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Hydrosilylation of a Silicon(II) Hydride: Synthesis and Characterization of a Remarkable Silylsilylene

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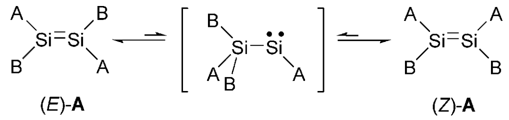
Dedicated to Professor Herbert W. Roesky

Abstract: The synthesis and characterization of novel monomeric silylsilylenes $[\{PhC(N\textit{t}Bu)_2\}Si{-}Si\{(N\textit{t}Bu)_2C(H)Ph\}R]$ (R = Cl (**2**), H (**4**)) are described. Compound **2** was prepared by the treatment of $[\{PhC(N\textit{t}Bu)_2\}SiHCl_2]$ (**1**) with two equivalents of potassium graphite, whereas compound **4** was synthesized by the treatment of **1** with four equivalents of potassium graphite. The results suggest that silicon(II) hydride intermediate $[\{PhC(N\textit{t}Bu)_2\}SiH]$ was formed in the reduction, which underwent a hydrosilylation with the amidinate ligand of $[\{PhC(N\textit{t}Bu)_2\}SiR]$ (R = Cl or H) to form **2** and **4**, respectively. The existence of $[\{PhC(N\textit{t}Bu)_2\}SiH]$ in solution was demonstrated by the treatment of $[\{PhC(N\textit{t}Bu)_2\}SiCl]$ (**3**) with $[K\{HB(\textit{i}Bu)_3\}]$. Compounds **2** and **4** have been characterized by X-ray crystallography and NMR spectroscopy. The results show that compounds **2** and **4** are stable in solution or the solid state, and do not dimerize to form the corresponding disilene. DFT calculations show that the Si–Si bonds in **2** and **4** do not have multiple-bond character.

Keywords: carbene homologues • N ligands • silicon • silylenes

Introduction

Disilenes $[(A)(B)Si{=}Si(A)(B)]$ (A and B are supporting substituents) can undergo *E*,*Z* isomerization under mild conditions.[1] For example, dissolving the crystals of (*E*)-$[(Si^A)(Si^B)Si{=}Si(Si^A)(Si^B)]$ ($Si^A = Si\textit{t}BuMe_2$, $Si^B = Si\textit{i}Pr_2Me$) in [D$_8$]toluene afforded a mixture of (*E*)- and (*Z*)-$[(Si^A)(Si^B)Si{=}Si(Si^A)(Si^B)]$ at 273 K.[2] Kira and co-workers showed that the *E*,*Z* isomerization of disilenes by 1,2-migration of a substituent to form the corresponding silylsilylene is less feasible (Scheme 1)[3] because it requires very high activation energy. DFT calculations show that the activation energy for the rearrangement of disilene $[H_2Si{=}SiH_2]$ to silylsilylene $[{:}Si(H)(SiH_3)]$ is rather high (17.3 kcal mol^{-1} at the MP3/6-31G(d,p)//HF/6-31G(d) level).[4] Tokitoh et al. showed that $[(Bbt)BrSi{=}SiBr(Bbt)]$ (Bbt = C_6H_2-2,6-$\{CH(SiMe_3)_2\}_2$-4-$\{C(SiMe_3)_3\}$) undergoes a 1,2-migration of a bromine atom in [D$_6$]benzene at 100 °C for 10 h to form silylsilylene intermediate $[\{(Bbt)(Br)_2Si\}(Bbt)Si{:}]$ and the low-valent silicon center was then inserted into the C–H bond of the Bbt ligand to form a cyclized compound. $[(Bbt)BrSi{=}SiBr(Bbt)]$ was calculated to be more stable than $[\{(Bbt)(Br)_2Si\}(Bbt)Si{:}]$ by 14.0 kcal mol^{-1} (B3LYP/6-31G(3d) for Si, 6-31G(d) for C and H).[5] Sekiguchi et al. demonstrated that disilylsilylene $[{:}Si\{SiMe(SiMe\textit{t}Bu_2)_2\}_2]$ is unstable and undergoes a 1,2-silyl migration to form disilene $[\{(\textit{t}Bu_2MeSi)_2MeSi\}(Si^C)Si{=}Si(Me)(Si^C)]$ ($Si^C = Si\textit{t}BuMe_2$).[6] To the best of our knowledge, stable monomeric silylsilylene is rarely found.



