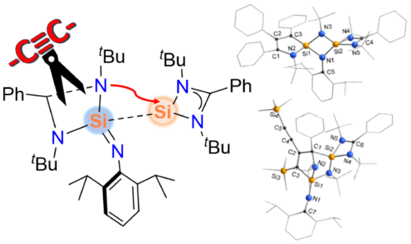
Unconventional Insertions of Internal Alkynes into a Mixed-Valent Silaiminyl-Silylene

Da Jin, Xiaofei Sun,* Alexander Hinz, and Peter W. Roesky*

ABSTRACT: The reactivity of a mixed-valent silaiminyl-silylene [LSi−Si(NDipp)L] (L = $PhC(N^tBu)_2$, Dipp = 2,6-^iPr-C_6H_3) toward various substituted internal alkynes was investigated. In contrast to previous reports that primarily yield [Si(μ-C_2)Si]-modified rings via 1,2-addition of two silylenes in the center of the molecule, our study reveals a novel reaction pathway. The introduction of [R_1−C≡C−R_2] (R_1 = Ph or $SiMe_3$, R_2 = Ph or C≡$CSiMe_3$) gave unconventional insertion into one of the amidinate ligands, followed by migration of the {N^tBu} group to bridge two Si atoms. This results in the formation of diverse expanded silacycles.



INTRODUCTION

The synthesis of silacycles has gained considerable attention due to their potential applications in diverse scientific fields, including biological chemistry, pharmaceuticals, and materials science.[1−5] Conventional methods involve the reactions of chlorosilanes with lithium alkyls or Grignard reagents, leading to silicon−carbon bond formation, cyclization, and subsequent transformations.[6−8] Additionally, transition metal-catalyzed cross-coupling reactions offer an alternative strategy for silacycle synthesis.[9−11] In contrast to these traditional approaches, the reaction of silylenes with unsaturated small molecules provides an efficient pathway to diverse silacycles with unconventional structures.[12−14]

In the realm of small molecule activation, extensive research has focused on understanding the interaction between mono(silylenes) and alkynes. These investigations have revealed that mono(silylenes) for example readily undergo cycloaddition reactions, forming three-membered [SiC_2] rings (Figure 1, **A**) in a 1:1 ratio[15−19] or four-membered [Si(μ-C_2)Si] rings (Figure 1, **B**) in a 2:1 ratio reaction.[20] Conversely, studies on reactions involving bis(silylene) and alkyne remain limited. Notable examples include the facile insertion of alkynes between silicon atoms. For instance, H. Roesky,[21] So[22] and Zhu[23] reported the formation of 1,4-disilabenzenes (Figure 1, **C**) through the reaction of [LSi−SiL] (L = $PhC(N^tBu)_2$) with [PhC≡CPh] or [Me_3SiC≡C−C≡$CSiMe_3$]. Driess et al.[24] recently isolated 1,3-disilapyrroles (Figure 1, **D**), which serve as triplet diradicals, generated through the cycloaddition of N,N-bis(silylenyl)aniline with diphenylacetylenes. Li et al.[25] reported the reaction of bis(silylene) [$(LSi)_2C_2B_{10}H_{10}$] with arylalkynes, yielding bis(silylium) carborane adducts with a [Si(μ-C_2)Si] structure.

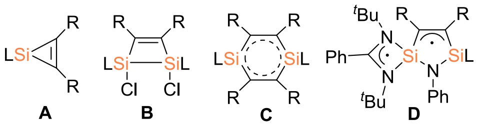


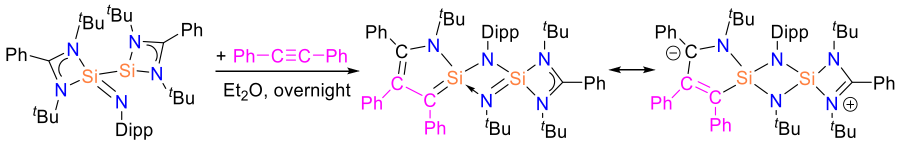
Figure 1. Representative silacycles derived from the reactions of silylenes with alkynes.

Motivated by the potential diverse reactivity exhibited by various substituted silylenes when reacted with alkynes, our focus shifted to the mixed-valent silaiminyl-silylene [LSi−Si(NDipp)L] (L = $PhC(N^tBu)_2$, Dipp = 2,6-$^iPrC_6H_3$), a hidden or masked bis(silylene). This compound is characterized by the presence of two silicon atoms in distinct formal oxidation states of +I and +III, allowing for facile switching between mono- and bis(silylene) motifs in response to external stimuli.[26] Moreover, the Dipp-iminyl group directly bonded to the silicon atom imparts specific electronic and steric properties to the silylene. Although initially identified as a minor side product by So and coworkers,[27] our group has successfully established an unconventional yet highly efficient one-pot reaction for the multigram-scale synthesis of this compound.[26] Notably, unlike the reactivity of the above-mentioned silylenes, including the diaminochlorosilyl-substituted silylsilylene,[28] the introduction of alkynes in our study results in the cleavage of the supporting amidinate ligand, thereby leading to the formation of various silacycles.

