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Dehydrochlorination to Silylenes by N-Heterocyclic Carbenes

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Reaction of cyclic diaminochlorosilanes with 1,3-bis(*tert*-butyl)imidazol-2-ylidene resulted in the facile formation of the corresponding stable and transient diaminosilylenes. This novel dehydrochlorination route could be applied for the generation of four- and five-membered N-heterocyclic silylenes with a range of different substituents under very mild conditions. Activation of an olefinic C−H bond and reduction of a cyclic diaminochlorosilane have been observed for these new transient silylenes.

Introduction

Silylenes are of considerable current interest owing to their fundamental interest and potential applications in transition metal catalysis.[1] Since the first stable N-heterocyclic silylene was reported by West in 1994,[2] several other cyclic silylenes have been synthesized and fully characterized by Lappert, Kira, and others.[3] At present, the number of stable N-heterocyclic silylenes is still very small and the factors that control the stability and chemical behavior of silylenes have yet to be investigated. This situation may be largely associated with very limited available synthetic approaches. The earlier routes to transient silylenes commonly involved photolytic and high-temperature exclusion of small organic fragments from appropriate silanes,[4] but the most versatile route is reduction of substituted silicon dihalides with highly reducing reagents such as alkali metals and naphthalene lithium in solution phase.[2,3] All of the known synthetic routes require either harsh conditions or highly reactive metallic reagents. Hence, the development of alternative routes to silylenes under mild conditions is highly desirable.

The reaction of trichorosilane with various amines for the generation of $SiCl_3$ anion has been exclusively discussed in a review.[5] The mechanistic studies suggested that $[SiCl_3]^-$ was generated by the initial deprotonation of $HSiCl_3$ by an appropriate amine. Recently, Karsch and co-workers demonstrated that the reaction of trichlorosilane with tertiary amines in the presence of diazabutadienes yielded 1,4-diazasilacyclopentene derivatives. In this system, dichlorosilylene has been proposed to be the key intermediate generated via the dissociation of one chloride ligand from $[SiCl_3]^-$.[6] In view of these earlier reports on the deprotonation of trichlorosilane with organic bases, it is anticipated that substituted hydrocholorosilanes could also be deprotonated by suitable strong bases to yield the corresponding silylenes.

N-Heterocyclic carbenes are well-known strong bases and have been used as HCl acceptors by Roesky's group for the preparation of β-diketiminato divalent germanium species and aluminum diamide from the corresponding halides.[7,8] Herein, we report on the facile route to cyclic silylenes via dehydrochlorination of cyclic diaminohydrochlorosilanes by the bulky heterocyclic carbene 1, 3-bis(*tert*-butyl)imidazol-2-ylidene. Our preliminary results showed that this method can be applied for the generation of stable and transient four- and five-membered heterocyclic silylenes with a range of different substituents on the ring backbones under very mild conditions. To the best our knowledge, this method represents the first approach for the generation of heterocyclic silylenes under mild conditions in the absence of metallic reagents.

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Experimental Section

All operations were carried out under an atmosphere of dry argon or nitrogen by using modified Schlenck line and glovebox techniques. All solvents were freshly distilled from Na and degassed immediately prior to use. Elemental analyses were carried out on an Elemental Vario EL analyzer. The ^{1}H, ^{13}C, and ^{29}Si NMR spectra were recorded on Bruker AV300 and AV400 spectrometers. Infrared spectra were recorded on a Bio-Rad FTS 6000 spectrometer. $Me_2Si(ArNH)_2$ (Ar=2,6-*i*-$Pr_2C_6H_3$),[9] $PhB(ArNLi)_2$,[10] $(CH)_2$(*t*-BuN)$_2$,[11] $(CH)_2(NCy)_2$,[12] 1,2-[N$(SiMe_3)]_2C_6H_4$,[13] and 1,3-bis(*tert*-butyl)imidazol-2-ylidene[14] were synthesized according to published procedures.

