

NHC-Stabilized Silicon–Carbon Mixed Cumulene

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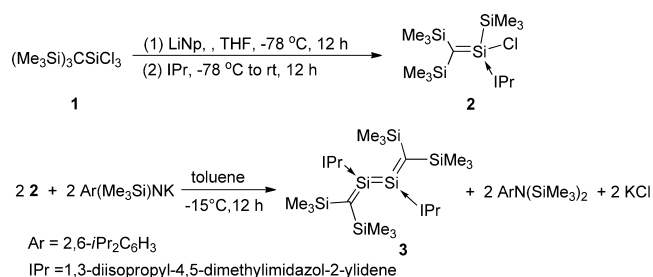
S Supporting Information

ABSTRACT: The NHC-stabilized silicon–carbon mixed cumulene $(\text{Me}_3\text{Si})_2\text{C}=\text{Si}(\text{IPr})=\text{Si}(\text{IPr})=\text{C}(\text{SiMe}_3)_2$ (**3**, IPr = 1,3-diisopropyl-4,5-dimethyl-imidazol-2-ylidene) has been prepared by reaction of $\text{Ar}(\text{SiMe}_3)\text{NK}$ with the NHC-stabilized silene $(\text{Me}_3\text{Si})_2\text{C}=\text{Si}(\text{SiMe}_3)\text{Cl}(\text{IPr})$ (**2**) in toluene at low temperature via the elimination of trimethylsilyl and chloride groups from **2**. X-ray crystal analysis of **3** indicated the formal $\text{C}=\text{Si}=\text{Si}=\text{C}$ cumulene skeleton with the short Si–Si double bond distance of 2.1896(10) Å. DFT calculations disclosed its zwitterionic character. Reaction of **3** with diphenylacetylene resulted in the formation of a silatriafulvene with an exocyclic NHC-stabilized silene moiety.

The chemistry of multiply bonded silicon species has been expanded rapidly in the past several decades since the pioneering work on the isolation of the first silene ($\text{R}_2\text{Si}=\text{CR}_2$) and disilene ($\text{R}_2\text{Si}=\text{SiR}_2$).^{1,2} By taking advantage of kinetic stabilization with super bulky groups, even disilynes with a Si–Si triple bond have been reported by Wiberg, Sekiguchi, and Tokitoh et al.³ Recently, base-stabilization concept has been proved to be very successful for the stabilization of multiply bonded silicon species such as remarkable base-stabilized silicon oxide and diatomic Si_2 , reported by Robinson et al.⁴ In this context, *N*-heterocyclic carbenes are among the most effective base for the stabilization of multiply bonded and low valent silicon compounds.^{4,5} Despite these significant advances, the silicon-containing π systems with consecutive double bonds have been much less studied. This is mainly due to the much less effective sp-hybridization of silicon atom in comparison with carbon atom. Nevertheless, the silicon analogue of an allene with the bent $\text{R}_2\text{Si}=\text{Si}=\text{SiR}_2$ geometry stabilized by a bulky cyclic dianionic alkyl group has been reported by Kira et al.^{6a} In addition, tetrasilabutadienes with conjugated Si–Si double bonds have been reported by Weidenbruch and Sekiguchi.^{6b,c} However, the silicon-containing cumulenes are still elusive.

Herein, we report the synthesis and structure of the isolable crystalline NHC-stabilized 2,3-disilabutatriene derivative (**3**, Scheme 1) containing a formal $\text{R}_2\text{C}=\text{Si}=\text{Si}=\text{CR}_2$ cumulene skeleton stabilized by complexation of the two silicon atoms with 1,3-diisopropyl-4,5-dimethyl-imidazol-2-ylidene (IPr, Scheme 1). It was prepared by the reaction of the NHC-stabilized chlorosilylsilene $(\text{Me}_3\text{Si})_2\text{C}=\text{SiCl}(\text{SiMe}_3)(\text{IPr})$ (**2**) with the potassium amide $\text{Ar}(\text{Me}_3\text{Si})\text{NK}$ (Ar = 2,6-*i*Pr₂C₆H₃, Scheme 1) via the cleavage of the Si–Si and Si–Cl bonds in **2**. Addition of diphenylacetylene to **3** led to the formation of an

Scheme 1. Synthesis of **2** and **3**



NHC-stabilized 1-silatriafulvene with an exocyclic $\text{Si}=\text{C}$ double bond.

