

# [[ $(\text{Me}_3\text{Si})_2\text{CH}$ ] $_2^i\text{PrSi}(\text{NHC})\text{Si}=\text{Si}(\text{Me})\text{Si}^i\text{Pr}[\text{CH}(\text{SiMe}_3)_2]_2]^+$ : A Molecule with Disilyl Cation Character

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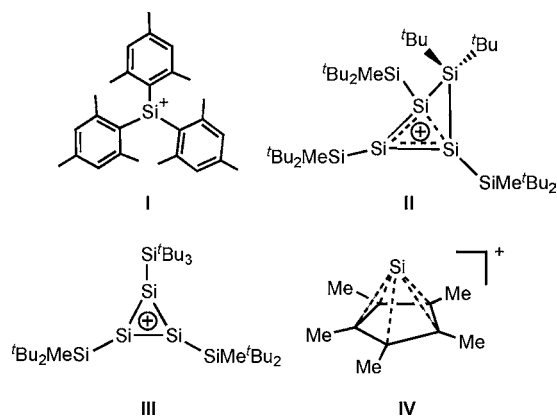
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**S** Supporting Information

**ABSTRACT:** Reaction of the disilyne–NHC complex **1** [ $\text{RLSi}=\text{SiR}$ : ( $\text{R} = \text{Si}^i\text{Pr}[\text{CH}(\text{SiMe}_3)_2]_2$ ,  $\text{L} = \text{NHC}$ )] with  $\text{MeOTf}$  gave the cation **2** [ $\text{RLSi}=\text{SiRMe}$ ] $^+$ , which is the first example of a base-stabilized heavy group 14 element analogue with vinyl cation character. Cation **2** has been fully characterized by multinuclear NMR spectroscopy and X-ray diffraction analysis. The molecular structure indicates that there are significant contributions from the NHC-stabilized cationic resonance structure **2A**, the disilene-like structure **2B**, and even some contribution from the silylene-like structure **2C**.

Heavy group 14 cations are an important topic in main group chemistry.<sup>1</sup> In contrast to carbocations,<sup>2</sup> isolation of tricoordinate silyl cations *free* of interaction with the solvent or counterion is difficult. This difference is primarily due to the low electronegativity and large atomic size of Si. During the past decade, several examples of tricoordinate silyl cations have been isolated.<sup>3</sup> The free trimesitylsilyl cation (**I**), [ $(\text{Mes})_3\text{Si}$ ] $^+$  where  $\text{X} = \text{B}(\text{C}_6\text{F}_5)_4^-$  or  $\text{CHB}_{11}\text{Me}_5\text{Br}_6^-$ , has been synthesized<sup>3a</sup> and structurally characterized<sup>3c</sup> by Lambert and Reed (Chart 1). In the past few years we have reported several

Chart 1. Trimesitylsilyl Cation (**I**) and Conjugated Silyl Cations (**II–IV**)



examples of conjugated free silyl cations; a cyclooctasilylium ion with homoaromatic (**II**)<sup>3b</sup> or allylic character,<sup>3g</sup> the cyclotrisilylium ion (**III**),<sup>3c</sup> and the disilacyclopropenylium ion (Chart 1).<sup>3f</sup> The cyclic  $\pi$ -conjugated cation,  $(\eta^5\text{-Me}_5\text{C}_5)\text{Si}^+$  (**IV**) was also prepared by Jutzi et al. (Chart 1).<sup>3d</sup> Furthermore, a hydrogen-bridged disilyl cation with a 1,8-naphthalenediyl

backbone and the ion-like  $\text{Et}_3\text{Si}(\text{CHB}_{11}\text{H}_5\text{Cl}_6)$  have been found to work as catalysts in C–F bond activation reactions.<sup>4</sup>

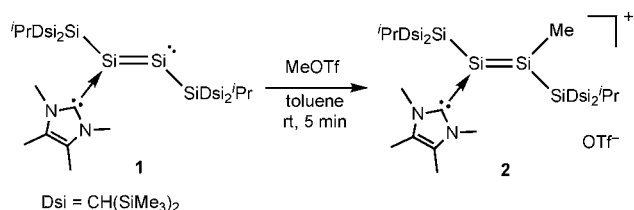
Despite numerous accomplishments in trivalent silyl cation chemistry, studies of divalent disilyl cations ( $\text{R}_2\text{Si}=\text{Si}^+\text{R}$ ), Si analogues of vinyl cations, have not been reported except for the theoretical study<sup>5</sup> and mass spectrometric observation<sup>6</sup> of  $\text{H}_3\text{Si}_2^+$ . Disilyl cations are intriguing targets because they possess two highly reactive functional groups, a silyl cation and a disilene, and as such should have interesting physical, electronic, and reactive properties. Vinyl cations on the other hand have been synthesized and even isolated in the solid state by the intramolecular reaction of a silyl cation with an alkyne.<sup>7</sup> Unfortunately, a similar synthetic method cannot be used for disilyl cations because the silicon analogues of alkynes and disilynes<sup>8</sup> are rare and only accessible with a limited number of substituents. In fact, the first disilynes were synthesized and reported concurrently in 2004 by one of us<sup>8a</sup> and Wiberg et al.<sup>8b</sup> Both of these examples have bulky silyl substituents to stabilize the very reactive triple bond. More recently, one example of an aryl-substituted disilyne has also been reported.<sup>8c</sup> The limitations on substituents preclude the intramolecular synthetic pathway used for vinyl cations. Although disilyl cations remain an intriguing target, an alternate strategy is required.

