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The structures and stability of silylenoids RBrSiLi$_2$ (R=CH$_3$, C(SiH$_3$)$_3$)

Yuhua Qi · Chongjuan Xu · Bing Geng · Maoxia He

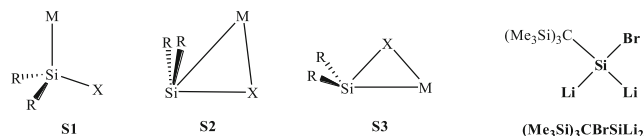**Abstract** The structures and stabilities of RBrSiLi$_2$ (R=CH$_3$, C(SiH$_3$)$_3$) have been studied using *ab initio* and DFT methods. CH$_3$BrSiLi$_2$ and C(SiH$_3$)$_3$BrSiLi$_2$ have three possible structures, the p-complex, the plain, and the folded structures. The plain and the folded structures are different from those of known structures of silylenoids. The energy of the plain structure is the lowest and nearly equals to that of the folded structure. The plain and the folded structures, which can isomerize into each other, are the most stable and possibly detected ones in chemical reactions. The essential of the insertion reactions with Me$_3$SiCl is the same. The insertion barriers are in the order of H$_2$SiLiBr > C(SiH$_3$)$_3$BrSiLi$_2$ > CH$_3$BrSiLi$_2$. The C(SiH$_3$)$_3$ group makes the insertion of C(SiH$_3$)$_3$BrSiLi$_2$ more difficult.

Keywords *Ab initio* · DFT · Insertion reactions · Silylenoids · Theoretical Study

Introduction

Silylenoids, R$_2$SiMX (X=halogen, M=alkali metal), are important intermediates in silicon hybrid and organosilicon chemistry [1, 2]. Previous research works have shown that silylenoids can be regarded as a silylene complex, in which a

Y. Qi (✉) · C. Xu · B. Geng · M. He
Key Laboratory of Fluorine Chemistry and Chemical Materials of Shandong Province, School of Chemistry and Chemical Engineering, University of Jinan, Jinan 250022, People's Republic of China
e-mail: chm_qiyh@ujn.edu.cn

M. He
Environment Research Institute, Shandong University, Jinan 250100, People's Republic of China

leaving group X and a metal atom M are bound to the same silicon atom. Clark et al. [3] have carried out the first theoretical study on the simplest silylenoid H$_2$SiLiF. During recent years, the silylenoids such as R$_2$SiMX (R=CH$_3$, C$_2$H$_5$, NH$_2$, OH, H; X=F, Cl, Br; M=Li, Na, K) have been systematically studied [4–10]. Their structures, stabilities, and the factors of influencing their existence have been investigated in detail. These research works show that though silylenoids are very reactive, they are detectable and their stable structures are not "classical" tetrahedral structures (**S1**), but are p-complex (**S2**) and three-membered ring (**S3**) structures. These results will provide useful and important theoretical information for the understanding of their reaction mechanisms.

As a kind of active species, the preparation of silylenoids is difficult. In 1995, Tamao et al. experimentally detected the existence of silylenoid Ph$_2$SiLi(OBu-t) for the first time [11]. Most recently, a great breakthrough in the research of silylenoids has been made. Lee et al. reported the syntheses of stable halosilylenoids (Tsi)X$_2$SiLi (Tsi=C(SiMe$_3$)$_3$, X=Br, Cl) at room temperature [12].

Recently, Myong Euy Lee reported his experimental research on the reaction of silylenoids (Me$_3$Si)$_3$CBrSiLi$_2$ in Shandong University. (Me$_3$Si)$_3$CBrSiLi$_2$ is another kind of silylenoid. At present, the structures and chemical properties of this silylenoid have not been studied. According to the components of the silylenoid, it can be expected that (Me$_3$Si)$_3$CBrSiLi$_2$ certainly has its own specific properties.

