

Theoretical Studies on the Alkylidene Silylenoid $\text{H}_2\text{C}=\text{SiLiF}$ and Its Insertion Reaction with R-H (R = F, OH, NH_2)

Xiaojun Tan,* Weihua Wang,[†] Ping Li,[†] Qingyan Li, Lei Cheng, Shufen Wang, Weiwang Cai, and Jinping Xing

College of Medical and Life Science, University of Jinan, Jinan, Shandong, 250022. P.R. China

*E-mail: chm_tanxj@ujn.edu.cn

[†]College of Chemistry Science, Qufu Normal University, Qufu, Shandong, 273165 P.R. China

Received September 10, 2009, Accepted January 26, 2010

The geometries and isomerization of the alkylidene silylenoid $\text{H}_2\text{C}=\text{SiLiF}$ as well as its insertion reactions with R-H (R = F, OH, NH_2) have been systematically investigated at the B3LYP/6-311+G* level of theory. The potential barriers of the three insertion reactions are 97.5, 103.3, and 126.1 kJ/mol, respectively. Here, all the mechanisms of the three reactions are identical to each other, i.e., an intermediate has been formed first during the insertion reaction. Then, the intermediate could dissociate into the substituted silylene ($\text{H}_2\text{C}=\text{SiHR}$) and LiF with a barrier corresponding to their respective dissociation energies. Correspondingly, the reaction energies for the three reactions are -36.4, -24.3, and 3.7 kJ/mol, respectively. Compared with the insertion reaction of $\text{H}_2\text{C}=\text{Si}$: and R-H (R = F, OH and NH_2), the introduction of LiF makes the insertion reaction occur more easily. Furthermore, the effects of halogen (F, Cl, Br) substitution and inorganic salts employed on the reaction activity have also been discussed. As a result, the relative reactivity among the three insertion reactions should be as follows: H-F > H-OH > H- NH_2 .

Key Words: Alkylidene silylenoid ($\text{H}_2\text{C}=\text{SiLiF}$), Insertion reaction, Density functional theory (DFT)

Introduction

Silylenes are significant, highly reactive organosilicon compounds.¹ The chemistry of silylenes has enjoyed a few decades of explosive growth, and stable silylenes have been reported.²⁻⁴

Similar to carbenoid, silylenoid is the complex formed between the silylene and inorganic salt, which can be denoted as $\text{R}_1\text{R}_2\text{SiMX}$ (M = alkali metal, X = halogen). Early in the 1960s, silylenoids were postulated as intermediates in some organosilicon reactions.^{5,6} Since then people tried to detect, even to obtain some silylenoid species as well as to probe into their structures and properties.⁷⁻¹³ However, as a kind of very reactive species, the preparation of silylenoids is very difficult. Until 1995, Tamao *et al.*¹⁴ reported the first experimental study of silylenoid chemistry, detected the existence of [(*tert*-butoxy)diphenylsilyl]lithium, $\text{Ph}_2\text{SiLi}(\text{O}i\text{Bu}-t)$, and investigated its chemical properties. In 1998, Tanaka *et al.*¹⁵ studied the self-condensation reaction of lithium (alkoxy)silylenoid as a model of $\text{Ph}_2\text{SiLi}(\text{O}i\text{Bu}-t)$ using ab initio method. In 2004, Lee *et al.*¹⁶ reported the synthesis of stable halosilylenoids (Tsi) X_2SiLi ($\text{Tsi} = \text{C}(\text{SiMe}_3)_3$; X = Br, Cl) at room temperature. Thus, a great breakthrough has been experimentally made in the research of silylenoids. The theoretical studies on silylenoids were lagged. In 1980, Clark *et al.*¹⁷ studied theoretically the isomers of lithiofluorosilylenoid H_2SiLiF by ab initio calculations for the first time. Feng *et al.* have studied some silylenoids such as $\text{R}_1\text{R}_2\text{-SiMX}$ ($\text{R}_1, \text{R}_2 = \text{H, F, OH, NH}_2, \text{Me, Et}$; X = F, Cl, Br; M = Li, Na, K, *etc.*) by quantum chemistry theory on their structures, stability, isomerization, insertion reactions, and addition reactions *etc.*¹⁸⁻²¹ Furthermore, the theoretical study of the structures and isomerization of silylenoid $\text{Ph}_2\text{SiLi}(\text{O}i\text{Bu}-t)$ have been performed by Feng's group,²² they found the calculated result is well consistent with the experimental presuming. Both experimental

and theoretical results show that silylenoids have ambiphilic character, nucleophilicity and electrophilicity, and can take part in many reactions. Such reactions as insertion, addition, and polymerization were recognized as important and effective methods for preparation of the new silicon-bonded and heterocyclic silicon compounds. Therefore, further thorough investigations on silylenoids will be of important theoretical and practical values.

