

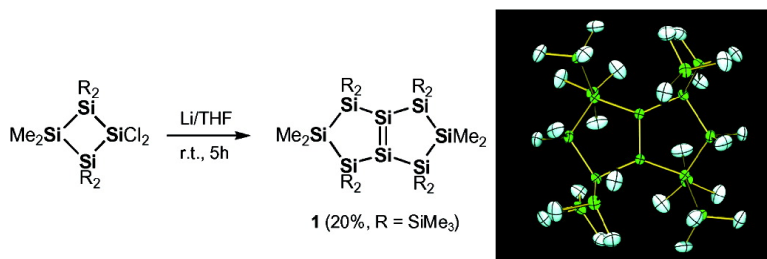
Communication

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## A Stable Fused Bicyclic Disilene as a Model for Silicon Surface

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Since the first isolation of a stable disilene (silicon–silicon doubly bonded compound) by West et al. in 1981,<sup>1</sup> great progress has been made in the chemistry of stable disilenes; endocyclic, exocyclic, and spirocyclic disilenes, trisilaallenes, and tetrasila-butadienes have become accessible recently.<sup>2</sup> Fused cyclic disilenes are one of the fascinating unknown disilenes because an active site of the Si(001) surface is considered to have a fused Si=Si double bond-like structure in the rigid polycyclic frameworks with five- and six-membered silicon rings.<sup>3</sup> Although functionalization of the Si(001) surface has attracted much attention in recent years,<sup>3,4</sup> the fundamental understanding of the structure and reactions of the Si(001) surface is not always clear at the atomic and molecular levels. Fused cyclic disilenes should play important roles to elucidate the structural characteristics and chemical behavior of small molecules bound to the Si(001) surface. We report herein the synthesis, X-ray analysis, and reactions of bicyclo[3.3.0]octasil-1(5)-ene **1** as the first stable fused bicyclic disilene. Disilene **1** represents topologically a partial structure of the Si(001) surface up to the third layer.

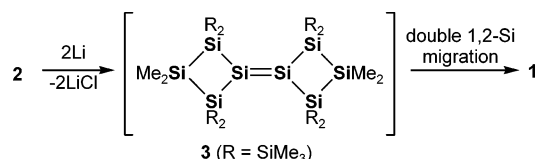
The reduction of 1,1-dichlorocyclotetrasilane **2**<sup>5</sup> with lithium metal in THF gave disilene **1** as air-sensitive but thermally stable orange crystals (mp 336 °C under argon) in 20% yield (eq 1).<sup>7</sup>



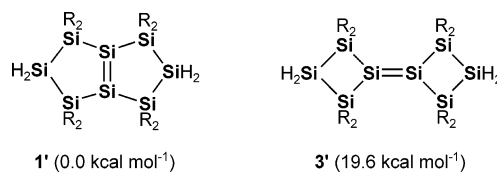
Formation of fused bicyclic disilene **1** from monocyclic precursor **2** is interesting. Although the mechanism for formation of **1** remains still open, a plausible mechanism involves the reductive coupling of **2** leading to bicyclic tetrasilanylidene **3** followed by isomerization of **3** to **1** via double 1,2-silyl migration<sup>8,9</sup> (Scheme 1). The driving force of the isomerization is ascribed to the intrinsic instability of the molecular skeleton of **3** compared to that of **1**. Model compound **3'** is 19.6 kcal/mol higher in energy than **1'** at the B3LYP/6-31G(d) level (Chart 1), mainly due to the relatively high strain energy of cyclotetrasilane units.<sup>10</sup> High migratory aptitude of trialkylsilyl groups<sup>11</sup> compared with that of alkyl and aryl groups would make the isomerization kinetically feasible.

The molecular structure of **1** determined by X-ray analysis is shown in Figure 1.<sup>12</sup> Disilene **1** has a crystallographic C<sub>2</sub> axis passing through the center of the double bond and perpendicular to both Si1–Si1\* and Si3–Si3\* axes. The five-membered ring skeleton adopts the envelope conformation with out-of-plane Si2 atom; the dihedral angle between the planes of Si1–Si2–Si3 and the least-squares plane of Si1–Si1\*–Si4–Si3 is 22.1°. The steric

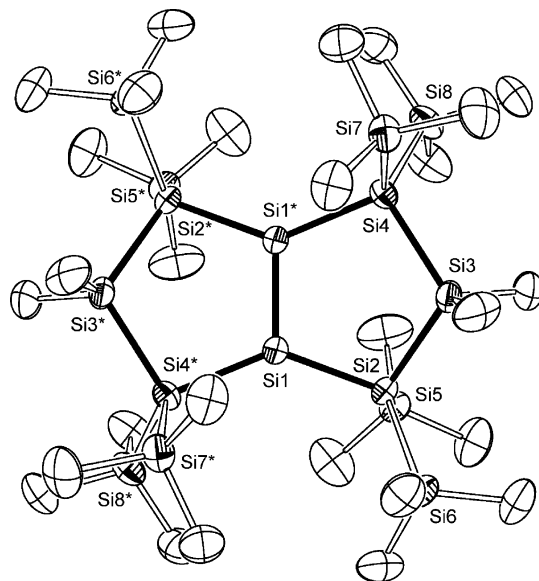
### Scheme 1. A Possible Mechanism for the Formation of **1**



