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## REACTIONS OF AN OVERCROWDED SILYLENE WITH PYRIDINES: FORMATION OF A NOVEL 2*H*-1,2-AZASILEPINE AND ITS FURTHER CYCLOADDITION

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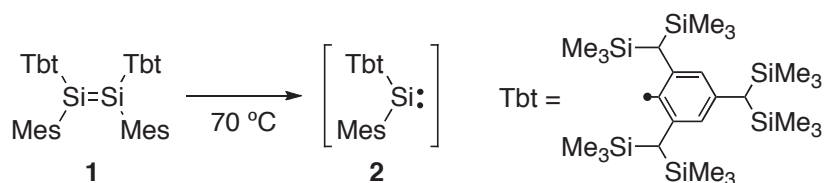
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**Abstract** – The reactions of an overcrowded silylene [Tbt(Mes)Si:] with two types of pyridines were performed. In the case using pyridine, a unique 2:2 adduct bearing five, six, and seven-membered rings was obtained. On the other hand, the reaction with *N,N*-dimethyl-4-aminopyridine (DMAP) afforded the corresponding 1:1 adduct having a 2*H*-1,2-azasilepine skeleton.

# Dedicated to Dr. Albert Padwa on the occasion of his 75th birthday.

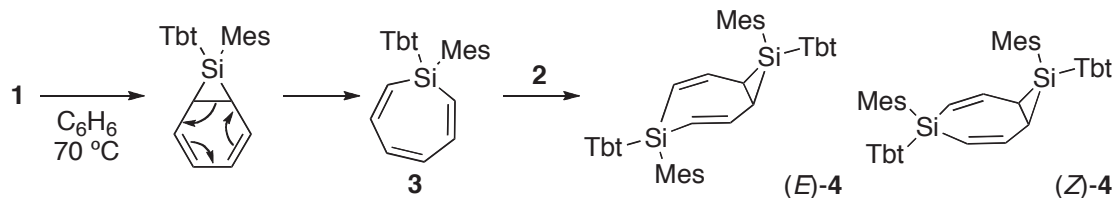
Silylenes (>Si:) are heavier congeners of carbene (>C:), that is, divalent silicon species without any electronic charge. They are usually postulated as reactive intermediates and the examples were quite limited for isolable and/or stable silylenes.<sup>1</sup>



Scheme 1. Thermal dissociation of disilene **1**.

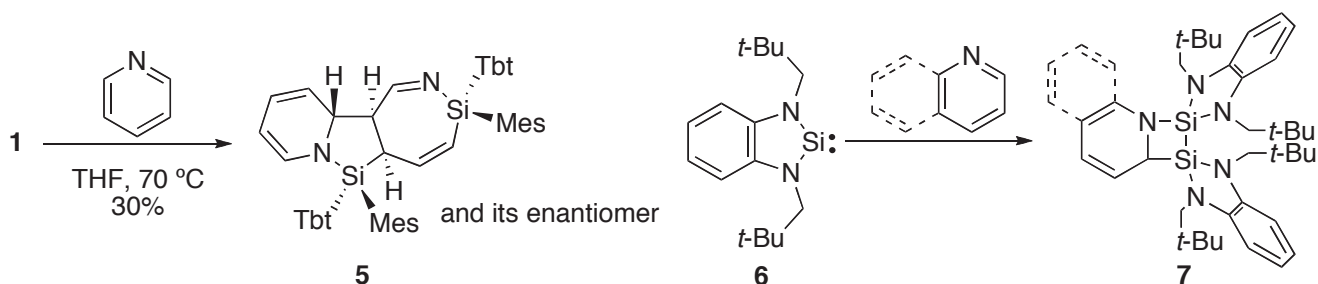
The reactivity of silylenes has been widely investigated, and various kinds of cycloaddition and insertion reactions have been reported.<sup>1</sup> Among them, we have already reported the synthesis of the extremely hindered disilene **1** and revealed its thermal dissociation into the corresponding silylene **2** for the first time (Scheme 1).<sup>2,3</sup> Silylene **2** was found to react even with inert arenes, e.g., benzene, naphthalene, giving the corresponding 2:1 adducts.<sup>3</sup> In the case of benzene, [1+2] cycloadduct was generated initially, and then the ring expansion giving silepin **3** and the successive addition of another silylene occurred to

afford **4** (Scheme 2). Similar reactivity in photochemical conditions was reported by Kira and his co-workers, and the corresponding silepins were isolated.<sup>4</sup> In the course of our research on the synthetic utility of silylene **2**, we found here the unique reactivity of **2** towards pyridines.



Scheme 2. Reaction of silylene **2** generated from **1** with benzene.