What are the structures and chemical properties of (Me$_3$Si)$_3$CBrSiLi$_2$? To get insight into these questions and provide useful theoretical information for the deep studying of analogues

of (Me$_3$Si)$_3$CBrSiLi$_2$, CH$_3$BrSiLi$_2$, and C(SiH$_3$)$_3$BrSiLi$_2$ are nvestigated and analyzed by density functional theory in the present paper.

Theoretical methods

The structures of reactants, transition states, and products were fully optimized at the B3LYP/6-31G(d) level [13–16]. The corresponding harmonic vibrational frequency calculations were carried out in order to characterize all stationary points as either local minima (no imaginary frequencies) or transition states (one imaginary frequency). Each transition state was verified to connect the designated reactants and products by performing an intrinsic reaction coordinate (IRC) analysis (The step size is 0.1 amu$^{1/2}$-Bohr. The number of steps is 70.) [17, 18]. Based on the optimized geometries, energies were obtained and natural bond orbital (NBO) [19–21] analyses were then used to study the nature of different interactions between atoms and groups. The solvent effects, which were simulated using the self-consistent reaction field (SCRF) method with Tomasi's polarized continuum model (PCM) [22–31], were investigated at the same level. The structures of CH$_3$BrSiLi$_2$ and C(SiH$_3$)$_3$BrSiLi$_2$ are also optimized at the MP2 (full)/6-31G(d) level [32] and G3(MP2) [33] theory was used for calculations of molecular energies. The Gaussian 03 [34] series of programs were employed in all calculations.

Results and discussion

Isomer structures of silylenoids

The structures of CH$_3$BrSiLi$_2$, C(SiH$_3$)$_3$BrSiLi$_2$ in vacuum are located at the B3LYP/6-31G(d) and the MP2(full)/6-31G(d) levels firstly. The PCM method is used to determine the structures in THF at the B3LYP/6-31G(d) level. Based on the MP2(full)/6-31G(d) geometries, energies were obtained using the G3(MP2) theory. Standard orientations and thermodynamic results of stationary points, imaginary frequencies of transition states are listed in Supporting information. The B3LYP/6-31G(d), MP2(full)/6-31G(d), and G3(MP2) energies are shown in Tables 1 and 2. Figures 1 and 2 indicate the calculated structures at the B3LYP/6-31G(d) level. For convenience, the central Si atom in silylenoids is marked as Si^1.

Structures of silylenoids in vacuum

Figure 1 shows the structures of CH$_3$BrSiLi$_2$ and C(SiH$_3$)$_3$BrSiLi$_2$ in vacuum at the B3LYP/6-31G(d) level. Unless otherwise specified, the following results are based on the calculations at the B3LYP/6-31G(d) level.

CH$_3$BrSiLi$_2$ Two structures of CH$_3$BrSiLi$_2$ are located. One is the p-complex structure **1a**, the other is the plain structure **1b**. **1a** can be regarded as the result of the interaction between the negative Br of LiBr and the empty p-orbital of Si in CH$_3$LiSi. The strong interaction between Br and Si makes **1a** very stable. The energy of **1a** is 128.2 kJ mol^{-1} lower than the sum of the separated LiBr and CH$_3$LiSi molecules. **1a** is similar to that of the p-complex structure of H$_2$SiLiBr [3–9]. In the plain structure **1b**, the Si^1 atom is sp^2 hybridized. Three sp^2 hybridized orbitals are connected with C and two Li atoms, respectively. Si^1, C, Br, and two Li atoms are all in the same plain. Their natural charges are −1.213 (C), −0.204 (Si^1), −0.825 (Br), 0.740 (Li). NBO analyses indicate that the main parts of HOMO and LUMO in **1b** are situated on the Si^1 atom. The main HOMO is localized on the p-orbital of the Si^1-Li-Br-Li plain (occupied number: 0.502), and the main LUMO is on the p-orbital vertical to the plain (occupied number: 0.506). **1b** is 66.4 kJ mol^{-1} lower in energy than **1a**. To the best of our knowledge, the structure of **1b** is different from any known structures of silylenoids.

