

# The Cycloadditions of Various Substituted Carbenes, Silylenes, and Germylenes onto the Diamond (100) Surface: A Theoretical Exploration

Yi-Jun Xu,<sup>\*,†</sup> Yong-Fan Zhang,<sup>‡</sup> and Jun-Qian Li<sup>†</sup>

School of Chemistry, Main Building, Cardiff University, Cardiff, CF10 3AT, United Kingdom, and  
Department of Chemistry, Fuzhou University, Fuzhou, 350002, China

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The cycloadditions of 21 singlet substituted carbenes, silylenes, and germylenes onto the diamond (100) surface have been theoretically studied by means of density functional theory coupled with effective cluster models. The calculated reaction energies and reaction pathways have disclosed that the substituents play an important effect on the reaction profiles for the additions of carbenes, silylenes, and germylenes onto the diamond (100) surface. Our theoretical investigations illustrate that, irrespective of carbenes, silylenes, and germylenes, the cycloadditions of those with electropositive substituents (such as H and CH<sub>3</sub>) onto diamond (100) are much more favorable than those with electronegative and  $\pi$ -donating substituents (such as F and NH<sub>2</sub>) both thermodynamically and kinetically. In broad perspective, we believe that a similar reactivity trend can also be extended to that of Si (100), Ge (100), fullerene, single-walled carbon nanotube, disilenes, digermenes, silenes, and germenes because all of these materials feature an analogous bonding motif.

## 1. Introduction

As one of the most promising materials for a number of potential applications, diamond has been attracting tremendous interest and attention because of its fascinating and unique mechanical, electrical, thermal, and optical properties, for example, extreme hardness, large band gap, biocompatibility, high breakdown voltage, and the ability to have a negative electron affinity.<sup>1–4</sup> The organic functionalization of the diamond surface can introduce new physical and chemical properties, thus leading to the improvement of its behavior for specific applications.<sup>5</sup> This interest largely arises from the significant potential that the vast range of functions of organic molecules can potentially be incorporated into the diamond surface.<sup>5,6</sup> Therefore, the new diamond-based organic–inorganic hybrid material can be achieved, which possesses the physical functions of diamond as well as the chemical functions of organic functional groups. As a result, diamond may well find its novel applications in a wide variety of technological fields, including molecular electronics, nonlinear optics, and biological sensors. In fact, such an active integration of organic and inorganic building blocks has drawn a broad interdisciplinary attention because this approach to innovative materials bears versatile flexibility of achieving desirable functionalities in a fine-tuning manner.

Against this background, research works regarding the organic functionalization of diamond surface have been reported both experimentally and theoretically.<sup>5–9</sup> For example, by means of density functional theory with effective cluster models, it has theoretically been reported that the famous Diels–Alder reactions and 1,3-dipolar cycloaddition reactions in organic chemistry can readily occur on the diamond (100) surface.<sup>6a–d</sup> More fascinating is the experimental work reported by Wang et al. and Hovis et al.,<sup>6e,f</sup> who found that 1,3-butadiene can react with the C (100) surface to form a Diels–Alder adduct and the “symmetry-forbidden” [2+2] cycloaddition of cyclopentene with

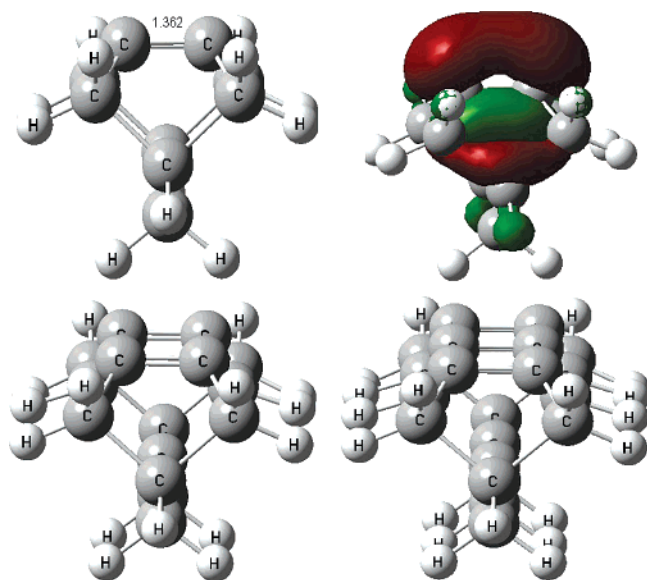
alkenes can occur on the C (100) surface. Thus, the diamond (100) surface can be vividly depicted as a “high reactive and big organic molecular alkene, but specifically has the biradical character in the surface C=C dimer.” More importantly, these pioneering findings strongly demonstrate the feasibility of functionalizing diamond surface by means of synthetic organic chemistry, which may consequently lead to a breakthrough in the fabrication of diamond films.<sup>5–9</sup> *Indeed, as is often the case with large steps forward in experimental techniques, current fundamentals mostly rest on the new application of an established well-known reaction.* In this respect, theoretical computations can be very useful for predicting the unknown reaction and unveiling the reaction pathways at the molecular level, thus providing instructive information for experiments.

