

# Self-Condensation Reaction of Lithium (Alkoxy)silylenoid: A Model Study by *ab Initio* Calculation

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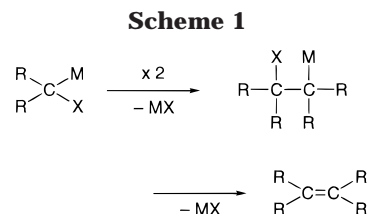
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A theoretical study on the reaction mechanism of the self-condensation reaction of lithium (methoxy)silylenoid (MeO)<sub>2</sub>SiLi (**4**) has been performed using MP2//HF/6-31G\*\*. Stable geometries of the unsolvated **4**, bis-solvated **4**·(H<sub>2</sub>O)<sub>2</sub>, and tris-solvated species **4**·(H<sub>2</sub>O)<sub>3</sub> are found. A stable geometry of **4**·(Me<sub>2</sub>O)<sub>2</sub> is also investigated. The self-condensation reaction path is followed using two molecules of **4**·(H<sub>2</sub>O)<sub>2</sub> to yield the reactive intermediate, the transition state, and the product. In the transition state, one silicon center functions as a nucleophile and the other as an electrophile. In the electrophilic part the lithium-assisted ionization of the Si–O bond lowers the energy of the σ\*(Si–O) orbital. The interaction between the lobe of the HOMO which localizes on the silicon atom in the nucleophilic part and the backside lobe of the σ\*(Si–O) orbital in the electrophilic part leads to the formation of the Si–Si bond and the breaking of the Si–O bond. Finally, the (disilanyl)lithium (MeO)-H<sub>2</sub>SiSiH<sub>2</sub>Li and lithium methoxide are obtained. The reaction proceeds via an S<sub>N</sub>2 type displacement with retention of the configuration of silicon in the nucleophilic part but with inversion of the configuration of silicon in the electrophilic part.

## Introduction

Carbenoids (X)R<sub>2</sub>CM show an ambiphilic character because a leaving group X as well as a metal atom M is bound to the same carbon atom.<sup>1,2</sup> Lithium is a typical metal atom, and halogen and alkoxy groups are possible leaving groups. Whereas carbenoids react with nucleophiles as well as electrophiles, they also undergo bimolecular self-condensation reactions as shown in Scheme 1.<sup>3</sup> In many cases, the self-condensation product undergoes β-elimination successively to give the corresponding olefin.<sup>1,2c,4</sup> Recently, the nitrogen ana-



logues, nitrenoids (X)RNLi,<sup>5</sup> and the oxygen analogues, oxenoids (X)OLi (X = alkoxy group),<sup>6</sup> have also been studied.

In addition, the silicon analogues, silylenoids (X)R<sub>2</sub>-SiM, have been discussed in comparison with the divalent silylenes. In 1980, Clark and Schleyer theoretically studied the stable geometries of (F)H<sub>2</sub>SiLi by *ab initio* calculation and mentioned the electrophilic character of the silicon atom.<sup>7</sup> Some (halo)silylenoids have been postulated as intermediates in the reduction of dihalosilanes with alkali metals.<sup>8</sup> In 1995, Tamao and Kawachi experimentally revealed that [(*tert*-butoxydiphenyl)silyl]lithium (**1**) exhibited ambiphilic character: **1** underwent a self-condensation reaction to give [2-(*tert*-butoxy)disilanyl]lithium derivative **2** in THF as shown in Scheme 2 and also a nucleophilic substitution reaction with *n*-butyllithium.<sup>9</sup> In this case, the self-condensation product **2** undergoes no β-elimination

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(1) Pertinent reviews: (a) Köbrich, G. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 473. (b) Maercker, G. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1023. (c) Boche, G.; Lohrenz, J. C. W.; Opel, A. In *Lithium Chemistry*; Space, A.-M., Schleyer, P. v. R., Eds.; John-Wiley & Sons: New York, 1995; pp 195–226. (d) Braun, M. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 430.