C(SiH$_3$)$_3$BrSiLi$_2$ Calculation results show that C(SiH$_3$)$_3$BrSiLi$_2$ has three isomers, the p-complex structure (**2a**), the plain structure (**2b**), and the folded structure (**2c**). Similar to **1a**, **2a** can be regarded as the complex of LiBr and C(SiH$_3$)$_3$LiSi. The energy of **2a** is 125.1 kJ mol^{-1} lower than the sum of the separated LiBr and C(SiH$_3$)$_3$LiSi molecules. The structure **2b** is similar to **1b**. Relative to the methyl in **1b**, **2b** bears the stronger electron-donating group, C(SiH$_3$)$_3$. The natural charges of Si^1 (−0.439) in **2b** is lower than that (−0.204) in **1b**. Similar to **1b**, the main parts of HOMO and LUMO of **2b** are situated on the atom Si^1. One is the p-orbital of the Si-Li-Br-Li plain (occupied number: 0.485), the other is the p-orbital vertical to the plain (occupied number: 0.637). The energy of **2b** is 64.4 kJ mol^{-1} lower than that of **2a**. In **2c**, Si^1, Br and two Li atoms are in one plain and the bond of Si^1-C is almost vertical to the plain. The main structure difference between **2b** and **2c** is the position of the C(SiH$_3$)$_3$ group. The Si^1 atom is also sp^2 hybridized in **2c**. Two sp^2 hybridized orbital of Si^1 are connected with two Li atoms, respectively, and the p-orbital of Si^1 interacts with the C atom of the C(SiH$_3$)$_3$ group. **2c** isomerizes into **2b** via **2cbts** with only a small barrier of 7.0 kJ mol^{-1}; 22.9 kJ mol^{-1} is needed for **2b** to isomerize into **2c**. So, it is shown that structure **2b** is more stable than **2c**. The energy of **2c** is 15.9 kJ mol^{-1} higher than that of **2b**. The main parts of HOMO and LUMO in **2c** are also localized on the central Si^1. The occupied number of the p-orbital on the Si-Li-Br-Li plain (HOMO) is 0.486, and the occupied number of the p-orbital vertical to the plain (LUMO) is 0.441.

In summary, **1a** and **2a** can be regarded as the complexes of silylenes and LiBr, resulted from the interaction between the empty p-orbital of the Si^1 atom and the negative Br atom. In **1b**, **2b**, and **2c**, the Si^1 atom, which is sp^2 hybridized, is the active center. The

Table 1 Total energies (a.u.) and relative energies (kJ mol^{-1}, in parentheses) for CH$_3$SiLi$_2$Br,C(SiH$_3$)$_3$SiLi$_2$Br in vacuum and in THF at the B3LYP/6-31G(d) level

Molecules	E	ZPE	E + ZPE
In vacuum			
1a	−2916.21319(0.0)	0.04050	−2916.17270(0.0)
1b	−2916.23829(−65.9)	0.04029	−2916.19800(−66.4)
CH$_3$LiSi + LiBr	−2916.16140(135.9)	0.03755	−2916.12385(128.2)
2a	−3788.31767(0.0)	0.08796	−3788.22971(0.0)
2b	−3788.34142(−62.3)	0.08719	−3788.25423(−64.4)
2cbts	−3788.33255(−39.1)	0.08704	−3788.24552(−41.5)
2c	−3788.33607(−48.3)	0.08790	−3788.24818(−48.5)
C(SiH$_3$)$_3$LiSi + LiBr	−3788.26759(131.5)	0.08554	−3788.18206(125.1)
In THF			
1a	−2916.24406(0.0)	0.03989	−2916.20416(0.0)
1b	−2916.25718(−34.4)	0.03937	−2916.21781(−35.8)
1c	−2916.25423(−26.7)	0.03930	−2916.21494(−28.3)
2a	−3788.34478(0.0)	0.08684	−3788.25794(0.0)
2b	−3788.35998(−39.9)	0.08598	−3788.27400(−42.2)
2c	−3788.35736(−33.0)	0.08682	−3788.27054(−33.1)

