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# An Isolable NHC-Stabilized Silylene Radical Cation: Synthesis and Structural Characterization

Hiroaki Tanaka, Masaaki Ichinohe, and Akira Sekiguchi*

Department of Chemistry, Graduate School of Pure and Applied Sciences, University of Tsukuba, Tsukuba, Ibaraki 305-8571, Japan

*Supporting Information*

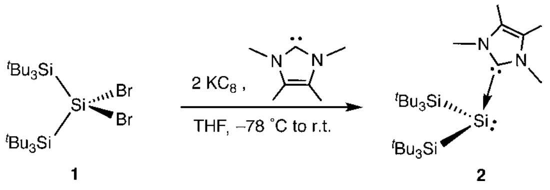
**ABSTRACT:** The silyl-substituted silylene−NHC complex bis(tri-*tert*-butylsilyl)silylene−(1,3,4,5-tetramethylimidazol-2-ylidene) [$({}^t\mathrm{Bu}_3\mathrm{Si})_2\mathrm{Si}{:}\leftarrow\mathrm{NHC}^{\mathrm{Me}}$, **2**] was synthesized and isolated as air- and moisture-sensitive orange crystals by reductive debromination of the dibromosilane $({}^t\mathrm{Bu}_3\mathrm{Si})_2\mathrm{SiBr}_2$ (**1**) with 2.0 equiv of $\mathrm{KC}_8$ in the presence of $\mathrm{NHC}^{\mathrm{Me}}$. In addition, the silylene−NHC complex **2** cleanly underwent one-electron oxidation with 1.0 equiv of $\mathrm{Ph}_3\mathrm{C}^+\cdot\mathrm{Ar}_4\mathrm{B}^-$ ($\mathrm{Ar}_4\mathrm{B}^-$ = tetrakis[4-(*tert*-butyldimethylsilyl)-2,3,5,6-tetrafluorophenyl]borate) in benzene to afford the NHC-stabilized silylene radical cation $[({}^t\mathrm{Bu}_3\mathrm{Si})_2\mathrm{Si}\leftarrow\mathrm{NHC}^{\mathrm{Me}}]^{\bullet+}\cdot\mathrm{Ar}_4\mathrm{B}^-$ (**3**). The radical cation **3** was isolated as air- and moisture-sensitive yellow crystals and structurally characterized by X-ray crystallography and electron paramagnetic resonance spectroscopy, which showed that **3** has a planar structure with a $\pi$-radical nature.

The chemistry of stable metallylenes (the heavier group 14 element analogues of carbenes) and the corresponding radical ions is one of the most fascinating topics of recent years.[1] Several group 14 element-centered metallylenes as well as the radical anions $\mathrm{R}_2\mathrm{E}{:}^{\bullet-}$ (E = Si, Ge, Sn) have been observed by electron paramagnetic resonance (EPR) spectroscopy.[2] Among them, the lithium salt of bis(di-*tert*-butylmethylsilyl)silylene anion radical $[({}^t\mathrm{Bu}_2\mathrm{MeSi})_2\mathrm{Si}{:}]^{\bullet-}$ has been structurally characterized by both X-ray crystallography and EPR spectroscopy.[2d] As for the silylene radical cation, the hydrogen complex of the parent species, $\mathrm{H}_2\mathrm{Si}^{\bullet+}\cdots\mathrm{H}_2$, generated under neon matrix deposition at 4 K by the photoionization of $\mathrm{SiH}_4$, has been reported.[3] To date, however, the isolation and structural characterization of metallylene radical cations have not been achieved because of their high reactivity and instability. We have succeeded in synthesizing a silyl-substituted silylene−NHC complex **2** (NHC = N-heterocyclic carbene) that readily undergoes one-electron oxidation, giving the isolable silylene−NHC radical cation $[({}^t\mathrm{Bu}_3\mathrm{Si})_2\mathrm{Si}\leftarrow\mathrm{NHC}^{\mathrm{Me}}]^{\bullet+}$ (**3**) ($\mathrm{NHC}^{\mathrm{Me}}$ = 1,3,4,5-tetramethylimidazol-2-ylidene), which we report here.