RESULTS AND DISCUSSION

The mixed-valent silaiminyl-silylene [LSi−Si(NDipp)L] **1** was prepared in a single step according to our previously published

Scheme 1. Reaction between [LSi−Si(NDipp)L] and [PhC≡CPh]



1 **2** (51%) **2'**

method[26] from the amidinato chlorosilylene [LSiCl][19] and [DippN(H)Li][29] as yellow powder in 90% yield. The treatment of **1** with an equivalent of diphenylacetylene [PhC≡CPh] in Et_2O at room temperature resulted in a gradual color change from yellow to dark brown. After overnight stirring, a large amount of crystalline precipitate formed as compound **2** in 51% yield (Scheme 1). In contrast to reported reactions that alkynes insert into the Si−Si bond (Figure 1, **C** and **D**), here one of the amidinate ligands is cleaved via insertion of the alkyne C−C moiety. This is accompanied by the migration of the {N^{t}Bu} group along the Si−Si bridge and both Si atoms undergo oxidation. The difference in steric bulk of the DippN moiety in **1** compared to the PhN moiety in **D** makes a key difference here.

Single crystals for X-ray diffraction analysis were obtained from a concentrated solution of **2** in Et_2O at room temperature and its molecular structure is depicted in Figure 2. The newly formed five-membered (SiC_3N) ring and four-membered (Si_2N_2) ring are twisted at the Si1 atom and arranged nearly perpendicular to each other with a dihedral angle of 81.3°. Both rings are nearly planar, with the sum of the inner angles totaling 359.72° for the four-membered ring and 539.62° for the five-membered one, respectively. The two distinct Si atoms, Si1 and Si2, adopt a distorted tetrahedral geometry. The Si1−C3 bond distance (1.797(2) Å) in the five-membered ring (SiC_3N) is slightly longer than that in reported structures such as Brook's silene [$(Me_3Si)_2Si{=}C(OSiMe_3)$-2-Ad] (1.764 Å),[30] Driess' dibenzo[a,e]disilapentalene (1.769 Å)[31] and our group's binol functionalized cyclic silene (1.759 Å),[32] but much shorter than typical Si−C single bonds (1.86−1.93 Å),[33] indicating the partial Si=C double bond character. The C1−C2 bond distance (1.366(3) Å) is consistent with that of reported double bonds in silacycles.[17,34] In the central four-membered Si_2N_2 ring, the Si−N bond distances range from 1.667 to 1.848 Å, with the longest bond distance observed for the Si1−N1 bond and the shortest for Si2−N3. These observed bond distances show significant variations within the ring, particularly when compared with other reported examples featuring a centrally planar [Si_2N_2] motif with nearly equal bond lengths.[35−38]

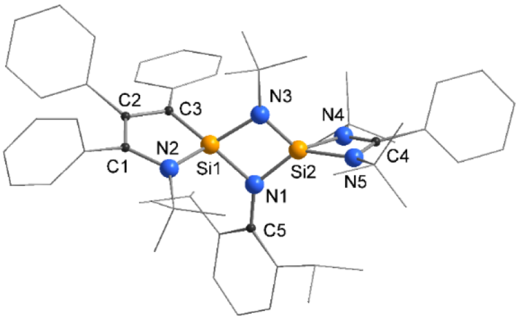


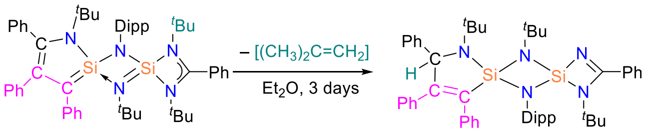
Figure 2. Molecular structure of **2** in the solid state. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles [°]: Si1−N1 1.848(2), Si1−N2 1.757(2), Si1−N3 1.797(2), Si1−C3 1.797(2), Si2−N1 1.711(2), Si2−N3 1.667(2), N2−C1 1.442(3), C1−C2 1.366(3), C2−C3 1.448(3); N2−Si1−C3 94.74(10), N1−Si1−N3 82.06(9), N1−Si2−N3 90.20(9), Si1−N1−Si2 92.08(9), Si1−N3−Si2 95.39(9), C1−N2−Si1 108.24(15), C2−C1−N2 114.4(2), C2−C3−Si1 105.5(2), C1−C2−C3 116.7(2).

After crystallization, compound **2** showed limited solubility in C_6D_6. In the ^1H NMR spectrum, the singlet signals at δ 1.89, 1.37, 1.20, and 0.93 ppm are assigned to the ^{t}Bu protons, and the two broad signals at 4.86 and 3.45 ppm for the ^{i}PrC*H* proton. The $^{29}Si\{^1H\}$ NMR spectrum exhibits two singlets at δ −26.1 (Si=C, calc. −31 ppm) and −50.1 ppm (SiN_4, calc. −54 ppm), which are shifted compared to those of silylene **1** (δ −61.2 and 32.4 ppm), with the former aligning closely with those reported for silenes.[32,39]

To understand the electronic characteristics of **2**, we utilized natural resonance theory (NRT) calculations. The result showed 20 resonance structures with contributions >1%, of which top six contribute 6−13% each (see Figure S23), which underscores the high degree of electron delocalization in **2**. However, it is noteworthy that one of the dominant structures shows a negative formal charge on the nitrogen-adjacent C atom of the five-membered heterocycle (Scheme 1, **2'**), which is relevant for the following reaction:

A solution of compound **2** in C_6D_6 underwent a striking color change from dark brown to colorless over a period of 3 days, accompanied by the disappearance of initially present undissolved precipitates (Scheme 2). This experiment could be repeated on a preparative scale in Et_2O. Analysis by $^{29}Si\{^1H\}$ NMR spectroscopy revealed two distinct chemical shifts at δ −27.7 and −38.8 ppm, deviating from those observed in compound **2**, suggesting that further reaction had occurred. In addition, the C*H* signals of the two ^{i}Pr groups are shifted to δ 4.48 and 3.36 ppm compared to compound **2** (δ 4.86 and 3.45 ppm). Interestingly, two new resonances at δ 5.24 and 4.75 ppm arise (Figure S3). Notably, the latter signal is accompanied by a peak at high field at δ 1.60 ppm, can be assigned to the isobutylene [$(CH_3)_2C{=}CH_2$]. This was further confirmed by $^{13}C\{^1H\}$ NMR analysis (δ 141.97, 111.12, and 24.11 ppm) (Figure S4). Additionally, three singlets at δ 0.96, 1.31, and 1.93 ppm are attributed to three nonequivalent ^{t}Bu substituents.

Scheme 2. Formation of Compound 3



2 **3** (49%)

Concentration of the C_6D_6 solution yielded compound **3** as colorless crystals. The molecular structure of **3** (Figure 3)

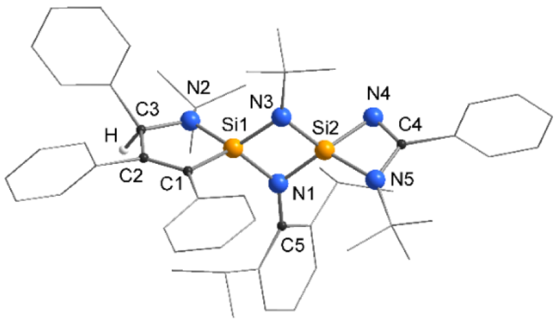


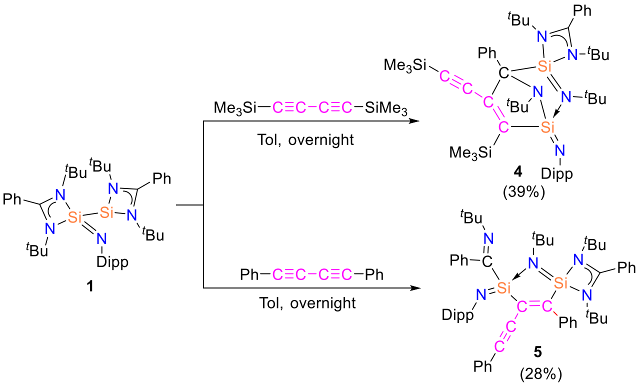
Figure 3. Molecular structure of **3** in the solid state. Hydrogen atoms (except for C3*H*) are omitted for clarity. Selected bond lengths (Å) and bond angles [°]: Si1−C1 1.8689(14), Si1−N1 1.7766(12), Si1−N2 1.7251(12), Si1−N3 1.7351(12), Si2−N1 1.7282(12), Si2−N3 1.7031(12), Si2−N4 1.7705(13), Si2−N5 1.7658(12), C1−C2 1.347(2), N1−C5 1.437(2), N2−C3 1.466(2), C2−C3 1.522(3), N4−C4 1.303(2), N5−C4 1.403(2); N2−Si1−C1 94.07(6), N1−Si1−N3 85.27(6), N1−Si2−N3 87.78(6), N4−Si2−N5 78.36(6), Si1−N1−Si2 92.29(6), Si1−N3−Si2 94.63(6), C5−N1−Si1 139.32(9), C5−N1−Si2 128.17(9), C3−N2−Si1 111.81(9), C2−C1−Si1 107.39(10), C1−C2−C3 117.61(12), N2−C3−C2 109.00(11).

indicates the loss of one ^{t}Bu group from the amidinate moiety, with one released H being attached to the nucleophilic carbon in **2**. This observation is in agreement with the presence of isobutylene in the NMR spectra. In **3**, the Si1−C1 bond distance (1.8689(14) Å) is significantly longer than that in **2**, falling within the range expected for a single bond. Meanwhile, the C2−C3 (1.522(3) Å) and C1−C2 (1.347(2) Å) bond distances in the five membered ring ($SiNC_3$) correspond to single and double bonds, respectively, which is in consistent with the molecular geometry. Regarding the [Si2N4C4N5] moiety, the N4−C4 bond (1.303(2) Å) is significantly shorter than the N5−C4 bond (1.403(2) Å), suggesting the assignment as a double bond and single bond, respectively. In the central four-membered unit (Si_2N_2), the Si−N bond distances (average 1.736 Å) are more closely aligned compared to those in **2** and are comparable to those observed in the reported dicationic *N*,*N*′-dimethyl-cyclodisilazane[40] and [*μ*-[^{i}PrN(Ph)CN]$_2$($SiMe_2$)$_2$].[41] The elimination of isobutylene from the {N^{t}Bu} molecular moiety has been previously reported.[42,43]

To systematically investigate the reaction outcomes and elucidate the underlying mechanism, various alkyne substituents were explored. However, when reacting silylene **1** with the differently substituted internal alkynes [$Me_3SiC{\equiv}CSiMe_3$], [$Me_3SiC{\equiv}CPh$], [$EtC{\equiv}CEt$] and [$MeC{\equiv}CMe$], no reaction took place as determined by NMR spectroscopy, even at elevated temperatures. Subsequently, two diynes with different steric hindrance were employed. Treatment of silylene **1** with diynes [$Me_3SiC{\equiv}C{-}C{\equiv}CSiMe_3$] and [$PhC{\equiv}C{-}C{\equiv}CPh$] resulted in the isolation of compounds **4** and **5**, respectively (Scheme 3).