Scheme 1. Mechanism for *E*,*Z* isomerization.

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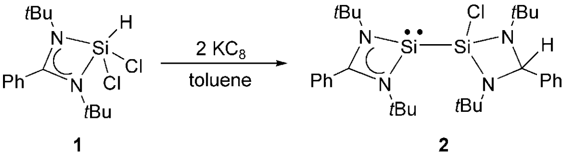
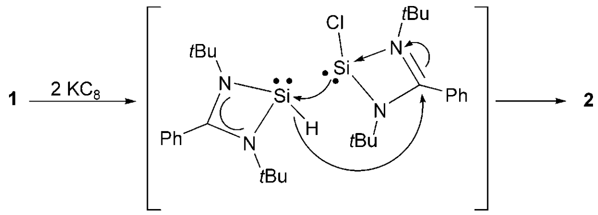
Herein, the synthesis and characterization of base-stabilized silylsilylenes [{PhC(N*t*Bu)$_2$}Si–Si{(N*t*Bu)$_2$C(H)Ph}R] (R = Cl (**2**), H (**4**)) are reported. We also demonstrate the existence of silicon(II) hydride [{PhC(N*t*Bu)$_2$}SiH] in solution.

Results and Discussion

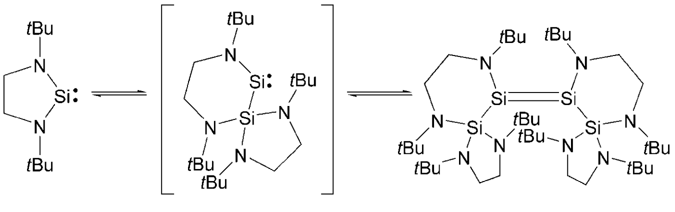
The treatment of [{PhC(N*t*Bu)$_2$}SiHCl$_2$] (**1**)[7] with two equivalents of potassium graphite in toluene for 2 h afforded novel monomeric silylsilylene [{PhC(N*t*Bu)$_2$}Si–Si{(N*t*Bu)$_2$C(H)Ph}Cl] (**2**; Scheme 2). It is suggested that hydrido- and chlorosilylene intermediates [{PhC(N*t*Bu)$_2$}SiR] (R = H, Cl) are formed by the reduction of **1** with potassium graphite. Intermediate [{PhC(N*t*Bu)$_2$}SiH] then reacts with the amidinate ligand of intermediate [{PhC(N*t*Bu)$_2$}SiCl] to form **2** (Scheme 3). The insertion of a silylene into the supporting ligand of another silylene was reported. West et al. showed that stable diaminosilylene [:Si{N(*t*Bu)CH$_2$CH$_2$N(*t*Bu)}] inserted into the Si–N bond of another diaminosilylene to form the intermediate aminosilylsilylene, which further dimerized to form the diaminodisilyldisilene (Scheme 4).[8] Theoretical calculations at the B3LYP/6-31G* level show that the dimerization of the aminosilylsilylene into the diaminodisilyldisilene is highly exothermic (27.3 kcal mol^{-1}). It is worth noting that compound **2** does not dimerize to form the corresponding disilene. DFT calculations also show that intermediates [{PhC(N*t*Bu)$_2$}SiR] (R = H, Cl) do not dimerize to form disilene [{PhC(N*t*Bu)$_2$}(H)Si=Si(Cl){(N*t*Bu)$_2$CPh}], which is not a stable minimum on the potential energy surface.