A large number of metallylenes of heavier group 14 elements with various substituents, such as alkyl, aryl, amino, and halogens, have been reported,[1] whereas metallylenes bearing electropositive substituents, such as silyl, germyl, and stannyl groups, have rarely been reported. Recently, the strong $\sigma$ donation of NHCs has been used to stabilize low-coordinate main group element compounds.[4] The parent metallylene complexes $\mathrm{LA}\leftarrow\mathrm{MH}_2\leftarrow\mathrm{NHC}$ [M = Si,[5a] Ge,[5b] Sn;[5b] LA = borane fragment, $\mathrm{BH}_3$, or $\mathrm{W(CO)}_5$] have also been reported. Escudié and co-workers recently reported the synthesis and structural characterization of the stable germylene−$\mathrm{NHC}^{\mathrm{iPr}}$ complex $[(\mathrm{Me}_3\mathrm{Si})_3\mathrm{Sn}]_2\mathrm{Ge}{:}\leftarrow\mathrm{NHC}^{\mathrm{iPr}}$ and the stannylene complexes $[(\mathrm{Me}_3\mathrm{Si})_3\mathrm{E}]_2\mathrm{Sn}{:}\leftarrow\mathrm{NHC}^{\mathrm{iPr}}$ (E = Si, Ge, Sn; $\mathrm{NHC}^{\mathrm{iPr}}$ = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene).[5c] Dihalosilylene−NHC complexes have also been isolated and structurally characterized,[5d,e] but such species with electropositive silyl substituents, $(\mathrm{R}_3\mathrm{Si})_2\mathrm{Si}{:}\leftarrow\mathrm{NHC}$, are unprecedented. The silylene center in this type of complex is expected to have a lone pair at a higher energy level than that of $\mathrm{X}_2\mathrm{Si}{:}\leftarrow\mathrm{NHC}^{\mathrm{Dip}}$ [X = Cl,[5d] Br;[5e] $\mathrm{NHC}^{\mathrm{Dip}}$ = 1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene]. This prompted us to prepare a silyl-substituted silylene−NHC complex with very bulky tri-*tert*-butylsilyl substituents by debromination of the dibromosilane $({}^t\mathrm{Bu}_3\mathrm{Si})_2\mathrm{SiBr}_2$ (**1**) in the presence of $\mathrm{NHC}^{\mathrm{Me}}$.[6]

Treatment of **1** with 2.0 equiv of $\mathrm{KC}_8$ in the presence of $\mathrm{NHC}^{\mathrm{Me}}$ resulted in a color change from colorless to red. After filtration of graphite and inorganic salts, recrystallization from tetrahydrofuran (THF) gave the silyl-substituted silylene−NHC complex $({}^t\mathrm{Bu}_3\mathrm{Si})_2\mathrm{Si}{:}\leftarrow\mathrm{NHC}^{\mathrm{Me}}$ (**2**) in 43% yield as air- and moisture-sensitive orange crystals (Scheme 1).[7,8] It is reasonable to assume the initial formation of the silylenoid $({}^t\mathrm{Bu}_3\mathrm{Si})_2\mathrm{Si(K)(Br)}$ followed by $\alpha$-elimination of KBr and coordination of the NHC to form **2**.[9] This can be contrasted with the free silylene $({}^t\mathrm{Bu}_3\mathrm{Si})_2\mathrm{Si}{:}$, which has previously been reported to have a triplet ground state.[10a,b] This indicates that the electronic structure of $({}^t\mathrm{Bu}_3\mathrm{Si})_2\mathrm{Si}{:}$ would change from a triplet to a singlet upon coordination of an NHC. Additionally, the free triplet rearranges into a disilacyclobutane, which was not observed in the synthesis of **2**.[10a,c] Therefore, it seems clear that the free silylene is not an intermediate in this reaction.

