

## Cycloaddition reactions of silacyclopropylidenoids to ethylene

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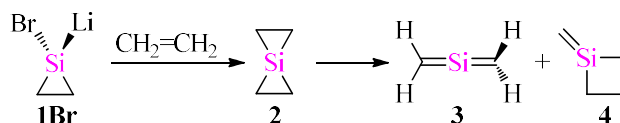
**Abstract:** The cycloaddition reactions of silacyclopropylidenoids (C<sub>2</sub>H<sub>4</sub>SiXLi, X = F, Cl, Br) to ethylene have been investigated separately to gain insights into halogen and solvation effects on the energetic of the proposed reactions at the B3LYP/6-311+G(d,p) level of theory. The calculations reveal that the addition of silacyclopropylidenoids to ethylene occurs via stepwise mechanisms. The required initial energy barriers for the conversion of silacyclopropylidenoids to silaspiropentanes are determined to be  $\Delta G = 77.4$  kJ/mol, 9.6 kJ/mol, and 9.2 kJ/mol for F, Cl, and Br, respectively. Furthermore, the gas phase calculations show that the reactions are not spontaneous at room temperature, whereas those of THF solvated models indicate that the formations of silaspiropentanes are spontaneous in the cases of X = Br and Cl. Additionally, the findings show that the silacyclopropylidene addition to ethylene is determined to be exergonic in both gas and THF phases by  $\Delta G = -42.6$  kJ/mol and  $-39.3$  kJ/mol, respectively.

**Keywords:** Silacyclopropylidenoids; silylenoid; silaspiropentane; reaction mechanism; DFT. ©2018 ACG Publications. All rights reserved.

### 1. Introduction

Carbenoids are compounds which have an electropositive metal and halogen are bound to the same carbon atom and have been known as highly reactive carbon species in organic chemistry.<sup>1-3</sup> The silicon analogue of simple carbenoids, H<sub>2</sub>SiLiX, X = F, Cl, or Br,<sup>4,5</sup> are most often key intermediates in many organometallic and organosilicon reactions and having considerable attention due to their applications to experimental and theoretical fields.<sup>6-11</sup> In 1995, Tamao and Kawachi explored the existence of a silylenoid and examined its chemical properties.<sup>11</sup> However, only limited stable silylenoids have been characterized up to now because of their highly reactive nature. A number of halosilylenoid compounds from the reaction of TsiSiX<sub>3</sub> [Tsi = C(SiMe<sub>3</sub>)<sub>3</sub>, X = Br, Cl] with lithium naphthalenide were published by Lee et al.<sup>13</sup> Apeloig et al. disclosed formation of fluorosilylenoid from the reaction of bromofluorosilane with silyl lithium in 2006.<sup>12</sup> Despite considerable potential in this regard,<sup>9,14,15</sup> reports on those of cyclic analogues (C<sub>2</sub>H<sub>4</sub>SiLiX, X = F, Cl, or Br) are still rare.<sup>16-18</sup> Very recently, we have performed a series of theoretical calculations on the formation and rearrangement of silaspiropentane **2** from addition of lithium-bromosilacyclopropylidenoid **1Br** to ethylene (Scheme 1).<sup>18</sup> The nature of the addition reaction of **1** to ethylene is found to be endergonic by  $\Delta G = 33.9$  kJ/mol, whereas the formation process of **4** is exergonic by  $\Delta G = -60.6$  kJ/mol at the B3LYP/6-31+G(d,p) level of theory.

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**Scheme 1.** General representation of the proposed intermolecular addition of **1Br** to **2** and intramolecular rearrangement of **2** to **3** and **4**.

