate was proposed, which further reacts with another molecule of organic azide to form azidosilane or silatetrazolin.

We have recently reported on the high yield access of Lewis base-stabilized silylenes,[13−16] L^2SiCl_2 (**2**) (L^2 = :C[N(2,6-$iPr_2C_6H_3$)CH]$_2$),[13] L^3SiCl (**3**) ($L^3 = PhC(NtBu)_2$),[14] and $L^3SiN(SiMe_3)_2$ (**4**)[15,16a] using very mild reducing agents. In the course of our studies on dichlorosilylene L^2SiCl_2 (**2**), we focused on probing the reactions with various organoazides. With sterically encumbered terphenyl azides $(2,6\text{-}Ar_2C_6H_3)N_3$ (Ar = 2,6-$iPr_2C_6H_3$, 2,4,6-$iPr_3C_6H_2$) **2** smoothly afforded the corresponding silaimine compounds.[17] However, when treated with AdN_3, it led to a functionalized *N*-heterocyclic carbene through the formation of unstable dichlorosilaimine as an intermediate.[18] From these observations it is evident that the alkyl or aryl substituent at the nitrogen atom of azides has a significant role in these reactions. This observation is further augmented by the reaction of L^3SiCl (**3**) with $CH(SiMe_3)N_2$, which resulted in a four-membered Si_2N_2 derivative via the formation of a silaimine complex that dimerizes in a [2 + 2] cycloaddition reaction due to its kinetic instability.[19a] A similar behavior was observed in the dehydrohalogenation of a silicon(IV) substituted diphenyl hydrazone derivative, where an unstable hydrosilaimine undergoes dimerization to afford a four-membered Si_2N_2 core.[19b] These results indicate that the steric protection is a crucial factor for obtaining stable silaimine compounds due to the polarized nature of the Si−N bond. This steric protection might be introduced by choosing either a

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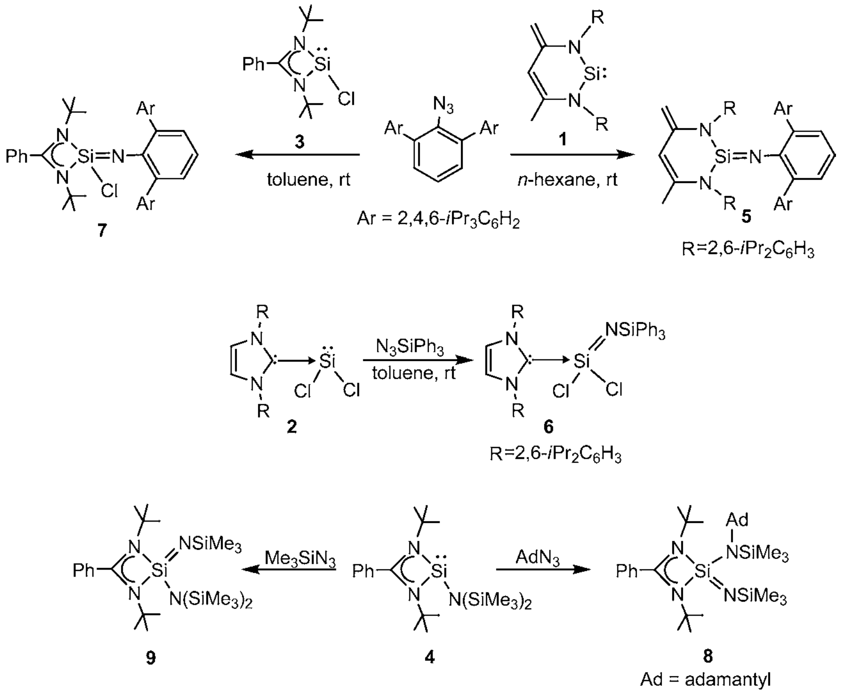
Scheme 1. Synthesis of Compounds 5−9



bulky ligand at the silicon atom or a sterically crowded substituent at the nitrogen atom. We recently prepared a stable bis-silaimine compound with terminal trimethylsilyl groups.[20a] Moreover, Kira et al. reported four base free silaimines with terminal Ph, CH$_2$Ph, SiMe$_3$, and Ad groups.[20b]