The formation of **4** follows a similar pattern to that of **2**, involving the cleavage of the C−N bond in one amidinate ligand through insertion of one alkyne C≡C fragment. In this instance, insertion of the diyne between the Si and C atoms leads to the formation of a heterocyclic [Si_2NC_3] ring bridged by a {N^{t}Bu} group, resulting in a norbornadiene type structure in the center. In the resulting molecular structure of **4** (Figure 4), the six-membered $Me_3SiC_4SiMe_3$ chain remains intact, with C2−C3 (1.366(3) Å) having double bond and C4−C5 (1.201(3) Å) having triple bond character. This reactivity shown here is different from that with the chlorosilylene [L(Cl)Si], as a symmetrical alkyne-linked bis(silene) has formed.[44] The central motif of **4** comprises two puckered five-membered Si_2N_2C and $SiNC_3$ heterocycles, forming the norbornadiene type structure. Both Si1 and Si2 adopt a distorted tetrahedral geometry and are surrounded by three N atoms and one C atom. The Si2−N3 bond distance (1.682(2) Å) is significantly shorter than that of Si1−N3 (1.796(2) Å), similar to the observation in compound **2**.

Scheme 3. Reactions between [LSi−Si(NDipp)L] and Diynes



However, for the formation of compound **5**, both Si atoms add to one of the C≡C bonds of the diyne, forming a [Si(*μ*-C_2)Si] bridge. This is accompanied by the migration of a {N^{t}Bu} group from one amidinate ligand to bridge both Si atoms. The molecular structure (Figure 4) exhibits a planar central [Si_2NC_2] ring with a sum of the inner angles of 539.3°. The Si2−N3 (1.667(2) Å) bond distance is consistent with that of Si2−N3 in **2** and **4**. The C1−C2 (1.354(3) Å) bond distance is longer than that of C3−C4 (1.202(3) Å), and they are identified as double and triple bonds, respectively, similar to those in **4**.

Compounds **4** and **5** were further characterized by NMR spectroscopy. In the ^{1}H NMR spectrum of **4**, two singlets are observed at high field δ 0.85 and 0.11 ppm for the $SiMe_3$ groups, along with four singlets at δ 1.72, 1.30, 1.21, and 0.90 ppm corresponding to the four different ^{t}Bu groups. In the ^{29}Si{^{1}H} NMR spectrum, four signals are detected at δ −8.9, −19.7, −68.0, and −85.3 ppm, with the former two attributed to the $SiMe_3$ groups (Si3 and Si4), as confirmed by ^{1}H-^{29}Si HMBC spectrum (Figure S11) and the latter two resonances result from Si1 and Si2, respectively. Similarly, in the ^{1}H NMR spectrum of **5**, four singlets at δ 1.90, 1.47, 1.25, and 1.04 ppm are assigned to four different ^{t}Bu groups. In the ^{29}Si{^{1}H} NMR spectrum, two signals at δ −28.1 (calc. −28 ppm, $SiCN_3$) and −66.8 ppm (calc. −80 ppm, SiC_2N_2) are observed, showing a downfield shift compared to those of **4**.

The distinct behavior of various alkynes toward **1** poses a question regarding the mechanisms of formation of **2**, **4** and **5**, respectively. The thermodynamic data show that in principle, for each of the alkynes the structural motif **2** should be the energetic minimum (see Figure S25 and Table S2), so the formation of **4** and **5** is due to kinetic reasons. A likely pathway (see Figure S26) includes the initial [2 + 1] cycloaddition of a triple bond at the silylene. Subsequently, a [2.1.1]bicyclic species could be formed which simultaneously alleviates steric