The unsaturated silylenoids $\text{R}_1\text{R}_2\text{C}=\text{SiMX}$ and $\text{HN}=\text{SiMX}$ are another kinds of silylenoids. At present, their existence, structures, and chemical properties have not been studied experimentally. Recently, Li *et al.* have studied the geometries and isomerization reaction of unsaturated silylenoid $\text{H}_2\text{C}=\text{SiNaF}$ ²³ and $\text{H}_2\text{C}=\text{SiNaBr}$ theoretically,²⁴ Wang *et al.*²⁵ have studied the geometries and insertion reaction with R-H of $\text{HN}=\text{SiMX}$.

Similarly, alkylidene silylenoid $\text{H}_2\text{C}=\text{SiLiF}$ is one of the simplest unsaturated silylenoids. However, its relevant geometries and reaction activities with R-H type molecules are still lack. By using $\text{H}_2\text{C}=\text{SiLiF}$ as a model, a detail theoretical study on its structures, stability, and insertion reaction with R-H (R = F, OH, and NH_2) will be reported in present study. Hopefully, the present results would be helpful for further experimental and theoretical studies on silylenoids.

Calculation Method

The popular hybrid density functional B3LYP method, namely Becke's three-parameter nonlocal exchange functional²⁶ with the nonlocal correlation functional of Lee, Yang, and Parr,²⁷ and 6-311+G* basis set including diffuse and polarization functions have been employed comprehensively. The B3LYP/6-311+G* level of theory has been proved relatively accurate to treat with the relevant insertion reactions in our previous study.²⁸ To furth-

er evaluate the validity of it, the relevant $\text{H}_2\text{C}=\text{SiLiF}$ complexes have been calculated using the advanced MP2/6-311+G* level of theory. Overall, both levels of theory can give the parallel results consistently. Considering the compromise between computational cost and accuracy and especially for comparison with the $\text{HN}=\text{SiNaF}$ system on the same benchmark, the results of B3LYP/6-311+G* level of theory have been discussed below if not noted otherwise. Subsequently, frequency analyses have been carried out to confirm the nature of the minima and transition states. Moreover, intrinsic reaction coordinate (IRC) calculations have also been performed to further validate the calculated transition states connecting reactants and products. Additionally, relevant energy quantities, such as reaction energy and barrier energies, have been corrected with zero-point vibrational energy (ZPVE) corrections.

All the calculations have been performed using Gaussian 98 programs.²⁹

Results and Discussion

Similar to the unsaturated carbene $\text{H}_2\text{C}=\text{C}:$, silylene $\text{HN}=\text{Si}:$,²⁵ the most stable alkylidene silylene $\text{H}_2\text{C}=\text{Si}:$ is also in singlet, where the singlet state is more favorable about 246.8 kJ/mol in energy relative to that of triplet state at the B3LYP/6-311+G* level of theory. Thus, the singlet state of $\text{H}_2\text{C}=\text{Si}:$ has been discussed in the following study. As displayed in Figure 1, Si atom adopts sp hybridization, where one of sp hybridization orbitals of Si forms σ bond with C atom and two electrons of Si occupy the other sp hybridization orbital. As for the two vertical p orbitals of Si atom, one forms π bond with the corresponding p orbital of C atom and the other is the empty orbital without electron. Obviously, the empty p orbital and the sp hybridization orbital in Si atom have electrophilicity and nucleophilicity, respectively. Expectedly, the complexation between the double func-

tionality of Si atom and the strong polar inorganic salts (eg., NaF and LiF) should lead to the different complexes. As a result, full geometry optimizations suggest that three stable equilibrium structures for $\text{H}_2\text{C}=\text{SiLiF}$ directly associated with the Si atom have been located as well as two transition states connecting them (in Figure 2). Correspondingly, the complexation processes of three stable complexes are schematically displayed in Figure 3.