Apart from the chemistry of dichlorosilylene **2**, we have also investigated the reactions of two functionalized silylenes **3** and **4**, each of which possesses the same benzamidinato backbone,[1e] but no reactions with organic azides are known. Inspired by the varied reactivity shown by silylenes and in search for the silaimines with a three- and four-coordinate silicon atom, and for those with less bulky substituents at nitrogen, we carried out the reaction of the stable silylenes **1−4** with various organic substituted azides. Treatment of L^{1}Si (**1**) with 2,6-bis(2,4,6-triisopropylphenyl)phenyl azide resulted in the silaimine L^{1}SiN(2,6-Triip$_2$-C$_6$H$_3$) (**5**) (Triip = 2,4,6-triisopropylphenyl) containing a three-coordinate silicon atom. The reaction of base-stabilized dichlorosilylene L^{2}SiCl$_2$ (**2**) with Ph$_3$SiN$_3$ afforded L^2(Cl$_2$)SiNSiPh$_3$ (**6**) possessing a four-coordinate silicon atom. Similarly, treatment of stable monochlorosilylene L^{3}SiCl (**3**) with 2,6-Triip$_2$C$_6$H$_3$N$_3$ yields the four-coordinate silaimine L^3(Cl)SiN(2,6-Triip$_2$C$_6$H$_3$) (**7**). The reactions of L^{3}SiN(SiMe$_3$)$_2$ (**4**) with adamantyl and trimethylsilyl azides furnished four-coordinate silaimine compounds L^3(N(Ad)-SiMe$_3$)SiN(SiMe$_3$) (**8**) (Ad = adamantyl) and L^3(N(SiMe$_3$)$_2$)-SiN(SiMe$_3$) (**9**), respectively. Silaimines **5−9** are stable under an inert atmosphere and were fully characterized by physical methods. The molecular structures of **5**, **6**, **8**, and **9** were established unambiguously by single-crystal X-ray structure analyses.

■ RESULTS AND DISCUSSION

The reaction of **1** with 2,6-bis(2,4,6-triisopropylphenyl)phenyl azide in equimolar ratio afforded the three-coordinate silaimine derivative **5** (Scheme 1). Compound **5** is soluble in all common organic solvents. The ^{29}Si NMR spectrum of **5** shows a single resonance (δ −44.29), which is shifted upfield when compared to that of **1** (δ 88.4).[11] The γ-C*H* proton for compound **5** in the ^{1}H NMR spectrum is observed at δ 5.20 and is upfield shifted when compared to that of **1** (δ 5.44). The NCC*H*$_2$ protons in **5** exhibit sharp singlets at δ 3.36 and 3.91 (for **1** δ 3.32 and 3.91). The molecular ion of **5** is exhibited in its EI-mass spectrum at *m*/*z* 940. Compound **5** crystallizes in the monoclinic space group *P*2$_1$/*c*, and the structure is shown in Figure 1. In **5** the silicon atom is three-coordinate and in a planar geometry comprising three nitrogen atoms (two from the supporting ligand). There is a shortening of bonds observed between the Si atom and the nitrogen atoms of the supporting ligand. The average bond distance between Si1−N1 and Si1−

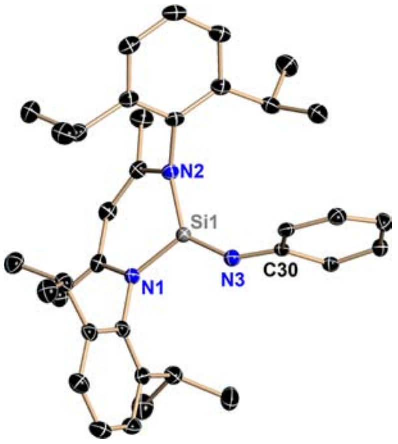


Figure 1. Molecular structure of **5**. The anisotropic displacement parameters are depicted at the 50% probability level. The bulky substituents at the phenyl group attached to N3 and all hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [deg]: Si1−N1 1.7051(13), Si1−N2 1.7206(13), Si1−N3 1.5698(13), C30−N3 1.3848(18); N1−Si1−N2 106.44(6), N1−Si1−N3 120.58(6), N2−Si1−N3 132.86(6), Si1−N3−C30 148.68(11).