### Chart 1. Relative Energy of Model Compounds **1'** and **3'** (R = SiH<sub>3</sub>)



repulsions between Me<sub>3</sub>Si groups would be responsible for the envelope conformation and twist geometry around the Si=Si double bond (angle between two Si(sp<sup>3</sup>)–Si(sp<sup>2</sup>)–Si(sp<sup>3</sup>) planes, 16.7°) of the five-membered rings of **1**.<sup>13</sup> The Si=Si bond distance of **1** (2.180(3) Å) is close to those of the five-membered ring disilenes (2.173–2.198 Å).<sup>14</sup> The Si=Si double bond of **1** adopts a slightly *cis*-bent geometry with the bent angle  $\theta$  of 3.6°, where the angle  $\theta$  is defined as an angle between the Si(sp<sup>3</sup>)–Si(sp<sup>2</sup>)–Si(sp<sup>3</sup>) plane and the Si(sp<sup>2</sup>)–Si(sp<sup>2</sup>) bond of **1**; to the best of our knowledge, all disilenes whose structures were determined by X-ray analysis so far have *trans*-bent or planar geometry.<sup>15</sup>



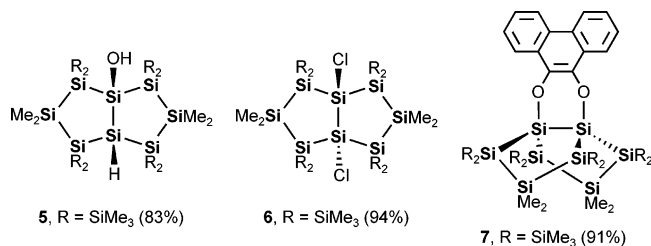
**Figure 1.** ORTEP drawing of **1**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (°): Si1–Si1\* 2.180(3), Si1–Si2 2.330(2), Si1–Si4\* 2.323(2), Si2–Si3 2.380(2), Si3–Si4 2.360(2); Si1\*–Si1–Si2 112.40(11), Si1–Si1\*–Si4 110.24(10), Si2–Si1–Si4\* 137.35(9), Si1–Si2–Si3 100.01(8), Si2–Si3–Si4 111.61(8), Si1\*–Si4–Si3 100.09(8).

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**Chart 2.** Products and Their Yields of the Reactions of **1** (R = SiMe<sub>3</sub>)



In contrast to the solid-state structure, <sup>1</sup>H NMR spectrum of **1** in benzene-*d*<sub>6</sub> showed a highly symmetric pattern involving two singlet signals due to eight SiMe<sub>3</sub> and two SiMe<sub>2</sub> groups. The spectral pattern remained unchanged between room temperature and -80 °C in THF-*d*<sub>8</sub>, indicating facile flipping of the bicyclic skeleton in solution. The <sup>29</sup>Si NMR resonance for the unsaturated silicon nuclei in **1** appears at 167.4 ppm.

Disilene **1** showed an intense absorption band at 468 nm due to π-π\* transition. The absorption maximum of **1** is considerably red-shifted by about 50 nm relative to those for typical silyl-substituted disilenes (412–425 nm).<sup>11,16</sup> The red-shift suggests significant σ-π interaction between the Si=Si π-bonding orbital and one of the π-type orbitals composed of eight neighboring Si(ring)-Si(substituent) σ-bonding orbitals; similar σ-π interaction has been observed for hexakis(*tert*-butyldimethylsilyl)cyclotetrasilene (**4**, 465 nm).<sup>17</sup>

Because the disilene moiety in the reconstructed Si(001) surface is known to have unsymmetric and significantly *cis*-bent structure,<sup>3,18</sup> fused bicyclic disilene **1** may not be an ideal model for the silicon surface. Nevertheless, investigation of the reactions of **1** with various small compounds would be useful to predict the reactivity of the silicon surface. The reactions of **1** with a trace amount of water in hexane provided *cis*-bicyclo[3.3.0]octasilanol **5** in good yield (Chart 2).<sup>19</sup> The observed *syn*-addition is in good accord with that reported for the reaction of Si(001) surface with water<sup>20</sup> and the reactions of disilenes with alcohols at low concentration of alcohols.<sup>21</sup> Disilene **1** reacted with carbon tetrachloride gave *trans*-1,5-dichlorobicyclooctasilane **6** similar to other stable disilenes,<sup>22</sup> while the reaction of the Si(001) surface with carbon tetrachloride has never been reported. Because the *anti*-addition on the silicon surface is prohibited, the reaction of the silicon surface with carbon tetrachloride may occur via a way different from that of the corresponding reaction of **1**. Disilene **1** reacted with 9,10-phenanthrenequinone (PQ) to give a [4 + 2] adduct **7** in 91% yield.<sup>23</sup> X-ray analysis of **7** clearly shows that PQ binds to the Si=Si bond of **1** through carbonyl oxygen atoms.<sup>19</sup> The structural characteristics of compound **7** are in good accord with the proposed structure of PQ adsorbed on the Si(001) surface.<sup>24</sup> The π-π stacking of the two molecules in the crystal structure of **7** is compatible with the PQ molecule pairs on the Si(001) surface observed by STM.

Further work is in progress.

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**Supporting Information Available:** Details for the synthesis and reactions of **1**, preparation of **2**, the X-ray analysis of **5**, **6**, and **7**, UV-vis spectra of **1** and **7**, and optimized atomic coordinates of **1'** and **3'**. The X-ray crystallographic data are also available in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (13) Two energy minima with slightly *cis*-bent (C<sub>2v</sub> symmetry) and planar (C<sub>i</sub> symmetry) Si=Si double bonds were found for model compound **1'** at the B3LYP/6-31G(d) level. Unlike the puckering mode observed for the five-membered rings of **1**, two five-membered rings for **1'** (C<sub>2v</sub> and **1'**-C<sub>i</sub>) are slightly puckered at the 3- and 7-positions. See Supporting Information for the details.
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