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# Do Silylenes Always Dimerize to Disilenes? Novel Silylene Dimers with Unusual Structures<sup>†</sup>

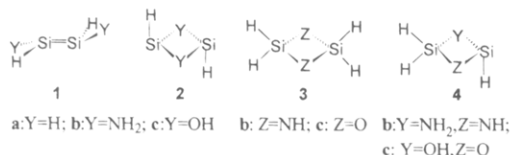
Yitzhak Apeloig\* and Thomas Müller

Department of Chemistry  
Technion—Israel Institute of Technology  
Haifa 32000, Israel

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The isolation of the first indefinitely stable disilene by West, Fink, and Michl in 1981<sup>1</sup> has prompted substantial experimental<sup>2</sup> and theoretical<sup>3</sup> activity, leading to the isolation of stable disilenes **1** with aryl,<sup>1,2</sup> alkyl,<sup>2</sup> amino,<sup>4</sup> and silyl<sup>5</sup> substituents. All of these disilenes **1** were synthesized via the dimerization of the corresponding silylenes (Scheme 1, path a). However, in principle the dimerization of two silylenes can lead also to the bridged isomer **2** (Scheme 1, path b). Are unconventional isomers of disilenes such as **2** thermodynamically and kinetically stable? Can they be observed?

In this paper we study silylene dimers of type **2** using high level *ab initio* calculations. We find that for Y = NH<sub>2</sub> the hetero-bridged **2** is thermodynamically more stable than the isomeric disilene and for Y = OH the two isomers have nearly the same energy. Furthermore, high barriers separate these novel unusual molecules, possessing a three-coordinated silicon bonded to a hypercoordinated O or N atom, from the isomeric thermodynamically more stable conventional isomers **3**, suggesting that **2**, Y = NH<sub>2</sub> and OH, are viable targets for synthesis. We predict that such bridged species are indeed obtained in the dimerization of a recently reported stable silylene.<sup>6</sup>

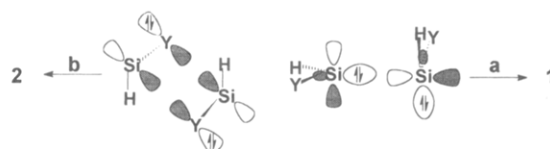


Extensive *ab initio* calculations of the potential energy surface (PES) of Si<sub>2</sub>H<sub>4</sub> showed that, in addition to disilene **1a** and silylsilylene, the unusual hydrogen-bridged isomers (Z)- and (E)-HSi(μ-H)<sub>2</sub>SiH (**2a**) are also minima on the PES, lying only 22.5 ((E)-**2a**) and 25.2 kcal/mol ((Z)-**2a**) (CI/DZP)<sup>7b</sup> higher in energy than **1a**.<sup>7c</sup> Similar bridged species exist also on the Si<sub>2</sub>H<sub>2</sub> PES.<sup>8</sup> We have recently suggested,<sup>9a</sup> in contrast to the original interpretation,<sup>9b</sup> that a species of type **2**, Y = F, has been actually observed by low-temperature NMR.<sup>9b</sup> Si<sub>2</sub>Cl<sub>4</sub> and Si<sub>2</sub>F<sub>4</sub> were also calculated to have bridged structures.<sup>10</sup>

<sup>†</sup> In memory of Prof. D. Becker (Technion).

- (1) West, R.; Fink, M. J.; Michl, J. *Science* **1981**, *214*, 1343.
- (2) (a) For leading references, see: *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, 1989. (b) Review: Raabe, G.; Michl, J. In ref 2a, Chapter 17, p 1015.
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## Scheme 1



Two major considerations directed this study to systems with Y = NH<sub>2</sub>, OH: (1) The lone-pair electrons on Y are expected to favor path b in Scheme 1 over path a. (2) NH<sub>2</sub> and OH substitution has a dramatic effect on the structure and energy of disilenes.<sup>11</sup> Thus, the degree of pyramidalization in H<sub>2</sub>-Si=SiH<sub>2</sub> is very high ( $\phi = 64.1^\circ$ ) and the Si=Si bond dissociation energy (40 kcal/mol) is considerably smaller than in H<sub>2</sub>Si=SiH<sub>2</sub> (57.2 kcal/mol).<sup>11</sup>

Several isomers of Si<sub>2</sub>H<sub>2</sub>Y<sub>2</sub> (Y = OH, NH<sub>2</sub>) were calculated using standard *ab initio* methods,<sup>12,13</sup> and their calculated geometries and total and relative energies are given in the supplementary material. For the discussion we use the MP4/6-311G\*\*//6-31G\*\* (for Y = NH<sub>2</sub>, 6-31G\* for Y = OH) values corrected for zero-point energy (ZPE) contributions.