Recently, employing prototype singlet carbene (CH<sub>2</sub>), silylene (SiH<sub>2</sub>), and germylene (GeH<sub>2</sub>) as modeling molecules, we have predicted that the C (100) surface can be chemically functionalized by the well-known addition reactions of carbenes to alkenes in organic chemistry.<sup>7</sup> However, it still remains unclear for the effect of various substituents of carbenes, silylenes, and germylenes on the addition reaction pathways and reaction energetics. Moreover, from the standpoint of experimental technology, simple reagents, CH<sub>2</sub>, SiH<sub>2</sub>, and GeH<sub>2</sub>, are lower in kinetic stability than other substituted carbenes, silylenes, and germylenes, such as CCl<sub>2</sub>, SiCl<sub>2</sub>, and GeCl<sub>2</sub>. Therefore, further theoretical calculations regarding the additions of various substituted carbenes, silylenes, and germylenes onto diamond (100) are necessary. To address this issue will not only help us understand the effect of substituents on the reaction profiles of the additions of carbenes, silylenes, and germylenes onto the diamond (100) surface, but also strongly suggest the feasibility that the famous additions of carbenes to alkenes in organic chemistry can be used as a new type of reaction to modify the diamond (100) surface. In addition, a fundamental understanding of the reactivity trend of the additions of various substituted carbenes, silylenes, and germylenes onto the diamond (100) surface would provide a qualitative outline of reactivity trend

\* Corresponding author. E-mail: xuy7@cf.ac.uk.

<sup>†</sup> Cardiff University.

<sup>‡</sup> Fuzhou University.



**Figure 1.** B3LYP/6-31G(d) optimized geometries (units in angstroms for bond length) of C<sub>9</sub>H<sub>12</sub>, C<sub>15</sub>H<sub>16</sub>, and C<sub>21</sub>H<sub>20</sub> clusters and the highest occupied molecular orbital (HOMO) of C<sub>9</sub>H<sub>12</sub> cluster.

for analogous additions of carbenes, silylenes, and germylenes onto the single-walled carbon nanotube (SWNCT) and fullerene, although the surface C=C dimer of diamond (100) is much more reactive than that of SWNCT and fullerene.<sup>7–9</sup>

The purpose of this paper is the following: (a) to undertake a systematic investigation of the cycloadditions of 21 singlet substituted CX<sub>2</sub>, SiX<sub>2</sub>, and GeX<sub>2</sub> (X = H, F, Cl, Br, CH<sub>3</sub>, NH<sub>2</sub>, and OH) species onto the diamond (100) surface to explore the effect of substituents on the reaction pathways and reaction energetics, and (b) to establish the general reactivity trend for the additions of various substituted carbenes, silylenes, and germylenes onto diamond (100), hence providing instructive information for other theoretical work. The calculated results illustrate that the substituents have an important effect on the addition profiles of carbenes, silylenes, and germylenes onto diamond (100) and reinforce the general feasibility that the additions of carbenes, silylenes, and germylenes onto diamond (100) can potentially be employed as a new type of surface reaction to functionalize the diamond surface at low temperature.