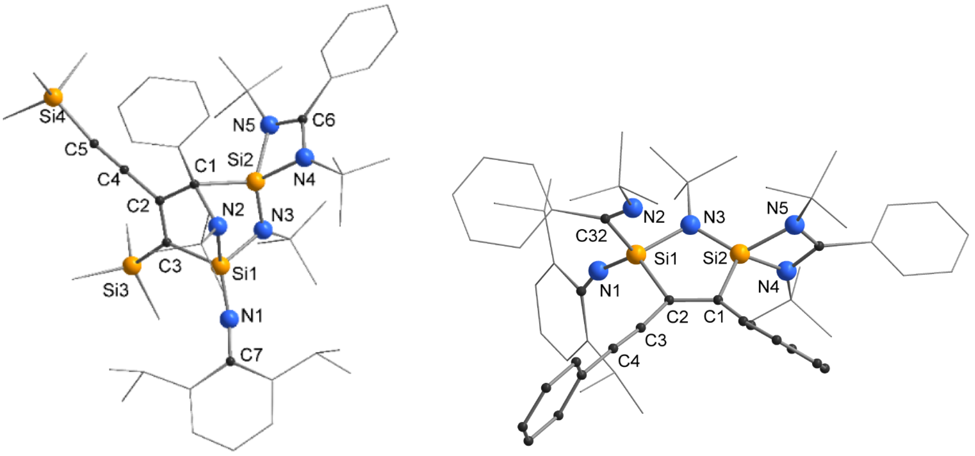


Figure 4. Molecular structures of **4** (left) and **5** (right) in the solid state. All hydrogen atoms and cocrystallized solvent molecules are omitted for clarity. Selected bond lengths (Å) and bond angles [°]: **4**: Si1–N1 1.589(2), Si1–N3 1.796(2), Si1–N2 1.855(10), Si1–C3 1.885(2), Si2–N3 1.682(2), Si2–N4 1.803(2), Si2–N5 1.880(2), Si2–C1 1.901(2), Si3–C3 1.872(2), Si4–C5 1.838(3), N5–C6 1.323(3), N4–C6 1.355(3), N1–C7 1.366(3), C2–C3 1.366(3), C2–C4 1.434(3), C4–C5 1.201(3), C1–C2 1.544(3), C1–N2 1.543(11); N3–Si1–C3 100.64(9), N4–Si2–N5 71.39(8), N3–Si2–C1 106.09(9), Si1–N3–Si2 100.91(9), C6–N5–Si2 89.65(13), C6–N4–Si2 91.96(13), C3–C2–C1 117.4(2), C2–C3–Si1 106.3(2), N4–C6–N5 106.8(2), C1–N2–Si1 101.7(6). **5**: Si1–N1 1.603(2), Si1–N3 1.804(2), Si1–C2 1.923(2), Si1–C32 1.908(3), Si2–N3 1.667(2), Si2–N4 1.811(2), Si2–N5 1.809(2), Si2–C1 1.831(2), N2–C32 1.279(3), C1–C2 1.354(3), C2–C3 1.428(3), C3–C4 1.202(3); C2–Si1–N3 94.83(9), C1–Si2–N3 104.73(10), Si1–N3–Si2 111.88(9), C2–C1–Si2 110.09(14), C1–C2–Si1 117.70(15).

and ring strain. This could also be viewed as formal [3 + 2] cycloaddition of the alkyne across a SiN_2C moiety. Up to this point, an aminosilylene-iminosilane equilibrium may still be invoked. As this is still a strained bicycle, there is a driving force for ring opening which could lead to the formation of a SiC_3N monocycle with an exocyclic iminosilane functionality. This is viewed as a key step, as in each instance an amidinate moiety is cleaved. From this intermediate, **2**, **4** and **5** could be formed by various rearrangements that are driven by the minimization of steric repulsion. The complex reactivity pattern that emerges should be comprehensively studied in future works that take into account the interplay of various bulky groups at the amidinates, the imino substituent in **1** as well as the alkyne substituents.

CONCLUSIONS

In summary, we investigated reactions between the mixed-valent silaiminyl-silylene [LSi–Si(NDipp)L] and internal alkynes, observing varied outcomes depending on the substituent of the alkynes used. In all cases examined, cleavage of one of the amidinate ligands occurred. This was accompanied by the migration of the {N^{t}Bu} group, which bridges both Si atoms in all cases studied. By reaction of [LSi–Si(NDipp)L] with [PhC≡CPh] and [$Me_3SiC≡C–C≡CSiMe_3$], insertion into the broken amidinate ligand was observed, with the former displaying instability and elimination of isobutylene [$(CH_3)_2C=CH_2$]. Conversely, the reaction with [PhC≡C–C≡CPh] resulted in addition of both Si atoms. These findings highlight the versatility and complexity of silylene-alkyne reactions, emphasizing the crucial role of substituents in dictating reaction pathways and product formation as subtle changes in sterics can lead to a variety of products.

EXPERIMENTAL SECTION

General Procedures. All manipulations of water- and air-sensitive compounds were performed with exclusion of moisture and oxygen in flame-dried Schlenk-type glassware either on a dual manifold Schlenk line, interfaced to a high vacuum (10^{-3} mbar) line or in an argon-filled MBraun glovebox. All solvents were dried by using a MBraun solvent purification system (SPS 800). C_6D_6 were dried over Na–K alloy and degassed by freeze–pump–thaw cycles. NMR spectra were recorded on Bruker spectrometers (Avance Neo 300 MHz, Avance Neo 400 MHz or Avance III 400 MHz) at 298 K. Chemical shifts are referenced internally using signals of the residual protio solvent (^{1}H) or the solvent (^{13}C{^{1}H}) and are reported relative to tetramethylsilane (^{1}H, ^{13}C{^{1}H}). The multiplicity of the signals is indicated as s = singlet, d = doublet, t = triplet, m = multiplet and br = broad. Assignments were determined on the basis of unambiguous chemical shifts, coupling patterns and ^{13}C DEPT experiments or 2D correlations (^{1}H–^{1}H COSY, ^{1}H–^{13}C HMQC and ^{1}H–^{13}C HMBC). Elemental analyses were carried out with an Elementar Vario Micro cube from Elementar Analysensysteme GmbH. IR spectra were obtained on a Bruker Tensor 37 spectrometer equipped with a room temperature DLaTGS detector, a diamond ATR (attenuated total reflection) unit and a nitrogen-flushed chamber. In terms of their intensity, the signals were classified into different categories (vs = very strong, s = strong, m = medium, w = weak, and sh = shoulder).