The reaction of silylene **2** generated from disilylene **1** with pyridine afforded the 2:2 adduct **5** in 30% yield (Scheme 3).<sup>5</sup> Interestingly, expected 2:1 adduct like **4** was not generated, but another pyridine molecule got involved in the skeleton of **5**. Although various stereoisomers are considerable for the structure of **5**, only one pair of the enantiomers was generated in this reaction as judged by the <sup>1</sup>H NMR spectrum of the crude mixture. The structure of **5** was reasonably supported by the <sup>1</sup>H and <sup>13</sup>C NMR and mass spectra, and finally determined by X-ray crystallographic analysis.<sup>6</sup> The whole and core structures of **5** are shown in Figure 1. The reactions of diamino-substituted silylene **6** with pyridine or quinoline were performed by Lappert and his co-workers (Scheme 3).<sup>7</sup> In contrast to our results, 2:1 adducts **7** having a disilane moiety were obtained, and no C–N bond cleavage occurred.



Scheme 3. Reaction of silylene **2** generated from **1** with pyridine and the related reactions.

Possible reaction pathways for the formation of **5** are summarized in Scheme 4. Taking account into consideration of the cleavage of not C–C but C–N bond on a pyridine molecule, silylene-pyridine complex **8** is considered to be generated initially. Its lone pair on the silicon atom could attack the *ortho*-carbon of the pyridine ring giving [1+2] adduct **9** and then ring-expanded compound, 2*H*-1,2-azasilene **10**. As for the base-stabilized silylene such as compound **8**, we have already reported the silylene–isocyanide complexes as thermally stable compounds by the reaction of **2** with isocyanides.<sup>8</sup> In addition, since silylene **2** can react with pivalonitrile to afford the corresponding [1+2] adduct, that is, SiNC three-membered ring compound, 2*H*-1,2-azasilirene,<sup>9</sup> it is possible to form intermediate

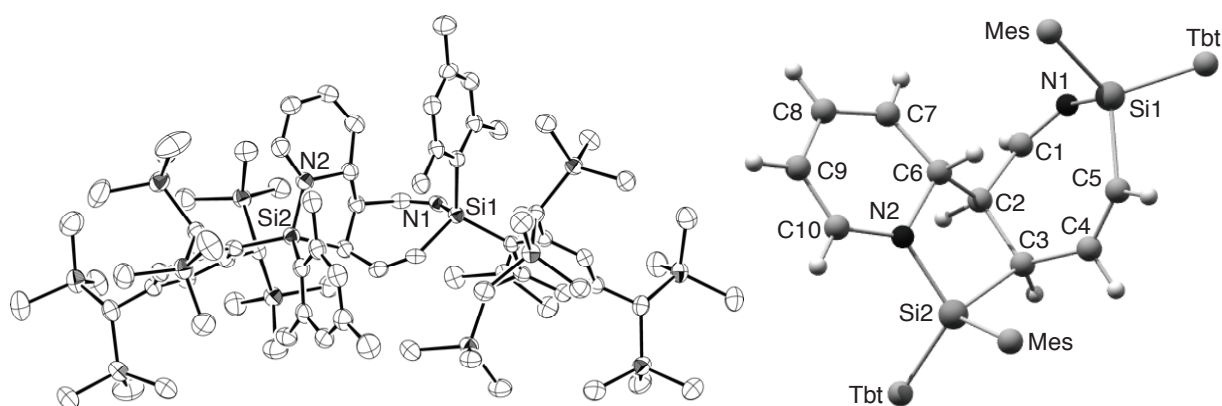
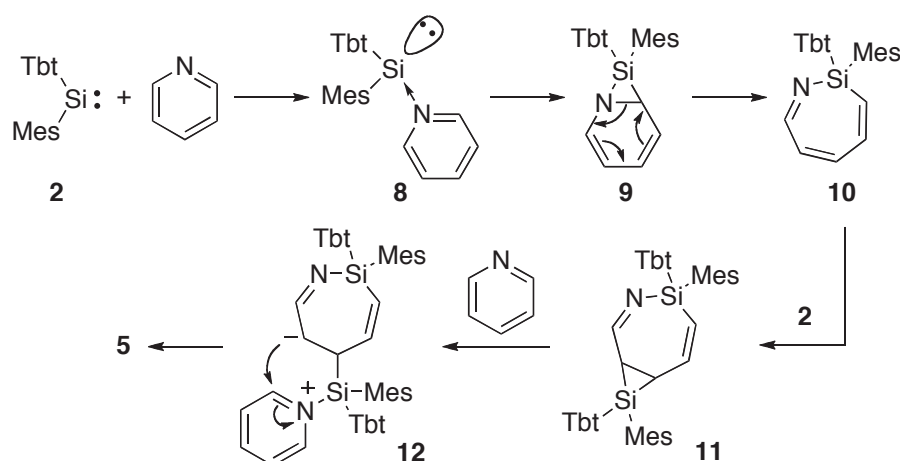