The silene $(\text{Me}_3\text{Si})_2\text{C}=\text{SiCl}(\text{SiMe}_3)(\text{IPr})$ (**2**) was synthesized in ca. 40% yield by the reduction of $(\text{Me}_3\text{Si})_3\text{CSiCl}_3$ (**1**)⁷ with lithium naphthalenide (LiNp) in the presence of IPr (Scheme 1). It has been reported that the similar reduction of **1** in the absence of NHCs yielded the corresponding silylenoid $(\text{Me}_3\text{Si})_3\text{CSiCl}_2(\text{Li})$.⁸ The silene **2** is very likely to be formed by the base-induced elimination of LiCl from the silylenoid followed by silyl migration from the carbon to the central silicon atom. Compound **2** is a new type of NHC-stabilized silene with a chloride ligand on the silicon atom.⁹ Attempts to substitute the chloride with the bulky potassium amide $\text{Ar}(\text{Me}_3\text{Si})\text{NK}$ in toluene at low temperature led to the immediate formation of a deep green solution, from which compound **3** was crystallized as deep green crystals at -40 °C from toluene in high yield with the concomitant formation of $\text{ArN}(\text{SiMe}_3)_2$ and KCl. Compound **3** is thermally unstable in solution and in the solid state above -5 °C and immediately decomposed when the temperature was raised to 5 °C. However, its cooled solution in toluene (below -5 °C) could be stored for several days under an inner atmosphere.

The formation of **3** is noteworthy since the reaction may involve the NHC-stabilized silavinylidene $(\text{SiMe}_3)_2\text{C}=\text{Si} \leftarrow \text{IPr}$ intermediate via the cleavage of the Si–SiMe₃ and Si–Cl bonds in **2** with the elimination of Me_3Si^+ and Cl^- groups. Unsaturated silylene $\text{R}_2\text{C}=\text{Si}$ (silavinylidene), isomeric with silaalkyne $\text{RC}\equiv\text{SiR}$, has been the subject of numerous theoretical and experimental investigations.¹⁰ However, silavinylidenes have only been detected and proposed as reactive intermediates, and their isolation has been unsuccessful to date. We reasoned that **3** is very likely to be formed by the dimerization of the NHC-stabilized silavinylidene intermediate.

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The cleavage of the Si–SiMe₃ and Si–Cl bonds with the elimination of KCl and the silylamine represents a new approach for the generation of low valent silicon species.

NHC-stabilized silene **2** was isolated as yellow crystals from toluene and has been fully characterized by ¹H, ¹³C, and ²⁹Si NMR spectra, elemental analysis, and X-ray single crystal analysis (for crystallographic data, see Table S1 in the SI). The ²⁹Si NMR spectrum displays three singlets at –17.2, –11.5, and –9.4 ppm, assignable to the resonances for the Si=C, Si–SiMe₃, and C–SiMe₃. The structure of **2** is given in Figure S1 in the Supporting Information with the relevant bond parameters. The Si1 atom in **2** adopts a distorted tetrahedral geometry, while C2 is almost planar (the sum of the bond angles = 359.72). The Si1–C2 bond length of 1.759(3) Å is much shorter than a Si–C single bond.

Since compound **3** is thermally labile, it has been characterized by ¹H, ¹³C, and ²⁹Si NMR and UV-vis spectroscopy at 263 K. The structure of **3** was finally confirmed by X-ray single crystal analysis. The structural analysis of **3** disclosed the NHC-stabilized 2,3-disilabutatriene skeleton as shown in Figure 1. The Si1–Si2 bond length of 2.1896(10) Å is

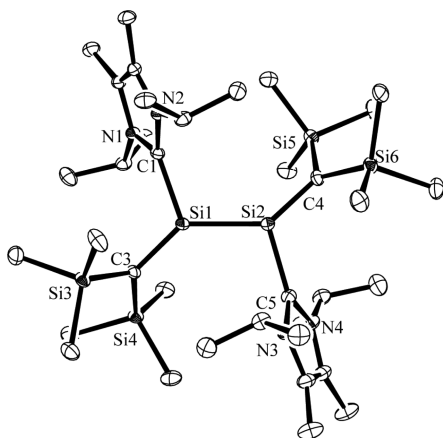


Figure 1. Ortep drawings of **3** with 30% thermal ellipsoid. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Si1–Si2 2.1896(10), Si1–C3 1.774(2), Si2–C4 1.776(2), Si1–C1 1.928(2), Si2–C5 1.941(2), C3–Si3 1.822(2), C3–Si4 1.816(2), C4–Si5 1.816(2), C4–Si6 1.827(2); C1–Si1–Si2 109.50(8), C1–Si1–C3, 114.74(11), Si2–Si1–C3 135.56(9), Si1–Si2–C4 135.50(9), Si–Si2–C5 106.25(8), C4–Si2–C5 116.50(11).