energies are in the orders of **1a > 1b,2a > 2c > 2b**. The energy difference between **1a** and **1b** (66.4 kJ mol^{-1}) is almost as large as that between **2a** and **2b** (64.4 kJ mol^{-1}). However, the energy difference (15.9 kJ mol^{-1}) between **2b** and **2c** is much smaller. Both the calculated structures and energies of CH$_3$BrSiLi$_2$ and C(SiH$_3$)$_3$BrSiLi$_2$ indicate that the plain structure is close to the folded structure and has large difference from the p-complex structure. **1b** and **2b** are the most stable and possibly detectable ones in chemical reactions.

The calculated structures of CH$_3$BrSiLi$_2$ and C(SiH$_3$)$_3$BrSiLi$_2$ at the MP2(full)/6-31G(d) level are similar to those calculated at the B3LYP/6-31G(d) level. The MP2(full)/6-31G(d) level and G3(MP2) energies also indicate that the order of **1a > 1b,2a > 2c > 2b.**

Table 2 Total energies (a.u.) and relative energies (kJ mol^{-1}, in parentheses) for CH$_3$SiLi$_2$Br,C(SiH$_3$)$_3$SiLi$_2$Br in vacuum

Molecules	MP2(full)/6-31G(d)	G3 (MP2)
1a	−2913.71678 (0.0)	−2913.76479(0.0)
1b	−2913.73958(−58.9)	−2913.78751(−59.5)
CH$_3$LiSi + LiBr	−2913.65884(152.1)	−2913.70895(146.6)
2a	−3784.21165(0.0)	−3784.32385(0.0)
2b	−3784.23111(−51.2)	−3784.34265(−49.4)
2cbts	−3784.22756(−41.8)	−3784.33898(−39.7)
2c	−3784.22933(−46.5)	−3784.34136(−46.0)
C(SiH$_3$)$_3$LiSi + LiBr	−3784.15118(158.7)	−3784.26772(147.2)

Structures of silylenoids in THF

The PCM model at the B3LYP/6-31G(d) level is used to calculate the structures of CH$_3$BrSiLi$_2$ and C(SiH$_3$)$_3$BrSiLi$_2$ (see Supporting information). The results can be summarized as follows:

(1) Three structures, the p-complex, the plain, and the folded structures of CH$_3$BrSiLi$_2$ and C(SiH$_3$)$_3$BrSiLi$_2$ in THF are located. These structures are similar to their corresponding ones in vacuum.

(2) Different from that in vacuum, the folded structure **1c** of CH$_3$BrSiLi$_2$ is located in THF. Just like **2c** resembling **2b**, **1c** is close to **1b** both in their energies (see Table 1) and in their structures.

(3) The thermal stabilities of the structures are lower in THF than in vacuum. The energies in THF are in the same order of **1a > 1c > 1b, 2a > 2c > 2b** as those in vacuum.

Insertion reactions with Me$_3$SiCl

To gain a further understanding about the stability of these silylenoids, the insertion reactions of CH$_3$BrSiLi$_2$, C(SiH$_3$)$_3$BrSiLi$_2$ with Me$_3$SiCl have been investigated at the B3LYP/6-31G(d) level. The insertion of the simplest model of silylenoid, H$_2$SiLiBr, is also studied for comparison. The optimized geometries are shown in Figs. 2 and 3 and Supporting information. The total energies together with the zero-point energies (ZPEs) and relative energies (relative to the corresponding reactants) of all stationary points are