N2 in **5** is 1.7129(13) Å, whereas the corresponding distance in **1** is 1.7349(11) Å. The bite angle (N−Si−N) at the silicon atom with the backbone ligand is 106.44(6)°, as compared to 99.31(5)° in **1**. The Si1−N3 bond length of 1.5698(13) Å indicates a double bond character.[8a]

The reaction of dichlorosilylene L^{2}SiCl$_2$ (**2**) with triphenylsilyl azide in equimolar ratio afforded the four-coordinate silaimine derivative **6** (Scheme 1). Like **5**, this compound is also soluble in toluene, benzene, and THF. The ^{29}Si NMR spectrum of **7** shows resonances at δ −29.64(*Si*Ph$_3$) and −75.25(*Si*Cl$_2$). The molecular structure of **6** is shown in Figure 2. Compound **6** crystallizes in the monoclinic space group $P2_1/c$. Here, the silicon atom is four-coordinate and displays a distorted tetrahedral geometry. The silicon coordination environment is derived from one carbon atom of the NHC, two chlorine atoms, and one nitrogen atom. The average Si−Cl distance in **6** is 2.0745(11) Å [Si−Cl$_{av}$ of **2** is 2.1664(16) Å]. Compound **6** exhibits a Si−C bond distance of 1.924(3) Å, which is shorter when compared to that of **2** [Si−C 1.985(4) Å]. The Si−N bond length of **6** (1.581(2) Å) is consistent with those reported for silaimine species with four-coordinate silicon atoms.[17]

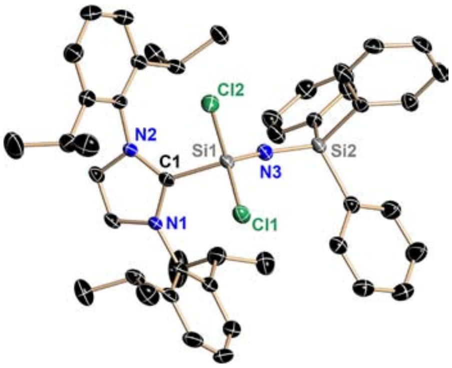
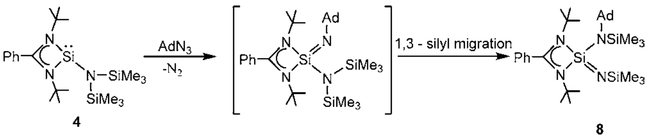


Figure 2. Molecular structure of **6**. The anisotropic displacement parameters are depicted at the 50% probability level. Hydrogen atoms and disordered toluene solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [deg]: C1−Si1 1.924(3), Si1−N3 1.581(2), Si1−Cl1 2.0783(11), Si1−Cl2 2.0698(10), Si2−N3 1.658(2); C1−Si1−N3 109.17(11), Si1−N3−Si2 156.73(15), Cl1−Si1−N3 117.24(9), Cl2−Si1−N3 118.78(9), Cl1−Si1−Cl2 100.57(4).

The reaction of 2,6-bis(2,4,6-triisopropylphenyl)phenyl azide with **3** in an equimolar amount afforded the four-coordinate silaimine derivative **7** (Scheme 1). The ^{29}Si NMR spectrum of **6** shows a resonance at δ −104.78, which is upfield shifted when compared to that of **3** (δ 14.6).[14] The *t*Bu protons of compound **7** in the ^{1}H NMR spectrum exhibit a singlet that is observed at δ 0.75. In addition, **7** shows its molecular ion in the mass spectrum at *m*/*z* 790.