Synthesis of $Me_2Si(ArN)_2SiHCl$ (1). A solution of *n*-BuLi (8 mL, 2.5 M in *n*-hexane) was added to a stirred solution of $Me_2Si(ArNH)_2$ (4.10 g, 10 mmol) in *n*-hexane (50 mL) at −78 °C. The mixture was slowly warmed to room temperature and stirred for 6 h. It was cooled to −78 °C, and neat $HSiCl_3$ (1.34 g, 10 mmol) was added. The mixture was allowed to warm to room temperature and stirred for 12 h. It was filtered and evaporated. The residue was extracted with *n*-hexane (30 mL × 2). The combined extracts were pumped to dryness to afford a white powder of **1** (3.6 g, 76%), mp 205 °C. Anal. Calcd for $C_{26}H_{41}ClN_2Si_2$ (472.25): C, 65.99; H, 8.73; N, 5.92. Found: C, 66.17; H, 8.54; N, 6.10. ^{1}H NMR (300 MHz, C_6D_6): δ 0.17, 0.51 (s, 6H, $SiMe_2$), 1.25 (d, 12H, $CH(CH_3)_2$), 1.34 (d, 12H, $CH(CH_3)_2$), 3.92 (sept, 4H, $CH(CH_3)_2$), 6.26 (s, 1H, SiH). ^{13}CNMR (75 MHz, C_6D_6): δ 0.79 ($SiMe_2$), 4.05 ($SiMe_2$), 25.51 ($CH(CH_3)_2$), 28.35 ($CH(CH_3)_2$), 124.25 (C_{meta}), 134.42 (C_{ipso}), 146.90 (C_{para}). ^{29}Si NMR ($CDCl_3$): δ 11.2, −34.4 (d, $^1J_{Si-H}$ = 307 Hz). IR: ν 2181 cm^{-1} (Si−H).

Synthesis of $PhB(ArN)_2SiHCl$ (2). Neat $SiHCl_3$ (0.75 g, 5.5 mmol) was slowly added to a solution of $PhB(ArNLi)_2$ (2.26 g, 5.0 mmol) in *n*-hexane (60 mL) at −78 °C. The solution was slowly warmed to room temperature, whereupon a white precipitate formed. After 12 h, it was filtered, and the filtrate was concentrated (ca. 20 mL) and stored at −40 °C for 24 h to give white crystals of **2** (2.1 g, 83.5%), mp 83−85 °C. Anal. Calcd for $C_{30}H_{40}BClN_2Si$: C, 71.63; H, 8.02; N, 5.57. Found: C, 71.45; H, 7.89; N, 5.34. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.07 (d, 3H, $CH(CH_3)_2$, 1.12 (d, 3H, $CH(CH_3)_2$), 1.19 (d, 3H, $CH(CH_3)_2$), 1.35 (d, 3H, $CH(CH_3)_2$), 3.59 (sept, 1H, $CH(CH_3)_2$), 3.91 (sept, 1H, $CH(CH_3)_2$), 6.35 (s, 1H, Si-H), 6.71 (t, 2H, Ar-H), 6.87 (t, 1H, Ar-H), 7.09−7.19 (7H, Ar-H), 7.27 (d, 2H, Ar-H). ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 23.52, 24.00, 24.85, 25.13 (s, $CH(CH_3)_2$), 28.97, 29.33 (s, $CH(CH_3)_2$), 123.91, 124.42, 126.24, 131.66, 135.09, 136.38, 144.69, 145.78 (s, Ar-C). ^{29}Si NMR ($CDCl_3$): δ −26.1 (d, $^1J_{Si-H}$ = 299 Hz). IR (cm^{-1}): ν 2216 (Si-H). MS: *m*/*z* 502.1 $[PhB(NAr)_2SiHCl]^+$.

Synthesis of $Me_2Si(ArN)_2SiH[(C_3N_2)H(t\text{-}Bu)_2]$ (3). A solution of $Me_2Si(ArN)_2SiHCl$ (0.47 g, 1.0 mmol) in THF (30 mL) was slowly added to a solution of I(*t*-Bu) (= 1,3-bis(*tert*-butyl)-imidazol-2-ylidene) (0.36 g, 2 mmol) in THF (10 mL) at −20 °C in 10 h. The mixture was allowed to warm to room temperature and stirred for 10 h. It was filtered and all volatiles were removed *in vacuo*. The residue was extracted with *n*-pentane (10 mL × 2), and the combined extracts were concentrated (ca. 5 mL) and stored in a freezer at 4 °C for 5 days to give colorless crystals of **3** (0.26 g, 40%), mp 183−185 °C. Anal. Calcd for for $C_{37}H_6N_4Si_2$ (616.44): C, 72.02; H, 9.80; N, 9.08. Found: C, 71.95; H, 9.84; N, 8.82. ^{1}H NMR (400 MHz, C_6D_6): δ 0.25, 0.54 (s, 6H, $Si(CH_3)_2$), 1.03, 1.22, 1.34, 1.39 (d, 24H, $CH(CH_3)_2$), 1.40, 1.63 (s, 18H, $C(CH_3)_3$), 3.88, 4.05 (sept, 4H, $CH(CH_3)_2$), 6.66 (s, 1H, SiH), 7.92 (s, 1H, C=CHN). ^{13}C NMR (100 MHz, C_6D_6): δ 1.07, 4.98 ($SiMe_2$), 25.17, 25.29, 26.05 ($C(CH_3)_2$), 28.36, 28.61 ($C(CH_3)_2$), 31.61, 32.54 ($C(CH_3)_3$), 56.22, 57.90 ($C(CH_3)_3$), 124.25, 125.00, 128.74, 136.73, 146.65 (Ar-C), 217.90 (C:). ^{29}Si NMR (C_6D_6): δ −29.9 (d, SiH, $^1J_{Si-H}$ = 302 Hz), 10.0 ($SiMe_2$). IR (cm^{-1}): ν 2188 (SiH).

