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Communication

[1 + 2] Cycloaddition of a Cyclic (Alkyl)(amino)silylene and a Disilyne Providing a 3-Aminocyclotrisilene

Taichi Koike, Shunya Honda, Shintaro Ishida, and Takeaki Iwamoto*

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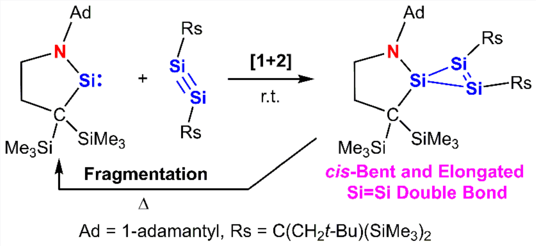
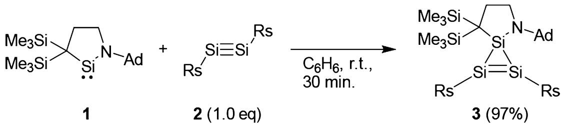
ABSTRACT: Despite the notable progress in the chemistry of cycloaddition reactions of silylenes toward unsaturated bonds, such reactions toward a Si$\equiv$Si triple bond remain unknown. Herein, we report [1 + 2] cycloaddition of a cyclic (alkyl)(amino)silylene (**1**) and a dialkyldisilyne (**2**) to form a 3-aminocyclotrisilene (**3**). Cyclotrisilene **3** adopts a slightly cis-bent geometry with a relatively long Si=Si double bond in the solid state, suggesting a π(Si=Si)−σ^*(Si−N) interaction. Thermolysis of **3** regenerated silylene **1**, which was trapped as Et_3SiH and toluene adducts at high temperatures.



Silylenes, silicon analogues of carbenes, are key intermediates in thermal and photochemical reactions of silicon compounds. Numerous reactions of silylenes resulting from their intrinsic Lewis basicity and acidity due to the lone pair and vacant 3p orbitals on the divalent silicon atom have been reported to date.[1] Some of the most well examined reactions of silylenes are cycloaddition reactions toward unsaturated compounds, e.g. alkenes, alkynes, dienes, and disilenes,[2] to form the corresponding silacycles.[3,4] The reversibility of the reaction[5] has made such compounds serve as synthetic equivalents to silylenes and have been widely applied to molecular transformations in organic synthesis.[6] Although various cycloadditions of silylenes have been reported, the cycloaddition reaction toward Si$\equiv$Si triple-bonded species, disilynes,[7] remains unknown. Herein, we report that the [1 + 2] cycloaddition of cyclic (alkyl)(amino)silylene **1** and dialkyldisilyne **2**, both of which were reported by our group, cleanly furnished 3-amino-substituted cyclotrisilene **3**.

The reaction of silylene **1**[8] and disilyne **2**[7d] at room temperature in benzene for 30 min provided a yellow solution. Removing the volatiles afforded cyclotrisilene **3** in 97% yield (Scheme 1).[9] **3** was identified by multinuclear NMR spectroscopy as well as high-resolution mass spectrometry. **3** is very stable in air: **3** does not decompose even after 1 month in the air in the solid state, implying that the silicon skeleton is well protected by the bulky substituents. The formation of the [1 + 2] cycloadduct is in contrast with the reaction of a disilyne with an N-heterocyclic carbene providing the corresponding NHC-disilyne complex instead of the [1 + 2] cycloadduct.[10]

Scheme 1. [1 + 2] Cycloaddition of Silylene 1 and Disilyne 2



(Ad= 1-adamantyl, Rs = 1,1-bis(trimethylsilyl)-3,3-dimethylbutyl)

Figure 1 shows the molecular structure of **3** determined by single-crystal X-ray diffraction (XRD) analysis. **3** has a longer