The reactions of **4** with AdN$_3$ and Me$_3$SiN$_3$ led to the four-coordinate silaimines **8** and **9**, respectively (Scheme 1). It is interesting to mention that treatment of AdN$_3$ with **2** showed a functionalized *N*-heterocyclic carbene through the formation of an unstable dichlorosilaimine as the intermediate.[18] In the present study the reaction of **4** with AdN$_3$ resulted in a silaimine compound with terminal SiMe$_3$ group through an unexpected migration of one SiMe$_3$ group. The route of this migration remains unclear. However, we propose that an unstable silaimine compound with a terminal adamantyl group has been formed as an intermediate under the elimination of dinitrogen. Subsequently, there is a 1,3-migration of one of the SiMe$_3$ groups from one nitrogen atom to the other nitrogen. The proposed mechanism is illustrated in Scheme 2.

Scheme 2. Formation of Compound 8



4

8

The ^{1}H NMR spectrum of **8** exhibits three single resonances at δ 0.59, 0.87, and 1.22, which correspond to two SiMe$_3$ groups and one *t*Bu group, respectively. In the ^{1}H NMR spectrum of **9**, four single resonances have been observed (δ 0.41, 0.57, 0.73, and 1.15). The first three belong to the SiMe$_3$ groups, whereas the latter one correponds to the *t*Bu protons, which is shifted slightly high-field when compared to that of **4** (δ 1.23).[6] The ^{29}Si NMR spectrum of **8** shows three resonances (δ −64.53, −24.14, and 1.78) for the three chemically different Si atoms. While the first one corresponds to the Si atom that is coordinated by the amidinate ligand, the second one originates from the SiMe$_3$ group that is bonded to the Si═N unit, and the third one from the remaining SiMe$_3$ moiety attached to the N−Ad group. Similarly, in the ^{29}Si NMR spectrum of **9**, the Si atom that is coordinated by the amidinate ligand resonates at δ −65.35, and the SiMe$_3$ group attached to the Si═N unit displays a resonance at δ −23.68. The latter two resonances (δ −1.76, and 4.16) correspond to the remaining SiMe$_3$ groups in **9**. In the EI-mass spectra of **8** and **9**, the molecular ions are observed as the most abundant peaks at *m*/*z* 568 and 506. The molecular structures of **8** and **9** were established by single-crystal X-ray diffraction studies. Figures 3 and 4 portray the molecular representation of **8** and **9**, respectively. Both **8** and **9** crystallize in the triclinic space group $P\bar{1}$. The central Si atoms in **8** and **9** are four-coordinate and exhibit a distorted tetrahedral geometry with the sum of the bond angles of 345.52° and 347.12°, respectively. The Si1−N3 bond lengths for **8** and **9** (1.5936(14) and 1.5885(14) Å) are slightly longer when compared to those of L^{2}Si(Cl)$_2$N−2,6-*i*Pr$_2$C$_6$H$_3$

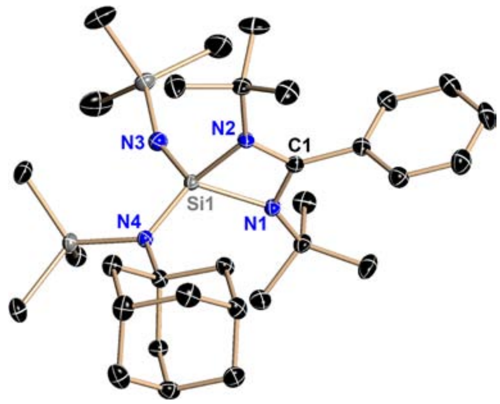


Figure 3. Molecular structure of **8**. The anisotropic displacement parameters are depicted at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [deg]: Si1−N1 1.8482(13), Si1−N2 1.8447(13), Si1−N3 1.5936(14), Si1−N4 1.7202(13); N3−Si1−N4 114.25(7), N3−Si1−N2 116.73(7), N4−Si1−N2 114.54(6), N3−Si1−N1 115.97(7), N4−Si1−N1 117.73(6), N2−Si1−N1 70.88(6), N3−Si1−C1 119.21(7), N4−Si1−C1 126.50(6), N2−Si1−C1 35.53(5), N1−Si1−C1 35.70(5).