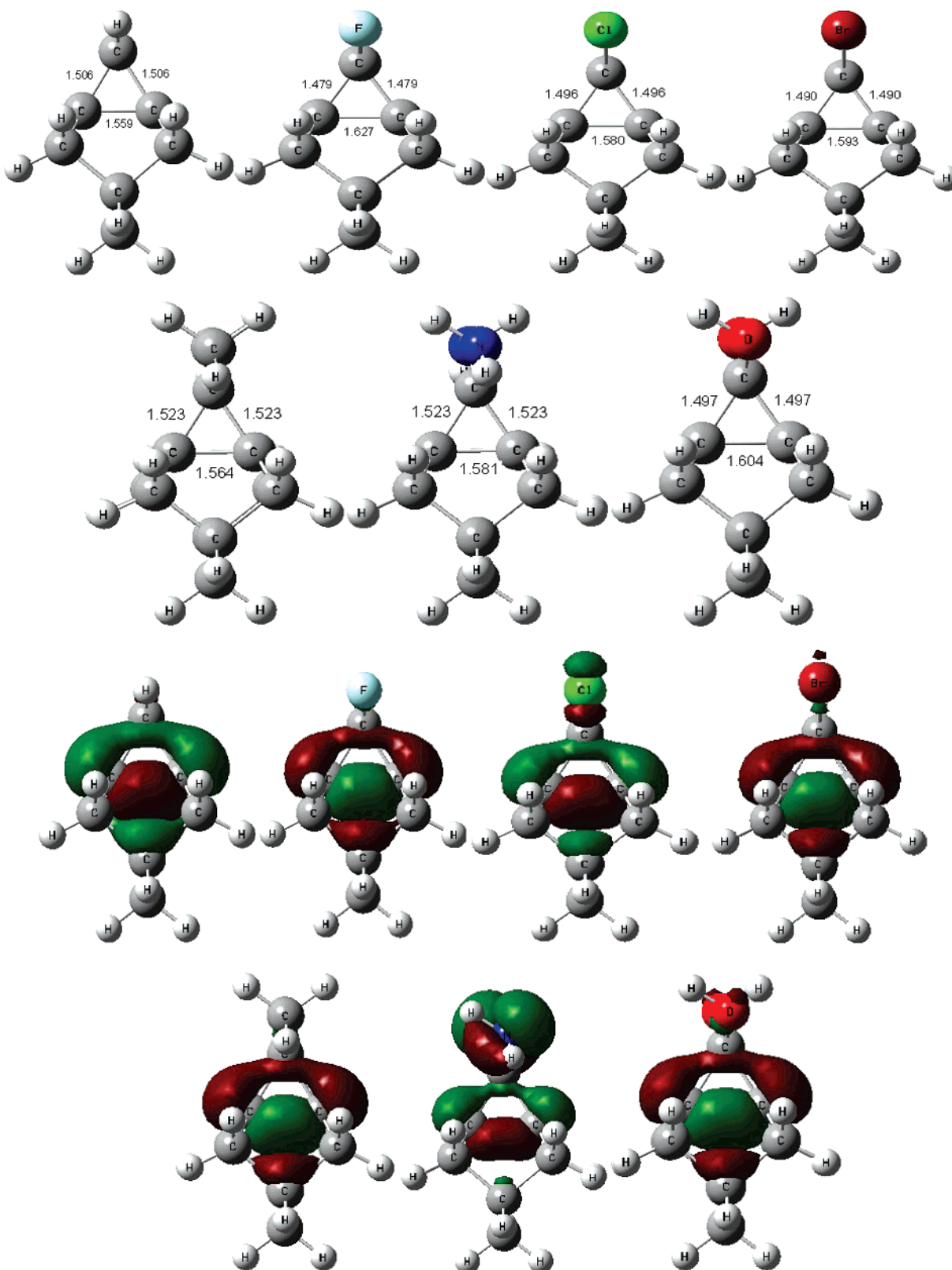
## 2. Computational Details and Models

To examine the effect of substituents, 21 kinds of singlet carbenes, silylenes, and germylenes, that is, CX<sub>2</sub>, SiX<sub>2</sub>, and GeX<sub>2</sub> (X = H, F, Cl, Br, CH<sub>3</sub>, NH<sub>2</sub>, and OH), were considered. An effective C<sub>9</sub>H<sub>12</sub> cluster model was employed to represent a dimer site on the C (100)-2 × 1 surface.<sup>6a–d,7–9</sup> Larger cluster models C<sub>15</sub>H<sub>16</sub> and C<sub>21</sub>H<sub>20</sub> were used to consider the effect of the cluster size on the calculated reaction energies and confirm the results obtained with a C<sub>9</sub>H<sub>12</sub> cluster (see Figure 1). This surface model has been used in our recent theoretical prediction of the additions of carbenes<sup>7</sup> and nitrenes<sup>8</sup> onto the C (100) surface, and the epoxidation of the C (100) surface with dioxiranes and subsequent ring-opening reactions with nucleophiles.<sup>9</sup> The same modeling scheme was also successfully used in theoretical studies of the Diels–Alder reactions<sup>6a,b</sup> and the 1,3-polar cycloadditions<sup>6c,d</sup> on the C (100) surface. Theoretically, this surface model fulfills the requirements of the stoichiometry principle, neutrality principle, and coordination principle so that it can be concluded as a good model of choice.<sup>10a,f,g</sup> In principle, cluster models calculations ought to be the most straightforward method to theoretically study surface processes by which the description of electronic properties is done in terms of local orbitals.<sup>10a,d,f,g,k</sup> Cluster model calculations tend to simulate single isolated adsorbed species in the low surface coverage regime, while slab calculations are better suited to model adsorbate overlayers and the substrate band structure at higher coverage. Objectively speaking, both methods have their respective advantages and can offer complementary information.<sup>10a,d,k</sup> Furthermore, cluster models present the advantage in terms of a compromise between accuracy and computational cost if clusters are properly selected.<sup>7–10</sup>