Scheme 2. Synthesis of **2**.

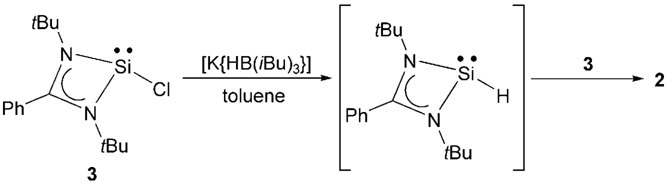


Scheme 3. Proposed mechanism for the formation of **2**.



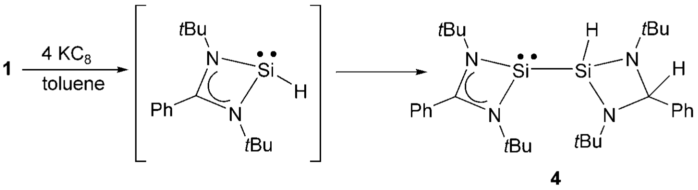
Scheme 4. Insertion of the diaminosilylene.

The treatment of [{PhC(N*t*Bu)$_2$}SiCl] (**3**) with [K{HB(*i*Bu)$_3$}] afforded compound **2** (Scheme 5). The results suggest that intermediate [{PhC(N*t*Bu)$_2$}SiH] is formed in solution which reacts with the amidinate ligand of **3** to form **2**. Because compound **2** was also afforded in the reaction of **1** with KC$_8$ (Scheme 2), it is suggested that intermediate [{PhC(N*t*Bu)$_2$}SiH] and **3** are formed in the reduction (Scheme 3). Recently, Roesky and co-workers have reported that stable germanium(II) or tin(II) hydrides [HC(CMeNAr)$_2$MH] (M = Ge or Sn, Ar = C$_6$H$_3$-2,6-*i*Pr$_2$) can be prepared by the treatment of [HC(CMeNAr)$_2$MCl] (M = Ge or Sn) with [K{HB(*i*Bu)$_3$}].[9] In contrast, [{PhC(N*t*Bu)$_2$}SiH] is highly reactive and cannot be stabilized by the amidinate ligand. However, chloro- and bromosilylene [{PhC(N*t*Bu)$_2$}SiX] (X = Cl (**3**), Br) were synthesized successfully and structurally characterized.[10] [{PhC(N*t*Bu)$_2$}SiCl] (**3**) was synthesized by the treatment of [{PhC(N*t*Bu)$_2$}SiCl$_3$] with potassium in THF, whereas [{PhC(N*t*Bu)$_2$}SiBr] was afforded by the treatment of [{PhC(N*t*Bu)$_2$}Si]$_2$ with bromine.



Scheme 5. Synthesis of **2** from [{PhC(N*t*Bu)$_2$}SiCl] (**3**).

The treatment of **1** with four equivalents of potassium graphite in toluene for 6 h afforded [{PhC(N*t*Bu)$_2$}Si–Si{(N*t*Bu)$_2$C(H)Ph}H] (**4**; Scheme 6). The results suggest that only the [{PhC(N*t*Bu)$_2$}SiH] intermediate was generated in the reaction. The reaction proceeded through the hydrosilylation of [{PhC(N*t*Bu)$_2$}SiH] with the amidinate ligand of another [{PhC(N*t*Bu)$_2$}SiH] molecule. It also suggests that the [{PhC(N*t*Bu)$_2$}SiH] intermediate may not undergo intramolecular 1,3-H shift to form diaminosilylene [{PhCH-



Scheme 6. Synthesis of **4**.