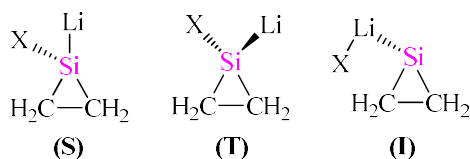
In the present computational study, we would like to distil a general message for the effects of halogen and solvent (Tetrahydrofuran, THF) on the possible cycloaddition reactions of silacyclopropylidenoids ( $C_2H_4SiLiX$ , denoted as **1X** with  $X = C, Si,$  or  $Ge$ ) to  $C=C$  double bond of ethylene. As we will show, the reactions proceed in stepwise manner in all case. The nature of the reactions is shown to depend heavily on the phase (Gas or THF) and halogen ( $X = F, Cl,$  or  $Br$ ) of the calculations.

## 2. Experimental

All the computations were carried out by Gaussian 09W packed program.<sup>19</sup> Density functional theory (B3LYP with 6-311+G(d,p) basis set) was employed to locate the studied compounds on their potential energy surface. The optimized structures were determined by characterization of their Hessian matrix as a minimum (no imaginary frequency) or transition state. The intrinsic reaction coordinate (IRC) procedure was carried out for the identification of the connectivity of stationary points on the respective potential energy surfaces with the algorithm of Gonzalez-Schlegel.<sup>20,21</sup> The frequency calculations of THF (Tetrahydrofuran) solvated models have been done for the optimized structures with using polarized continuum model (PCM) solvation model to estimate solvent effect on the energetic of the reactions.<sup>22</sup> The optimized structures were visualized by using the GaussView 3.0 program.<sup>23</sup>

## 3. Results and Discussion

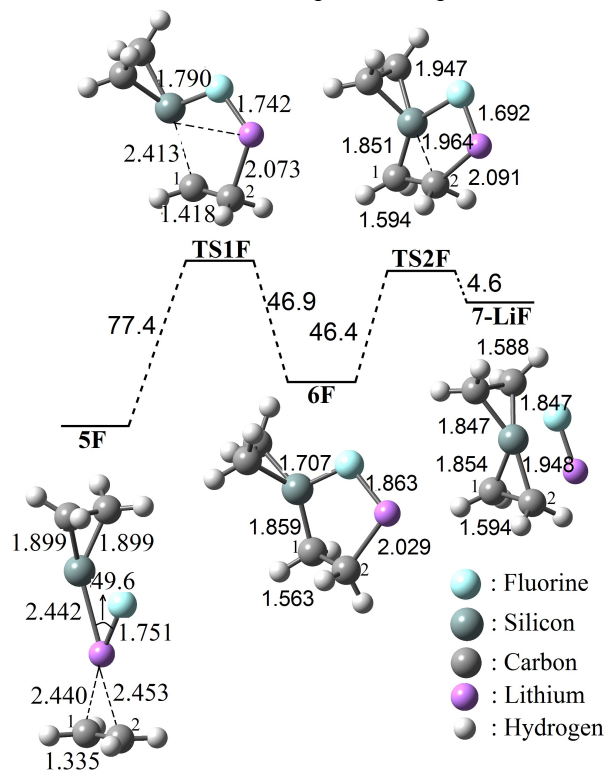
Hence, we have started optimization of most stable **S** form of  $C_2H_4SiLiX$  from silacyclopropylidenoid (**S**), tetrahedral (**T**), and inverted (**I**) forms (Scheme 2).<sup>24</sup>



**Scheme 2.** The silacyclopropylidenoid (**S**), tetrahedral (**T**), and inverted (**I**) forms of  $C_2H_4SiLiX$  (where  $X = F, Cl, Br$ ).