The hybrid density functional B3LYP method,<sup>11</sup> that is, Becke's three-parameter nonlocal-exchange functional with the correlation functional of Lee–Yang–Parr, was employed. Geometry optimizations without constrained degrees of freedom were carried out using analytical gradients and the Berny algorithm at the B3LYP/6-31G(d) level of theory. Because the B3LYP/6-31G(d) method tends to overestimate the Si–C and Ge–C bond strength,<sup>10a</sup> the single-point energies calculated at the B3LYP/6-311G(2d,2p)//B3LYP/6-31G(d) level of theory were used to compare the effect of substituents on the reaction energetics. Reported energies were zero-point vibrational energy

**TABLE 1: Calculated Reaction Energies ( $\Delta E_r$ , in kcal/mol) for the Additions of Various Substituted Carbenes, Silylenes, and Germylenes onto the C (100)-2 × 1 Surface**

system	$\Delta E_r$	system	$\Delta E_r$	system	$\Delta E_r$
CH <sub>2</sub> + C <sub>9</sub> H <sub>12</sub>	–132.7	CH <sub>2</sub> + C <sub>15</sub> H <sub>16</sub>	–132.1	CH <sub>2</sub> + C <sub>21</sub> H <sub>20</sub>	–132.2
CF <sub>2</sub> + C <sub>9</sub> H <sub>12</sub>	–78.6	CF <sub>2</sub> + C <sub>15</sub> H <sub>16</sub>	–77.3	CF <sub>2</sub> + C <sub>21</sub> H <sub>20</sub>	–77.5
CCl <sub>2</sub> + C <sub>9</sub> H <sub>12</sub>	–90.4	CCl <sub>2</sub> + C <sub>15</sub> H <sub>16</sub>	–89.8	CCl <sub>2</sub> + C <sub>21</sub> H <sub>20</sub>	–90.0
CBr <sub>2</sub> + C <sub>9</sub> H <sub>12</sub>	–92.5	CBr <sub>2</sub> + C <sub>15</sub> H <sub>16</sub>	–91.6	CBr <sub>2</sub> + C <sub>21</sub> H <sub>20</sub>	–91.8
C(CH <sub>3</sub> ) <sub>2</sub> + C <sub>9</sub> H <sub>12</sub>	–109.5	C(CH <sub>3</sub> ) <sub>2</sub> + C <sub>15</sub> H <sub>16</sub>	–108.3	C(CH <sub>3</sub> ) <sub>2</sub> + C <sub>21</sub> H <sub>20</sub>	–108.7
C(NH <sub>2</sub> ) <sub>2</sub> + C <sub>9</sub> H <sub>12</sub>	–47.2	C(NH <sub>2</sub> ) <sub>2</sub> + C <sub>15</sub> H <sub>16</sub>	–46.4	C(NH <sub>2</sub> ) <sub>2</sub> + C <sub>21</sub> H <sub>20</sub>	–46.8
C(OH) <sub>2</sub> + C <sub>9</sub> H <sub>12</sub>	–66.4	C(OH) <sub>2</sub> + C <sub>15</sub> H <sub>16</sub>	–65.9	C(OH) <sub>2</sub> + C <sub>21</sub> H <sub>20</sub>	–66.2
SiH <sub>2</sub> + C <sub>9</sub> H <sub>12</sub>	–74.8	SiH <sub>2</sub> + C <sub>15</sub> H <sub>16</sub>	–74.0	SiH <sub>2</sub> + C <sub>21</sub> H <sub>20</sub>	–74.2