Structures and relative stabilities of $\text{H}_2\text{C}=\text{SiLiF}$. As displayed in Figure 2, complex **1** is characterized by a four-membered ring structure. Obviously, as shown in Figure 3, complex **1** was formed when lone pair of F^- in LiF molecule transfers to the empty sp -orbital of Si accompanying the electron transfer from C to Li^+ . Here, the hybridization of C atom has been changed from sp^2 to sp^3 upon complexation. From the bond lengths, it can be seen that the C=Si and Li-F bonds of complex **1** are weaker than those corresponding monomers, where both bonds are elongated by about 0.061 and 0.188 Å upon complexation, respectively. Overall, the stability of complex **1** has been enhanced through the donating of partial sp^3 electrons of C atom to the positive Li atom and the feedback of an electron lone pair of F atom to the sp -orbital of Si atom, resulting in the formation of the electron circle of $\text{F} \rightarrow \text{Si} \rightarrow \text{C} \rightarrow \text{Li}$. As shown in Table 1, complex **1** has been stabilized by about 161.3 kJ/mol relative to those of monomers, which is the most stable one among the available

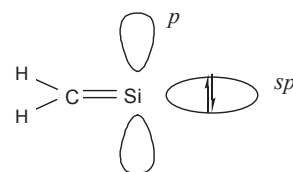


Figure 1. Schematic diagram of singlet silylene $\text{H}_2\text{C}=\text{Si}:$.

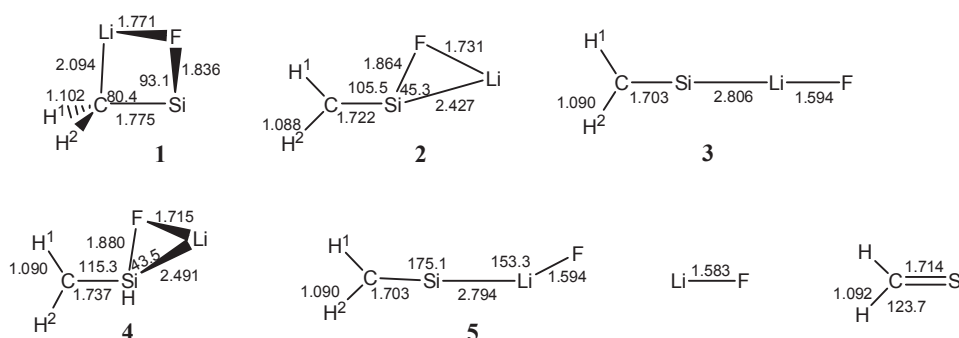


Figure 2. The geometries of $\text{H}_2\text{C}=\text{SiLiF}$, where the bond length and bond angle are in angstrom and degree, respectively.

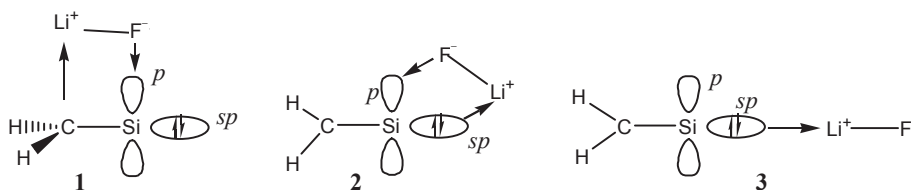


Figure 3. Complexation process between $\text{H}_2\text{C}=\text{Si}:$ and LiF.

Table 1. Relative energies of the complexes $H_2C=SiLiF$ (in kJ/mol)

Species	$H_2C=Si: + LiF$	1	2	3	4	5
B3LYP/6-311+G*	0.0	-161.3	-110.9	-19.7	-105.5	-19.6
MP2/6-311+G*	0.0	-170.2	-116.0	-22.5	-110.6	-21.7

complexes.

Complex **2** is characterized by a three-membered ring structure formed among Si, Li, and F atoms, which is in C_s symmetry. Similar to complex **1**, Si atom adopt sp hybridization. Complex **2** can be regarded as a product originating from the interaction between Li^+ and F^- in LiF and the sp occupied and p empty orbital in Si, resulting in the formation of the donor-acceptor bonds of $Si \rightarrow Li$ and $F \rightarrow Si$, respectively. Relative to the respective monomers, the $C=Si$ and $Li-F$ bonds have been slightly shortened and elongated by 0.008 and 0.148 Å upon complexation, respectively. Obviously, the three-membered ring structure has more ring strain compared with complex **1**. As a result, complex **2** has been stabilized by about 110.9 kJ/mol relative to the corresponding monomers.