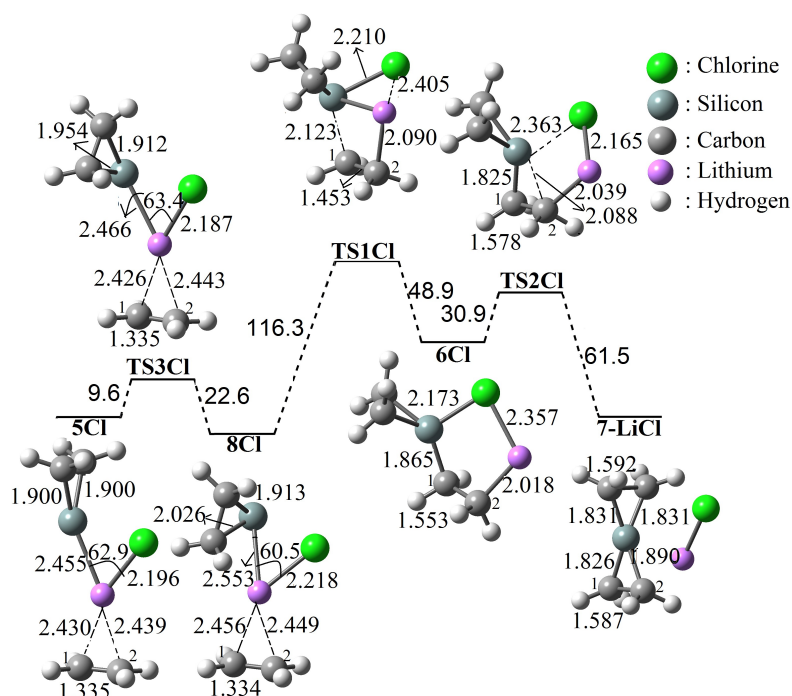
Then, the **S** forms with  $F, Cl,$  and  $Br$  are selected as reactant for the proposed reactions and those of van der Waals complexes (**5F**, **5Cl**, and **5Br**) are optimized on their potential energy surfaces (PES) at the B3LYP/6-311+G(d,p) level of theory (Figure 1–3). The  $C1-Li$  and  $C2-Li$  bond distances of **5F** are determined to be 2.440 Å and 2.453 Å, respectively (Figure 1). As the addition reaction continues, **TS1F** is formed by  $\Delta G^\ddagger = 94.6$  kJ/mol. The theoretical computations indicate that the  $C2$  atom of the ethylene unit becomes connected (2.073 Å) to counter ion  $Li^+$  and the  $Si$  atom of the silacyclopropylidenoid moiety moves to the  $C1$  atom to form a related **TS1F** structure along the potential energy surface. As it can be seen from Figure 1, the  $C2-Li$  bond distance in **TS1F** is considerably shortened as compared to that of **5F** (2.433 Å), whereas  $C1-C2$  bond length in **5F** is elongated with 0.083 Å. The geometry changes along with **TS1F** promotes formation of **6F**. The calculated energy barrier from **6F** to **TS1F** was obtained to be  $\Delta G^\ddagger = 46.9$  kJ/mol. A newly formed  $\sigma$ -

bond between Si–C1 is existed with a bond length of 1.859 Å in **6F**. Subsequently, the liberation of **LiF** from the resulting intermediate **6F** to generate silacyclopropene–LiF complex **7–LiF** via **TS2F** needs energy barrier of  $\Delta G^\ddagger = +46.4$  kJ/mol. Compared with **6F**, the Si–C2 and Li–F bond lengths in **TS2F** are decreased by 0.807 Å and Å 0.171 Å, respectively. Then, the three-membered ring moiety of **7–LiF** is formed by the backward energy of  $\Delta G = 4.6$  kJ/mol, so that the overall pathway for **7–LiF** is decidedly endergonic by  $\Delta G = 72.3$  kJ/mol (Figure 1). Collectively, the mechanistic pathway of **1F** is appeared to bear a reasonable resemblance to our previous report on **1Br** reaction.<sup>18</sup>