Fig. 1 The B3LYP/6-31G(d) geometries (in Å and (°)) for CH_3SiLi_2Br, $C(SiH_3)_3SiLi_2Br$, and the transition state 2cbts in vacuum. The central Si atom in silylenoids is marked as Si^1
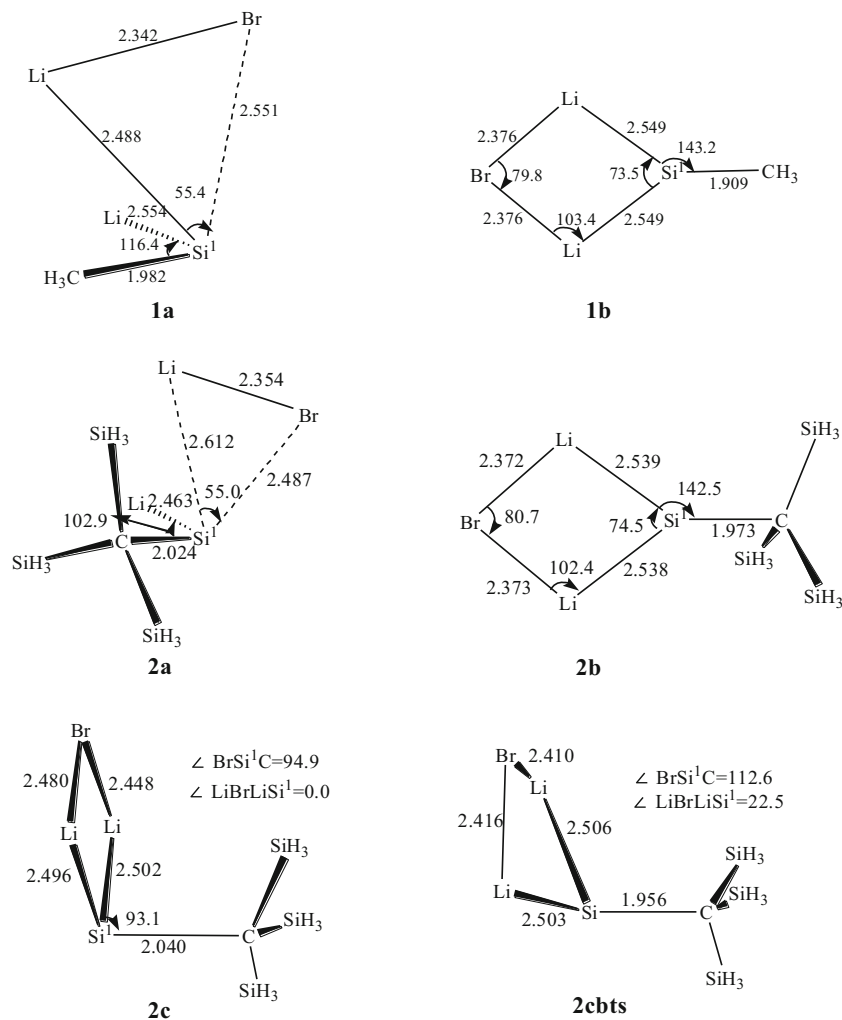
described by Table 3. For convenience, the Si atom in Me_3SiCl is marked as Si^2.

Insertion reaction of $H_2SiLiBr$ with Me_3SiCl

The previous calculations [3–9] show that silylenoid $H_2SiLiBr$ has four equilibrium isomers, the three-membered ring, the p-complex, the σ-complex (linear), and the "classical" tetrahedral structures. The three-membered ring structure is the most stable and possibly detectable one in chemical reactions. So the three-membered ring structure of silylenoid $H_2SiLiBr$ is adopted in this study.

Transition state Two electron donation effects contribute to the proceeding of the insertion reaction. One is the donation of the electrons of Cl into the p-orbital on the Si^1 atom. The other is the donation of the σ electrons on the Si^1 atom to the positive Me_3Si^2 group. The electron donations make the formation of the transition state **INts**. The insertion barrier is 64.1 kJ mol^{-1}.

Insertion product After getting over the transition state **INts**, **INpro** are gradually formed with the LiBr moiety leaving from the Si^1 atom. In fact, **INpro** is a complex of **silane1** and LiBr. The energy of **INpro** is 34.9 kJ mol^{-1} lower than the sum of **silane1** and LiBr.