The silaiminyl-silylene [LSi–Si(NDipp)L] was prepared following literature procedures.[26] [PhC≡CPh], [$SiMe_3C≡C–C≡CSiMe_3$] and [PhC≡C–C≡CPh] are commercially available and used without further purification.

Synthesis of 2. Et_2O (10 mL) was added to a mixture of silylene [LSi–Si(NDipp)L] (0.150 g, 0.216 mmol) and [PhC≡CPh] (0.038 g, 0.216 mmol) at room temperature. The color of the reaction mixture gradually changed from yellow to dark brown. After overnight stirring, crystalline precipitates formed. These brown precipitates were isolated by filtration, then dried *in vacuo* for 1 h to obtain compound **2**. Crystals suitable for X-ray diffraction studies were obtained by slow evaporation of the concentrated solution of **2** in Et_2O at room temperature. Yield (based on crystalline precipitates): 0.096 g (0.110 mmol), 51%. Anal. Calcd for $C_{56}H_{73}N_5Si_2$ (872.41 g/mol): C, 77.10; H, 8.43; N, 8.03. Found: C, 77.15; H, 7.94; N, 7.67. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ (ppm) = 7.81 (d, J = 8.6 Hz, 1H), 7.58 (br, 2H), 7.31 (d, J = 7.6 Hz, 2H), 7.22 (d, J = 7.7 Hz, 2H), 7.10–6.93 (m, 11H), 6.98–6.77 (m, 4H), 6.60 (br, 1H), 4.86 (br, 1H, Dipp–C*H*), 3.45 (br, 1H, Dipp–C*H*), 1.89 (s, 9H), 1.76 (br, 3H), 1.42 (br, 3H), 1.37 (s, 9H), 1.20 (s, 12H), 0.93 (s, 9H), 0.88 (br, 3H). ^{13}C{^{1}H} NMR: Upon crystallization, compound **2** exhibited inadequate solubility in C_6D_6 and insufficient stability in THF-d_8

(due to the fast reaction to **3**), precluding the acquisition of identifiable signals in the $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR spectrum. $^{29}\mathrm{Si}\{^1\mathrm{H}\}$ NMR (79.5 MHz, C_6D_6, 298 K): δ (ppm) = −26.1 (*Si*=C), −50.1 ($\mathit{Si}\mathrm{N}_4$). IR (ATR): $\tilde{\nu}$(cm^{-1}) = 3067 (w), 3019 (sh), 2965 (vs), 2927 (m), 2867 (m), 2277 (w), 2169 (w), 1578 (s), 1520 (w), 1478 (s), 1438 (m), 1388 (vs), 1343 (s), 1226 (m), 1194 (vs), 1130 (w), 1107 (m), 1087 (w), 1063 (w), 1031 (w), 993 (w), 965 (s), 847 (s), 795 (m), 775 (m), 703 (s), 670 (m), 535 (w), 497 (m).

Synthesis of 3. Compound **2** (0.050 g, 0.057 mmol) was dissolved in Et_2O (15 mL) and stirred for 3 days. During this period, the color of the solution changed from dark brown to colorless, and all undissolved precipitates disappeared. Crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of the Et_2O solution of **3** at room temperature. This process was also carried out in the NMR tube using C_6D_6, and subsequent NMR spectra were obtained, demonstrating nearly quantitative transfer. Yield (based on crystals): 0.023 g (0.028 mmol), 49%. Anal. Calcd for $C_{52}H_{65}N_5Si_2$ (816.30 g/mol): C, 76.51; H, 8.03; N, 8.58. Found: C, 76.30; H, 8.35; N, 8.01. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ (ppm) = 8.00 (br, 1H), 7.89 (dd, *J* = 15.3, 6.9 Hz, 4H), 7.26 (dd, *J* = 7.6, 2.1 Hz, 1H, Dipp−C*H*), 7.15−7.01 (m, 8H), 6.96 (t, *J* = 7.3 Hz, 1H), 6.92−6.86 (m, 3H), 6.85−6.77 (m, 3H), 6.73 (s, 1H), 6.53 (s, 1H, Dipp *p*−H), 5.24 (s, 1H, C*H*), 4.48 (sept, *J* = 6.6 Hz, 1H, Dipp−C*H*), 3.36 (sept, *J* = 6.5 Hz, 1H, Dipp−C*H*), 1.93 (s, 9H, ^{t}Bu), 1.62 (d, *J* = 6.5 Hz, 3H, Dipp−CH_3), 1.50 (d, *J* = 6.5 Hz, 3H, Dipp−CH_3), 1.31 (overlap, 12H, ^{t}Bu + Dipp−CH_3), 0.96 (s, 9H, ^{t}Bu), 0.69 (d, *J* = 6.5 Hz, 3H, Dipp−CH_3). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (101 MHz, C_6D_6, 298 K): δ (ppm) = 182.4 (NCN), 158.7 (CH−C═C), 145.2 (CH−Ph−C_q), 144.7 (Dipp−C_q), 143.7 (Dipp−C_q), 140.1, 138.41, 138.39, 138.3 (Dipp−C_q), 132.7 (above signals are C_q), 130.9, 130.4, 129.8, 129.3, 128.35 (from ^{13}C DEPT), 128.0 (from ^{13}C DEPT), 127.6, 127.04, 129.64, 126.7, 126.6, 125.8 (Dipp−C_m), 125.0 (Dipp−C_m), 124.0, 68.9(CH), 54.8 ($C(CH_3)_3$), 52.3 ($C(CH_3)_3$), 51.9 ($C(CH_3)_3$), 33.1 ($(CH_3)_3$), 32.4 ($(CH_3)_3$), 32.2 ($(CH_3)_3$), 28.7 (Dipp−CH), 28.4 (Dipp−CH), 28.1 (Dipp−CH_3), 27.0 (Dipp−CH_3), 25.8 (DippCH_3), 23.9 (Dipp-CH_3). $^{29}\mathrm{Si}\{^1\mathrm{H}\}$ NMR (79.5 MHz, C_6D_6, 298 K): δ (ppm) = −27.7 ($\mathit{Si}\mathrm{CN}_3$), −38.8 ($\mathit{Si}\mathrm{N}_4$). IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3057 (w), 3030 (w), 2968 (s), 2867 (w), 2167 (w), 1588 (w), 1523 (m), 1478 (m), 1460 (m), 1433 (m), 1393 (w), 1363 (w), 1325 (w), 1225 (s), 1197 (vs), 1154 (w), 1101 (s), 1043 (w), 1013 (w), 945 (m), 890 (s), 812 (w), 771 (w), 755 (w), 700 (m), 626 (w), 553 (w), 499 (w), 442 (w).