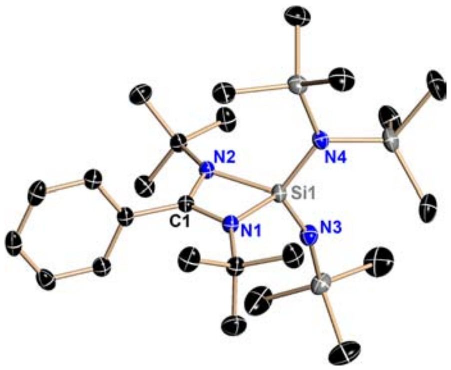


Figure 4. Molecular structure of **9**. The anisotropic displacement parameters are depicted at the 50% probability level. Hydrogen atoms and disordered toluene lattice molecules are omitted for clarity. Selected bond lengths [Å] and angles [deg]: Si1−N1 1.8360(13), Si1−N2 1.8326(14), Si1−N3 1.5885(14), Si1−N4 1.7218(14); N3−Si1−N4 116.58(7), N3−Si1−N2 117.46(7), N4−Si1−N2 113.10(7), N3−Si1−N1 118.04(7), N4−Si1−N1 112.50(6), N2−Si1−N1 71.25(6), N3−Si1−C1 121.63(7), N4−Si1−C1 121.79(6), N2−Si1−C1 35.87(6), N1−Si1−C1 35.64(5).

(1.545(2) Å)[17] and $L^3Si(Cl)N{-}2,6\text{-}iPr_2C_6H_3$ (1.545(2) Å).[21] The Si2−N3 bond distances in **8** and **9** (1.6594(15) and 1.6575(15) Å) correspond to the Si−N single bond lengths.[19,22] The geometry about N3 can best be described as distorted trigonal planar, with two sites being occupied by two Si atoms.

■ CONCLUSION

Stable silaimine $L^1SiN(2,6\text{-}Triip_2\text{-}C_6H_3)$ (**5**) with three-coordinate silicon atom has been prepared using the bulky azide, 2,6-bis(2,4,6-triisopropylphenyl)phenyl azide. Lewis base-stabilized chlorosilaimines $L^2(Cl_2)SiN(SiPh_3)$ (**6**) and $L^3(Cl)SiN(2,6\text{-}Triip_2C_6H_3)$ (**7**) were synthesized by the reaction of chlorosilylenes with appropriate azides. We obtained the unusual silaimine compound $L^3(N(Ad)SiMe_3)SiN(SiMe_3)$ (**8**) (Ad = adamantyl) under the 1,3-migration of one $SiMe_3$ group and $L^3(N(SiMe_3)_2)SiN(SiMe_3)$ (**9**) featuring a terminal $SiMe_3$ group. A recent communication from our laboratory documented the reduction of dichlorosilaimines resulting in the formation of dimeric silaisonitriles.[20a] The herein reported chlorosilaimines are expected to be valuable precursors for the preparation of various silaisonitriles.

■ EXPERIMENTAL SECTION

Syntheses were carried out under an inert gas atmosphere of dinitrogen in oven-dried glassware using standard Schlenk techniques. Other manipulations were accomplished in a dinitrogen filled glovebox. Solvents were purified by the MBRAUN solvent purification system MB SPS-800. All chemicals were purchased from Aldrich and used without further purification. Compounds **1**,[11] **2**,[13] **3**,[14] and **4**[15] were prepared as reported in literature. Triphenylsilyl azide[23] and $2,6\text{-}Triip_2C_6H_3N_3$[24] were prepared as reported in the literature. ^1H and ^{29}Si NMR spectra were recorded with a Bruker Avance DPX 200, Bruker Avance DRX 300, or a Bruker Avance DRX 500 spectrometer, using C_6D_6 as solvent. Chemical shifts δ are given relative to $SiMe_4$. EI-MS spectra were obtained using a Finnigan MAT 8230 instrument. Elemental analyses were done in the Institut für Anorganische Chemie, Universität Göttingen. For elemental analysis, the compounds were under vacuum for 6 h to remove the solvent molecules. Melting points were measured in a sealed glass tube on a Büchi B-540 melting point apparatus.