(2) <sup>13</sup>C NMR: (a) Seebach, D.; Sigel, H.; Gabriel, J.; Hässig, R. *Helv. Chim. Acta* **1980**, *63*, 2046. (b) Seebach, D.; Hässig, R.; Gabriel, J. *Helv. Chim. Acta* **1983**, *66*, 308. (c) Boche, G.; Bosold, F.; Lohrenz, J. C. W.; Opel, A.; Zulauf, P. *Chem. Ber.* **1993**, *126*, 1873. X-ray: (d) Boche, G.; Marsch, M.; Müller, A.; Harms, K. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1032. (e) Boche, G.; Harms, K.; Marsch, M.; Müller, A. *J. Chem. Soc., Chem. Commun.* **1994**, 1393. (f) Müller, A.; Marsch, M.; Harms, K.; Lohrenz, J. C. W.; Boche, G. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1518. Stereochemistry: (g) Topolski, M.; Duraisamy, M.; Rachon, J.; Gawronsky, J.; Gawronska, K.; Goedlken, V.; Walborsky, H. M. *J. Org. Chem.* **1993**, *58*, 546. Calculations: (h) Clark, T.; Schleyer, P. v. R. *J. Chem. Soc., Chem. Commun.* **1979**, 883. (i) Clark, T.; Schleyer, P. v. R. *Tetrahedron Lett.* **1979**, 4963. (j) Mareda, J.; Rondan, N. G.; Houk, K. N. *J. Am. Chem. Soc.* **1983**, *105*, 6997.

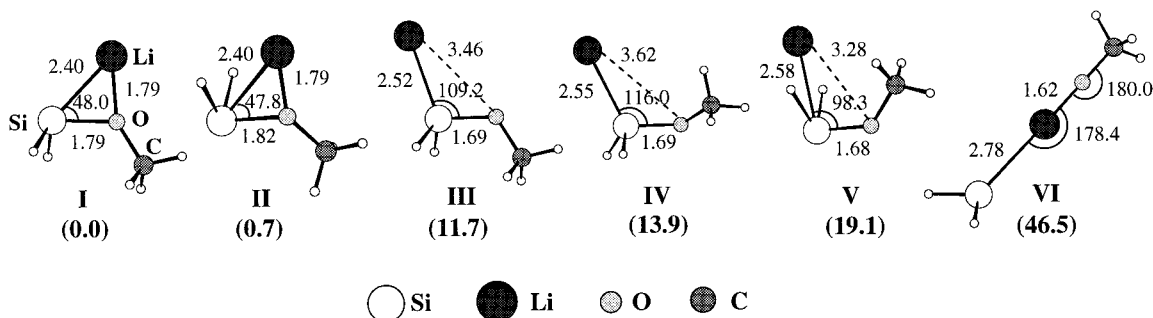
(3) Although the term "dimerization" has often been used for describing this type of bimolecular reaction, "self-condensation" seems to be more suitable in our opinion.

(4) Schöllkopf, U.; Eisert, M. *Liebigs Ann. Chem.* **1963**, 664, 76.

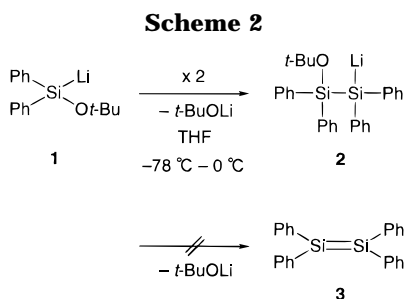
(5) Boche, G.; Boie, C.; Bosold, F.; Harms, K.; Marsch, M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 115.

(6) (a) Julia, M.; Saint-Jalmes, V. P.; Verpeaux, J.-N. *Synlett* **1993**, 233. (b) Boche, G.; Bosold, F.; Lohrenz, J. C. W. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1161. (c) Boche, G.; Möbus, K.; Harms, K.; Lohrenz, J. C. W.; Marsch, M. *Chem. Eur. J.* **1996**, *2*, 604.

(7) Clark, T.; Schleyer, P. v. R. *J. Organomet. Chem.* **1980**, *191*, 347.



**Figure 1.** Optimized geometries and relative energies (kcal/mol) for  $(\text{MeO})_2\text{H}_2\text{SiLi}$  (**4**) at MP2//HF/6-31G\*\*. Bond lengths are in angstroms and bond angles in degrees.



perhaps due to the low stability of the corresponding elimination product, disilene **3**.