$(\mathrm{N}t\mathrm{Bu})_2\}\mathrm{Si}\!:]$. Roesky et al. showed that germanium(II) and tin(II) hydrides $[\mathrm{HC(CMeNAr)_2MH}]$ (M = Ge or Sn) underwent hydrogermylation or hydrostannylation with unsaturated molecules, such as carbon dioxide, ketones, and alkynes.[9] The treatment of $[\mathrm{HC(CMeNAr)_2SnH}]$ with CyN=C=NCy (Cy = cyclohexyl) afforded $[\mathrm{HC(CMeNAr)_2Sn\{(NCy)_2CH\}}]$.[9c] Power and co-workers showed that the treatment of [ArGeCl] (Ar = $\mathrm{C_6H_3}$-2,6-($\mathrm{C_6H_3}$-2,6-$i\mathrm{Pr_2}$)$_2$) with L-selectride and $\mathrm{PMe_3}$ afforded $[\mathrm{Ar(Me_3P)Ge\text{-}Ge(H)_2Ar}]$.[11] The treatment of [Ar*SnCl] (Ar* = 3,5-$i\mathrm{Pr_2}$-$\mathrm{C_6H}$-2,6-($\mathrm{C_6H_2}$-2,4,6-$i\mathrm{Pr_3}$)$_2$) with $i\mathrm{Bu_2AlH}$ afforded [Ar*Sn−Sn(H)$_2$Ar*].[12]

Compound **2** was isolated as a highly air- and moisture-sensitive colorless crystalline solid that is soluble in toluene and $\mathrm{Et_2O}$. It is stable in both solution and the solid state at room temperature under an inert atmosphere, and has been characterized by elemental analysis and spectroscopic methods. The ^{1}H and ^{13}C NMR spectra of **2** display resonances due to the amidinate and amido ligand. The ^{1}H NMR spectrum of **2** shows a singlet at $\delta = 5.86$ ppm for the NC(H)N proton of the amido ligand. The ^{29}Si NMR spectrum of **2** exhibits two singlets at $\delta = 9.95$ and 26.8 ppm for the silyl substituent and low-valent silicon center, respectively, and the ^{29}Si NMR resonances of **2** lie between the two-coordinate silicon in [Si{N(tBu)CHCHN(tBu)}][13] ($\delta = 78.3$ ppm) and the five-coordinate silicon in **1** ($\delta = -96.6$ ppm). The ^{29}Si NMR signals of **2** also show an upfield shift compared with that of the Si=Si atoms in the diaminodisilyldisilene ($\delta = 119.5$ ppm).[8] It is suggested that compound **2** is monomeric in solution. The UV/Vis spectrum of **2** in toluene at room temperature shows absorption bands at $\lambda = 311$ and 294 nm in the ultraviolet region.

Compound **4** was isolated as a highly air- and moisture-sensitive orange crystalline solid that is soluble in toluene and $\mathrm{Et_2O}$. It is stable in both solution and the solid state at room temperature under an inert atmosphere. The ^{1}H and ^{13}C NMR spectra of **4** display resonances due to the amidinate and amido ligand. The ^{1}H NMR spectrum of **4** shows two singlets at $\delta = 5.58$ and 6.70 ppm for the NC(H)N proton of the amido ligand and silicon hydride, respectively. The ^{29}Si NMR spectrum of **4** exhibits two singlets at $\delta = 2.59$ (J(Si,H) = 145.7 Hz) and 45.6 ppm (^2J(Si,H) = 18.0 Hz) for the silyl substituent and low-valent silicon center, respectively. The ^{29}Si NMR signals of **4** are comparable with those of **2**. Thus, compound **4** is monomeric in solution. The infrared spectrum of **4** shows a ν(Si−H) absorption at 1962 cm^{-1}, which is shifted to lower frequency by 163 cm^{-1} relative to that of $\mathrm{Ph_3SiH}$ (2125 cm^{-1}). The UV/Vis spectrum of **4** in toluene at room temperature shows absorption bands at $\lambda = 320$ and 279 nm in the ultraviolet region.