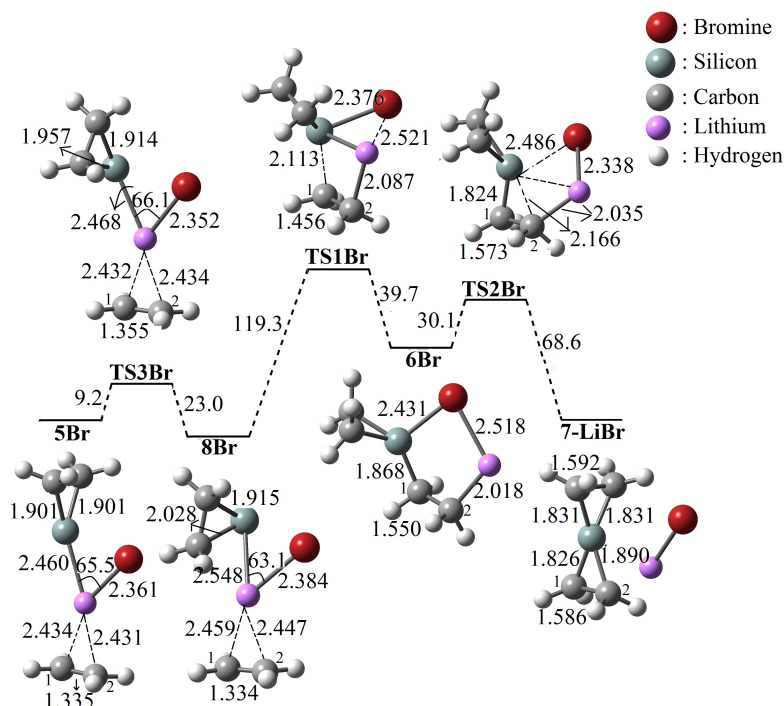


**Figure 1.** The proposed addition reaction mechanism of **1F** to ethylene.

The exchange of the halogen atom with chlorine and bromine ( $X = \text{Cl}$  or  $\text{Br}$ ) has a minor mechanistic impact: instead of two steps mechanisms now three steps processes via **8X** ( $X = \text{Cl}$  or  $\text{Br}$ ) lead to silaspiropentane compound. The initial required energy barriers to **8X** ( $X = \text{Cl}$  or  $\text{Br}$ ) are determined to be very similar by  $\Delta G^\ddagger = +9.6$  kJ/mol and 9.2 kJ/mol, respectively (Figure 2 and 3). The structure **8X** can be described as distorted form of **5X** with the obtained structural properties. For instance, the C1–Li (2.456 Å), C2–Li (2.449 Å), and C1–C2 (1.334 Å) bond lengths in **8Cl** are determined to be very similar as compared to those of in **5Cl** (2.430 Å, 2.439 Å, and 1.335 Å), respectively (Figure 2). The required energy barriers for the coordination of Si and  $\text{Li}^+$  atoms to the C1 and C2 atoms to form related intermediates **6X** via **TS1X** were calculated to be  $\Delta G^\ddagger = 116.3$  and 119.3 kJ/mol for  $X = \text{Cl}$  and  $\text{Br}$ , respectively. The intermediates **6X** follow cyclization step to form **7–LiX** complexes via **TS2X** by  $\Delta G^\ddagger = 30.9$  kJ/mol for  $\text{Cl}$  and 30.1 kJ/mol for  $\text{Br}$ . The results indicate that formations of **7–LiCl** and **7–LiBr** are endergonic by 23.8 kJ/mol and 27.3 kJ/mol, respectively. Thus, the gas phase calculations at room temperature suggest that the reactions are plausible but not spontaneous at room temperature.



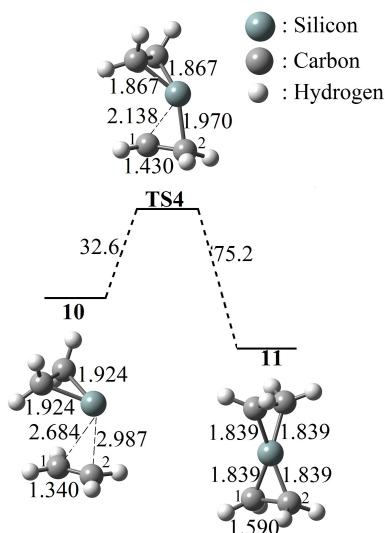
**Figure 2.** The proposed addition reaction mechanism of **1Cl** to ethylene.