We have been interested in elucidation of the mechanism of the self-condensation reaction because it provides a new reaction mode of silicon-silicon bond formation. Two paths are plausible: (A) two molecules of **1** directly react with each other, one of which functions as a nucleophile and the other as an electrophile; (B) one molecule of **1** undergoes  $\alpha$ -elimination to give the corresponding silylene  $\text{Ph}_2\text{Si:}$ , which is inserted into the Si-Li bond of another molecule of **1**.<sup>10</sup> Path B may be excluded by our previous experimental evidence to show that no silylene was trapped in the presence of various silylene-trapping agents.<sup>9</sup> Thus, we investigated the self-condensation reaction based on path A. In the present ab initio calculations we searched for stable geometries of model compound  $(\text{MeO})_2\text{H}_2\text{SiLi}$  (**4**), its bis-solvated species  $4 \cdot (\text{H}_2\text{O})_2$  (**5**), and tris-solvated species  $4 \cdot (\text{H}_2\text{O})_3$  (**6**), and followed the self-condensation reaction of **5** by bringing the two molecules closer. Our main interest is the origin of electrophilicity of the silylenoid as well as the reaction mechanism.<sup>11</sup>

### Method and Model

**Method.** All calculations were performed with the Gaussian 94 program package.<sup>12</sup> Stationary points on the potential energy surface were optimized at the HF/6-31G\*\* level, and

(8) (a) Boudjouk, P.; Samaraweera, U.; Sooriyakumaran, R.; Chrusciel, J.; Anderson, K. R. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1355. (b) Tsumuraya, T.; Batcheller, S. A.; Masamune, S. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 902. (c) Corriu, R. J. P.; Lanneau, G.; Priou, C.; Soulaïrol, F.; Auner, N.; Probst, R.; Conlin, R.; Tan, C. J. *J. Organomet. Chem.* **1994**, *466*, 55. (d) Recently Kira et al. reported that [bis(*tert*-butylsilyl)bromosilyl]lithium was obtained by reduction of bis(*tert*-butylsilyl)dibromosilane with lithium naphthalenide: Sawa, Y.; Ichinohe, M.; Kira, M. In the 73rd annual meeting of the Chemical Society of Japan, 1997, September, Morioka, Japan.

(9) (a) Tamao, K.; Kawachi, A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 818. (b) Tamao, K.; Kawachi, A. *Organometallics* **1995**, *14*, 3108.

(10) Armitage, D. A. In *Comprehensive Organometallic Chemistry II*; Davies, A. G., Ed.; Elsevier Science Ltd.: Oxford, 1995; Vol. 2, pp 1-44.

single-point energies at the optimized stationary points were calculated at the MP2/6-31G\*\* level: energy minima exhibited all positive eigenvalues of the Hessian matrix, and the transition state exhibited one negative eigenvalue of the Hessian matrix. Vibrational zero-point energies (ZPE) were not included.

**Model.** Although  $(t\text{-BuO})\text{Ph}_2\text{SiLi}$  (**1**) was used experimentally,<sup>9</sup>  $(\text{MeO})_2\text{H}_2\text{SiLi}$  (**4**) was used as a model of **1** to reduce the number of atoms treated in the present calculations: inactive phenyl groups of **1** were replaced with hydrogens, and the *tert*-butoxy group was replaced with a methoxy group. Although the structure of **1** in solution has not been clarified experimentally, most of the silyllithiums in THF reported so far exist as a monomer, in which lithium is coordinated with THF molecules.<sup>13</sup> Thus we treated  $4 \cdot (\text{H}_2\text{O})_2$  (**5**) as a monomer containing two water molecules on the lithium atom as a model of the solvated species. We also treated  $4 \cdot (\text{H}_2\text{O})_3$  (**6**) as a model of the solvated species. Water molecules have frequently been used as models of ethereal solvents in ab initio calculations on the chemistry of organolithium and silyllithium compounds to give successful results.<sup>2f,14</sup> For comparison we also calculated  $4 \cdot (\text{Me}_2\text{O})_2$  (**7**) containing two dimethyl ether molecules.

### Results and Discussion

**Stable Geometries of  $(\text{MeO})_2\text{H}_2\text{SiLi}$  (**4**).** First we examined the stable geometries of  $(\text{MeO})_2\text{H}_2\text{SiLi}$  (**4**). Starting from the tetrahedral geometry and from four local minima geometries found for  $(\text{F})\text{H}_2\text{SiLi}$ ,<sup>7</sup> six local minima I-VI were found as shown in Figure 1.