Synthesis of 5. *n*-Hexane (60 mL) was placed in a Schlenk flask (100 mL) containing **1** (0.36 g, 0.81 mmol) and 2,6-bis(2,4,6-triisopropylphenyl)phenyl azide (0.43 g, 0.82 mmol). The reaction mixture was stirred at room temperature for 12 h. The solution was filtered, and the solvent was reduced in vacuo to 20 mL and stored in a freezer at −26 °C for 3 days to obtain single crystals of **5** (0.50 g, 64%). Mp 196−198 °C. Anal. Calcd for $C_{65}H_{89}N_3Si$ (940.51): C, 83.01; H, 9.54; N, 4.47. Found: C, 82.85; H, 9.49; N, 4.45. ^1H NMR (300 MHz, C_6D_6, 25 °C): δ 0.39−1.47 (m, 60H, $CH(CH_3)_2$), 2.26 (m, 1H, $CH(CH_3)_2$), 2.56 (m, 1H, $CH(CH_3)_2$), 2.66−2.98 (m, 4H, $CH(CH_3)_2$), 3.12 (m, 1H, $CH(CH_3)_2$), 3.36 (s, 1H, $NCCH_2$), 3.43 (m, 1H, $CH(CH_3)_2$), 3.54−3.79 (m, 2H, $CH(CH_3)_2$), 3.91 (s, 1H, $NCCH_2$), 5.20 (s, 1H, γ-CH), 6.54−7.28 (m, 13H, ArH) ppm. $^{29}Si\{^1H\}$ NMR (59.63 MHz, C_6D_6, 25 °C): δ −44.29 ppm. EI-MS: m/z 940 [M^+].

Synthesis of 6. Toluene (60 mL) was added to a Schlenk flask (100 mL) containing **2** (0.49 g, 1.01 mmol) and triphenylsilyl azide (0.30 g, 1.00 mmol). The reaction mixture was stirred at room temperature for 12 h. The solution was filtered, and the solvent was reduced in vacuo to about 30 mL and stored at −26 °C in a freezer for 5 days to obtain colorless single crystals of **6** (0.60 g, 78.9%). Mp 171−174 °C (decomp). Anal. Calcd for $C_{45}H_{51}Cl_2N_3Si_2$ (760.98): C, 71.02; H, 6.74; N, 5.52. Found: C, 71.05; H, 6.71; N, 5.38. ^1H NMR (200 MHz, C_6D_6, 25 °C): δ 0.93 (d, 12 H, $CH(CH_3)_2$), 1.20 (d, 12 H, $CH(CH_3)_2$), 2.82 (m, 4H, $CH(CH_3)_2$), 6.36 (s, 2H, CH), 6.98−7.20 (m, 12H ArH), 7.68−7.82 (m, 9H ArH) ppm. $^{29}Si\{^1H\}$ NMR (99.36 MHz, C_6D_6, 25 °C): δ −29.64 ($SiPh_3$), −75.25 ($SiCl_2$) ppm.

Synthesis of 7. Toluene (60 mL) was added to a Schlenk flask (100 mL) containing **3** (0.30 g, 1.02 mmol) and 2,6-bis(2,4,6-triisopropylphenyl)phenyl azide (0.53 g, 1.01 mmol). The reaction mixture was stirred at room temperature for 12 h. The solution was filtered, and the solvent was reduced in vacuo to about 30 mL and stored at −26 °C in a freezer for a week to obtain **7** as a crystalline solid (0.60 g, 75%). Mp 161−164 °C. Anal. Calcd for $C_{51}H_{72}ClN_3Si$ (790.68): C, 77.47; H, 9.18; N, 5.31. Found: C, 77.39; H, 9.15; N, 5.38. ^1H NMR (500 MHz, C_6D_6, 25 °C): δ 0.75 (s, 18H, $C(CH_3)_3$), 1.19−1.41 (m, 30H, $CH(CH_3)_2$), 1.53 (d, 6H, $CH(CH_3)_2$), 2.80−3.10 (m, 4H, $CH(CH_3)_2$), 3.48 (m, 2H, $CH(CH_3)_2$), 6.80−7.24 (m, 12H, ArH) ppm. $^{29}Si\{^1H\}$ NMR (99.36 MHz, C_6D_6, 25 °C): δ −104.78 ppm. EI-MS: m/z 790 [M^+].