Synthesis of $Me_2Si(ArN)_2(Cl)SiSi(H)(NAr)_2SiMe_2$ (4). A solution of I(*t*-Bu) (0.18 g, 1 mmol) in toluene (20 mL) was added to a solution of $Me_2Si(ArN)_2SiHCl$ (0.94 g, 2 mmol) in toluene (20 mL) at −20 °C. The mixture was warmed to room temperature and stirred for 10 h. After filtration, the filtrate was pumped to dryness. The residue was extracted with *n*-hexane (2 × 30 mL). The extract was concentrated (ca. 10 mL) and stored overnight in a freezer at −25 °C to afford a white solid of **4** (0.56 g, 62%), mp 285 °C. Anal. Calcd for $C_{52}H_{81}ClN_4Si_4$ (908.52): C, 68.63; H, 8.97; N, 6.16. Found: C, 69.03; H, 9.75; N, 6.30. ^{1}H NMR (C_6D_6): δ 0.00, 0.38 (s, 12H, $Si(CH_3)_2$), 1.13, 1.19, 1.23 (d, 24H, $CH(CH_3)_2$), 3.72, 3.89 (sept, 8H, $CH(CH_3)_2$), 5.48 (s, 1H, SiH). ^{13}C NMR (100 MHz, C_6D_6): δ 0.14, 4.34 ($SiMe_2$), 24.35, 24.56, 25.33, 26.40 ($C(CH_3)_2$), 27.78, 28.32 ($C(CH_3)_2$), 123.89, 124.00, 125.08, 135.94, 146.44, 146.63 (Ar(C)). IR (cm^{-1}): ν 2179 (Si−H). MS (ESI): 909.5 $[M + 1]^+$.

Synthesis of $PhB(ArN)_2(Cl)SiSi(H)(NAr)_2BPh$ (5). A solution of I(*t*-Bu) (0.36 g, 2.0 mmol) in *n*-hexane (20 mL) was added to a solution of **2** (2.0 g, 4.0 mmol) in *n*-hexane (40 mL). The mixture was stirred for 12 h at room temperature, and a white precipitate was formed. After filtration, the colorless filtrate was concentrated (ca. 10 mL) and stored at −40 °C for 24 h to give white crystals of **5** (1.5 g, 77.5%), mp 206−208 °C. Anal. Cacld for $C_{60}H_{79}B_2ClN_4Si_2$: C, 74.33; H, 8.21; N, 5.78. Found: C, 74.12; H, 8.05; N, 5.72. ^{1}H NMR (C_6D_6): δ 0.64 (d, 3H, $CH(CH_3)_2$), 0.67 (d, 3H, $CH(CH_3)_2$), 1.09 (d, 3H, $CH(CH_3)_2$), 1.10 (d, 3H, $CH(CH_3)_2$), 1.17 (d, 3H, $CH(CH_3)_2$), 1.19 (d, 3H, $CH(CH_3)_2$), 1.42 (d, 3H, $CH(CH_3)_2$), 1.47 (d, 3H, $CH(CH_3)_2$), 3.09 (sept, 1H, $CH(CH_3)_2$), 3.63 (sept, 1H, $CH(CH_3)_2$), 3.836 (sept, 1H, $CH(CH_3)_2$), 4.066 (sept, 1H, $CH(CH_3)_2$), 6.63 (s, 1H, Si-H), 6.67 (t, 2H, Ar-H), 6.82 (qua, 1H, Ar-H), 7.01 (d, 1H, Ar-H), 7.05 (t, 1H, Ar-H), 7.11 (d, 1H, Ar-H), 7.18 (d, 2H, Ar-H), 7.21 (t, 2H, Ar-H). ^{13}C NMR (C_6D_6, 100.6 MHz): 21.50, 21.96, 23.91, 24.29, 24.42, 24.81, 25.53, 25.83 (s, $CH(CH_3)_2$), 28.70, 29.36, 30.47, 31.96 (s, $CH(CH_3)_2$), 123.58, 123.94, 124.48, 125.05, 126.00, 126.10, 127.48, 27.58, 131.29, 131.71, 135.28, 136.17, 137.90,, 138.82, 143.24, 145.04, 145.34, 146.15 (s, Ar-C). ^{29}Si NMR ($CDCl_3$): δ −54.7 (d, SiH, $^1J_{Si-H}$ = 295 Hz), −22.0 (SiCl). IR (cm^{-1}): ν 2109 (Si-H).