**Scheme 1. Reduction of Dibromosilane 1 with $\mathrm{KC}_8$ To Give Silylene−NHC Complex 2**



The molecular structure of **2** was unambiguously characterized by X-ray crystallographic analysis (Figure 1).[7] The

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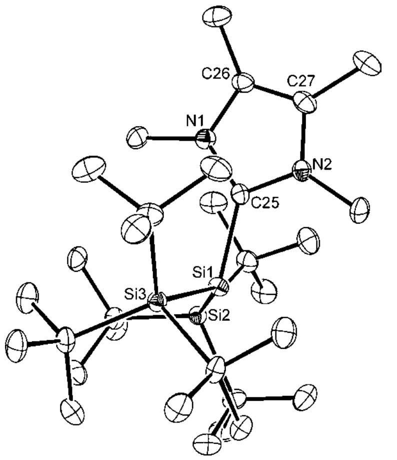


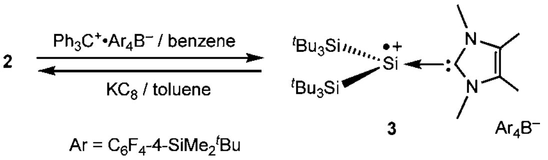
**Figure 1.** ORTEP drawing of **2** (50% thermal ellipsoids). There are two crystallographically independent molecules of **2** in the unit cell, of which one is shown here. H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Si1−C25, 1.933(4); Si1−Si2, 2.4542(15); Si1−Si3, 2.4419(14); N1−C25, 1.369(5); N1−C26, 1.385(5); N2−C25, 1.368(5); N2−C27, 1.385(5); C26−C27, 1.370(6); C25−Si1−Si2, 103.48(12); C25−Si1−Si3, 106.04(12); Si2−Si1−Si3, 134.81(6); N1−C25−N2, 103.6(3); N1−C25−Si1, 122.2(3); N2−C25−Si1, 134.2(3).

tricoordinate silicon center in the solid-state structure of **2** has a pyramidal geometry (sum of the bond angles at Si1 = 344.3°). The geometry of **2** is similar to those of dihalosilylene−NHC$^{Dip}$ complexes $X_2Si{:}\leftarrow NHC^{Dip}$ [sum of the bond angles around the tricoordinate silicon atom = 290.7° (X = Cl)[5d] and 292.7° (X = Br)[5e]] and that of the tricoordinate silylenoid $(^tBu_2MeSi)_2Si(F)(Li)$ previously reported by Apeloig and co-workers[11] (sum of the bond angles around the central silicon atom = 307.6°). The central silicon atom is less pyramidalized in **2** than in these compounds primarily for steric reasons. The $Si_{silylene}$−$C_{carbene}$ bond length in **2** [Si1−C25 = 1.933(4) Å] is shorter than those in the dihalosilylene−NHC complexes [1.985(4) Å (X = Cl)[5d] and 1.989(3) Å (X = Br)[5e]] because of the smaller methyl groups on the NHC in our case.

The $^1H$ NMR spectrum of **2** shows a 1:1 ratio between the $(^tBu_3Si)_2Si{:}$ fragment and the NHC.[7] The signals of the two $^tBu_3Si$ groups and the two sets of methyl groups on the nitrogen atoms and the C=C double bond in NHC$^{Me}$ are equivalent in **2** because of fast rotation around the $Si_{silylene}$−$C_{carbene}$ bond. This is in contrast to the corresponding $E_{metallylene}$−$C_{carbene}$ bonds in $[(Me_3Si)_3Sn]_2Ge{:}\leftarrow NHC^{iPr}$ and $[(Me_3Si)_3E]_2Sn{:}\leftarrow NHC^{iPr}$ (E = Si, Ge, Sn), which are static on the NMR time scale because of the bulky substituents.[5c] In the $^{13}C$ NMR spectrum of **2**, the signal of the carbene carbon coordinated to the electropositive silicon atom is shifted significantly upfield (172.6 ppm) compared with that of the "free" NHC$^{Me}$ (212.7 ppm).[6] The $^{29}Si$ NMR resonances of **2** appear at 34.0 ppm ($^tBu_3$*Si*) and −128.9 ppm [$(^tBu_3Si)_2$*Si*$:\leftarrow NHC^{Me}$]. The resonance at −128.9 ppm is shifted significantly upfield compared with those in the dihalosilylene−NHC complexes $X_2Si{:}\leftarrow NHC^{Dip}$ [19.1 ppm (X = Cl)[5d] and 10.1 ppm (X = Br)[5e]] because the silyl groups of **2** are electron-dononating groups, in contrast to the halogen atoms. The UV−vis spectrum of **2** in hexane exhibits an absorption band assignable to the n−π* transitions at 558 nm (ε = 74 $M^{-1}$ $cm^{-1}$).[7]