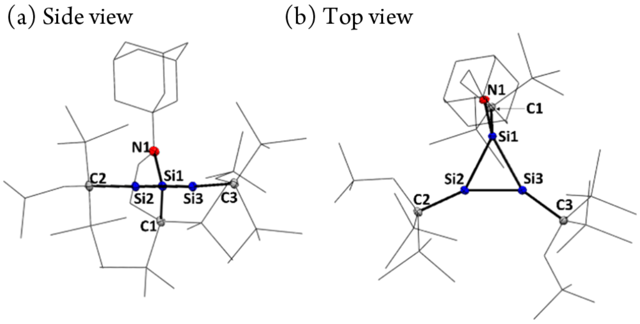


Figure 1. ORTEP drawing of **3** (atomic displacement parameters set at 50% probability; hydrogen atoms and disordered neopentyl moiety omitted for clarity). Selected bond lengths (Å) and angles (deg): Si1−N1 1.7472(13), Si1−C1 1.9284(15), Si1−Si2 2.3269(5), Si1−Si3 2.3616(5), Si2−Si3 2.1676(6), Si2−C2 1.9484(15), Si3−C3 1.9630(14), N1−Si1−C1 93.13(6), N1−Si1−Si2 119.74(5), N1−Si1−Si3 130.57(4), C1−Si1−Si2 128.99(5), C1−Si1−Si3 129.85(5), Si2−Si1−Si3 55.067(16), Si1−Si2−Si3 63.280(17), Si1−Si3−Si2 61.652(17), C2−Si2−Si1 142.04(5), C2−Si2−Si3 154.66(5), C3−Si3−Si1 155.37(5), C3−Si3−Si2 142.56(5).

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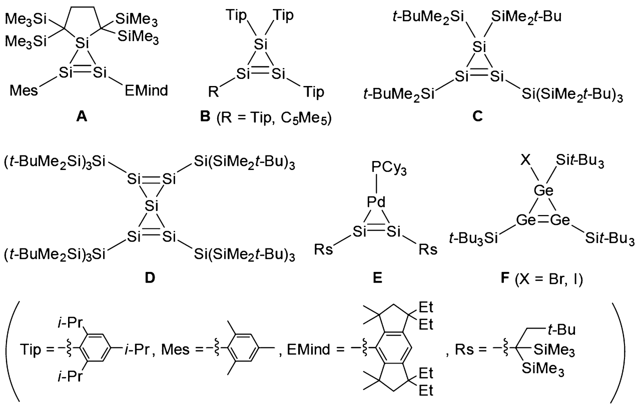
Si═Si double bond (2.1676(6) Å) in comparison to other reported cyclotrisilenes such as **A** (2.1283(6) Å),[4f] **B** (R = Tip = 2,4,6-tri(isopropyl)phenyl), 2.118(1) Å),[4e] and **C** (2.132(2) Å),[4a,d] with the exception of the highly strained and spiro-conjugated spiropentasiladiene **D** (2.186(3) Å) (Chart 1).[4c]

Chart 1. Examples of Reported Disilenes with Three-Membered Rings and Cis-Bent Digermenes



Notably, the Si═Si double bond in **3** adopts a slightly cis-bent geometry (cis-bent angles: 1.0° (Si2), 7.8° (Si3)) in contrast to the structurally related **A** or η^2-disilyne-Pd complex **E** that exhibit a trans-bent geometry (trans-bent angles: 11.9 and 3.9° for **A**, 14.9 and 16.6° for **E**). Cyclotrisilene **3** also displays an unsymmetrical geometry around the silicon skeleton (Si1−Si2 2.3269(5) Å, Si1−Si3 2.3616(5) Å) probably due to steric demands as seen in unsymmetrically substituted cyclotrisilenes **A** and **C**.

A cis-bent geometry around the double bond of heavier group 14 elements was found in some disilenes and 3-halo-substituted cyclotrigermenes **F**.[11] While such geometry exhibited for the cis-bent disilenes is mainly explained by steric effects of the substituents around the Si═Si double bond, a cis-bent and elongated Ge═Ge double bond of **F** was explained by substantial interactions between the π orbital of the Ge═Ge double bond and the low-lying σ^* orbital of the exocyclic Ge−X bond.[12] Overlap of the two orbitals is enhanced when the substituents are oriented toward the Ge−X bond, which results in the cis-bent configuration. As **3** also has an electronegative nitrogen introduced to the saturated position of the silicon skeleton, it is reasonable to hypothesize that the similar electronic effects of the amino group could contribute to the observed cis-bent and elongated Si═Si double bond in **3** (Figure 2a).

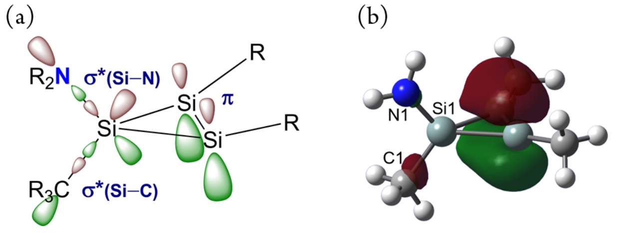


Figure 2. (a) Schematic representation of π(Si═Si)−σ^*(Si−N) and π(Si═Si)−σ^*(Si−C) interactions in a 3-aminocyclotrisilene. (b) Frontier Kohn−Sham orbital of $\mathbf{5}_{opt}$ (HOMO, isosurface value 0.05 e$^-$/au^3).