Synthesis of $[(CH)_2(NMes)_2]SiHCl$ (7). Lithium (0.18 g, 25 mmol) was added to a solution the diimine $(CH)_2(NMes)_2$ (Mes = 2,4,6-$Me_3C_6H_2$, 2.92 g, 10 mmol) in THF (30 mL). The mixture was stirred for 2 days to give an orange-red suspension. It was filtered, and the filtrate was cooled to −78 °C. To the cooled solution was added neat $HSiCl_3$ (10 mmol) in 5 min. The resulting solution was warmed to room temperature and stirred for 12 h. It was filtered, and the volatiles were removed *in vacuo*. The residue was extracted with *n*-hexane (50 mL), and the extract was stored in a freezer at −40 °C overnight to give white crystals of **7** (2.5 g, 70%), mp 125−127 °C. Anal. Calcd for $C_{20}H_{24}N_2Si$: C, 67.29; H, 7.06; N, 7.85. Found: C, 66.93; H, 7.35; N, 7.42. ^{1}H NMR ($CDCl_3$): δ 2.35 (s, 6H, *p*-CH_3), 2.46 (s, 12H, *o*-CH_3), 5.78 (s, 2H, CHCH), 6.41 (s, 2H, Si-H), 6.99 (s, 4H, Ar-H). ^{13}C NMR ($CDCl_3$): δ 18.7 (*p*-CH_3), 20.9 (*o*-CH_3), 117.9 (HCCH), 128.9, 129.4, 136.0, 136.7 (Ar-C). ^{29}Si NMR ($CDCl_3$): δ −39.3 (d, $^1J_{Si-H}$ = 285 Hz).

Synthesis of $[(CH)_2(NCy)_2]SiHCl$ (8). Lithium chunks (0.25 g, 36.3 mmol) were added to a solution of the diimine $(CHNCy)_2$ (4.0 g, 18.2 mmol) in THF (50 mL) at −78 °C. The mixture was allowed to warm to room temperature and stirred overnight to give a red solution. Neat $HSiCl_3$ (1.83 mL, 18.2 mmol) was added to the solution at −78 °C, and the mixture was allowed to

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warm to room temperature in 20 h. It was filtered, and the volatiles were removed *in vacuo*. The residue was extracted with 60 mL of *n*-hexane. After filtration and removal of solvents, the remaining colorless oil was distilled under reduced pressure (101 °C, 0.3 mbar) to afford **8** as a colorless oil (1.45 g, 28%). Anal. Calcd for $C_{14}H_{25}ClN_2Si$: C, 59.02; H, 8.84; N, 9.83. Found: C, 58.76; H, 8.76; N, 9.24. ^1H NMR ($CDCl_3$): δ 6.48 (s, 1H, Si-*H*), 5.68 (s, 2H, C*H*=C*H*), 2.87 (m, 2H, cyclohexyl-C*H*), 2.07, 1.93, 1.55, 1.40, 1.00 (m, 20H, cyclohexyl-CH_2). ^{13}C NMR($CDCl_3$): δ 114.9 (*C*H=*C*H), 56.3, 35.4, 34.8, 25.9 (cyclohexyl). ^{29}Si NMR ($CDCl_3$): δ −36.1 (d, $^1J_{Si-H}$ = 320 Hz). MS (EI): 284.3 (M^+).