One technique that has been widely used to stabilize low-valent heavier group 14 cations, such as  $\text{RE}^+$  and  $\text{E}^{2+}$ , is the use of a Lewis base to either intra- or intermolecularly stabilize the reactive center.<sup>9,10</sup> Lewis basic carbenes,<sup>11</sup> especially N-heterocyclic carbenes (NHCs), have proven to be particularly powerful tools to coordinate and stabilize a variety of reactive species, including a  $\text{Ge}^+$  center<sup>10c</sup> and a variety of low-valent silicon species.<sup>12</sup> In fact, we recently found that an NHC (1,3,4,5-tetramethylimidazol-2-ylidene) can coordinate a stable disilyne,  $\text{RSi}\equiv\text{SiR}$  ( $\text{R} = \text{Si}^i\text{Pr}[\text{CH}(\text{SiMe}_3)_2]_2$ ),<sup>8a</sup> to give the isolable disilyne–NHC complex **1** (Scheme 1).<sup>13a</sup> Crystallographic studies show that **1** has a *trans* geometry about a  $\text{Si}=\text{Si}$  double bond and a lone pair of electrons residing on one of the doubly bonded Si atoms.<sup>13a</sup> The lone pair on silicon is a Lewis base and can coordinate to  $\text{ZnCl}_2$ . This reactivity led us to investigate if **1** could be used as a precursor for an NHC-stabilized disilyl cation. This strategy involves addition of a cation ( $\text{R}'^+$ ) to the nucleophilic Si center of **1**, which should lead directly to the desired  $[\text{R}(\text{NHC})\text{Si}=\text{SiRR}']^+$ -type cation. Herein, we report the synthesis and structure of **2**, the first

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## Scheme 1. Synthesis of NHC-Stabilized Cation 2

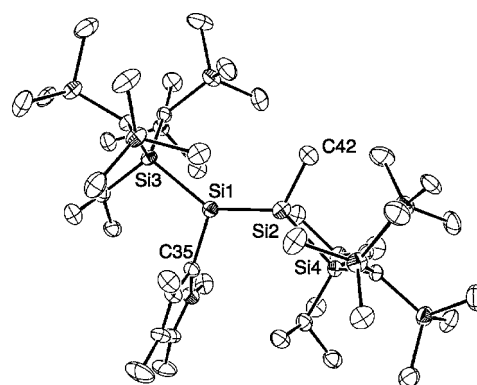


isolable species with significant disilyl cation character, by the methylation of the disilyne–NHC complex **1** (Scheme 1).

The reaction of **1** with methyl triflate (MeOTf) immediately proceeded to give a pale-orange solution of the NHC-coordinated disilyl cation **2**, which was isolated as air- and moisture-sensitive yellow crystals in 66% yield (Scheme 1).<sup>14</sup> This solid was dissolved in C<sub>6</sub>D<sub>6</sub> and analyzed by multinuclear NMR spectroscopy. In the <sup>1</sup>H NMR spectrum, the signals for four magnetically nonequivalent Dsi groups [Dsi = CH(SiMe<sub>3</sub>)<sub>2</sub>] are evident as well as the two signals corresponding to the NHC. In addition, there is a signal at 1.23 ppm that can be attributed to the =Si–CH<sub>3</sub> protons. This methyl group is also visible in the <sup>13</sup>C NMR spectrum with a chemical shift of 5.1 ppm. The carbene carbon signal is apparent at 149.7 ppm, which is indicative of a coordinated NHC and similar to both **1** (160.9 ppm) and **1**·ZnCl<sub>2</sub> (157.1 ppm).<sup>13a</sup> The characteristic low-field shifted <sup>29</sup>Si NMR signals of the doubly bonded Si atoms are observed at 54.0 ppm (NHC–Si=Si) and 168.8 ppm (NHC–Si=Si), respectively. The chemical shift of the NHC-coordinated silicon atom is slightly low-field shifted from that of **1** (28.7 ppm) and close to that of **1**·ZnCl<sub>2</sub> (66.9 ppm). Although the chemical shifts of free silylium ions (tricoordinate silyl cations) are generally observed at very low field (e.g., the <sup>29</sup>Si NMR chemical shift of [Me<sub>3</sub>Si][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] is 225.5 ppm),<sup>3a</sup> those of coordinated silyl cations are shifted considerably upfield [e.g., Et<sub>3</sub>Si(toluene)[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]: 92.3 ppm].<sup>15</sup> With this in mind, the observed chemical shift of 54.0 ppm is not abnormal for an NHC-stabilized cationic silicon center. To confirm this, gauge-including atomic orbitals (GIAO) calculations of the Me<sub>3</sub>Si-substituted model compound [Me<sub>3</sub>Si(NHC)Si=Si(Me)SiMe<sub>3</sub>]<sup>+</sup> **2'** were performed, and the calculated chemical shifts of both doubly bonded silicon atoms (69.7, 215.5 ppm) were found to reasonably reproduce the experimentally observed values.<sup>14</sup>