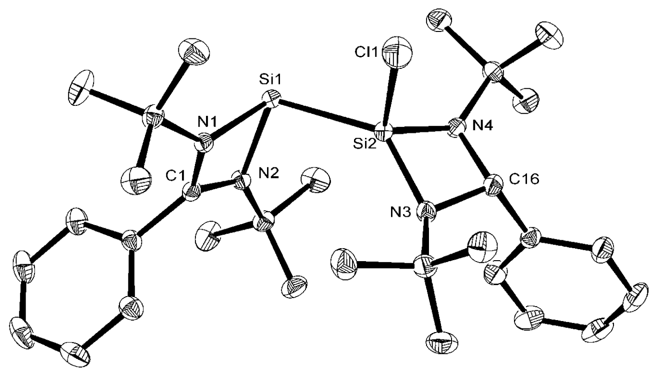


Figure 1. Molecular structure of **2**. Thermal ellipsoids are drawn at the 50% probability level and hydrogen atoms are omitted for clarity. Selected bond distances [Å] and angles [°]: Si1−Si2 2.381(7), Si1−N1 1.877(2), Si1−N2 1.848(2), C1−N1 1.346(3), C1−N2 1.338(2), Si2−Cl1 2.146(8), Si2−N3 1.730(2), Si2−N4 1.735(2), C16−N3 1.491(2), C16−N4 1.489(2); N1-Si1-Si2 103.5(5), N2-Si1-Si2 103.4(6), N1-Si1-N2 70.0(7), Si1-N1-C1 90.9(1), N1-C1-N2 105.5(2), C1-N2-Si1 92.5(1), Si1-Si2-Cl1 101.1(3), Si1-Si2-N3 135.3(6), N3-Si2-N4 78.2(8), Si2-N3-C16 91.3(1), N3-C16-N4 94.2(1), C16-N4-Si2 91.1(1).

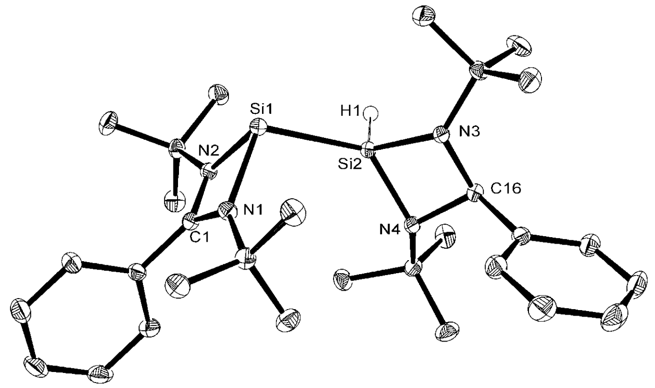


Figure 2. Molecular structure of **4**. Thermal ellipsoids are drawn at the 50% probability level and hydrogen atoms are omitted for clarity, except for H1. Selected bond distances [Å] and angles [°]: Si1−Si2 2.377(5), Si1−N1 1.851(1), Si1−N2 1.874(1), C1−N1 1.341(2), C1−N2 1.350(2), Si2−H1 1.42(2), Si2−N3 1.753(1), Si2−N4 1.759(1), C16−N3 1.483(2), C16−N4 1.487(2); N1-Si1-Si2 104.3(4), N2-Si1-Si2 100.4(4), N1-Si1-N2 69.9(5), Si1-N1-C1 92.8(8), N1-C1-N2 105.0(1), C1-N2-Si1 91.5(8), Si1-Si2-H1 104.7(7), Si1-Si2-N3 119.6(4), N3-Si2-N4 77.5(5), Si2-N3-C16 91.0(7), N3-C16-N4 95.5(8), C16-N4-Si2 90.7(7).