Insertion reaction of $CH_3BrSiLi_2$ with Me_3SiCl

Precursor complex Different from the process of $H_2SiLiBr$ insertion, there is the precursor complex **1INpre** formed in the insertion reaction of $CH_3BrSiLi_2$ with Me_3SiCl. In the beginning of the insertion, the negative Cl of Me_3SiCl approaches the p-orbital of Si^1 from one side of the $LiSi^1Li$ plain, and the precursor complex **1INpre** forms. In **1INpre**, the $Cl⋯Si^1$ distance is 2.921 Å, and the $Cl…Si^2$ distance (2.140 Å) is only slightly different from that of Me_3SiCl. In fact, the interaction between $CH_3BrSiLi_2$ and Me_3SiCl moieties in **1INpre** is very weak. The energy of **1INpre** is only 19.7 kJ mol^{-1} lower than the sum of $CH_3BrSiLi_2$ and Me_3SiCl.

Fig. 2 The B3LYP/6-31G(d) geometries (in Å and (°)) for some stationary points in the insertion reaction of CH_3SiLi_2Br with Me_3SiCl. The central Si atom in silylenoids and the Si atom in Me_3SiCl are marked as Si^1 and Si^2, respectively

1INpre

1INts

1INpro

silylenoid1
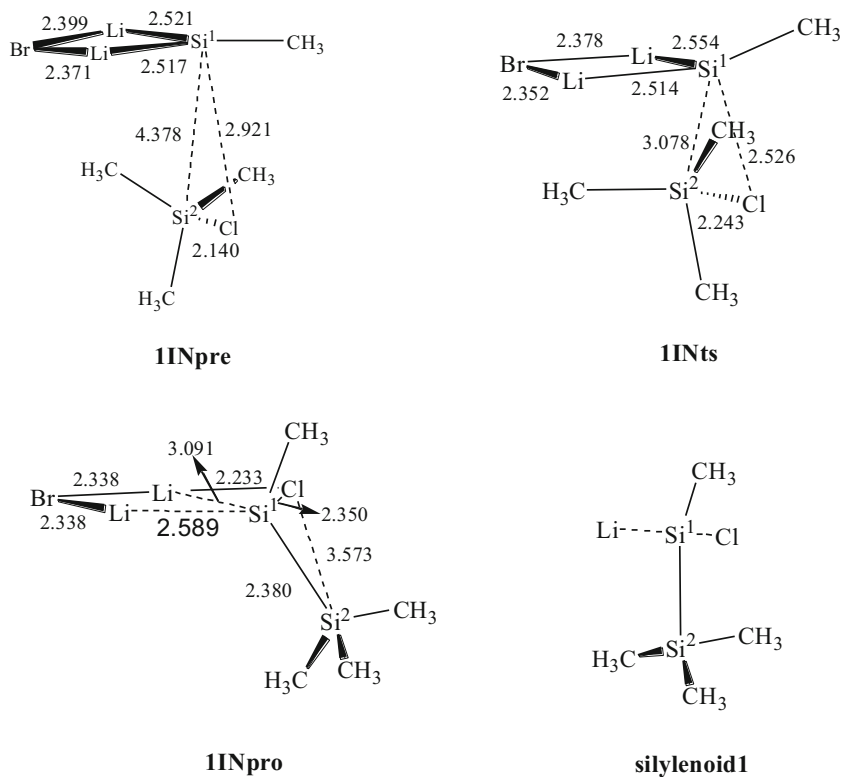
Transition state As the Cl···Si^1 interaction becomes strong, the positive Me_3Si group of Me_3SiCl simultaneously interacts with

the negative Si^1 atom of $CH_3BrSiLi_2$. The insertion reaches the transition state **1INts**. In **1INts**, the Si^1-Cl and Si^1-Si^2 distances