To determine if the anion interacts with the cationic silicon moiety in solution, the <sup>29</sup>Si NMR spectrum was recorded in THF-*d*<sub>8</sub>, a considerably more polar solvent. Virtually no solvent effect is present, most notably for the two disilyl silicon centers (168.8 vs 168.0 ppm and 54.0 vs 51.1 ppm in C<sub>6</sub>D<sub>6</sub> and THF-*d*<sub>8</sub>, respectively).<sup>14</sup> The lack of a solvent effect strongly indicates that there are negligible cation solvent interactions and that the cation does not interact with the counterion in solution.

The molecular structure of **2** determined by X-ray crystallography is shown in Figure 1.<sup>14</sup> In the solid state, no interactions between the skeletal silicon atoms and the triflate anion are observed. The closest Si–F interaction (Si1–F3) is 5.6 Å, while the nearest Si–O interaction (Si1–O3) is 5.9 Å, both of which are longer than the sum of the van der Waals radii.<sup>16</sup> A closer look at the Si1–Si2 bond shows that the addition of the methyl group does not significantly affect the bond length [2.192(2) Å in **2** compared with 2.1989(6) Å in **1**]. This length is typical of a Si=Si double bond.<sup>17</sup> Both Si1

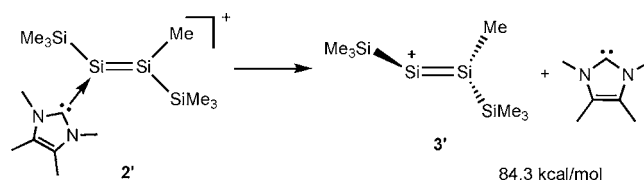


**Figure 1.** ORTEP drawing of **2**·(C<sub>6</sub>H<sub>5</sub>F)<sub>0.5</sub>(toluene) (50% thermal ellipsoids). Hydrogen atoms, TfO<sup>−</sup> anion as a counterion, and C<sub>6</sub>H<sub>5</sub>F and toluene as crystallization solvents are omitted for clarity. Selected bond lengths (Å) and angles (°): Si1–Si2, 2.192(2); Si1–Si3, 2.4342(18); Si2–Si4, 2.4064(19); C35–Si1, 1.904(5); C42–Si2, 1.865(5); C35–Si1–Si2, 106.47(15); C35–Si1–Si3, 112.71(15); Si2–Si1–Si3, 139.87(8); C42–Si2–Si1, 117.61(18); C42–Si2–Si4, 111.84(17); Si1–Si2–Si4, 130.14(8).

and Si2 atoms are nearly planar (359.1° for the sum of bond angles around Si1, 359.6° for the sum of bond angles around Si2). The cationic nature of the Si1 atom causes the C35–Si1 bond length [1.904(5) Å] to decrease slightly compared with the starting material [1.9221(16) Å]. However, the C35–Si1 bond length is longer than the (NHC)C–Si bond length of [Br<sub>3</sub>Si(Idipp)]<sup>+</sup>·Br<sup>−</sup> [1.880(9) Å, Idipp = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene],<sup>12e</sup> which indicates that the NHC–Si interaction in **2** may be relatively weak.