As for complex **3**, it is characterized by a linear structure, which is in $C_{\infty v}$ symmetry. Here, as displayed in Figure 3, Si atom takes sp hybridization and the complex **3** was formed when the electrons of the sp -occupied orbital in Si migrate to Li^+ . As a result, the $C=Si$ and $Li-F$ bonds have been shortened and elongated by about 0.011 and 0.011 Å upon complexation, respectively. As shown in Table 1, complex **3** has been only sta-

bilized about 19.7 kJ/mol relative to the monomers of $H_2C=Si:$ and LiF .

Isomerization reactions of $H_2C=SiLiF$. As displayed in Figure 2, two transition-state structures **4** and **5** have been located. Further IRC calculations suggest that they are the true transition states for the isomerization reactions between complexes **1-2** and **2-3**, respectively. Vibration analysis calculations indicate that the unique imaginary frequencies of structures **4** and **5** are 101.2i and 18.1i cm^{-1} , respectively.

As presented in Table 1, the potential barrier from complex **1** to **2** is 55.8 kJ/mol and the reverse reaction is only 5.4 kJ/mol, implying the easy isomerization from the latter to the former. Similarly, the potential barrier from complex **2** to complex **3** is 141.7 kJ/mol and the reverse is only 0.1 kJ/mol. Thus, complex **1** should be the predominant form of $H_2C=SiLiF$ in the gas phase thermodynamically and kinetically.

As mentioned above, we have also investigated the relevant $H_2C=SiLiF$ species at the MP2/6-311+G* level of theory. As shown in Table 1, the validity of the B3LYP/6-311+G* level of theory can be confirmed from the consistent tendency between MP2 and B3LYP method. Thus, in the following study, complex **1** has been selected to investigate its insertion reactions with some small molecules $R-H$ ($R=F, OH,$ and NH_2) at the B3LYP/6-311+G* level of theory.

Insertion reactions of $H_2C=SiLiF$ and $R-H$.

The structures and energies of the transition states: As mentioned above, complex **1** is characterized by a four-membered ring structure and there is an exposed space that can be attacked

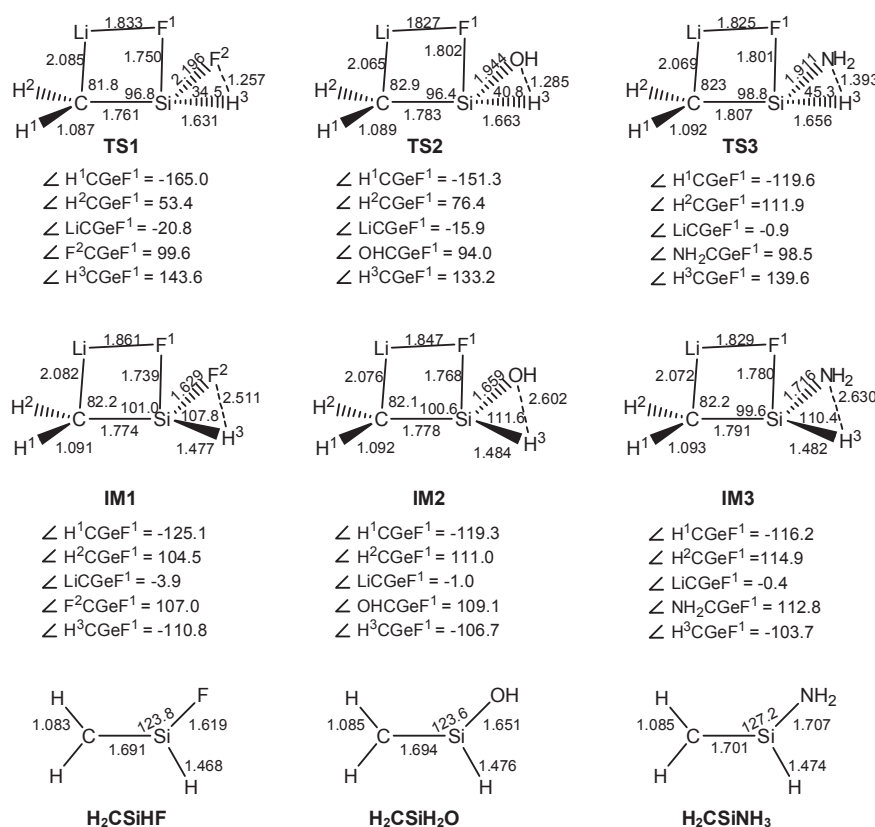
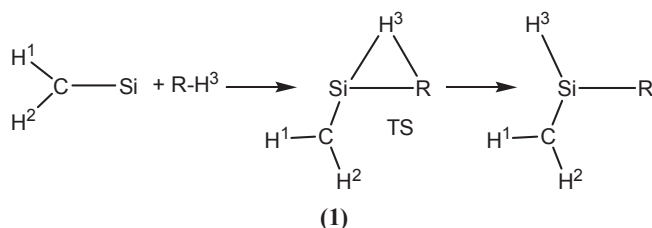
**Figure 4.** Optimized structures of TSs, intermediates, and products, where the bond length and bond angle are in angstrom and degree, respectively.