Dimerization of H<sub>2</sub>Si,<sup>14</sup> HSi(NH<sub>2</sub>), and HSi(OH), either along path a in Scheme 1 leading to **1** or along path b leading to **2**, is exothermic and barrierless. The hetero-bridged species HSi(μ-NH<sub>2</sub>)<sub>2</sub>SiH (**2b**) and HSi(μ-OH)<sub>2</sub>SiH (**2c**) are minima on the PES, and both are substantially bound relative to the corresponding silylenes (by 27.6 and 22 kcal/mol, respectively, Figure 1).<sup>15</sup> Furthermore, **2b** is more stable than disilene **1b** by 10.0 kcal/mol, and **2c** is by only 3.2 kcal/mol less stable than **1c**.

However, the global minima on the H<sub>2</sub>Si<sub>2</sub>Y<sub>2</sub> PES, the conventional cyclodisilazane (**3b**) and cyclodisiloxane (**3c**), are substantially more stable than **2b** and **2c**, i.e., by 46.0 and 78.6 kcal/mol, respectively (Figure 1). Furthermore, **2b** and **2c** can isomerize to **3b** and **3c** by two simple consecutive 1,2-H-shifts. Are the hetero-bridged **2b** and **2c** kinetically stable? *The calculations show surprisingly that the barriers for these highly exothermic 1,2-H-shifts are quite high* (53.8 and 39.5 kcal/mol for **2b** and **2c**, respectively)<sup>16</sup> and that these barriers are actually higher than the barriers for dissociation of **2b** and **2c** into two isolated silylenes (Figure 1). Furthermore, **4b** and **4c**, the first intermediates along the rearrangement path, are also separated

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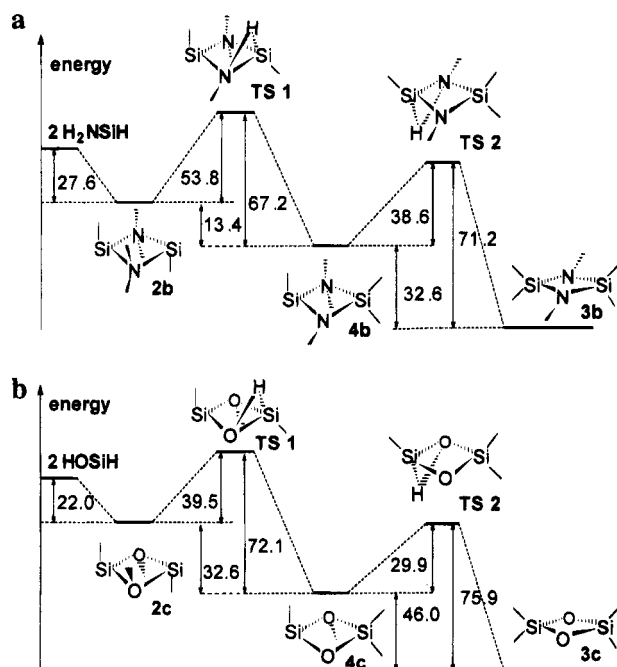
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- (13) Geometries were initially fully optimized at the Hartree–Fock level with the 6-31G\*\* (Y = NH<sub>2</sub>) or the 6-31G\* (Y = OH) basis sets and in some cases also with the MP2 and CISD methods. Frequency analysis was used to characterize stationary points. Transition state (TS) structures were located using the eigenvector following method and the intrinsic reaction coordinate (IRC) method. The energies of the calculated structures were evaluated at MP4STDQ/6-311G\*\*.

- (14) Ohta, K.; Davidson, E. R.; Morokuma, K. *J. Am. Chem. Soc.* **1985**, *107*, 3466.