consistent with a Si–Si double bond.¹¹ The Si–C3 and Si2–C4 bond lengths of 1.774 and 1.776(2) Å are slightly longer than that in **2** (1.759(3) Å) and lie in the Si=C double bond range. The Si1 and Si2 distances to the NHC central carbon atoms (1.928 and 1.941(2) Å) are slightly shortened compared to that in **2** (1.971(3) Å) probably due to the three-coordinate silicon atoms in **3**. The geometry of Si1 and Si2 atoms is almost planar (sum of the bond angles around Si1 and Si2 atoms is 359.8 and 358.25°, respectively), indicating the approximate sp² hybrid silicon atoms. The geometry of C3 and C4 atoms is also planar (sum of the angles around the C3 and C4 atoms is 359.79 and 359.35°, respectively). The Si1=Si2 double bond is twisted with the C3–Si1–Si2–C4 and C1–Si1–Si2–C5 torsion angles of 157.1 and 179.1°, respectively. The ²⁹Si NMR spectrum of **3** exhibited two singlets at 34.9 and –13.4 ppm, which can be assigned to the central unsaturated silicon atoms and the SiMe₃ groups, respectively. The former resonance at 34.9 ppm is significantly high-field shifted compared to those determined

for disilenes (ca. 90 ppm).¹¹ This chemical shift is close to the calculated value of 31.4 ppm (relative to SiMe₄) for the central silicon atom in **3** at RB3LYP/6-311+G(2d,p) level (see Figure S3 in the SI).

To understand the electronic structure and bonding situations in **3**, density functional theory (DFT) calculations on compound **3** at RB3LYP/6-311+G(d,p) level have been performed.¹² The optimized structure of **3** (Figure S2) features very similar bond parameters with the experimentally determined values for **3** (Table S2 in the SI). The calculated frontier orbitals for **3** are shown in Figure 2. The HOMO

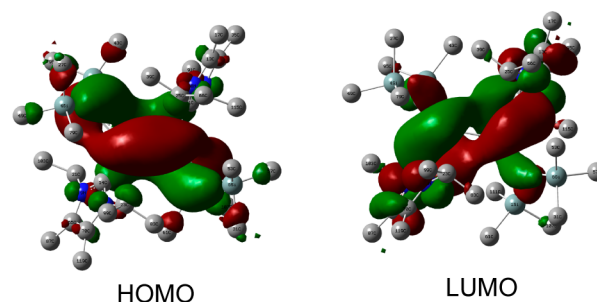
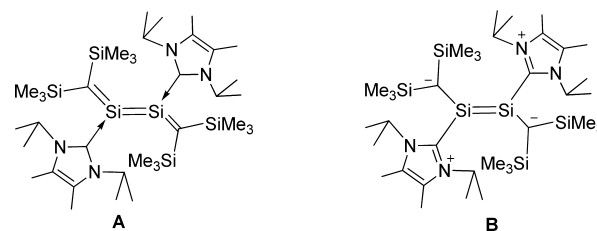


Figure 2. Frontier orbitals of **3** obtained by DFT calculations.

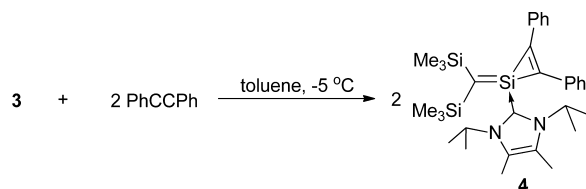
mainly corresponds to the Si–Si π bond and lone pairs on the two carbon atoms in the central CSiSiC skeleton, whereas the LUMO mainly involves the Si–C_{NHC} antibonding orbitals, the NHC nitrogen lone pairs, and the carbene C=C antibonding π orbitals. Natural bond order (NBO) analysis disclosed the highly filled σ bond (1.94e, sp^{1.80} hybrid orbitals) and π bond (1.81e, p orbitals) for the Si=Si double bond. The two Si–C bonds in the C=Si=Si=C skeleton are formed by the sp^{1.34} hybrid orbitals of the silicon atoms with sp^{2.14} orbitals of the carbon atoms. The lone pairs on the two carbon p orbitals in the CSiSiC unit have significant donor–acceptor interactions with the σ* (4.52 kcal/mol) and π* (12.15 kcal/mol) orbitals of the Si=Si bond, leading to the short C–Si bonds. Based on the structural features of **3** and DFT calculations, the structure of **3** can be rationalized by the major contribution from the zwitterionic form **B** and small contribution from the resonance form **A** (Chart 1).