Table 2. Relative energies of reactants, TSs, intermediates, and products in the insertion reactions for silylenoid and silylene with R-H (in kJ/mol)

Species	R = F	R = OH	R = NH ₂
H ₂ C = SiLiF + RH	0.0	0.0	0.0
TS (of H ₂ C = SiLiF + RH)	97.5	103.3	126.1
IM (of H ₂ C = SiLiF + RH)	-238.5	-216.3	-170.6
H ₂ C = SiHR + LiF	-36.4	-24.3	3.7
H ₂ C = Si: + RH	0.0	0.0	0.0
TS (of H ₂ C = Si: + RH)	378.6	384.6	365.6
H ₂ C = SiHR	-223.9	-185.6	-157.6

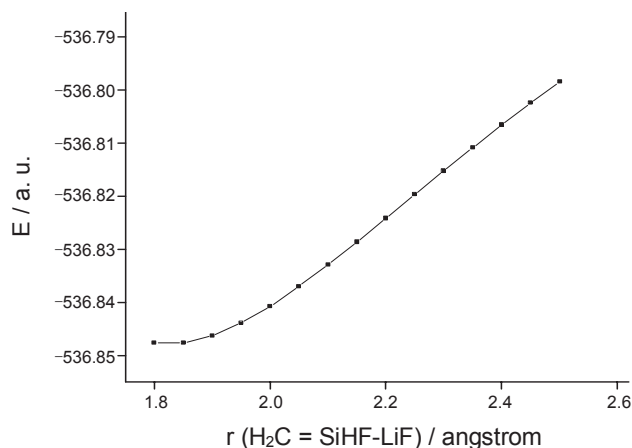
**Scheme 1.** The insertion reaction between H₂C = Si: and R-H.

by nucleophiles or electrophiles under the Si atom. Thus, the insertion reaction between H₂C = SiLiF and R-H should occur in this region.

As displayed in Figure 4, the calculated transition states **TS1**–**TS3** in the insertion reactions have the similar structures. Here, the calculated unique imaginary frequencies are 1289.5i, 1532.7i, and 1570.9i cm⁻¹ for **TS1**, **TS2**, and **TS3**, respectively. Compared with the isolated H₂C = SiLiF, the bond distance between Si and F¹ have been slightly shortened by 0.086, 0.034, and 0.035 Å when R is F, OH, and NH₂, respectively. On the other hand, the bond distance of R-H³ has been elongated significantly to 1.257, 1.285, and 1.393 Å, respectively. Thus, in these transition states, the R-H bond is to be broken and a new Si-H³ bond to be formed simultaneously. Correspondingly, relevant energy quantities about transition states have been summarized in Table 2.

For the sake of comparison, we have also investigated the insertion reaction between silylene H₂C = Si: and R-H (R = F, OH, and NH₂) at the same calculation level, which can be denoted as the Scheme (1) and relevant energy quantities have been summarized in Table 2. Similarly, the insertion reaction proceeds first through a transition state (TS), where the barriers are 378.6 (R = F), 384.6 (R = OH), and 365.6 kJ/mol (R = NH₂), respectively. Obviously, the barriers are higher 239.5 ~ 281.3 kJ/mol than those of reactions in the presence of LiF. Thus, the positive role of inorganic salts like LiF should be emphasized in the insertion reaction.

The structures and energies of the intermediates and products: As displayed in Figure 4, three intermediates have been located in the insertion reactions. Obviously, all of them have similar structures. In detail, there are an approximate plane composed by the atoms of C, Si, Li and F¹, and the R and H³ locate at the two sides of this plane. Compared with the isolated R-H, the R-H³ bonds have been elongated significantly by about 1.562

**Figure 5.** Energy changes in the dissociation process of **IM1** along with the distance between two fragments.

(R = F), 1.626 (R = OH), and 1.626 Å (R = NH₂), respectively, implying the broken of R-H³ bond. At the same time, the distance between Si and R atoms has been decreased significantly. For example, the corresponding bond lengths are 1.629 (R = F), 1.659 (R = OH), and 1.716 Å (R = NH₂), respectively. At the same time, they have been shortened by 0.567, 0.285, and 0.195 Å compared with the corresponding distance in the transition states, respectively, suggesting the formation of the new Si-R bonds.