The molecular structures of **2** and **4** are shown in Figures 1 and 2, respectively. The amidinate ligands are bonded in a N,N'-chelate fashion to the Si1 atoms in **2** and **4** and display a trigonal pyramidal geometry. The sum of bond angles at the Si1 centers (**2**: 276.9°; **4**: 274.5°) are comparable with that of the three-coordinated silylene [{PhC(NtBu)$_2$}SiCl] (260.7°).[10a] This geometry is consistent with a stereoactive lone pair at the Si1 atoms in **2** and **4**. The C1−N1 (**2**: 1.346(3) Å; **4**: 1.341(2) Å) and C1−N2 (**2**: 1.338(2) Å; **4**: 1.350(2) Å) bond lengths are approximately intermediate between the C=N and C−N(sp^2) bond lengths. This geometry shows considerable delocalization throughout the N1-C1-N2 skeletons in **2** and **4**. Therefore, the Si1 atoms in **2** and **4** are coordinated with an amidinate ligand. The Si1−Si2 bonds (**2**: 2.381(7) Å; **4**: 2.377(5) Å) are slightly shorter than that of disilylene [{PhC(NtBu)$_2$}Si]$_2$ (2.413(2) Å),[14] but they are comparable with typical Si−Si bond lengths (2.34 Å). It is suggested that the Si1−Si2 bonds in **2** and **4** do not have multiple-bond character. The geometry around the Si2 atoms in **2** and **4** are distorted tetrahedral. The C16−N3 (**2**:

1.491(2) Å; **4**: 1.483(2) Å) and C16–N4 (**2**: 1.489(2) Å; **4**: 1.487(2) Å) bonds are comparable to normal C–N bond. The Si2–N bonds (**2**: av. 1.733 Å; **4**: av. 1.756 Å) are significantly shorter than the Si1–N bonds (**2**: av. 1.863 Å; **4**: av. 1.863 Å). The Si2–N bonds in **2** and **4** are similar to the Si–N_{amide} bonds in [$SiCl_2${N(*t*Bu)C(Ph)C(Ph)N(*t*Bu)}] (av. 1.701 Å).[15] Thus, the Si2 atoms in **2** and **4** are coordinated with an amido ligand. The Si2–Cl1 bond (2.146(8) Å) in **2** is slightly longer than that in [$SiCl_2${N(*t*Bu)C(Ph)C(Ph)N(*t*Bu)}] (av. 2.055 Å).[15] The Si2–H1 bond (1.42(2) Å) in **4** is similar to that of Ph_3SiH (1.49(3) Å).[16]

To understand the bonding nature, a simple derivative [{HC$(NH)_2$}Si–Si{$(NH)_2CH_2$}Cl] (**2A**; Figure S1 in the Supporting Information) was investigated by means of quantum-chemical calculations. The calculations were performed by using DFT[17] at the B3LYP level[18] with the 6-311+G(d,p) basis set[19] as implemented in the Gaussian 03 program.[20] The calculated structural parameters (bond lengths [Å]: Si1–Si2 2.395, Si1–N1 1.926, Si1–N2 1.917, Si1–Cl1 2.156, Si2–N3 1.755, Si2–N4 1.743; bond angles [°]: N1-Si1-N2 67.3, N3-Si2-N4 78.2) are in good agreement with the crystallographic data. The natural-bond-orbital (NBO) analysis[21] (Table S1 in the Supporting Information) shows that the Si1 atom is almost nonhybridized. The Si1–N1 bond is formed by p-rich hybrids on the silicon atom ($sp^{11.06}$) and $sp^{2.05}$ hybrids on the nitrogen atom. The Si1–Si2 bond is formed by p-rich hybrids on the Si1 atom ($sp^{10.56}$) and $sp^{2.27}$ hybrids on the Si2 atom. The lone-pair electrons at the Si1 center are high in s character with some directionality ($sp^{0.32}$, occupancy 1.92). The Wiberg bond index (WBI)[22] of the Si1–Si2 bond (0.87) shows that it is a single bond.

The presence of a π bond in a molecule can be measured by the chemical shift anisotropy (CSA).[23] Large CSA values indicate the presence of π bonds. Comparing the calculated ^{29}Si CSA of **2A** ($\delta = 78.3$ (Si1), 112.7 ppm (Si2)) with that of [$H_2Si{=}SiH_2$] ($\delta = 362.6$ ppm; Table S2 in the Supporting Information), it is suggested that the Si–Si bonds in **2** and **4** do not have multiple-bond character.