Fig. 3 The B3LYP/6-31G(d) geometries (in Å and (°)) for some stationary points in the insertion reaction of $C(SiH_3)_3SiLi_2Br$ with Me_3SiCl. The central Si atom in silylenoids and the Si atom in Me_3SiCl are marked as Si^1 and Si^2, respectively
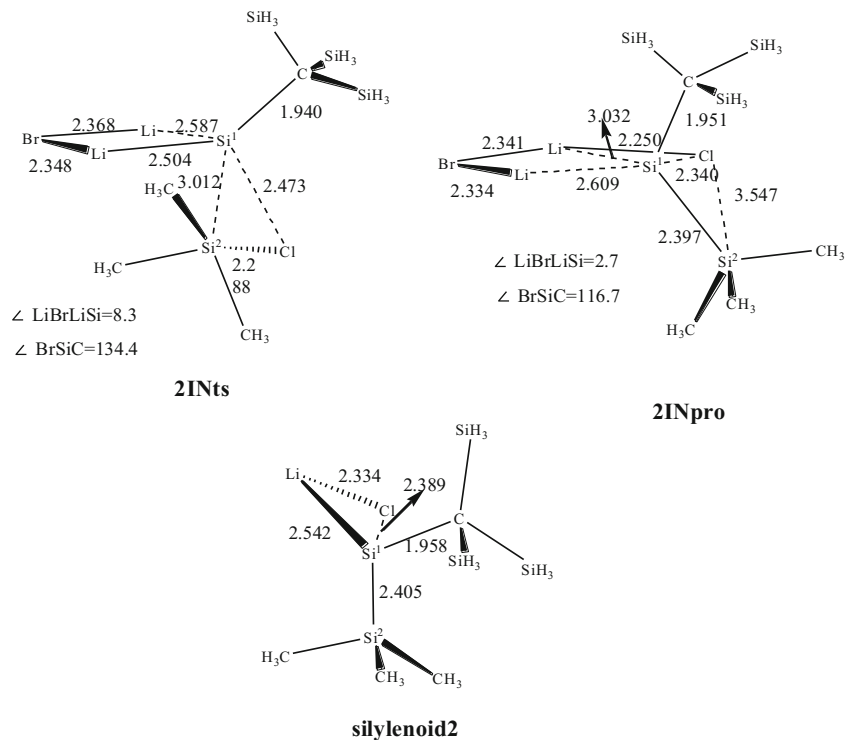

2INts

2INpro

silylenoid2

Table 3 Total energies (a.u.) and relative energies (kJ mol^{-1}, in parentheses) for reactants, intermediates, transition states, and products of the insertion reactions at the B3LYP/6-31G(d) level

Molecules	E	ZPE	E + ZPE
$H_2SiLiBr + Me_3SiCl$	−3739.50603(0.0)	0.13147	−3739.37456(0.0)
INts	−3739.48333(59.6)	0.13317	−3739.35016(64.1)
INpro	−3739.53878(−86.0)	0.13384	−3739.40494(−79.7)
Silane1+ LiBr	−3739.52417(−47.6)	0.13255	−3739.39162(−44.8)
1b + Me_3SiCl	−3785.76085(0.0)	0.15381	−3785.60704(0.0)
1INpre	−3785.76932(−22.2)	0.15478	−3785.61454(−19.7)
1INts	−3785.75644(11.6)	0.15511	−3785.60133(15.0)
1INpro	−3785.85495(−247.0)	0.15532	−3785.69963(−243.0)
Silylenoid1+ LiBr	−3785.77787(−44.7)	0.15379	−3785.62407(−44.7)
2b + Me_3SiCl	−4657.86398(0.0)	0.20071	−4657.66327(0.0)
2INts	−4657.84721(44.0)	0.20199	−4657.64522(47.4)
2INpro	−4657.94392(−209.8)	0.20271	−4657.74122(−252.0)
Silylenoid2 + LiBr	−4657.86803(−10.6)	0.20143	−4657.66659(−8.7)

are 0.395 and 1.300 Å shorter than those in **1INpre**, respectively. The breaking Cl-Si^2 distance is 2.243 Å. The energy of **1INts** is 15.0 kJ mol^{-1} relative to the sum of $CH_3BrSiLi_2$ and Me_3SiCl.