Synthesis of 8. Toluene (30 mL) was added to a Schlenk flask (100 mL) containing **4** (0.50 g, 1.19 mmol) and adamantyl azide (0.21 g, 1.19 mmol). The reaction mixture was stirred at room temperature for 6 h. The solvent was reduced in vacuo to about 15 mL and stored at −4 °C to obtain single crystals of **8** in a day (0.52 g, 77%). Mp 210−212 °C. Anal. Calcd for $C_{31}H_{56}N_4Si_3$ (569.06): C, 65.43; H, 9.92; N, 9.85. Found: C, 65.35; H, 9.83; N, 9.94. ^1H NMR (500 MHz, C_6D_6, 25 °C): δ 0.58 (s, 9H, $Si(CH_3)_3$), 0.87 (s, 9H, $Si(CH_3)_3$), 1.22 (s, 18H, *t*Bu), 1.59−1.67 (m, 6H, Ad CH_2), 2.02 (br, 3H, Ad CH), 2.35 (br, 6H, Ad CH_2), 6.87−6.96 (m, 5H, ArH) ppm. $^{29}Si\{^1H\}$ NMR (99.36 MHz, C_6D_6, 25 °C): δ −64.53 (LSi), −24.14 ($Si{=}NSiMe_3$), 1.776 ($Si{-}NSiMe_3$) ppm. EI-MS: m/z 568 [M^+].

Synthesis of 9. To a toluene (30 mL) solution of **4** (0.50 g, 1.19 mmol) in a Schlenk flask (100 mL) was added trimethylsilyl azide (0.14 g, 1.19 mmol) in toluene (10 mL) drop by drop at −40 °C. The solution was warmed to room temperature and stirred for 2 h. The solvent was reduced in vacuo to about 10 mL and stored at −4 °C to obtain single crystals of **9** in 2 days (0.48 g, 81%). Mp 192−194 °C. Anal. Calcd for $C_{24}H_{50}N_4Si_4$ (507.02): C, 56.85; H, 9.94; N, 11.05. Found: C, 56.71; H, 9.99; N, 11.18. ^1H NMR (500 MHz, C_6D_6, 25 °C): δ 0.41 (s, 9H, $Si(CH_3)_3$), 0.57 (s, 9H, $Si(CH_3)_3$), 0.73 (s, 9H, $Si(CH_3)_3$), 1.15 (s, 18H, *t*Bu), 6.86−7.01 (m, 5H, ArH) ppm. $^{29}Si\{^1H\}$ NMR (99.36 MHz, C_6D_6, 25 °C): δ −65.35 (LSi), −23.68 ($Si{=}NSiMe_3$), −1.76 ($Si{-}NSiMe_3$), 4.16 ($Si{-}NSiMe_3$) ppm. EI−MS: m/z 506 [M^+].

Crystal Structure Determination. Single crystals were selected from a Schlenk flask under an argon atmosphere and covered with perfluorated polyether oil on a microscope slide, which was cooled with a nitrogen gas flow using the X-TEMP2.[25] An appropriate crystal was selected using a polarized microscope, mounted on the tip of a

Table 1. Crystal and Structure Refinement Parameters for Compounds 5, 6, 8, and 9