Chart 1. Canonical Structures of **3**



The preliminary examination of reactivity of **3** with diphenylacetylene has been performed. Reaction of **3** with diphenylacetylene in toluene at –5 °C led to the slow color change from green to orange in 20 h. The NHC-stabilized 1-silamethylenecyclopropene (1-silatriafulvene) **4** with an exocyclic silene unit attached was isolated as orange crystals in ca. 40% yield after workup (Scheme 2). This reactivity is distinct from that reported for most disilenes but resembles that of silylenes, suggesting that the Si–Si double bond may dissociate

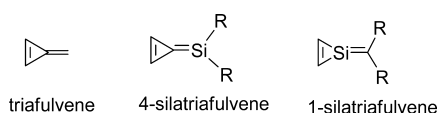
Scheme 2. Reaction of 3 with Diphenylacetylene



to the corresponding NHC-stabilized unsaturated silylene in solution. The calculated small dissociate energy of 4.23 kcal/mol for 3 obtained by DFT calculations (Table S3 in the SI) supports the dissociation mechanism. The reactions of disilenes with alkynes in general yielded disilacyclobutenes via a formal [2 + 2] cycloaddition.¹³ Nevertheless, it has been reported that reaction of a lattice framework disilene with alkynes gave the corresponding silacyclopropene due to the dissociation of the disilene in solution.¹⁴ The similar reaction from $-5\text{ }^{\circ}\text{C}$ to room temperature also yielded 4, indicating that the decomposition of 3 might proceed via the dissociation of the Si=Si bond.

As the smallest fulvene, triafulvene (Chart 2), has been the subject of considerable experimental and theoretical interest.

Chart 2



Kira et al. reported the synthesis and reactions of 4-silatriafulvenes (Chart 2) kinetically stabilized by bulky silyl groups on the exocyclic silicon atom.¹⁵ The silicon analogues with a silicon atom within the three-membered ring, 1-silatriafulvenes, have not been isolated so far. Compound 4 can be described as an NHC-stabilized 1-silatriafulvene.

Compound 4 has been fully characterized by NMR spectroscopy, elemental analysis, and X-ray single crystal analysis. The ²⁹Si NMR spectrum of 4 exhibits two resonances at δ 106.8 and 9.4 ppm. The structure of 4 is shown in Figure 3. The Si1–C21 bond length of 1.816(3) Å is longer than that in 2 (1.759(3) Å), whereas the Si1–C_{NHC} bond of 1.919(3) Å is shortened compared to those in 2 (1.971(3) Å). In the SiCC three-membered ring, the two Si–C bond lengths of 1.830 and

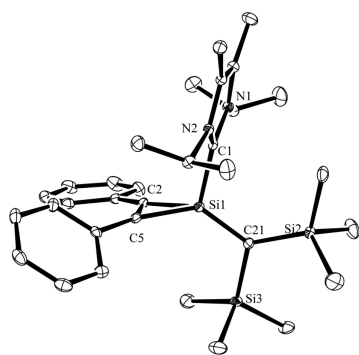


Figure 3. Ortep drawings of 4 with 30% thermal ellipsoid. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): C2–C5 1.354(4), Si1–C2 1.830(3), Si1–C5 1.841(3), Si1–C21 1.816(3), Si1–C1 1.919(3), C21–Si2 1.816(3), C21–Si3 1.834(3); C2–Si1–C5 43.29(12).

1.841(3) Å and the short C–C distance of 1.354(4) Å are in line with the silacyclopropene structure.¹⁶

In summary, we have developed a novel reaction pathway based on the potassium amide-induced Si–Si and Si–Cl bond cleavage for the generation of the elusive NHC-stabilized silicon–carbon mixed cumulene with a formal C=Si=Si=C skeleton. Its reaction with diphenylacetylene yielded the NHC-stabilized 1-silatriafulvene 4 via the cycloaddition with the unsaturated silylene intermediate (Me₃Si)₂C=Si(IPr). Compound 3 represents a novel class of silicon-containing cumulene, which features Si=Si double bond and significant zwitterionic character. Further investigation into the reactivity of 3 and trapping of the silylidene intermediate with unsaturated compounds are currently undertaken in our laboratory.

■ ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b06960.

Synthetic procedures, spectroscopic data, X-ray crystal structure of 2, and details of DFT calculations for 3 (PDF)

Compound 2 (CIF)

Compound 3 (CIF)

Compound 4 (CIF)

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Notes

The authors declare no competing financial interest.

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