Conclusion

Novel monomeric silylsilylene complexes [{PhC$(\mathrm{N}t\mathrm{Bu})_2$}Si–Si{$(\mathrm{N}t\mathrm{Bu})_2$C(H)Ph}R] (R = Cl (**2**), H (**4**)) were successfully synthesized by treating [{PhC$(\mathrm{N}t\mathrm{Bu})_2$}$SiHCl_2$] (**1**) with potassium graphite. It is suggested that the reaction proceeded through silicon(II) hydride intermediate [{PhC$(\mathrm{N}t\mathrm{Bu})_2$}SiH], which underwent a hydrosilylation with the amidinate ligand of another [{PhC$(\mathrm{N}t\mathrm{Bu})_2$}SiR] (R = Cl, H) molecule to form **2** and **4**, respectively. X-ray crystallography and NMR spectroscopy show that compounds **2** and **4** are stable in solution and the solid state, and do not dimerize to form the corresponding disilene. DFT calculations show that the Si–Si bonds in **2** and **4** do not have multiple-bond character.

Experimental Section

General procedure: All manipulations were carried out under an inert atmosphere of argon gas by using standard Schlenk techniques. Solvents were dried and distilled over Na/K alloy prior to use. Compounds **1** and **3** were prepared as described in the literature.[7,10a] The ^{1}H, ^{13}C, and ^{29}Si NMR spectra were recorded by using a JEOL ECA 400 spectrometer. The NMR spectra were recorded in [D$_6$]benzene. The chemical shifts (δ) are relative to $SiMe_4$ for ^{1}H, ^{13}C, and ^{29}Si. Elemental analyses were performed by the Division of Chemistry and Biological Chemistry, Nanyang Technological University. Melting points were measured in sealed glass tubes and were not corrected.

[{PhC(N*t*Bu)$_2$}Si-Si{(N*t*Bu)$_2$C(H)Ph}Cl] (2)

Method A: Toluene (30 mL) was added to a mixture of **1** (1.93 g, 5.83 mmol) and KC_8 (1.76 g, 13.0 mmol) at RT. The resulting red mixture was stirred for 2 h. The insoluble precipitate was then filtered off and the red filtrate was concentrated to afford **2** as colorless block crystals (yield: 0.25 g, 15.5 %).

Method B: [K{HB(*i*Bu)$_3$}] (1.02 mL, 1 M in THF) was added dropwise to a stirred solution of [{PhC(N*t*Bu)$_2$}SiCl] (**3**; 0.297 g, 1.01 mmol) in toluene (15 mL) at 0 °C. The resulting red mixture was warmed to ambient temperature and stirred for an additional 6 h. The insoluble precipitate was filtered off and the red filtrate was concentrated to give colorless crystals of **2** (yield: 0.18 g, 32.9 %).

Characterization data for **2**: M.p. 187.0 °C; ^{1}H NMR (395.9 MHz, 25 °C): $\delta = 1.30$ (s, 18H; *t*Bu), 1.35 (s, 18H; *t*Bu), 5.86 (s, 1H; NC(*H*)N), 6.86–7.14 (m, 6H; Ph), 7.16–7.35 (m, 3H; Ph), 8.17–8.19 ppm (m, 1H; Ph); ^{13}C{^{1}H} NMR (100.4 MHz, 25 °C): $\delta = 31.1$ (C*Me*$_3$), 31.4 (C*Me*$_3$), 50.8 (*C*Me$_3$), 53.6 (*C*Me$_3$), 79.1 (N*C*(H)N), 128.5, 128.6, 128.8, 129.3, 129.6, 130.3, 133.8, 146.9 (Ph), 157.2 ppm (N*C*N); ^{29}Si{^{1}H} NMR (78.7 MHz, 25 °C): $\delta = 9.95$, 26.8 ppm; UV/Vis (toluene): λ_{max} (ε) = 294 (7862), 311 nm (shoulder; 6825 dm^{3}mol^{-1}cm^{-1}); elemental analysis calcd (%) for $C_{30}H_{47}N_4ClSi_2$: C 64.89, H 8.54, N 10.10; found: C 64.59, H 8.38, N 9.82.