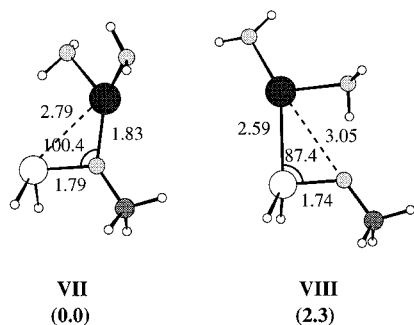
The most stable geometry, I (0 kcal/mol), includes  $\text{Li} \cdots \text{O}$  interaction (1.79 Å) as well as  $\text{Li} \cdots \text{Si}$  interaction (2.40 Å). Such lithium-bridged structures were also obtained as the most stable geometry for the carbenoids,<sup>2</sup> nitrenoids,<sup>5</sup> and oxenoids.<sup>6</sup> The  $\text{Li} \cdots \text{O}$  interaction elongates the Si-O bond (1.79 Å), compared to

(11) Dimerization of divalent silylenes was theoretically discussed: Apeloig, Y.; Müller, T. *J. Am. Chem. Soc.* **1995**, *117*, 5363.

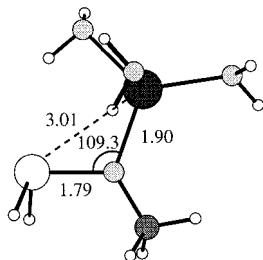
(12) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*, Revision D.3; Gaussian, Inc.: Pittsburgh, PA, 1995.

(13) (a) Tamao, K.; Kawachi, A. *Adv. Organomet. Chem.* **1995**, *38*, 1. (b) Pauer, F.; Power, P. P. In *Lithium Chemistry*; Space, A.-M., Schleyer, P. v. R., Eds.; John-Wiley & Sons: New York, 1995; pp 295-392, and references therein.

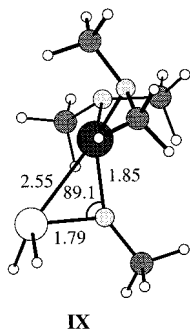
(14) (a) Bühl, M.; Hommes, N. J.; Hommes, R. v. E.; Schleyer, P. v. R.; Fleischer, U.; Kutzelnigg, W. *J. Am. Chem. Soc.* **1991**, *113*, 2459. (b) Nakamura, M.; Nakamura, E.; Koga, N.; Morokuma, K. *J. Am. Chem. Soc.* **1993**, *115*, 11016. (c) Koizumi, T.; Kikuchi, O. *Organometallics* **1995**, *14*, 987. (d) Koizumi, T.; Morihashi, K.; Kikuchi, O. *Organometallics* **1995**, *14*, 4018.



**Figure 2.** Optimized geometries and relative energies (kcal/mol) for  $(\text{MeO})_2\text{H}_2\text{SiLi}(\text{H}_2\text{O})_2$  (**5**) at MP2//HF/6-31G\*\*. Bond lengths are in angstroms and bond angles in degrees.



**Figure 3.** Optimized geometry for  $(\text{MeO})_2\text{H}_2\text{SiLi}(\text{H}_2\text{O})_3$  (**6**) at HF/6-31G\*\*. Bond lengths are in angstroms and bond angles in degrees.



**Figure 4.** Optimized geometry for  $(\text{MeO})_2\text{H}_2\text{SiLi}(\text{Me}_2\text{O})_2$  (**6**) at HF/6-31G\*\*. Bond lengths are in angstroms and bond angles in degrees.