Insertion product As the reaction proceeds, the Si^1-Cl and Si^1-Si^2 bonds are formed with the breaking of the Cl-Si^2 bond. The insertion product silane **1INpro** formed. **1INpro** can be decomposed into **silylenoid1** and LiBr. The energy (198.3 kJ mol^{-1}) needed for the dissociation of **1INpro** is far less than that given out by the process from **1INts** to **1INpro** (258.0 kJ mol^{-1}). So there is enough energy in the reaction system to dissociate **1INpro** into **silylenoid1** and LiBr.

The structures of **silylenoid1** are similar to those of $H_2SiLiBr$. The same as with $H_2SiLiBr$, **silylenoid1** can react with Me_3SiCl.

Insertion reaction of C(SiH₃)₃BrSiLi₂ with Me₃SiCl

The insertion of $C(SiH_3)_3BrSiLi_2$ with Me_3SiCl is similar to the insertion of $CH_3BrSiLi_2$ with Me_3SiCl, but there is no precursor complex formed in the insertion process of $C(SiH_3)_3BrSiLi_2$. The relative energy of the transition state **2INts** is 47.4 kJ mol^{-1}. The insertion product **2INpro** can decompose into **silylenoid2** and LiBr. Just like $H_2SiLiBr$, **silylenoid2** can react with Me_3SiCl.

The above discussion shows that the insertion processes of $H_2SiLiBr$, $CH_3BrSiLi_2$, and $C(SiH_3)_3BrSiLi_2$ with Me_3SiCl are similar. Essential to these insertions are the p-orbital and electrons of Si^1 in silylenoids which interact with the negative Cl and positive Me_3Si group, respectively. In the view of energy, the insertion barriers are in the order of $CH_3BrSiLi_2$ < $C(SiH_3)_3BrSiLi_2$ < $H_2SiLiBr$. This indicates that silylenoids of the $CH_3BrSiLi_2$ analogues are easier to insert with Me_3SiCl

than those of the $H_2SiLiBr$ style. The big $C(SiH_3)_3$ group makes the insertion of $C(SiH_3)_3BrSiLi_2$ more difficult than that of $CH_3BrSiLi_2$. NBO analyses indicate that the occupancy of p-orbital of Si^1 in $CH_3BrSiLi_2$ (0.048) is much lower than that in $C(SiH_3)_3BrSiLi_2$ (0.285). Calculations also show that the natural charge of Si^1 in $CH_3BrSiLi_2$ (−0.204) is higher than in that $C(SiH_3)_3BrSiLi_2$ (−0.439). The lower occupancy of p-orbital and the lower charge of Si^1 benefit to the insertion reaction of silylenoids. So the $C(SiH_3)_3$ group make the p-orbital accept electrons more difficult and the negative Si interact on positive groups easier. The combined effects result in the higher insertion barrier of $C(SiH_3)_3BrSiLi_2$.

Conclusions

In the present work, we have studied the structures of silylenoids $CH_3BrSiLi_2$, $C(SiH_3)_3BrSiLi_2$ and their insertion reactions with Me_3SiCl by *ab initio* and DFT theory.

(1) The calculations indicate that $CH_3BrSiLi_2$ and $C(SiH_3)_3BrSiLi_2$ have three possible structures: the p-complex, the plain, and the folded structures. The plain and the folded structures are different from those of known structures of silylenoids. The energy of the plain structure is the lowest and nearly equals to that of the folded structure. The plain and the folded structures are possibly the detected ones in chemical reactions of $CH_3BrSiLi_2$ and $C(SiH_3)_3BrSiLi_2$.

(2) The insertions of $H_2SiLiBr$, $CH_3BrSiLi_2$ and $C(SiH_3)_3BrSiLi_2$ into Si-Cl bond are similar. The essential of these insertion reactions is same. The insertion barriers are in the order of $H_2SiLiBr$ > $C(SiH_3)_3BrSiLi_2$ > $CH_3BrSiLi_2$. The $C(SiH_3)_3$ group makes the insertion more difficult.

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