Crystal data for **2**: [$C_{30}H_{47}ClN_4Si_2$]; $M_r = 555.35$; monoclinic; space group *P21/c*; $a = 11.5240(4)$, $b = 16.2230(6)$, $c = 17.0161(6)$ Å; $\alpha = 90$, $\beta = 94.828(2)$, $\gamma = 90°$; $V = 3169.9(2)$ Å^3; $Z = 4$; $\rho_{calcd} = 1.164$ mg m^{-3}; 41 542 measured reflections; 8415 independent reflections; 346 refined parameters; $R_1 = 0.0504$, $wR_2 = 0.1433$ ($I > 2\sigma(I)$).

[{PhC(N*t*Bu)$_2$}Si-Si{(N*t*Bu)$_2$C(H)Ph}H] (4): Toluene (32 mL) was added to a mixture of **1** (1.32 g, 4.0 mmol) and KC_8 (2.19 g, 16.17 mmol) at RT and stirred for 6 h. The insoluble precipitate was then filtered off and the red filtrate was concentrated to afford **4** as orange block crystals (yield: 0.017 g, 1.63 %). M.p. 151.4 °C; ^{1}H NMR (395.9 MHz, 25 °C): $\delta = 1.22$ (s, 18H; *t*Bu), 1.32 (s, 18H; *t*Bu), 5.58 (s, 1H; NC(*H*)N), 6.70 (s, 1H; SiH), 6.90–7.07 (m, 5H; Ph), 7.29 (t, 3H; Ph), 7.77–7.78 ppm (m, 2H; Ph); ^{13}C NMR (99.5 MHz, 25 °C): $\delta = 30.4$ (C*Me*$_3$), 31.2 (C*Me*$_3$), 49.7 (*C*Me$_3$), 53.1 (*C*Me$_3$), 79.5 (N*C*(H)N), 128.6, 129.3, 130.5, 134.4, 150.0 (Ph), 152.4 ppm (N*C*N); ^{29}Si NMR (78.6 MHz, 25 °C): $\delta = 2.59$ (J(Si,H) = 145.7 Hz) and 45.6 ppm (^2J(Si,H) = 18.0 Hz); UV/Vis (toluene): λ_{max} (ε) = 279 (1271), 320 nm (5700 dm^{3}mol^{-1}cm^{-1}); elemental analysis calcd (%) for $C_{30}H_{48}N_4Si_2$: C 69.19, H 9.30, N 10.76; found: C 68.71, H 8.93, N 10.64.

Crystal data for **4**: [$C_{30}H_{48}N_4Si_2$]; $M = 520.90$; orthorhombic; space group *P*2(1)2(1)2(1); $a = 9.9171(2)$, $b = 11.2382(3)$, $c = 27.6449(7)$ Å; $V = 3081.0(1)$ Å^3; $Z = 4$; $T = 103(2)$ K; $\rho_{calcd} = 1.123$ mg m^{-3}; 28 164 measured reflections; 9798 independent reflections; 341 refined parameters; $R_1 = 0.0361$, $wR_2 = 0.0823$ ($I > 2\sigma(I)$).

X-ray data collection and structural refinement: Intensity data for compounds **2** and **4** were collected by using a Bruker APEX II diffractometer. Reflections were measured at 103(2) K. The structures were solved by direct-phase determination (SHELXS-97) and refined for all data by full-matrix least-squares methods on F^2.[24] All nonhydrogen atoms were subjected to anisotropic refinement. The hydrogen atoms were generated geometrically and allowed to ride on their respective parent atoms; they were assigned appropriate isotopic thermal parameters and included in the structure-factor calculations.

CCDC-752319 (**2**) and −761095 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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