We examined the one-electron oxidation of **2** with $Ph_3C^+{\cdot}Ar_4B^-$ ($Ar_4B^-$ = tetrakis[4-(*tert*-butyldimethylsilyl)-2,3,5,6-tetrafluorophenyl]borate)[12] in the hope of obtaining the corresponding silylene radical cation. When a mixture of **2** and 1.0 equiv of $Ph_3C^+{\cdot}Ar_4B^-$ was stirred in benzene at room temperature, it formed a two-layer reaction mixture, accompanied by a color change from orange to dark-red. The lower layer was separated and washed with hexane, giving the NHC-stabilized silylene radical cation **3**, which was isolated by recrystallization from fluorobenzene in 86% yield as air- and moisture-sensitive yellow crystals (Scheme 2).[7] As expected, treatment of a toluene solution of **3** with 1.0 equiv of $KC_8$ caused rapid reversion to the neutral **2**.

**Scheme 2. One-Electron Oxidation of Silylene−NHC Complex 2 To Give NHC-Stabilized Silylene Radical Cation 3**



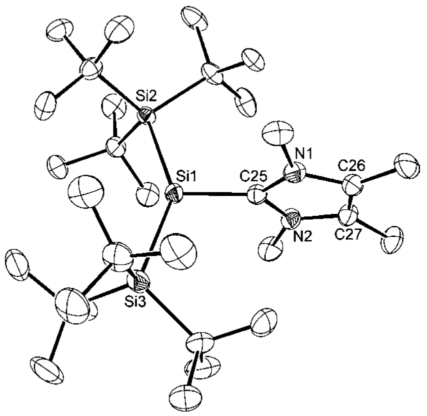


**Figure 2.** ORTEP drawing of **3** (50% thermal ellipsoids). The counteranion (tetrakis[4-(*tert*-butyldimethylsilyl)-2,3,5,6-tetrafluorophenyl]borate), crystallization solvent molecules (fluorobenzene), and H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Si1−C25, 1.915(3); Si1−Si2, 2.4664(11); Si1−Si3, 2.4659(10); N1−C25, 1.350(3); N2−C25, 1.355(3); N1−C26, 1.377(4); N2−C27, 1.390(4); C26−C27, 1.358(5); C25−Si1−Si2, 106.94(9); C25−Si1−Si3, 107.87(9); Si2−Si1−Si3, 144.96(4); N1−C25−N2, 104.9(2); N1−C25−Si1, 126.9(2); N2−C25−Si1, 128.1(2).

The structure of **3** was unambiguously characterized by X-ray crystallographic analysis and is depicted in Figure 2.[7] The solid-state structures of neutral **2** and radical cation **3** are quite different. The latter has a planar geometry around the tricoordinate silicon atom (sum of the bond angles at Si1 = 359.8°). As a result, the Si2−Si1−Si3 bond angle is widened from 134.81(6)° in the precursor **2** to 144.96(4)° in **3**. The Si2−Si1−Si3 plane and the NHC ring are nearly perpendicular to each other. The closest distance between the cationic silicon atom and any fluorine atom of the counteranion is greater than 5 Å, which is outside the range of van der Waals interactions. The tricoordinate silicon atom to carbene carbon bond length in **3** [Si1−C25 = 1.915(3) Å] is slightly shorter than that in the precursor **2** [1.933(4) Å]. This bond shortening can be explained by the increase in s character of the Si−C bond resulting from the change in hybridization of the central silicon atom, Si1. On the other hand, the Si1−Si2 and Si1−Si3 bond lengths in **3** [2.4664(11) and 2.4659(10) Å] are slightly longer than those in **2** [2.4542(15) and 2.4419(14) Å] because steric repulsion between the extremely bulky $^t$Bu$_3$Si groups prevents bond shortening.