Synthesis of 4. Toluene (10 mL) was added to a mixture of [LSi−Si(NDipp)L] (0.150 g, 0.216 mmol) and [$SiMe_3C{\equiv}C{-}C{\equiv}CSiMe_3$] (0.042 g, 0.216 mmol) at room temperature. The color of the reaction mixture quickly changed from yellow to red. After overnight stirring, all volatiles were removed under reduced pressure. The resulting solid was then extracted with Et_2O (10 mL). Concentration of the Et_2O solution yielded crystalline material of compound **4**. Crystals suitable for X-ray diffraction studies were obtained from the concentrated solution of **4** in C_6D_6 at room temperature. Yield (based on crystals): 0.075 g (0.084 mmol), 39%. Anal. Calcd for $C_{52}H_{81}N_5Si_4$ (888.60 g/mol): C, 70.29; H, 9.19; N, 7.88. Found: C, 70.75; H, 9.42; N, 8.58. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ (ppm) = 7.44 (d, *J* = 7.5 Hz, 2H, Ph *m*−H), 7.35−7.28 (m, 1H, Ph *p*−H), 7.22−7.10 (m, 5H, 3H of which are overlapped with the residual protio signal of C_6D_6), 7.07 (t, *J* = 7.4 Hz, 1H, Ph *p*−H), 7.01−6.96 (m, 2H, Ph *m*−H), 6.94 (d, *J* = 8.6 Hz, 1H), 6.88−6.82 (m, 1H), 4.41 (br, 2H, Dipp−C*H*), 1.72 (s, 9H, ^{t}Bu), 1.55 (d, *J* = 6.7 Hz, 12H, Dipp−CH_3), 1.30 (s, 9H,^{t}Bu), 1.21 (s, 9H, ^{t}Bu), 0.90 (s, 9H, ^{t}Bu), 0.85 (s, 9H, SiMe_3), 0.11 (s, 9H, SiMe_3). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (101 MHz, C_6D_6, 298 K): δ (ppm) = 179.1 (NCN), 164.1 (C_q, $Me_3Si\mathit{C}{=}C$), 147.4 (C_q), 144.1 (C_q), 138.5 (C_q), 131.4, 131.2 (C_q), 128.7, 128.32 (from ^{13}C DEPT), 128.29 (from ^{13}C DEPT), 128.26 (from ^{13}C DEPT), 128.04 (from ^{13}C DEPT), 127.4, 127.1, 123.5, 115.2, 109.7 (C_q, $C\,{\equiv}CSiMe_3$), 104.3 (C_q, ${\equiv}CSiMe_3$), 67.5 (C_q), 61.8 ($C(CH_3)_3$), 56.7 ($C(CH_3)_3$), 55.9 ($C(CH_3)_3$), 52.7 ($C(CH_3)_3$), 34.9 ($(CH_3)_3$), 32.5 ($(CH_3)_3$), 32.3 ($(CH_3)_3$), 32.1 ($(CH_3)_3$), 27.3 (Dipp-CH and CH_3, overlap), 1.0 (SiMe_3), −0.4 (SiMe_3). Note: one C_q signal is not detected. $^{29}\mathrm{Si}\{^1\mathrm{H}\}$ NMR (79.5 MHz, C_6D_6, 298 K): δ (ppm) = −8.9 ($\mathit{Si}\mathrm{Me}_3$), −19.7 ($\mathit{Si}\mathrm{Me}_3$), −68.0 (DippN*Si*), −85.3 ($\mathrm{PhC(N^tBu)_2}\mathit{Si}$). IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2955 (s), 2932 (sh), 2905 (m), 2865 (w), 2138 (w), 1586 (w), 1472 (sh), 1452 (vs), 1389 (vs), 1367 (m), 1295 (w), 1242 (m), 1191 (m), 1155 (w), 1090 (w), 1062 (w), 1026 (w), 983 (w), 921 (w), 840 (vs), 795 (m), 748 (s), 705 (m), 662 (w), 633 (w), 594 (w), 574 (w), 549 (w), 506 (w), 457 (w).