parameters	5	6·toluene	8	(9·toluene)$_3$
CCDC no.	891040	891041	891042	891043
empirical formula	$C_{65}H_{89}N_3Si$	$C_{52}H_{59}Cl_2N_3Si_2$	$C_{31}H_{56}N_4Si_3$	$C_{93}H_{174}N_{12}Si_{12}$
formula weight	940.48	853.10	569.07	1797.52
crystal system	monoclinic	monoclinic	triclinic	triclinic
space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
unit cell dimensions	a = 20.144(2) Å b = 12.315(2) Å c = 22.761(3) Å β = 93.35(2)°	a = 12.102(2)Å b = 16.373(2) Å c = 24.055(3) Å β = 92.06(3)°	a = 9.875(2) Å b = 9.906(2) Å c = 19.285(2) Å α = 91.21(2)° β = 104.27(2)° γ = 111.65(2)°	a = 13.269(2) Å b = 16.300(2) Å c = 25.856(3) Å α = 87.86(2)° β = 82.51(2)° γ = 82.79(2)°
volume, Z	5636.7(13) Å^3, 4	4763.3(11) Å^3, 4	1686.1(5) Å^3, 2	5499.4(12) Å^3, 6
density (calcd)	1.108 g/cm^3	1.190 g/cm^3	1.121 Mg/m^3	1.086 Mg/cm^3
absorption coefficient	0.083 mm^{-1}	0.224 mm^{-1}	0.166 mm^{-1}	0.187 mm^{-1}
$F(000)$	2056	1816	642	1968
crystal size/mm	0.15 × 0.15 × 0.09	0.12 × 0.10 × 0.06	0.20 × 0.20 × 0.10	0.15 × 0.08 × 0.08
θ range for data collection	1.01–25.71°	1.50–25.39°	1.10–26.73°	1.26–26.04°
limiting indices	$-24 \le h \le 24$; $-15 \le k \le 15$; $-27 \le l \le 27$	$-14 \le h \le 14$; $-19 \le k \le 19$; $-28 \le l \le 28$	$-12 < h < 9$, $-12 < k < 12$, $-24 < l < 24$	$-16 \le h \le 16$; $-20 \le k \le 20$; $-31 \le l \le 31$
reflns collected	101 565	99 203	13 997	109 840
independent reflns	10 683 (R_{int} = 0.0447)	8737 (R_{int} = 0.1243)	7128 (R_{int} = 0.0258)	21 603 (R_{int} = 0.0357)
completeness to θ	99.6% (θ = 25.71°)	99.8% (θ = 25.39°)	99.4% (θ = 26.73°)	99.5% (θ = 26.04°)
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
data/restraints/parameters	10 683/76/660	8737/591/656	7128/0/355	21 603/415/1177
GOF on F^2	1.015	1.012	1.038	1.043
final R indices [$I > 2\sigma(I)$]	R1 = 0.0398, $wR2$ = 0.0926	R1 = 0.0481, $wR2$ = 0.1067	R1 = 0.0379, $wR2$ = 0.0928	R1 = 0.0368, $wR2$ = 0.0953
R indices (all data)	R1 = 0.0525, $wR2$ = 0.0995	R1 = 0.0841, $wR2$ = 0.1245	R1 = 0.0478, $wR2$ = 0.0985	R1 = 0.0490, $wR2$ = 0.1004
largest diff. peak and hole	0.306 and −0.354 e Å^{-3}	0.410 and −0.343 e Å^{-3}	0.472 and −0.252 e Å^{-3}	0.404 and −0.264 e Å^{-3}

MiTeGen MicroMount fixed to a goniometer head, and shock cooled by the crystal cooling device. The data for **5**, **6**, **8**, and **9** were collected from shock-cooled crystals at 100(2) K.[25] The data for **8** and **9** were collected on an Incoatec Mo microsource[26] with mirror optics and an APEX II detector with a D8 goniometer. The data for **5** and **6** were measured on a Bruker TXS Mo rotating anode with mirror optics and an APEX II detector with a D8 goniometer. Both diffractometers used Mo K$_\alpha$ radiation, λ = 71.073 pm. The data for all structures were integrated with SAINT,[27] and an empirical absorption correction (SADABS)[28] was applied. The structures were solved by direct methods (SHELXS-97)[29a] and refined by full-matrix least-squares methods against F^2 (SHELXL-97)[29b,c] within the SHELXLE GUI.[29d] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically on calculated positions using a riding model with their U_{iso} values constrained to equal 1.5 times the U_{eq} of their pivot atoms for terminal sp^3 carbon atoms and 1.2 times for all other carbon atoms. The disordered lattice toluene molecules in **6** and **9** and *i*Pr group in the para position of one of the Triip substituents attached to the phenyl group at N3 in **5** were refined using distance restraints and restraints for anisotropic displacement parameters. Crystallographic data (excluding structure factors) for the structures reported in this Article have been deposited with the Cambridge Crystallographic Data Centre. The CCDC numbers, crystal data, and experimental details for the X-ray measurements are listed in Table 1.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

CIF files of compounds **5**, **6**, **8**, and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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