Figure 1. Thermal ellipsoid plot of [**5**·hexane] (50% probability) and the ball and stick model of its core structure. In the thermal ellipsoid plot, hydrogen atoms and hexane molecule were omitted for clarity. Selected bond lengths (Å): Si1–N1 1.775(3), Si1–C5 1.886(3), N1–C1 1.210(4), C1–C2 1.546(4), C2–C3 1.537(4), C2–C6 1.544(4), C3–C4 1.512(4), C3–Si2 1.968(3), C4–C5 1.290(4), Si2–N2 1.746(3), N2–C10 1.386(4), N2–C6 1.493(4), C6–C7 1.500(4), C7–C8 1.317(4), C8–C9 1.454(5), C9–C10 1.324(4).

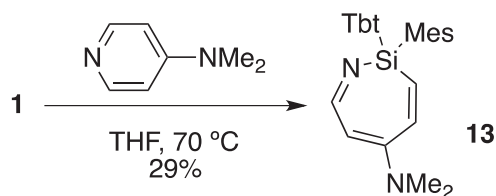
**9** bearing a three-membered ring similarly to the case of the reaction of **2** with benzene. Then, silylene **2** reacted with the less hindered C=C bond of **10** to afford **11**. Although the nitrogen atom of azasilapine **10** can interact with **2** and give the corresponding SiNC three-membered ring, steric and electronic (decrease of nucleophilicity due to the neighboring silicon atom) demands prevented such kind of reactivity. At the final stage, the nitrogen atom of a pyridine molecule attacked to the silicon atom of **11** resulting in the opening of the silacyclopropane ring and the formation of C–C bond. Release of the ring strain of the three-membered ring in **11** and the relative stability of the resulting carbanion are presumably the driving force of the ring-opening reaction followed by the second addition of pyridine molecule. On the other hand, (*E*)-**4** having a skeleton similar to that of **11** did not react with pyridine under similar conditions (10 equiv. of pyridine at 70 °C in THF for 10 h), suggesting that the ring strain of the silacyclopropane unit in **11** is not the dominant factor for the formation of final product **5** but the stabilization



Scheme 4. Plausible mechanisms for the generation of **5**.

of the ring-opened carbainon **12** by its imine unit is of great importance for the ring opening reaction and the regioselective ring annelation giving **5**.

In order to investigate the initial step, the reaction of **2** with DMAP (*N,N*-dimethyl-4-aminopyridine) was performed. Steric hindrance around the 5-position of the silepine skeleton and the electron-withdrawing character of  $\text{NMe}_2$  may suppress the second addition of silylene **2**. As expected, 1:1 adduct **13** having 2*H*-1,2-azasilepine skeleton was isolated as a stable product in 29% yield (Scheme 5).<sup>10</sup> As far as we know, this is the first example of a 2*H*-1,2-azasilepine skeleton. Compound **13** was fully characterized by the  $^1\text{H}$  and  $^{13}\text{C}$  NMR and mass spectra, and the molecular structure was finally determined by X-ray crystallographic analysis.<sup>11</sup> The whole and core structures of **13** are shown in Figure 2 together with the selected bond lengths. The  $\text{NMe}_2$  moiety and C1-4 atoms are almost in same plane, and N1, C5, and Si1 atoms are deviated from that plane.



Scheme 5. Reaction of silylene **2** generated from **1** with DMAP.