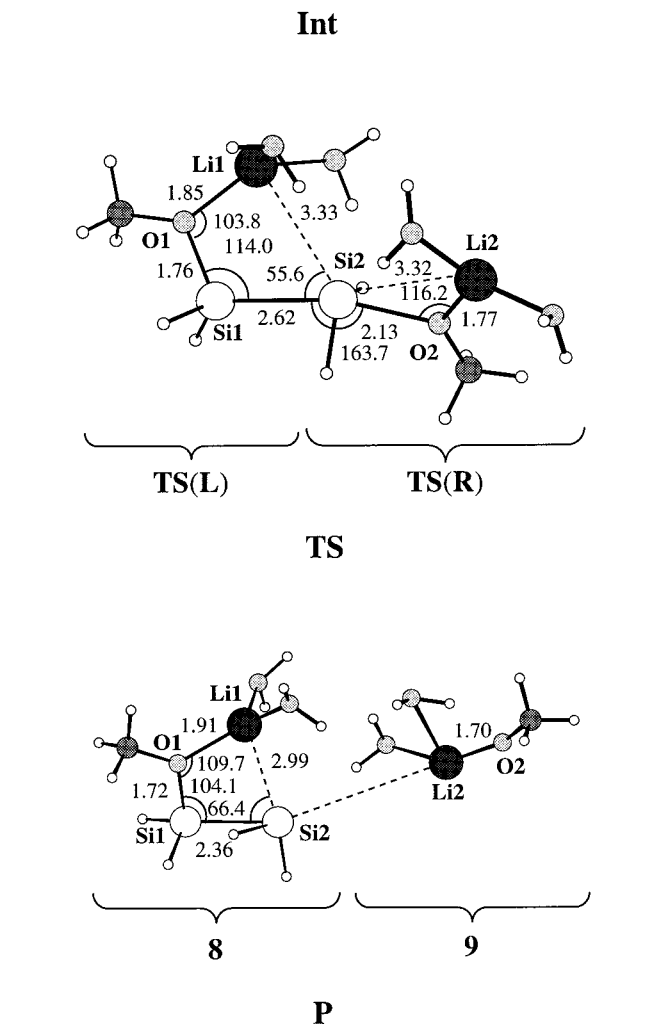
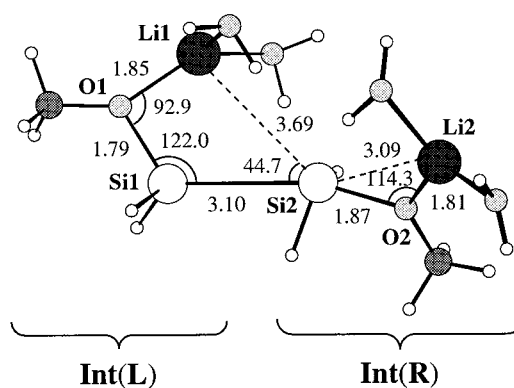
that in  $(\text{MeO})_2\text{H}_2\text{Si}-\text{H}$  (1.64 Å). Geometry II (+0.7 kcal/mol) includes an agostic  $\text{Li}\cdots\text{H}-\text{Si}$  interaction<sup>15</sup> in addition to the  $\text{Li}\cdots\text{O}$  interaction, in which the Si-O bond is further elongated to 1.82 Å. Geometry III (+11.7 kcal/mol) has a nearly tetrahedral geometry around the silicon atom, in which the  $\text{Li}\cdots\text{O}$  interaction is now broken and the Si-O bond (1.69 Å) is shorter than those in I and II. Geometries IV (+13.9 kcal/mol) and V (+19.1 kcal/mol) may be regarded as rotational isomers of III and II, respectively. Geometry VI (+46.5 kcal/mol) is the least stable among these six geometries. This geometry can be represented as a silylene-lithium methoxide complex, in which silylene acts as a donor and the lithium atom acts as an acceptor.<sup>16,17</sup>

**Stable Geometries of Bis-Solvated Silyllithium  $(\text{MeO})_2\text{H}_2\text{SiLi}(\text{H}_2\text{O})_2$  (**5**) and Tris-Solvated Silyllithium  $(\text{MeO})_2\text{H}_2\text{SiLi}(\text{H}_2\text{O})_3$  (**6**).** Next we examined

(15) A similar agostic interaction was observed in  $(\text{F})_2\text{H}_2\text{SiLi}$ ; see ref 7.

(16) For an example of silylene-Lewis acid complexes: Metzler, N.; Denk, M. *J. Chem. Soc., Chem. Commun.* **1996**, 2657.