Synthesis of [(CH)$_2$(N*t*-Bu)$_2$]Si (9). A solution of I(*t*-Bu) (0.19 g, 1.1 mmol) in THF (5 mL) was added to a solution of [(CH)$_2$(*t*-BuN)$_2$]Si HCl (0.25 g, 1.1 mmol) in THF (5 mL) at room temperature. The mixture was stirred overnight. It was filtered, the filtrates were removed under vacuum, and the remaining solid was extracted with 30 mL of *n*-hexane. The extract was concentrated (ca. 2 mL) and stored in a freezer at −40 °C overnight to give colorless crystals of **9** (0.15 g, 71.5%). ^1H NMR (C_6D_6): δ 6.75 (s, 2H, CH), 1.40 (s, 18H, CH_3). ^{13}C NMR (C_6D_6): δ 120.0 (CH), 54.1 ($C(CH_3)_3$), 33.1 ($C(CH_3)_3$). ^{29}Si NMR (C_6D_6): δ 77.8 (s).

Synthesis of [(CH)$_2$(NMes)$_2$]Si (10). To a solution of **7** (1.78 g, 5 mmol) in *n*-hexane (20 mL) was added a solution of I(*t*-Bu) (0.9 g, 5 mmol) in *n*-hexane (20 mL). The reaction mixture was stirred for 10 h. Filtration and subsequent concentration and storage at −40 °C overnight afforded yellow crystals of **10** (1.3 g, 81.2%), mp 110−112 °C. Anal. Calcd for $C_{20}H_{24}N_2Si$: C, 74.95; H, 7.55; N, 8.74. Found: C, 74.92; H, 7.41; N, 8.68. ^1H NMR (C_6D_6): δ 2.17 (s, 6H, *p*-CH_3), 2.25 (s, 12H, *o*-CH_3), 6.29 (s, 2H, C*H*C*H*), 6.83 (s, 4H, Ar-*H*). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 18.5 (*p*-*C*H_3); 21.0 (*o*-*C*H_3); 124.4 (H*C*=*C*H), 129.3, 134.8, 135.8, 140.3 (Ar-*C*). ^{29}Si NMR (C_6D_6): δ 77.8.

Synthesis of [(CH)$_2$(NCy)$_2$]SiH[(C_3N_2)H(*t*-Bu)$_2$] (11). I(*t*-Bu) (0.47 g, 2.58 mmol) in THF (5 mL) was added to a solution of **8** (0.37 g, 1.29 mmol) in THF (5 mL) at room temperature. The mixture was stirred overnight. After filtration and removal of volatiles *in vacuo*, the residues were extracted with 30 mL of *n*-hexane. The extract was concentrated and stored in a freezer at −40 °C overnight to afford colorless crystals of **11** (0.33 g, 60%), mp 136 °C. Anal. Calcd for $C_{25}H_{44}N_4Si$: C, 70.04; H, 10.34; N, 13.07. Found: C, 69.90; H, 10.39; N, 12.75. ^1H NMR ($CDCl_3$): δ 7.43 (s, 1H,), 6.46 (s, 1H), 5.72 (s, 2H), 2.90 (m, 2H), 1.96, 1.54, 1.34, 0.96 (m, 20H). ^{13}C NMR ($CDCl_3$): δ 221.97, 132.19, 115.09, 57.91, 56.19, 55.97, 34.85, 34.60, 32.33, 31.35, 26.05, 25.78. ^{29}Si NMR (C_6D_6): δ −38.7 (d, $^1J_{Si-H}$ = 238 Hz).

Synthesis of [C_6H_4(NSiMe$_3$)$_2$-1,2]SiHCl (12). *n*-BuLi (6.85 mL, 17.1 mmol, 2.5 M solution in *n*-hexane) was slowly added to a solution of [C_6H_4(HNSiMe$_3$)$_2$-1,2] (2.2 g, 8.56 mmol) in 50 mL of THF at −78 °C. The mixture was allowed to warm to room temperature and stirred overnight. To this precooled solution (−78 °C) was added $HSiCl_3$ (0.86 mL, 8.56 mmol), and the mixture was allowed to warm to room temperature and stirred for 12 h to yield a light yellow solution. All volatiles were removed *in vacuo*. The remaining residue was extracted with 60 mL of THF. After filtration and removal of the volatiles, the remaining light green oil was distilled under reduced pressure (105 °C, 0.2 mbar) to give colorless oil of **12** (2.1 g, 77.9%), which solidified in a couple of days, mp 58 °C. Anal. Calcd for $C_{12}H_{23}ClN_2Si_3$: C, 45.75; H, 7.36; N, 8.89. Found: C, 45.27; H, 7.87; N, 8.25. ^1H NMR ($CDCl_3$): δ 6.89 and 6.78 (m, 2H, Ar-*H*), 6.14 (s, 1H, Si-*H*), 0.43 (s, 18H, Si(CH_3)$_3$). ^{13}C NMR ($CDCl_3$): δ 140.6, 119.2, and 114.2 (Ar-*C*), 0.15 (Si(CH_3)$_3$). ^{29}Si NMR ($CDCl_3$): δ −16.3 (d, *Si*H, $^1J_{Si-H}$ = 315 Hz), 5.40 (SiMe$_3$). IR: 2250.4 (Si-*H*). MS (EI): 314.4 (M^+).