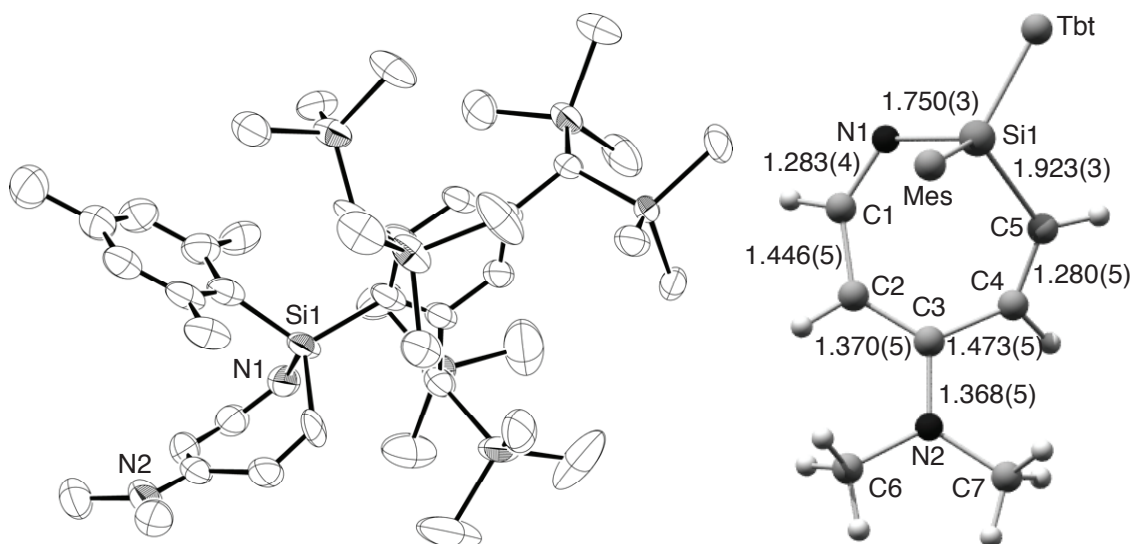


Figure 2. Thermal ellipsoid plot of **13** (50% probability) and ball and stick model of its core structure with selected bond lengths (Å). In the thermal ellipsoid plot, hydrogen atoms were omitted for clarity.

In summary, we have found the unique reactivity of an overcrowded silylene **2** with pyridines giving the first examples of 2*H*-1,2-azasilepine derivatives. These results indicated that a silylene can activate not only the  $\text{C}=\text{C}$  bond but also the  $\text{C}=\text{N}$  bond in an aromatic ring. Since silyl substituents are known to be removable under appropriate conditions, activation by silylenes has a potential leading to a novel method

for the chemical conversion of inactive bonds.

## ACKNOWLEDGEMENTS

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5. Experimental procedure and chemical data: The mixture of (*Z*)-**1** (111 mg, 0.0793 mmol) and pyridine (62.8 mg, 0.793 mmol) was stirred in THF at 70 °C for 10 h and the solvent was removed under reduced pressure. Hexane was added to the residue and the solution was filtered. The filtrate was evaporated and recrystallized from hexane/THF to afford **5** (37.5 mg, 0.0241 mmol, 30%) as colorless crystals. **5**: mp 241 °C (dec.); <sup>1</sup>H NMR (800 MHz, C<sub>6</sub>D<sub>6</sub>, 343 K):  $\delta$  0.04 (s, 18H), 0.17 (s, 36H), 0.19 (s, 18H), 0.29 (s, 36H), 1.48 (s, 1H), 1.49 (s, 1H), 2.07 (s, 3H), 2.12 (s, 3H), 2.22 (brs, 2H), 2.51 (s, 12H), 2.61 (brs, 2H), 3.18 (ddd, *J* = 5.4, 3.3, 2.4 Hz, 1H), 3.96 (ddd, *J* = 10.7, 5.4, 5.1 Hz, 1H), 4.29 (ddd, *J* = 9.8, 1.4, 0.6 Hz, 1H), 4.58 (ddd, *J* = 7.2, 5.4, 0.6 Hz, 1H), 4.78 (ddd, *J* = 10.7, 1.8, 1.4 Hz, 1H), 5.38 (ddd, *J* = 9.8, 5.4, 1.8 Hz, 1H), 5.81 (dd, *J* = 16.1, 2.4 Hz, 1H), 5.83 (dd, *J* = 16.1, 3.3 Hz, 1H), 6.38 (d, *J* = 7.2 Hz, 1H), 6.60 (brs, 4H), 6.70 (brs, 2H), 6.82 (brs, 2H), 9.32 (d, *J* = 5.1 Hz, 1H); <sup>13</sup>C NMR (200 MHz, C<sub>6</sub>D<sub>6</sub>, 343 K):  $\delta$  1.19 (q), 1.21 (q), 1.24 (q), 1.26 (q), 2.2 (q), 3.2 (q), 20.8 (q), 20.9 (q), 26.1 (q  $\times$  2), 27.8 (d), 27.9 (q  $\times$  2), 29.6 (d), 30.1 (d), 31.1 (d), 31.4 (d),