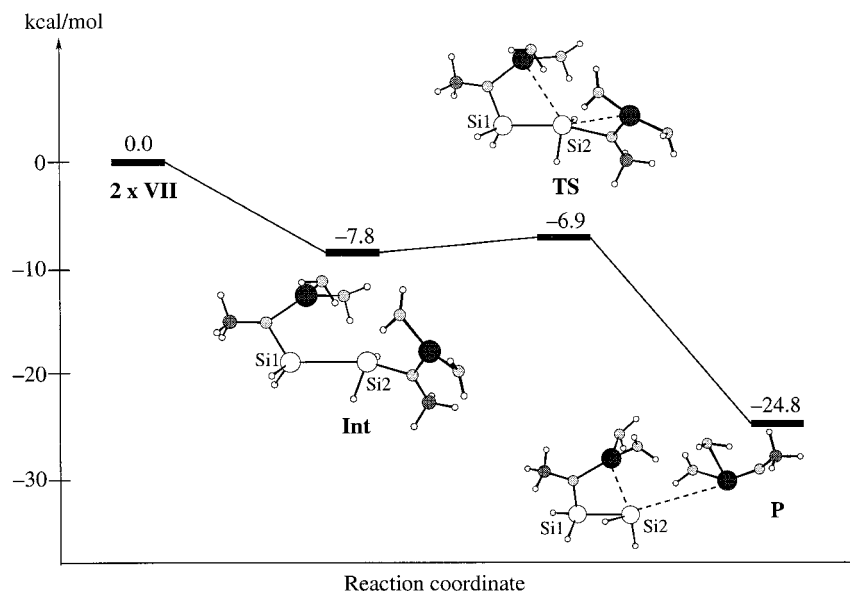
(17) Formation of the free silylene  $\text{H}_2\text{Si}$ : from the geometry I is estimated to be 59.0 kcal/mol unfavorable.



**Figure 5.** Optimized geometries for reactive intermediate (**Int**), transition state (**TS**), and product (**P**) at MP2//HF/6-31G\*\*. Bond lengths are in angstroms and bond angles in degrees.

the solvated species  $(\text{MeO})_2\text{H}_2\text{SiLi}(\text{H}_2\text{O})_2$  (**5**) based on the geometries obtained for **4**. Although the coordination number of lithium remains to be discussed, tetracoordination is the most popular, and tri- and dicoordination are sometimes observed.<sup>13,18</sup> Thus, two water molecules are coordinated to the lithium atom through  $\text{Li}\cdots\text{O}$  interaction in the most stable geometry I and in the tetrahedral geometry III, which are expected to give the tetra- and tricoordination of the lithium atom, respec-

(18) Setzer, W. V.; Schleyer, P. v. R. *Adv. Organomet. Chem.* **1985**, 24, 353.



**Figure 6.** Potential-energy profile for the self-condensation reaction at MP2//HF/6-31G\*\*.

tively. The second stable geometry, II, is excluded, because the agostic interaction is not feasible for **1**.

By the solvation of the lithium atom, the geometry I yields VII (Figure 2). The Si–Li bond is elongated to 2.79 Å, and accordingly the Si–O–Li angle increases to 100.4°. By the solvation of the lithium atom, the geometry III yields VIII. The Si–Li bond is slightly elongated to 2.59 Å, and the Li–O bond is shortened to 3.05 Å; accordingly, the Li–Si–O angle decreases to 87.4°. The geometry VII is 2.3 kcal/mol more stable than VIII. Thus we use the geometry VII as a reactant model of the self-condensation reaction.

We also calculated a tris-solvated species **4**·(H<sub>2</sub>O)<sub>3</sub> (**6**) by starting from the geometry I, as shown in Figure 3. The Si···Li bond in **6** (3.01 Å) is much longer than that of geometry VII (2.79 Å). Thus, the lithium atom is tetracoordinated by three water molecules and a methoxy group.

To confirm the reliability of the solvated model containing water molecules, we investigated the bis-solvated species containing dimethyl ether molecules, (MeO)H<sub>2</sub>SiLi(Me<sub>2</sub>O)<sub>2</sub> (**7**). The stable geometry IX based on the geometry I was obtained as shown in Figure 4.

In IX the Si–Li bond is elongated to 2.55 Å, and accordingly the Si–O–Li angle increases to 89.1° by the solvation, as observed in VII. Although the geometry IX is slightly different from VII, it was also found that the energy level of the HOMO and the  $\sigma^*$ (Si–O) orbital (see below for the importance of these orbitals) in both species are close to each other and the shapes of the orbitals are essentially the same in VII and IX. These results suggest that there is essentially no difference in the reactivity between VII and IX. Thus, it was concluded that the species **5** was reasonable as the solvated model in the present reaction.

**Self-Condensation Reaction of the Bis-Solvated Silyllithium 5.** We modeled the self-condensation reaction of **5** using the geometry VII as a reactant, in such a fashion that two reactants VII approach each other for the formation of the Si–Si bond.<sup>19</sup> The

geometries of the intermediate (**Int**), the transition structure (**TS**), and the product (**P**) are shown in Figure 5.