**Figure 3.** The proposed addition reaction mechanism of **1Br** to ethylene.

We also calculated the possible mechanism of the cycloaddition reaction between silacyclopropylidene **9** and ethylene to evaluate effect of **LiX**. DFT calculations on the mechanism predict free energy barrier of  $\Delta G^\ddagger = 32.6$  kJ/mol for **TS4** after formation of van der Waals complexes **10**, so that the overall pathway for **11** is decidedly exergonic by  $\Delta G = -42.6$  kJ/mol in gas phase (Figure 4). It can be seen that the nature of the reactions **1F**, **1Cl**, and **1Br** with ethylene are all endergonic, showing that the reactions are nonspontaneous and not favorable in gas phase, whereas the

addition of silacyclopropylidene **9** to ethylene is promising with exergonic character of the proposed reaction.



**Figure 4.** The proposed addition reaction mechanism of **9** to ethylene.

To obtain more insights on the energetics of the mechanisms, the implicit solvation models with PCM method was performed. It is well known from the literature that carbenes, carbenoids, and those of heavier analogues can be stabilized by using donor solvents, such as THF, diethyl ether, toluene, etc.<sup>12,13</sup> Based on these observations, tetrahydrofuran (THF) was chosen as solvent for the addition reactions to form **7-LiX**. The frequency calculations of the optimized structures estimate that the required activation energies are decreased for **TS1X** and **TS2X**, whereas those of **TS3X** forms are increased as compared to gas phase calculations (Table 1). Moreover, the final products **7-LiCl** and **7-LiBr** are determined to be considerably exergonic by the overall energies of  $\Delta G = -17.3$  kJ/mol and  $-12.6$  kJ/mol in the cases of  $X = \text{Cl}$  and  $\text{Br}$ . However, the structure of **7-LiF** has endergonic nature on its potential energy surface by  $\Delta G = -18.2$  kJ/mol.

**Table 1.** The solvent effect on the energetic of the reactions at B3LYP/6-311+G(d,p) level of theory (energies in kJ/mol, Solvent = THF).

	<b>TS3</b>	<b>TS1</b>	<b>TS2</b>	<b>TS4</b>	<b>The overall <math>\Delta G</math></b>
<b>5F</b>	–	50.6	21.8	–	+18.2
<b>5Cl</b>	14.6	96.5	27.5	–	-17.3
<b>5Br</b>	12.9	100.0	23.0	–	-12.6
<b>10</b>	–	–	–	33.8	-39.3

#### 4. Conclusion

The energetic of the addition reactions of silacyclopropylidenoids (**1X**,  $X = \text{F, Cl, or Br}$ ) are compared and the contribution of the halogens to the reactivity of the structures is simply discussed. The calculations depict that the reactions follow stepwise fashion for silacyclopropylidenoid (**1X**,  $X = \text{F, Cl, or Br}$ ) additions, whereas silacyclopropylidene **10** addition occurs in a concerted manner. The computed relative  $\Delta G$  energies indicate that the formation of silaspiropentanes **7-LiX** from additions of **1X** to ethylene are endergonic by  $\Delta G = 72.3$  kJ/mol, 23.8 kJ/mol, and 27.3 kJ/mol for F, Cl, and Br in gas phase, respectively. Conversely, the THF solvated systems for **1Cl** and **1Br** are determined to be exergonic by  $\Delta G = -17.3$  kJ/mol and  $-12.6$  kJ/mol, respectively. In the case of silacyclopropylidene **9** addition, the reaction is also exergonic in both gas and THF phases by  $\Delta G = -42.6$  kJ/mol and  $-39.3$

kJ/mol, respectively. On the basis of theoretical results, the THF solvated pathways with X = Cl and Br are more promising with exergonic characters of the proposed reactions.

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## Supporting Information

Supporting information accompanies this paper on <http://www.acgpubs.org/OC>

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