Synthesis of [C_6H_4(NSiMe$_3$)$_2$-1,2]SiH[(C_3N_2)H(*t*-Bu)$_2$] (13). I(*t*-Bu) (0.51 g, 2.8 mmol) in THF (5 mL) was added to a solution of **12** (0.44 g, 1.4 mmol) in THF (5 mL) at room temperature. **13** was obtained as colorless crystals (62%) following a similar procedure to that described for **11**, mp 166 °C. Anal. Calcd for $C_{23}H_{42}N_4Si_3$: C, 60.20; H, 9.23; N, 12.21. Found: C, 59.90; H, 9.39; N, 12.25. ^1H NMR (C_6D_6): δ 7.34 (s, 1H, C*H*), 6.93 and 6.82 (m, 4H, Ar-*H*), 6.13 (s, 1H, Si-*H*), 1.59 and 1.48 (s, 9H, C(CH_3)$_3$), 0.22 (s, 18H, Si(CH_3)$_3$). ^{13}C NMR (C_6D_6): δ 222.0 (carbene), 142.8, 119.5, and 114.7 (Ar-C), 133.1 (*C*H), 57.8 and 56.0 (*C*Me$_3$), 32.3 and 31.3 (C(*C*H$_3$)$_3$), 0.44 (Si(*C*H$_3$)$_3$). ^{29}Si NMR ($CDCl_3$): δ −22.3 (d, $^1J_{Si-H}$ = 229 Hz), 3.59. IR (cm^{-1}): ν 2156, 2098 (Si−H). MS (EI): 458.3 (M^+).

X-ray Structural Determination. All intensity data were collected with a Bruker SMART CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 113(2) K. The structures were resolved by direct methods and refined by full matrix least-squares on F^2. Hydrogen atoms were considered in calculated positions. All non-hydrogen atoms were refined anisotropically. Crystals of **3** suitable for X-ray analysis were grown from *n*-hexane. Crystallographic data for **3**: monoclinic, space group $P2_1/c$, a = 29.013(6) Å, b = 11.349(2) Å, c = 23.425(5) Å, β = 99.15(3)°, V = 7615(3) Å^3, Z = 8, 50 498 reflections, 13 373 unique (R_{int} = 0.0511), R_1 = 0.0549 ($I > 2\sigma(I)$), wR_2 = 0.1460 (all data). CCDC-731412 contains 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.

Results and Discussion

We have recently reported the isolation of two *N*-aryl-substituted heterocyclic silylenes via low-temperature reduction of their corresponding dihalides.[15] As a continuation of our search for stable silylenes featuring other frameworks, we designed to prepare four-membered heterocyclic silylenes of the type [E(NR)$_2$]Si (E = Me$_2$Si, PhB). It has been reported that the silylene [Me$_2$Si(N*t*-Bu)$_2$]Si could be observed by low-temperature matrix isolation spectroscopy,[16] and we attempted to study this type of silylenes in condensed phases. After our unsuccessful attempts using a reduction route with alkali metals, we turned our attention to dehydrohalogenation reaction with N-heterocyclic carbenes.

The four-membered cyclic diaminochlorosilanes [Me$_2$Si(NAr)$_2$]SiHCl (Ar = 2,6-*i*Pr$_2$C$_6$H$_3$, **1**) and [PhB(NAr)$_2$]SiHCl (**2**) were obtained by the respective reaction of Me$_2$Si(ArNLi)$_2$ and PhB(ArNLi)$_2$[10] with trichlorosilane. Reaction of the N-heterocyclic carbene I(*t*-Bu) (I(*t*-Bu) = 1,3-bis(*tert*-butyl)imidazol-2-ylidene)[14] with **1** in toluene at room temperature resulted in the rapid formation of a white precipitate, which was identified as 1,3-di-*tert*-butylimidazolium chloride. Analysis of the soluble materials by proton NMR spectroscopy indicates the formation of new species. Two species were isolated in pure form under the optimized conditions (Scheme 1); slow addition of a solution of **1** to 2 equiv of I(*t*-Bu) in THF or toluene followed by crystallization of the crude product from *n*-hexane yielded **3** in good yield, while addition of I(*t*-Bu) to 2 equiv of **1** in toluene or *n*-hexane gave the disilane **4**. Compounds **3** and **4** have been characterized by ^1H and ^{13}C NMR and IR spectroscopies and elemental analysis. The presence of silicon hydride in **3** and **4** was evident from their ^1H NMR and IR spectra. The IR bands at 2188 cm^{-1} for **3** and 2179 cm^{-1} for **4** can be assigned to Si−H stretch vibrations. The ^1H NMR signals due to the Si−*H* for **3** and **4** appear at δ 6.66 and