DFT calculations provided insight into the structural feature of **3**. Figure 3 displays the optimized structures of cyclotrisilene **3** ($\mathbf{3}_{opt}$) as well as model tetramethylcyclotrisilene $\mathbf{4}_{opt}$ and 3-aminotrimethylcyclotrisilene $\mathbf{5}_{opt}$ calculated at the B3LYP-D3/6-311G(d) level of theory. Table 1 shows the selected structural parameters of $\mathbf{3}_{opt}$−$\mathbf{5}_{opt}$ as well as of **3** obtained from XRD analysis. Cyclotrisilene $\mathbf{3}_{opt}$ adopts a cis-bent geometry around the Si═Si double bond (cis-bent angles 7.0 (Si2), 15.8° (Si3); Si═Si length 2.1646 Å), which was in good agreement with the structural features of **3** determined by XRD analysis. Notably, the model 3-aminocyclotrisilene $\mathbf{5}_{opt}$ showed a substantial cis-bent geometry (cis-bent angles: 11.1 (Si2), 11.2° (Si3)) and an elongated Si═Si double bond of 2.1441 Å, while $\mathbf{4}_{opt}$ displayed a planar geometry with a Si═Si length of 2.1254 Å.[12] While the HOMO of $\mathbf{5}_{opt}$ is the π(Si═Si) orbital with a small contribution of the σ^*(Si1−N1) and σ^*(Si1−C1) orbitals (Figure 2b), the stabilization energy for the π(Si═Si) → σ^*(Si1−N1) donation of $\mathbf{5}_{opt}$ (61.6 kJ mol^{-1}) obtained from a second-order perturbation theory analysis is greater than that of the π(Si═Si) → σ^*(Si1−C1) donation (49.4 kJ mol^{-1}). The stronger π(Si═Si)−σ^*(Si−N) interaction should contribute to the cis-bent structure and elongation of the Si═Si double bond of 3-aminocyclotrisilenes, resembling the case of 3-halo-substituted cyclotrigermenes **F**. Although the geometry around the Si═Si bond should be sensitive to the

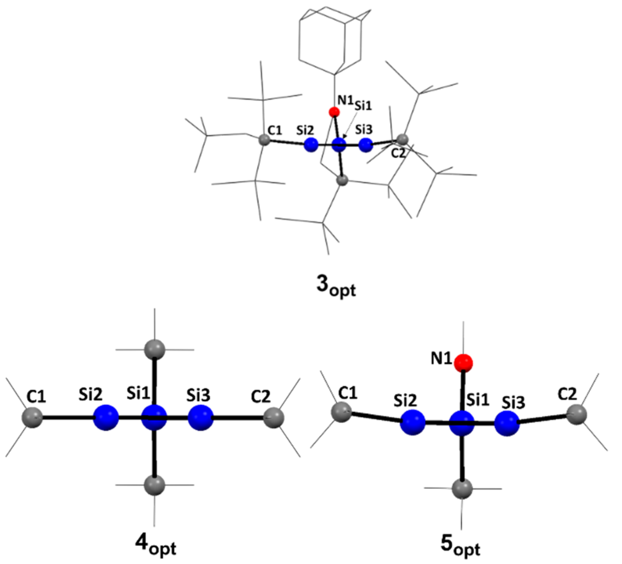


Figure 3. Calculated structures of $\mathbf{3}_{opt}$−$\mathbf{5}_{opt.}$ Hydrogen atoms of $\mathbf{3}_{opt}$ are omitted for clarity.

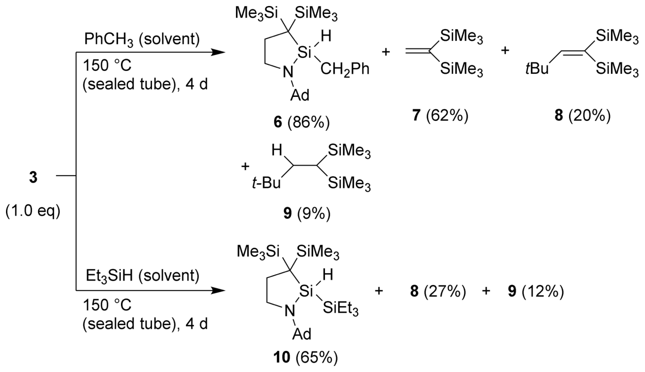
Table 1. Selected Structural Parameters of 3 and $\mathbf{3}_{opt}$−$\mathbf{5}_{opt}$