Further population analyses suggest that the net charges on Li (F¹) of intermediates are 0.578 (-0.396), 0.557 (-0.430), and 0.548 (-0.400) when R = F, OH, and NH₂, respectively. Thus, the intermediate can be a strong ionic complex formed by H₂C = SiHR, F⁻, and Li⁺ three fragments. With the increasing of the distance between H₂C = SiHR and LiF fragments, these intermediates can be dissociated. To investigate this dissociation process, the potential energy curve for the **IM1** has been constructed along the distance between H₂C = SiHR and LiF fragments. As displayed in Figure 5, the energy of the system increases continuously before dissociation. Actually, no transition state has been located for this dissociation process to our best ability. Thus, the dissociation energy should be the barrier height required for this dissociation process.

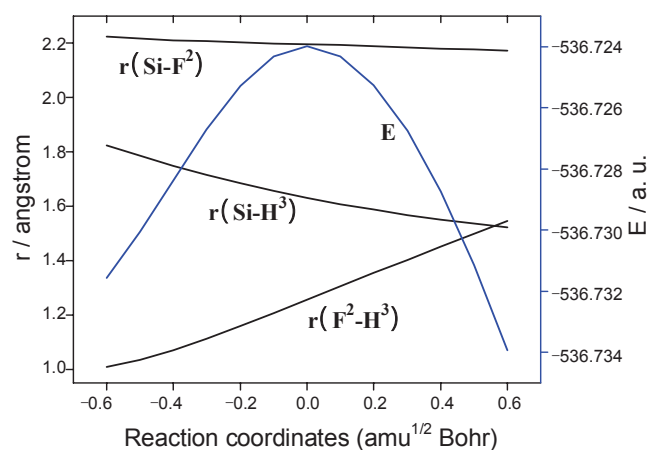
Additionally, as shown in Table 2, compared with the reactants, three intermediates have been stabilized by about 238.5 (R = F), 216.3 (R = OH), and 170.6 (R = NH₂) kJ/mol, respectively. Correspondingly, the relative energies of the final products are -36.4, -24.3, and 3.7 kJ/mol, suggesting that the insertion reactions of H₂C = SiLiF and RH (R = F, OH) should be exothermic processes, On the other hand, the reaction should be endothermic processes when R = NH₂. As a result, the relative order in reaction energies is as follows: R = F > R = OH > R = NH₂.

The mechanism of insertion reactions: Taking the process of inserting H-F bond as an example, IRC calculations have been performed on the basis of the calculated **TS1** to investigate the mechanism of the insertion process (see Figure 6). Correspondingly, charge distributions for the selected atoms along the reaction coordinates have been presented in Table 3.

As shown in Table 3, the charges at the Si and F² atoms in-

Table 3. Population analyses for the selected atoms in **TS1** along with the reaction coordinates

Rx.Coord	Si	F ²	H ³
-0.6	0.284	-0.244	0.275
-0.5	0.296	-0.253	0.265
-0.4	0.315	-0.267	0.253
-0.3	0.339	-0.285	0.241
-0.2	0.368	-0.306	0.229
-0.1	0.400	-0.331	0.216
0.0	0.435	-0.354	0.203
0.1	0.471	-0.377	0.192
0.2	0.503	-0.398	0.182
0.3	0.535	-0.418	0.173
0.4	0.566	-0.436	0.164
0.5	0.595	-0.453	0.156
0.6	0.622	-0.468	0.148

**Figure 6.** Energy changes in the dissociation process of **IM1** along with the distance between two fragments.

crease gradually when the insertion reaction proceeds. At the same time, as displayed in Figure 6, the distance between them decreases gradually, suggesting the formation of the Si-F² bond. On the other hand, as for the bond lengths of H³-F² and Si-H³, they increase and decrease with the proceeding of the reaction, implying the break of the former and the formation of the latter, respectively.