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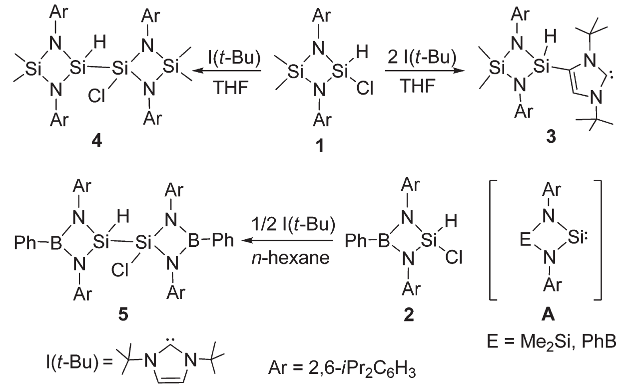
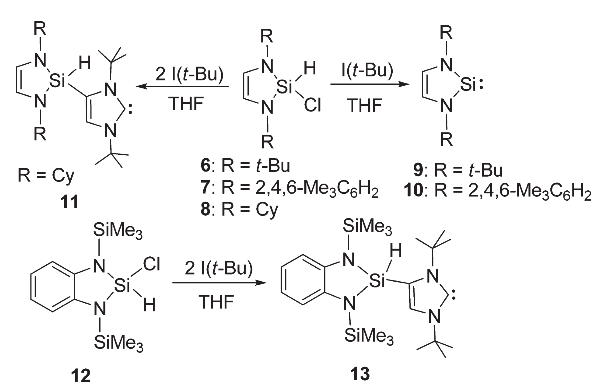
[16] Veith, M.; Werle, E.; Lisowsky, R.; Köppe, R.; Schnöckel, H. *Chem. Ber.* **1992**, *125*, 1375.

Scheme 1



Scheme 2



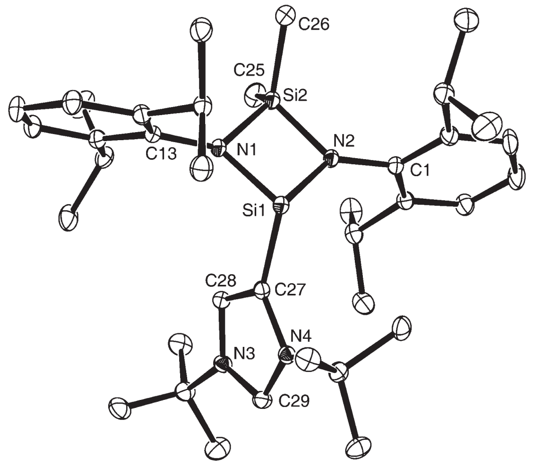


Figure 1. ORTEP drawing of **3** with 30% probability ellipsoids. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): N1−Si1 1.7402(18), N2−Si1 1.7298(18), Si1−C27 1.852(2), N3−C29 1.369(3), N4−C29 1.352(3); N1−Si1−N2 87.02(9), N3−C29−N4 103.52(18).

5.48 ppm. The structure of **3** has been confirmed by an X-ray single-crystal analysis (Figure 1). It is notable that the central silicon atom is bonded to one of the olefinic carbon atoms on the imidazol-2-ylidene ring. Most likely, the formation of **3** involves cleavage of one olefinic C−H bond on the ring.

Reaction of [PhB(NAr)$_2$]SiHCl (**2**) with I(*t*-Bu) in *n*-hexane also resulted in the rapid formation of the corresponding imidazolium chloride. However, the exclusive product is the disilane **5**, irrespective of the addition sequences, molar ratio, and solvents employed (Scheme 1). The disilane **5** has been ambiguously characterized by NMR, IR, and mass spectroscopies and elemental analysis. The ^{29}Si NMR spectrum of **5** gives one doublet at δ −54.7 ($^1J_{\mathrm{Si-H}}$ = 295 Hz) and one singlet at −22.0 ppm due to the two different silicon atoms. It has been reported that disilanes can also be generated by the reaction of a stable heterocyclic silylene with halocarbons.[17]