To take a closer look at the overall electronic and bonding nature of **2**, DFT calculations for the Me<sub>3</sub>Si-substituted model compound **2'** were carried out using the B3LYP/6-31G(d) basis set. The optimized structure of **2'** closely reproduced the experimentally observed structure of **2**. The frontier molecular orbitals of **2'** show that the highest occupied molecular orbital (HOMO) corresponds to the Si–Si π-bond, while the lowest unoccupied molecular orbital (LUMO) is the Si–Si π\*-orbital. These orbitals are similar to those of the NHC-disilyne complex **1** and **1**·ZnCl<sub>2</sub> and also of disilenes in general.<sup>13,17</sup> The UV–vis spectrum of **2** in THF has an absorption at 408 nm ( $\epsilon = 3600 \text{ M}^{-1} \text{ cm}^{-1}$ ), which should correspond to the π–π\* transition (see the Supporting Information). Time-dependent DFT (TD-DFT) calculations performed on the optimized structure of **2'** also show the π–π\* transition at 393 nm, which agrees with the experimentally observed results.

To gain a better understanding of the NHC–Si interaction, DFT calculations were also performed for the NHC and the free disilyl cation **3'** at the same level of theory. These results show that the dissociation of the NHC from **2'** to give the free disilyl cation **3'** is endothermic by 84.3 kcal/mol, which is indicative of a strong interaction (Scheme 2). An additional way to estimate the bonding interaction between the Si<sup>+</sup> center and

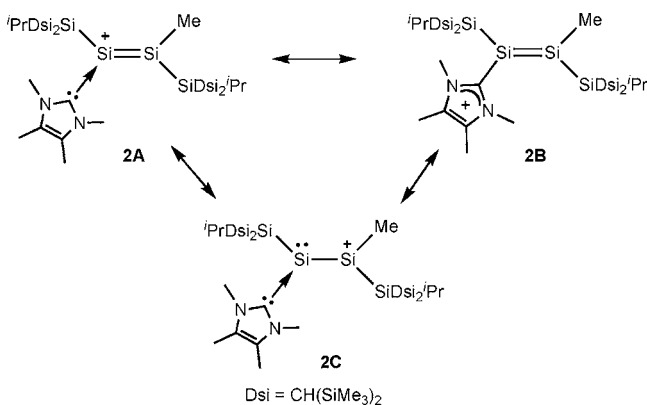
Scheme 2. Dissociation of NHC from **2'**

the NHC is to look at the Wiberg bond index (WBI). According to these calculations, the NHC–Si bond in **2'** is less than a single bond (WBI = 0.77). This can be compared with the Si–Me bond on the other side of the double bond, which has a WBI of 0.86. These calculations indicate that the NHC–Si interaction has donor/acceptor character.<sup>18</sup> This agrees with the experimental observation of an elongated NHC–Si bond (vide supra).

To obtain information on the charge distribution and polarity of the molecule, the natural population analysis (NPA) charges were examined. The sum of the charges on the two TMS groups and the Me substituent is nearly 0 (–0.0073), while the cationic charge is delocalized on the central Si=Si–NHC skeleton. The carbene moiety bears nearly half of the charge (0.45). The disilene moiety has the rest of the charge; however, the formally cationic Si1 center has only a small part of the charge (0.06), while the other disilene silicon center (Si2) bears the most significant portion of the charge (0.49). This charge delocalization contributes to the stability of **2** and also accounts for the lack of interaction of the triflate counterion with Si1.

From the experimental and theoretical results, three resonance structures seem to contribute to the overall structure of **2** (Chart 2): First, the NHC-stabilized disilanyl cation (**2A**) as indicated by NMR, X-ray, and WBI data. Second, the

Chart 2. Resonance Structures of **2**



imidazolium-substituted disilene (**2B**) as seen in the relatively strong bonding energy and NPA charge distribution. Finally, some contribution from structure **2C** is also seen in the NPA charges, but because of the planar structure and apparent disilene character of the Si1–Si2 bond, this structure can be at best a minor contributor to the overall properties of **2**.

In conclusion, a highly basic N-heterocyclic carbene has been used to stabilize **2**, a species with disilanyl cation character, which is the silicon analogue of the vinyl cation. This new type of cation is accessible from a stable disilyne, which further demonstrates the utility, both fundamentally and synthetically, of this type of heavy alkyne. The use of an NHC allows the cationic charge to be delocalized on the NHC and disilene skeleton and sufficiently stabilizes this species to allow it to be isolated and fully characterized, including by X-ray crystallographic analysis. Further studies on the reactivity of this new species and investigations into the synthesis of free disilanyl cations are currently under way.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

Experimental procedure of **2**, UV–vis spectral chart of **2**, computational results on the model compounds **2'** and **3'**, and tables of crystallographic data including atomic positional and thermal parameters for **2** (PDF/CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(14) For the experimental procedures, spectral data of **2**, crystal data of **2**, UV–vis chart of **2**, and details of the theoretical studies of **2'** and **3'** see the Supporting Information.

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