Synthesis of 5. Toluene (10 mL) was added to a mixture of [LSi−Si(NDipp)L] (0.150 g, 0.216 mmol) and [$PhC{\equiv}C{-}C{\equiv}CPh$] (0.038 g, 0.216 mmol) at room temperature. The color of the reaction mixture slowly changed from yellow to dark red. After overnight stirring, all volatiles were removed under reduced pressure. The resulting solid was extracted with Et_2O (10 mL) and then layered by pentane to yield needle-shaped crystalline material **5**. Crystals suitable for X-ray diffraction studies were obtained from the concentrated C_6D_6 solution of **5** at room temperature. Yield (based on crystals): 0.055 g (0.061 mmol), 28%. Anal. Calcd for $C_{58}H_{73}N_5Si_2$ (896.43 g/mol): C, 77.71; H, 8.21; N, 7.81. Found: C, 78.29; H, 8.08; N, 7.46. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ (ppm) = 8.01 (d, *J* = 7.7 Hz, 1H), 7.49 (d, *J* = 7.3 Hz, 2H), 7.32 (d, *J* = 7.8 Hz, 2H), 7.11−7.06 (m, 7H), 7.02−6.96 (m, 3H), 6.93−6.85 (m, 5H), 6.82 (t, *J* = 6.7 Hz, 2H), 6.70 (d, *J* = 7.3 Hz, 1H), 4.73 ((sept, *J* = 6.9 Hz, 2H, Dipp−C*H*)), 1.90 (s, 9H, ^{t}Bu), 1.71 (d, *J* = 6.8 Hz, 6H, Dipp−CH_3), 1.55 (d, *J* = 6.8 Hz, 6H, Dipp−CH_3), 1.47 (s, 9H, ^{t}Bu), 1.25 (s, 9H, ^{t}Bu), 1.04 (s, 9H, ^{t}Bu). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (101 MHz, C_6D_6, 298 K): δ (ppm) = 180.8 (NCN), 150.5 (C_q), 149.6 (Dipp−NC_q), 140.9 (C_q), 140.8 (Dipp−C_q), 140.2 (C_q, =C), 133.9, 131.6, 130.8, 130.3, 128.7, 128.6, 128.4 (from ^{13}C DEPT), 128.1 (from ^{13}C DEPT), 127.7, 127.5, 127.3, 126.9, 126.5, 126.4 (C_q), 122.9 (Dipp−C), 114.3, 106.1 (C_q, =C), 94.0 (C_q, ≡C), 86.8 (C_q, ≡C), 56.7 ($C(CH_3)_3$), 56.0 ($C(CH_3)_3$), 55.4 ($C(CH_3)_3$), 54.9 ($C(CH_3)_3$), 34.7 ($(CH_3)_3$), 33.5 ($(CH_3)_3$), 31.5 ($(CH_3)_3$), 31.0 ($(CH_3)_3$), 28.3 (Dipp−CH), 26.0 (Dipp−CH_3), 25.4 (Dipp−CH_3). Note: two C_q signals are not detected. $^{29}\mathrm{Si}\{^1\mathrm{H}\}$ NMR (79.5 MHz, C_6D_6, 298 K): δ (ppm) = −28.1 ($\mathit{Si}\mathrm{CN}_3$), −66.8 ($\mathit{Si}\mathrm{C}_2\mathrm{N}_2$). IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3056 (w), 2965 (s), 2928 (s), 2861 (m), 2204 (m), 2166 (w), 1598 (w), 1582 (w), 1563 (w), 1444 (sh), 1424 (s), 1385 (s), 1363 (vs), 1309 (w), 1246 (s), 1193 (s), 1132 (m), 1109 (w), 1058 (m), 1021 (m), 988 (m), 923 (w), 868 (m), 854 (sh), 794 (s), 762 (m), 748 (s), 705 (m), 694 (m), 618 (w), 576 (w), 542 (w), 507 (w), 461 (w).

Crystallographic Studies. A suitable crystal was covered in mineral oil (Aldrich) and mounted on a glass fiber. The crystal was transferred directly to the cold stream of a STOE StadiVari diffractometer. All structures were solved by using the program SHELXS/T[45,46] and Olex2.[47] The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least-squares techniques on F^2 by using the program SHELXL.[45,46] In each case, the locations of the largest peaks in the final difference Fourier map calculations, as well as the magnitude of the residual electron densities, were of no chemical significance. Summary of the crystal data, data collection and refinement for compounds are given in Table S1.

Accession Codes

CCDC 2361301−2361304 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif., or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033.

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Notes

The authors declare no competing financial interest.
No uncommon hazards are noted.

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