The most plausible explanation for the formation of the C−H activation product **3** and disilanes **4** and **5** may involve the initial generation of the transient four-membered heterocyclic silylenes **A** via a dehydrochlorination reaction (Scheme 1). The diaminosilylenes can either insert one of the olefinic C−H bonds on the imidazol-2-ylidene ring or reduce the hydrochlorosilanes **1** and **2**. The different reactivity observed for the two systems may arise from steric effects since the relatively short B−N bond (ca. 1.43 Å)[18] would result in the more open structure of the borylene-bridged diaminosilylene, which can be more easily attacked by **2**. Monitoring the reactions in C$_7$D$_8$ did not provide any information on the possible intermediates due to the rapid formation of the imidazolium chloride even at low temperature.

In order to gain further support for the formation of the silylene intermediates by the dehydrochlorination reaction, we attempted to prepare the known five-membered heterocyclic silylenes **9** and **10** via this route.[2,15] Indeed, the reactions of the diaminochlorosilanes **6**[6] and **7** with 1 equiv of I(*t*-Bu) in THF or *n*-hexane at room temperature cleanly yielded **9** and **10** in ca. 72% and 81% yields, respectively (Scheme 2). The spectroscopic data and physical properties of **9** and **10** are in good agreement with those reported. Obviously, this route is superior to the potassium reduction reaction previously employed for the synthesis of **9** and **10** in that the dehydrochlorination reaction can be easily carried out at room temperature in THF, *n*-hexane, and toluene, and the high yields are reproducible. It is noted that the reaction rate for the formation of the imidazolium chloride in *n*-hexane and toluene is slower that that in THF, suggesting that the dehydrohalogenation may go through a polarized intermediate. We postulate that the reaction involves the initial deprotonation of the diaminochlorosilanes by I(*t*-Bu) due to the strong basicity of the N-heterocyclic carbene. This could lead to the formation of cyclic diaminocholorosilyl anions, which then undergo dissociation of the chloride to give the silylenes. The near inertness of the dichorosilane [(CH)$_2$(*t*-BuN)$_2$]SiCl$_2$ to I(*t*-Bu) under similar conditions strongly supports the deprotonation pathway.

The dehydrohalogenation reaction can also be applied for the generation of a transient heterocyclic silylene with less hindered N-substituted groups and a benzo-fused heterocyclic silylene (Scheme 2). The reaction of the N-cyclohexyl-substituted diaminochlorosilane **8** with I(*t*-Bu) in THF yielded the C−H activation product **11**. Similarly, the reaction of the N-silyl-substituted substrate **12** with I(*t*-Bu) gave **13** in good yield. The new compounds **8** and **11**−**13** have been characterized by spectroscopic methods and elemental analysis. The ^{29}Si NMR spectra of the C−H activation products display the characteristic doublet (δ −38.7 ($^1J_{\mathrm{Si-H}}$ = 238 Hz) and −22.3 ppm ($^1J_{\mathrm{Si-H}}$ = 229 Hz) for **11** and **13**, respectively) for the central silicon atom. In the five-membered

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[18] Chivers, T.; Fedorchuk, C.; Parvez, M. *Inorg. Chem.* **2004**, *43*, 2643.

heterocyclic system, the formation of a disilane has not been observed probably due to the more hindered steric environment in the five-membered cyclic silylenes, which suppress the attack of the resulting silylene to the silicon center of the hydrochlorosilanes. Both the C–H activation products have been characterized by standard spectroscopic methods.

The formation of these C–H activation products and disilanes indicates that the sterically hindered environments around a divalent silicon center are essential for the protection of the heterocyclic silylene from attack by other substrates in the reaction medium. In the case of the N-silyl-substituted benzo-fused heterocyclic silylene, the destabilization may result from the reduced electron density on the nitrogen atoms due to the electron-withdrawing property of the silyl substituent.

Conclusion

A novel and facile dehydrohalogenation route by a stable N-heterocyclic carbene for the generation of N-heterocyclic silylenes under very mild conditions has been developed. This route has allowed the generation of stable and transient four- and five-membered cyclic diaminosilylenes with a range of different substituents on the ligand backbones in high yields. Most remarkably, these silylenes were obtained by a non-metallic route under very mild conditions for the first time. We are currently extending this methodology for the generation of other types of silylenes with various N-heterocyclic carbenes and investigating a detailed mechanism for this type of new reaction.

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Supporting Information Available: A cif file for compound **3**. This material is available free of charge via the Internet at http://pubs.acs.org.