The comparisons of the insertion reactions: As shown in Table 2, the calculated barrier heights are 97.5, 103.3, and 126.1 kJ/mol for the three different inserting reactions of R = F, OH, and NH₂, respectively, exhibiting their different reactivity. Correspondingly, the calculated reaction energies are -36.4, -24.3, and 3.7 kJ/mol, respectively. Thus, from the thermodynamic and kinetic viewpoints, the insertion reactions should occur easily in the order of H-F > H-OH > H-NH₂ under the same condition. This point is also consistent with the calculated positive charges on the H atoms of the electrophiles, where the charges on the H atoms are 0.417, 0.369, and 0.349 in HF, H₂O, and NH₃, respectively. However, the relative activity is almost reversed if the negative charges on the R atoms of the nucleophiles are

Table 4. Relative energies of reactants, TSs, intermediates, and products in the insertion reactions for silylenoid X'₂C = SiLiF into HF (in kJ/mol).

Species	X' = H	X' = F	X' = Cl	X' = Br
X' ₂ C = SiLiF ¹ + HF ²	0.0	0.0	0.0	0.0
TS	97.5	95.9	94.3	92.1
IM	-238.5	-213.4	-234.3	-239.4
X' ₂ C = SiLiF ² + LiF ¹	-36.4	-18.5	-7.8	-6.9

Table 5. Relative energies of reactants, TSs, intermediates, and products in the insertion reactions for silylenoid H₂C = SiMX into H-F (in kJ/mol).

Species	MX = not available	MX = LiF	MX = LiCl	MX = NaF	MX = NaCl
H ₂ C = SiMX + HF	0.0	0.0	0.0	0.0	0.0
TS	378.6	97.5	62.8	84.1	78.1
IM	-	-238.5	-269.7	-239.7	-239.4
H ₂ C = SiHF + MX	-223.9	-36.4	-30.3	-108.0	-107.9

considered. Here, the charges on the R atom are -0.417, -0.739, and -1.048 in HF, H₂O, and NH₃, respectively. Thus, it seems that the insertion reactions should be predominated by the electrophiles attack.

To get more insights into the reactive activity of the insertion reactions upon halogen substitution, we have also investigated the insertion reaction of silylenoid of X'₂C = SiLiF (X' = H, F, Cl, Br) into R-H. Taking the insertion reaction into HF as an example, as shown in Table 4, the barrier heights have been decreased more or less, suggesting the increase of the reactivity upon halogen substitution. At the same time, the halogen substituted cases have a similar reaction activity, which can be reflected from their similar barrier heights and reaction energies.

The influences of the inorganic salts in the insertion reactions: To investigate the role of different inorganic salts in the insertion reaction, the NaF, NaCl, and LiCl have been employed for comparison with LiF. Taking the insertion reaction into H-F as an example, as shown in Table 5, the barrier height has been decreased by about 281.1 ~ 315.8 kJ/mol in the presence of various inorganic salts, implying the positive role of the introduction of inorganic salts. Moreover, different inorganic salts have different influences on the reaction activity. For example, the barrier heights for the insertion reactions containing Cl atom are lower than those containing F atom. As a result, the positive role of LiCl is much clearer than other inorganic salts in the present study.

Conclusions

In the present study, the geometries and isomerization of unsaturated silylenoid H₂C = SiLiF as well as its insertion reactions with R-H (R = F, OH, NH₂) have been systematically investigated employing the B3LYP density functional method. Three stable complexes of H₂C = SiLiF have been located and the most stable one is characterized by a four-membered ring structure. The barrier heights of the three insertion reactions are

97.5, 103.3, and 126.1 kJ/mol at the B3LYP/6-311+G* level of theory, respectively. All the mechanisms of the three reactions are identical to each other, i.e., an intermediate has been formed first during the insertion reaction. Then, the intermediate could dissociate into the substituted silylene ($\text{H}_2\text{C} = \text{SiHR}$) and LiF with a barrier corresponding to their corresponding dissociation energies. As a result, the relative reactivity among the three insertion reactions should be as follows: $\text{H-F} > \text{H-OH} > \text{H-NH}_2$. The reaction activity of the insertion reaction of alkylidene silylene $\text{H}_2\text{C} = \text{Si}$: has been strengthened significantly upon introductions of various inorganic salts. Compared with the insertion reaction of $\text{HN} = \text{SiNaF}$ into R-H, alkylidene silylenoid $\text{H}_2\text{C} = \text{SiLiF}$ has higher reaction activity and is more easy to insert the R-H bond. Additionally, the halogen substitution effects on the reaction activity have also been discussed. Hopefully, the present results are expected to fill a void in the available data for the study of the interactions between the unsaturated silylenoid and the molecules possessing the R-H characteristics.