The EPR spectrum of **3** shows a quintet at a $g$ value of 2.00466 because of coupling with the two $^{14}$N nuclei ($I$ = 1) with a hyperfine coupling constant (hfcc) of $a(^{14}\mathrm{N})$ = 0.26 mT (Figure 3). The satellite signals with an hfcc of $a(^{29}\mathrm{Si})$ = 7.16 mT can be assigned to the coupling with the central $\alpha$-Si nucleus. This characteristic splitting pattern indicates the presence of a hyperfine interaction of the unpaired electron with both nitrogen atoms of the NHC. The $a(\alpha\text{-}^{29}\mathrm{Si})$ value of 7.16 mT is slightly greater than the values of typical persilyl-substituted silyl radicals (5.56−6.28 mT)[13] but much smaller than the $a(\alpha\text{-}^{29}\mathrm{Si})$ of 19.3 mT in the trialkyl-substituted silyl radical, which has a pyramidal geometry,[14] providing convincing evidence for the significant planar geometry of the radical center in **3**.

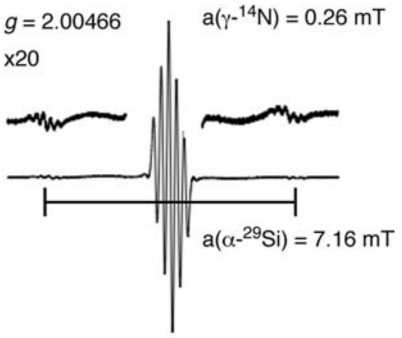
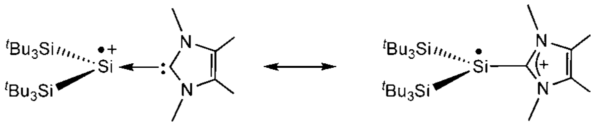


**Figure 3.** EPR spectrum of **3** in benzene at room temperature.

The atomic charges and spin densities were calculated by natural bond order (NBO) analysis at the (U)B3LYP/6-31G(d) level for neutral **2** and radical cation **3**. The results give important information about the electronic structures of **2** and **3**. On the basis of these DFT calculations, the NHC carries a charge of +0.32 in **2** and +0.38 in **3**, whereas the [($^t$Bu$_3$Si)$_2$Si] units carry charges of −0.32 in **2** and +0.62 in **3** (see the Supporting Information). This indicates that upon one-electron oxidation, the electron is removed from the silylene lone pair of **2**, resulting in a change in geometry to the planar structure. The spin density in **3** is mainly localized on the tricoordinate silicon atom.

The two possible resonance structures of **3** are depicted in Chart 1. On the basis of the experimental findings (X-ray diffraction analysis and EPR spectral data) and theoretical calculations, the NHC-stabilized silylene radical cation **3** can best be described as a $\pi$-radical cation with a nearly sp$^2$-hybridized central silicon atom on which most of the positive charge is localized.

**Chart 1. Resonance Structures of the NHC-Stabilized Silylene Radical Cation 3**



## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

The experimental procedures of **2** and **3**; UV−vis spectrum of **2**; natural population analysis of **2** and **3**; tables of crystallographic data, including atomic positional and thermal parameters, and CIFs for **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

## ■ AUTHOR INFORMATION

### Corresponding Author

sekiguch@chem.tsukuba.ac.jp

### Notes

The authors declare no competing financial interest.

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