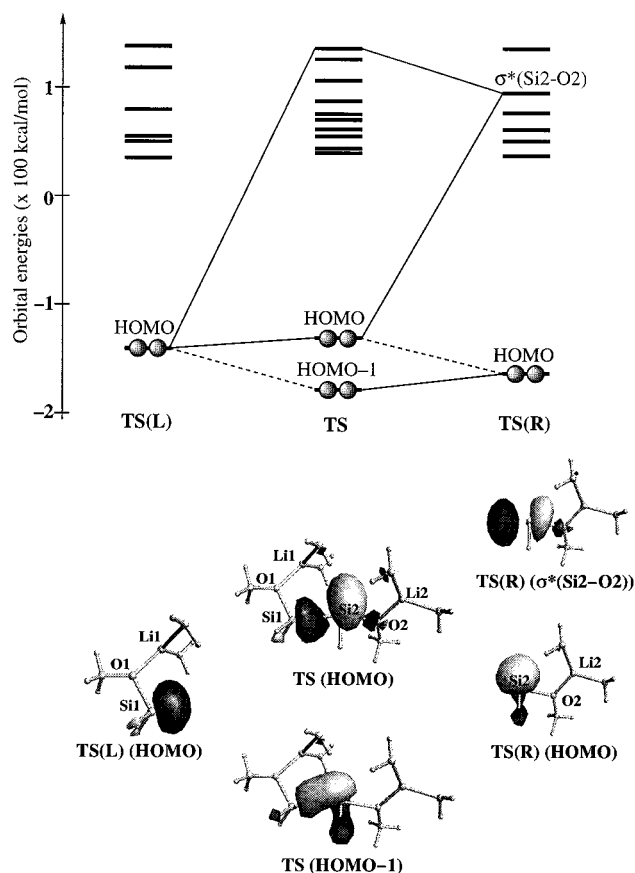
In the initial step, two reactants VII form a reactive intermediate (**Int**) at the Si1–Si2 distance of 3.10 Å. This complex is 7.8 kcal/mol more stable than the two reactants themselves. Compared to VII, the Li1–O1–Si1 angle in the left part (**Int(L)**) decreases from 100.4° to 92.9°, resulting in the approach of Li1 to Si2. In the right part (**Int(R)**), Li2 moves away from Si2 to O2 (Si2–Li2 = 3.09 Å; Li2–O2 = 1.81 Å). As a whole, it seems that Li1 leads Si1 to Si2 through an electrostatic interaction between Li1 and Si2, as Li2 leaves from Si2.<sup>6c</sup>

The transition state (**TS**) is formed at the Si–Si distance of 2.62 Å. The Si1 center in the left part (**TS(L)**) approaches Si2 in the right part (**TS(R)**) from the backside of the Si2–O2 bond at the Si1–Si2–O2 angle of 163.7°. Li1 also further approaches Si2 (Li1–Si2 = 3.33 Å) and Li2 completely migrates from Si2 to O2 (Si2–Li2 = 3.32 Å; Li2–O2 = 1.77 Å), resulting in the elongation of the Si2–O2 bond (2.13 Å) and the formation of lithium methoxide as a neutral leaving molecule. Thus, **TS** involves the formation of the Si1–Si2 bond and the breaking of the Si2–O2 bond. The small activation energy (0.9 kcal/mol) agrees with the experimental result that **1** easily undergoes a self-condensation reaction at low temperatures.

In the final step, product (**P**) is formed, where [2-(methoxy)disilanyl]lithium (**8**) and lithium methoxide (**9**) are involved. The product is 24.8 kcal/mol more favorable than the reactants. In **8**, Li1 still interacts with O1 (Li1–O1 = 1.91 Å) as well as Si2, and thus the Li1–Si2 bond (Li1–Si2 = 2.99 Å) is somewhat longer than the normal Si–Li bond length. Formation of the disilanyl lithium **8** is consistent with the experimental result.<sup>9</sup>

(19) We have also attempted to model the self-condensation reaction of the unsolvated species I at MP2/Huzinaga's double- $\zeta$  level using the Gaussian 92 program. However, no product suitable for the experiment was found because of the overestimation of an *intermolecular* Li···O(Me) interaction.