- 34.1 (d), 58.2 (d), 59.4 (d), 97.5 (d), 115.3 (d), 123.1 (d), 123.9 (d), 128.2 (s), 128.5 (d × 2), 129.4 (s), 129.9 (d × 2), 130.4 (s), 131.2 (d), 133.5 (d), 134.1 (s), 134.9 (s), 136.1 (d), 137.0 (d), 138.6 (d), 138.8 (d), 139.6 (s × 2), 139.7 (s × 2), 144.2 (s), 144.3 (s), 145.5 (s), 147.1 (d), 153.8 (s × 4), 171.7 (d); <sup>29</sup>Si NMR (160 MHz, C<sub>6</sub>D<sub>6</sub>, 343 K): δ -28.4, -3.0, 1.9, 2.1, 2.5, 2.7; HRMS (APPI-TOF) *m/z* calcd for C<sub>82</sub>H<sub>151</sub>N<sub>2</sub>Si<sub>14</sub> 1557.8658 ([M+H]<sup>+</sup>). Found: 1557.8665 ([M+H]<sup>+</sup>).
6. X-Ray crystallographic data for [**5**·hexane]: C<sub>82</sub>H<sub>150</sub>N<sub>2</sub>Si<sub>14</sub>·C<sub>6</sub>H<sub>14</sub>, *M* = 1643.47; triclinic; space group *P*-1 (no. 2); *a* = 13.5983(9), *b* = 13.5983(9), *c* = 20.7806(10) Å; α = 66.2556(19), β = 88.173(3), γ = 84.602(6)°; *V* = 5036.2(5) Å<sup>3</sup>; *Z* = 2; *D*<sub>calcd</sub> = 1.084 g/cm<sup>3</sup>; μ = 0.218 mm<sup>-1</sup>; 2θ<sub>max</sub> = 50°; *T* = 103 K; *R*<sub>1</sub> [*I* > 2σ(*I*)] = 0.0542; w*R*<sub>2</sub> (all data) = 0.1422; GOF = 1.034 for 17618 reflections and 981 parameters.
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10. Experimental procedure and chemical data: The mixture of (*Z*)-**1** (90.2 mg, 0.0645 mmol) and *N,N*-dimethyl-4-aminopyridine (39.3 mg, 0.322 mmol) was stirred in THF at 70 °C for 10 h, and the solvent was removed under reduced pressure. Hexane was added to the residue and the solution was filtered. The filtrate was evaporated and recrystallized from hexane/THF to afford **13** (31.2 mg, 0.0380 mmol, 29% yield) as pale yellow crystals. **13**: mp 211 °C (dec.); <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ 0.12 (s, 9H), 0.16 (s, 9H), 0.25 (s, 18H), 0.37 (s, 9H), 0.40 (s, 9H), 1.55 (s, 1H), 2.02 (s, 3H), 2.12 (s, 6H), 2.62 (s, 6H), 2.90 (s, 1H), 3.18 (s, 1H), 4.82 (d, *J* = 4.4 Hz, 1H), 6.52 (s, 2H), 6.60 (s, 1H), 6.66 (s, 2H), 6.73 (s, 1H), 8.53 (d, *J* = 4.4 Hz, 1H); <sup>13</sup>C NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ 1.16 (q), 1.20 (q), 1.5 (q), 1.9 (q), 2.2 (q), 20.9 (q), 27.1 (q × 2), 27.9 (d × 2), 30.8 (d), 39.5 (q × 2), 105.6 (d), 123.5 (d), 128.6 (d), 129.3 (d × 2), 133.6 (s), 136.5 (d), 136.7 (d), 138.8 (s), 144.2 (s), 144.3 (s), 144.5 (s × 2), 153.1 (s), 153.6 (s), 155.6 (s), 162.7 (d); <sup>29</sup>Si NMR (60 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ -20.8, 2.1, 2.4, 2.9. HRMS (APPI-TOF) *m/z* calcd for C<sub>43</sub>H<sub>81</sub>N<sub>2</sub>Si<sub>7</sub> 821.4779 ([M+H]<sup>+</sup>). Found: 821.4774 ([M+H]<sup>+</sup>).
11. X-Ray crystallographic data for **13**: C<sub>43</sub>H<sub>80</sub>N<sub>2</sub>Si<sub>7</sub>, *M* = 821.72; monoclinic; space group *C*2/*c* (no. 15); *a* = 21.3564(3), *b* = 25.7153(4), *c* = 19.2493(3) Å; β = 107.7834(8)°; *V* = 10066.3(3) Å<sup>3</sup>; *Z* = 8; *D*<sub>calcd</sub> = 1.084 g/cm<sup>3</sup>; μ = 0.219 mm<sup>-1</sup>; 2θ<sub>max</sub> = 50°; *T* = 103 K; *R*<sub>1</sub> [*I* > 2σ(*I*)] = 0.0685; w*R*<sub>2</sub> (all data) = 0.1887; GOF = 1.021 for 8867 reflections and 614 parameters.