- (15) (a) At HF/6-31G\*\*,  $\Delta S^\circ$  for the dimerization of two HSiNH<sub>2</sub> to **2b** is  $-43 \text{ cal/mol}\cdot\text{K}$ , leading to a calculated  $\Delta G^\circ(25^\circ\text{C, kcal/mol}) = -22.7 (\Delta H^\circ \text{ at } 25^\circ\text{C} + 12.8 (-T\Delta S^\circ) = -9.9 \text{ kcal/mol})$  ( $\Delta H^\circ(25^\circ\text{C, kcal/mol}) = -26.6 (0 \text{ K}) + 3.9 (\Delta E(\text{therm.}) \text{ at } 25^\circ\text{C}) = -22.7 \text{ kcal/mol}$ ). (b) (H<sub>2</sub>N)Si(μ-H)<sub>2</sub>Si(NH<sub>2</sub>) is a saddle point for the intermolecular hydrogen transfer between two HSiNH<sub>2</sub>, being 8.4 kcal/mol higher in energy than **1a** (MP4STDQ/6-311G\*\*//6-31G\*).

- (16) The relatively high barriers are probably associated with the fact that the rearrangements are symmetry forbidden, as they involve four electrons (two electrons on Si and two electrons of the N–H bond).



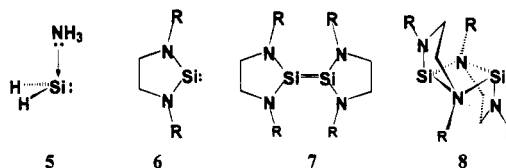
**Figure 1.** Calculated relative energies (kcal/mol): (a) for the interconversion of **2b** to **3b** (MP4/6-311G\*\*//6-31G\*\* + ZPE); (b) for the interconversion of **2c** to **3c** (MP4/6-311G\*\*//6-31G\*\* + ZPE).

from **3b** and **3c** by high barriers of 38.6 and 29.9 kcal/mol, respectively. **4b** and **4c** are also more stable than the corresponding disilenes, by 23.4 (**4b**) and 29.4 kcal/mol (**4c**). These results suggest (Figure 1) that, if **2b** (or **2c**) is formed by dimerization of two silylenes, it should be kinetically stable toward isomerization to **3b** (or **3c**) and therefore the *synthesis of bridged species of type 2 or 4 is conceivable*.

The bonding in **2** and **4** is of interest. In both **2b** and **2c**, the Si··Si separation (2.940 Å (**2b**); 2.923 Å (**2c**))<sup>17</sup> is much longer than even the longest known Si—Si bonding distances (e.g., 2.697 Å in *t*-Bu<sub>3</sub>SiSi-*t*-Bu<sub>3</sub>)<sup>18</sup>. Mulliken overlap population (MOP)<sup>12a</sup> as well as natural bond orbital (NBO) analyses<sup>19</sup> reveals insignificant electron density between the silicon atoms.<sup>20</sup> The same applies to **4b** and **4c**, even if they show shorter Si··Si separations, i.e., 2.727 and 2.650 Å (at HF/6-31G\*), respectively. Thus, the silicon atoms in **2b** and **2c** are best described as being three-coordinated with each silicon bearing a sp<sup>0.5</sup> hybridized lone pair. The Si—Y bond lengths (1.956 Å (**2b**); 1.920 Å (**2c**)) are much longer than “regular” Si—N or Si—O bond distances.<sup>22</sup> The SiN Wiberg bond index (WBI)<sup>21</sup> in **2b** (0.42) is only 60% of that in H<sub>3</sub>SiNH<sub>2</sub> (0.71), indicating a weaker bond. The resemblance between the geometrical parameters of **2b** and of the H<sub>2</sub>Si/NH<sub>3</sub> complex **5** (i.e., *r*(SiN), 1.956 Å (**2b**), 2.072 Å (**5**); *r*(SiH) and *α*(HSiN), 1.509 Å, 91.5° (**2b**), 1.513 Å, 88.0° (**5**); and their similar SiN WBI (0.33 (**5**), 0.42 (**2b**), 0.71 (H<sub>3</sub>SiNH<sub>2</sub>)) suggest that **2b** and **2c** are best described as donor–acceptor complexes. The binding energy of **2b** relative to two isolated (H<sub>2</sub>N)HSi: of 27.6 kcal/mol is ca. 4 times the complexation energy of (H<sub>2</sub>N)HSi: with NH<sub>2</sub>SiH<sub>3</sub> (–6.9 kcal/mol), pointing to a strong synergistic bonding effect in **2b**. However, this binding energy is only ca. 25% of the bond

dissociation energy of a regular SiN bond.<sup>23</sup> The bonding in **2b** is best described as resulting from a cyclic donor–acceptor interaction between a filled lone-pair orbital on the nitrogen of one silylene and an empty Si(3p) orbital of the other silylene, as shown in Scheme 1.<sup>24</sup>