		distance/Å		
compound	cis-bent angle/deg	Si2═Si3	Si1−Si2	Si1−Si3
3	Si2 1.0 Si3 7.8	2.1676(6)	2.3269(5)	2.3616(5)
$\mathbf{3}_{opt}$	Si2 7.0 Si3 15.8	2.1646	2.3236	2.3861
$\mathbf{4}_{opt}$	Si2 0.0 Si3 0.0	2.1254	2.3141	2.3141
$\mathbf{5}_{opt}$	Si2 11.1 Si3 11.2	2.1441	2.3143	2.3144

steric demand due to the shallow energy potential for the cis-bent deformation of the Si═Si double bond,[13c] the non-covalent interaction (NCI) analysis of 3_{opt} shows that strong steric repulsion does not exist between the Rs substituents and the silylene moiety (Figure S33), implying that steric effects do not contribute strongly to the cis-bent structure for **3**.

We investigated the retrocyclization reaction of **3** (Scheme 2). A toluene solution of **3** was heated at 150 °C in a sealed tube, providing a mixture of the toluene adduct of silylene **1** (**6**, 86%), bis(trimethyl)silylethylene (**7**) (62%), 2-(*tert*-butyl)-1,1-bis(trimethylsilyl)ethylene (**8**) (20%), and **9** (9%). When a Et_3SiH solution of **3** was heated, the corresponding Et_3SiH adduct of silylene **1** (**10**, 65%) was obtained along with **8** (27%) and **9** (12%). Formation of silylene adducts **6** and **10** in high yields indicate the generation of silylene **1** upon heating **3**. Compounds **7**−**9** may be degradation products of **2**. In the absence of toluene or Et_3SiH, silylene **1** was generated by only 3% together with the formation of **7** (117%), **8** (13%), and unidentified products, even though silylene **1** itself does not decompose at 150 °C, suggesting that generated **1** further reacted with **7** and **8**.[14] Although detailed mechanism of the thermal fragmentation reaction remains unclear,[15] the aforementioned results suggest that **3** could be an equivalent of silylene **1** that is stockable in the air.

Scheme 2. Thermal Reactions of Cyclotrisilene 3



In summary, we have succeeded in the reaction of cyclic (alkyl)(amino)silylene **1** and dialkyldisilyne **2** to furnish 3-amino-substituted cyclotrisilene **3** as the first example of a [1 + 2] cycloaddition reaction between a silylene and a disilyne. Cyclotrisilene **3** adopts a slightly cis-bent geometry with a relatively long Si═Si double bond. DFT calculations confirmed that the π(Si═Si)−σ*(Si−N) conjugation should play an important role in the observed structural features. When it is heated at 150 °C, **3** regenerates silylene **1**, which is trapped by Et_3SiH and toluene.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.9b00828.

Experimental details, NMR spectra, UV−vis absorption data, X-ray crystallographic information, and details of theoretical calculations (PDF)

Cartesian coordinates of the calculated structures (XYZ)

Accession Codes

CCDC 1969134 contains 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 336033.

■ AUTHOR INFORMATION

Corresponding Author

Takeaki Iwamoto − *Tohoku University, Sendai, Japan;* orcid.org/0000-0002-8556-5785;
Email: takeaki.iwamoto@tohoku.ac.jp

Other Authors

Taichi Koike − *Tohoku University, Sendai, Japan;* orcid.org/0000-0002-6713-4375
Shunya Honda − *Tohoku University, Sendai, Japan;* orcid.org/0000-0002-1721-5302
Shintaro Ishida − *Tohoku University, Sendai, Japan;* orcid.org/0000-0001-7832-912X

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.organomet.9b00828

Notes

The authors declare no competing financial interest.

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(14) A high-resolution mass spectrum (HRMS APCI) of the reaction mixture exhibits formation of silylene adducts of **7** and **8**.

(15) Disilyne **2** immediately isomerizes into a 1:1 mixture of diastereomeric bi(silacyclopropanes) via intramolecular C−H insertion at temperatures above room temperature.[7d] Heating the silacyclopropanes in the presence of silylene **1** at 150 °C resulted in the formation of ethylene **8** along with signs of numerous unidentified byproducts, suggesting the possibility of disilyne **2** regenerating in situ. However, direct decomposition of **3** as well as isomerization into a disilenyl silylene followed by further decomposition[4f,9c−e] could not be ruled out.