**Figure 7.** Molecular orbital analysis of **TS**. Orbital correlation energy diagram (above) and molecular orbitals of HOMO (**TS**, **TS(L)**, and **TS(R)**), HOMO-1 (**TS**), and  $\sigma^*(\text{Si2-O2})$  (**TS(R)**) (below).

The potential energy profile of the whole process is illustrated in Figure 6.

Molecular orbital analysis of **TS** helps in the understanding of the reaction mechanism. Figure 7 shows the correlations between the pertinent MOs of **TS(L)** and **TS(R)** to build the MO of the **TS** structure. (1) In **TS(L)** the lobe of the HOMO is localized on Si1, and its orbital energy (-141 kcal/mol) is 10 kcal/mol higher than that of VII (-151 kcal/mol), which suggests that the **TS(L)** moiety is acting as a nucleophile. (2) In **TS(R)**, the lobe of the  $\sigma^*(\text{Si2-O2})$  orbital develops around the backside of the Si2-O2 bond, and its orbital energy (95 kcal/mol) is 22 kcal/mol lower than that of VII (117 kcal/mol) due to the bonding interaction between Li2 and O2, which suggests that the **TS(R)** moiety is acting as an electrophile. This is the origin of the electrophilicity of the silylenoid. (3) The **TS(L)** moiety approaches the **TS(R)** moiety from the backside along the Si2-O2 bond axis, resulting in the bonding interaction between the lobe of the HOMO of the former and the backside lobe of the  $\sigma^*(\text{Si-O})$  orbital of the latter, which leads to formation of the Si1-Si2 bond and breaking of the Si2-O2 bond. This clearly illustrates an  $\text{S}_{\text{N}}2$  type substitution reaction on Si2 by the Si1 center in **TS(R)**. (4) Although there should be a four-electron repulsive interaction between the HOMO electrons on both moieties, this interaction appears to be minimized by the nearly orthogonal orientation of these two HOMO lobes. (5) There seems to be an electrostatic interaction between Li1 in **TS(L)** and Si2 in **TS(R)**

through the filled orbital on Si2 (HOMO) perpendicular to the Si1-Si2 bond axis. (6) Natural bonding orbital analysis shows that the Si1-Si2 bond is already present in **TS** (bonding/antibonding occupancy of 1.98581/0.05590), whereas the Si2-O2 bond is almost totally absent (bonding occupancy of < 0.1).

Finally, the stereochemistry of this reaction should be mentioned: this simulated reaction proceeds with retention of the configuration of the nucleophilic silicon center Si1 and with inversion of the configuration of the electrophilic silicon center Si2.<sup>20</sup> The inversion of the configuration of the electrophilic carbon center has been confirmed in carbenoid chemistry.<sup>2g</sup>

**Attempted Self-Condensation Reaction of Tris-Solvated Silyllithium (6).** We have also attempted to model the self-condensation reaction starting from **6** in a way similar to that of **5**, but no transition state could be found. The result may suggest that a vacant site on the lithium atom is essential for the self-condensation reaction, consonant with the Li1...Si2 electrostatic interaction mentioned above (comment 5).

## Conclusions

In the present theoretical study, we have found the stable geometries of the unsolvated, bis-solvated, and tris-solvated silyllithiums and followed the self-condensation reaction using the bis-solvated species  $(\text{MeO})_2\text{-SiLi}(\text{H}_2\text{O})_2$ . Several features of the reaction are as follows:

(1) A reactive complex is formed as an intermediate from two molecules of the bis-solvated (alkoxysilyl)-lithium before reaching the transition state at the Si...Si distance of 3.10 Å.

(2) The transition state is formed at the Si...Si distance of 2.62 Å in which one silicon center has become nucleophilic and the other electrophilic. The lithium-assisted ionization of the Si-O bond lowers the energy of the  $\sigma^*(\text{Si-O})$  in the electrophilic part. The interaction between the lobe of the HOMO in the nucleophilic part and the backside lobe of the  $\sigma^*(\text{Si-O})$  orbital in the electrophilic part leads to the formation of the Si-Si bond and the breaking of the Si-O bond.

(3) The reaction proceeds via an  $\text{S}_{\text{N}}2$  type displacement with retention of the configuration of silicon in the nucleophilic part but with inversion of the configuration of silicon in the electrophilic part.

(4) The [2-(alkoxy)disilanyl]lithium and lithium methoxide are finally formed, consistent with the experimental result.

An experimental study for confirmation of the expected stereochemistry is now in progress in our laboratory.

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