Mes[(TMS)<sub>2</sub>N]Si:<sup>25</sup> dimerizes to Mes[(TMS)<sub>2</sub>N]Si=Si–[N(TMS)<sub>2</sub>]Mes.<sup>4</sup> This observation is consistent with the computational finding that [(H<sub>3</sub>Si)<sub>2</sub>N]HSi=SiH[N(SiH<sub>3</sub>)<sub>2</sub>] is by 9.0 kcal/mol (HF/6-31G\* + ZPE) more stable than the corresponding bridged dimer of type **2** (the latter being by 5.8 kcal/mol more stable than two free [(H<sub>3</sub>Si)<sub>2</sub>N]HSi:). For (H<sub>2</sub>N)<sub>2</sub>Si:, the situation is predicted to be different. Thus, while (H<sub>2</sub>N)<sub>2</sub>Si=Si(NH<sub>2</sub>)<sub>2</sub> is *not a stationary point* on the HF/6-31G\*\* PES, the corresponding *bridged dimer is a local minimum*, being 15.3 kcal/mol more stable than two isolated diaminosilylenes (MP2-(fc)/6-31G\*/MP2(fc)/6-31G\*).<sup>26</sup> It was recently reported that the stable silylene **6**, R = *t*-Bu, reacts to give a dimer which was not yet characterized.<sup>6</sup> Calculations (HF/6-31G\*\* + ZPE) for the model **6**, R = H, show that, in analogy to (H<sub>2</sub>N)<sub>2</sub>Si=Si(NH<sub>2</sub>)<sub>2</sub>, the disilene **7**, R = H, is not a minimum on the PES, while the corresponding bridged dimer **8**, R = H, is a minimum lying 7.8 kcal/mol lower in energy than two isolated silylenes **6**, R = H. We therefore propose that the observed noncharacterized dimer of **6**, R = *t*-Bu<sup>6</sup> is *not a disilene, but it is a bridged cage-like structure, probably 8*, R = *t*-Bu.<sup>27</sup>



In conclusion, *hetero-bridged isomers of diamino- and dihydroxydisilenes are predicted to be unimolecularly kinetically stable, making these novel compounds viable targets for synthesis*. In fact we believe that several such species have already been observed<sup>6,9a</sup> although they were not recognized as such.<sup>6,9a</sup> We hope that this report will promote further experimental efforts to synthesize and to characterize these novel interesting compounds.

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**Supplementary Material Available:** Calculated geometries and total and relative energies of **1b,c**, **2b,c**, **3b,c**, and **4b,c** and the transition states for their interconversion, of **6** and **8**, and of the dimers of (H<sub>2</sub>N)<sub>2</sub>Si: and [(H<sub>3</sub>Si)<sub>2</sub>N]HSi: (10 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

JA944168U

(23) Walsh, R. In ref 2a, Chapter 5, p 385.

(24) A different model involving ionic bonds has been suggested for FSi(μ-F)<sub>2</sub>SiF<sub>2</sub><sup>10c</sup> but detailed MOP and NBO analyses for **2b** and **2c** show that the donor–acceptor model is better suited to describe the bonding in these compounds.

(25) Mes ≡ 2,4,6-trimethylphenyl.

(26) The fact that (H<sub>2</sub>N)<sub>2</sub>Si=Si(NH<sub>2</sub>)<sub>2</sub> is not at a minimum on the PES is in line with previous qualitative<sup>10a–c</sup> and quantitative<sup>11</sup> theoretical predictions based on the high singlet–triplet separation (80.4 kcal/mol at MP4SDTQ/6-311G\*\*//6-31G\*\*) in the silylene monomers.

(27) (a) Analogous dimeric structures of the type R<sub>2</sub>E(μ-NR<sub>2</sub>)<sub>2</sub>ER<sub>2</sub> are known for E = Al and other group 13 elements.<sup>27b</sup> However, in these compounds the Al is hypercoordinated while in **8** the silicon is low-valent. We are grateful to one of the referees for bringing this analogy to our attention. (b) Review: Taylor, M. J. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: Oxford, 1986; Chapter 25.

(17) MP2(fc)/6-31G\*\* values are quoted throughout.

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(20) For **2b**, the MOP is 0.024 and the WBI<sup>21</sup> is 0.022. Compare to MOP = 0.383 and WBI = 0.985 in H<sub>3</sub>SiSiH<sub>3</sub>.

(21) Wiberg, K. *Tetrahedron* **1968**, 24, 1083.

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