Acknowledgments. This work is supported by the Scientific Research Foundation of Jinan University (XKY0709) and Students Research Training of Jinan University (SRT A52).

References

1. Gaspar, P. P.; West, R. *The Chemistry of Organic Silicon Compounds: Part 3*, 2nd ed.; Wiley: New York, 1999; p 2463.
2. Denk, D.; Lennon, R.; Hayashi, R.; West, R.; Belyakov, A. V.; Verne, H. P.; Hannland, A.; Wangner, M.; Metzler, N. *J. Am. Chem. Soc.* **1994**, *116*, 2691.
3. Gerhus, B.; Lappert, M. F.; Heincke, J.; Boese, R.; Blaser, D. *J. Chem. Soc., Chem. Commun.* **1996**, 11931.
4. Kira, M.; Ishida, S.; Iwamoto, T.; Kabuto, C. *J. Am. Chem. Soc.* **1999**, *121*, 9722.
5. Gilman, H.; Peterson, D. J. *J. Am. Chem. Soc.* **1965**, *87*, 2389.
6. Nefedow, O. M.; Manakow, M. N. *Angew. Chem.* **1964**, *76*, 270.
7. Boudjouk, P.; Samaraweera, U.; Sooriyakumaran, R.; Chrusciel, J.; Anderson, K. R. *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1355.
8. Tsumuragua, T.; Batcheller, S. A.; Masamune, S. *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 902.
9. Tsumuragua, T.; Batcheller, S. A.; Masamune, S. *Angew. Chem.* **1991**, *103*, 916.
10. Tamao, K.; Kawachi, A.; Ito, Y. *J. Am. Chem. Soc.* **1992**, *114*, 3989.
11. Corriu, R.; Lanneau, G.; Priou, C.; Soulairol, F.; Auner, N.; Probst, R.; Conlin, R.; Tan, C. J. *J. Organomet. Chem.* **1994**, *466*, 55.
12. Kawachi, A.; Tamao, K. *Organometallics* **1996**, *15*, 4653.
13. Kawachi, A.; Doi, N.; Tamao, K. *J. Am. Chem. Soc.* **1997**, *119*, 233.
14. Tamao, K.; Kawachi, A. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 818.
15. Tanaka, Y.; Kawachi, A.; Hada, M.; Nakatsuji, H.; Tamao, K. *Organometallics* **1998**, *17*, 4573.
16. Lee, M. E.; Cho, H. M.; Lim, Y. M.; Choi, J. K.; Park, C. H.; Jeong, S. E.; Lee, U. *Chem. Eur. J.* **2004**, *10*, 377.
17. Clark, T.; Schleyer, P. R. *J. Organomet. Chem.* **1980**, *191*, 347.
18. Feng, S. Y.; Feng, D. C.; Li, J. H. *Chem. Phys. Lett.* **2000**, *316*, 146.
19. Feng, S. Y.; Zhou, Y. F.; Feng, D. C. *J. Phys. Chem. A* **2003**, *107*, 4116.
20. Xie, J.; Feng, D. C.; Feng, S. Y. *J. Organomet. Chem.* **2006**, *691*, 208.
21. Xie, J.; Feng, D. C.; Feng, S. Y.; Zhang, J. *Chemical Physics* **2006**, *323*, 185.
22. Feng, D. C.; Xie, J.; Feng, S. Y. *Chem. Phys. Lett.* **2004**, *396*, 245.
23. Li, W. Z.; Gong, B. A.; Cheng, J. B. *Acta Phys. Chim. Sin.* **2006**, *22*, 653.
24. Li, W. Z.; Gong, B. A.; Cheng, J. B. *Acta Chim. Sin.* **2007**, *65*, 1573.
25. Wang, W. H.; Li, P.; Tan, X. J. *Struct. Chem.* **2008**, *19*, 527.
26. He, S. G.; Tackett, B. S.; Clouthier, D. J. *J. Chem. Phys.* **2004**, *121*, 257.
27. Lee, C. W.; Yang, T.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.
28. Tan, X. J.; Wang, W. H.; Li, P.; Yang, X. L.; Zheng, G. X. *Theor. Chem. Acc.* **2007**, *118*, 357.
29. Frisch, M. J. *et al.*, Gaussian 98, Gaussian Inc., Pittsburgh, PA, 1998.