SiF <sub>2</sub> + C <sub>9</sub> H <sub>12</sub>	–52.3	SiF <sub>2</sub> + C <sub>15</sub> H <sub>16</sub>	–51.8	SiF <sub>2</sub> + C <sub>21</sub> H <sub>20</sub>	–52.0
SiCl <sub>2</sub> + C <sub>9</sub> H <sub>12</sub>	–53.6	SiCl <sub>2</sub> + C <sub>15</sub> H <sub>16</sub>	–52.9	SiCl <sub>2</sub> + C <sub>21</sub> H <sub>20</sub>	–53.1
SiBr <sub>2</sub> + C <sub>9</sub> H <sub>12</sub>	–54.8	SiBr <sub>2</sub> + C <sub>15</sub> H <sub>16</sub>	–54.2	SiBr <sub>2</sub> + C <sub>21</sub> H <sub>20</sub>	–54.5
Si(CH <sub>3</sub> ) <sub>2</sub> + C <sub>9</sub> H <sub>12</sub>	–73.2	Si(CH <sub>3</sub> ) <sub>2</sub> + C <sub>15</sub> H <sub>16</sub>	–72.0	Si(CH <sub>3</sub> ) <sub>2</sub> + C <sub>21</sub> H <sub>20</sub>	–72.4
Si(NH <sub>2</sub> ) <sub>2</sub> + C <sub>9</sub> H <sub>12</sub>	–45.7	Si(NH <sub>2</sub> ) <sub>2</sub> + C <sub>15</sub> H <sub>16</sub>	–44.7	Si(NH <sub>2</sub> ) <sub>2</sub> + C <sub>21</sub> H <sub>20</sub>	–45.2
Si(OH) <sub>2</sub> + C <sub>9</sub> H <sub>12</sub>	–51.0	Si(OH) <sub>2</sub> + C <sub>15</sub> H <sub>16</sub>	–50.3	Si(OH) <sub>2</sub> + C <sub>21</sub> H <sub>20</sub>	–50.6
GeH <sub>2</sub> + C <sub>9</sub> H <sub>12</sub>	–50.2	GeH <sub>2</sub> + C <sub>15</sub> H <sub>16</sub>	–50.6	GeH <sub>2</sub> + C <sub>21</sub> H <sub>20</sub>	–50.4
GeF <sub>2</sub> + C <sub>9</sub> H <sub>12</sub>	–16.4	GeF <sub>2</sub> + C <sub>15</sub> H <sub>16</sub>	–16.1	GeF <sub>2</sub> + C <sub>21</sub> H <sub>20</sub>	–16.3
GeCl <sub>2</sub> + C <sub>9</sub> H <sub>12</sub>	–20.7	GeCl <sub>2</sub> + C <sub>15</sub> H <sub>16</sub>	–19.9	GeCl <sub>2</sub> + C <sub>21</sub> H <sub>20</sub>	–20.6
GeBr <sub>2</sub> + C <sub>9</sub> H <sub>12</sub>	–21.3	GeBr <sub>2</sub> + C <sub>15</sub> H <sub>16</sub>	–21.4	GeBr <sub>2</sub> + C <sub>21</sub> H <sub>20</sub>	–21.1
Ge(CH <sub>3</sub> ) <sub>2</sub> + C <sub>9</sub> H <sub>12</sub>	–48.4	Ge(CH <sub>3</sub> ) <sub>2</sub> + C <sub>15</sub> H <sub>16</sub>	–48.1	Ge(CH <sub>3</sub> ) <sub>2</sub> + C <sub>21</sub> H <sub>20</sub>	–48.2
Ge(NH <sub>2</sub> ) <sub>2</sub> + C <sub>9</sub> H <sub>12</sub>	–14.2	Ge(NH <sub>2</sub> ) <sub>2</sub> + C <sub>15</sub> H <sub>16</sub>	–14.6	Ge(NH <sub>2</sub> ) <sub>2</sub> + C <sub>21</sub> H <sub>20</sub>	–14.4
Ge(OH) <sub>2</sub> + C <sub>9</sub> H <sub>12</sub>	–15.0	Ge(OH) <sub>2</sub> + C <sub>15</sub> H <sub>16</sub>	–15.5	Ge(OH) <sub>2</sub> + C <sub>21</sub> H <sub>20</sub>	–15.2



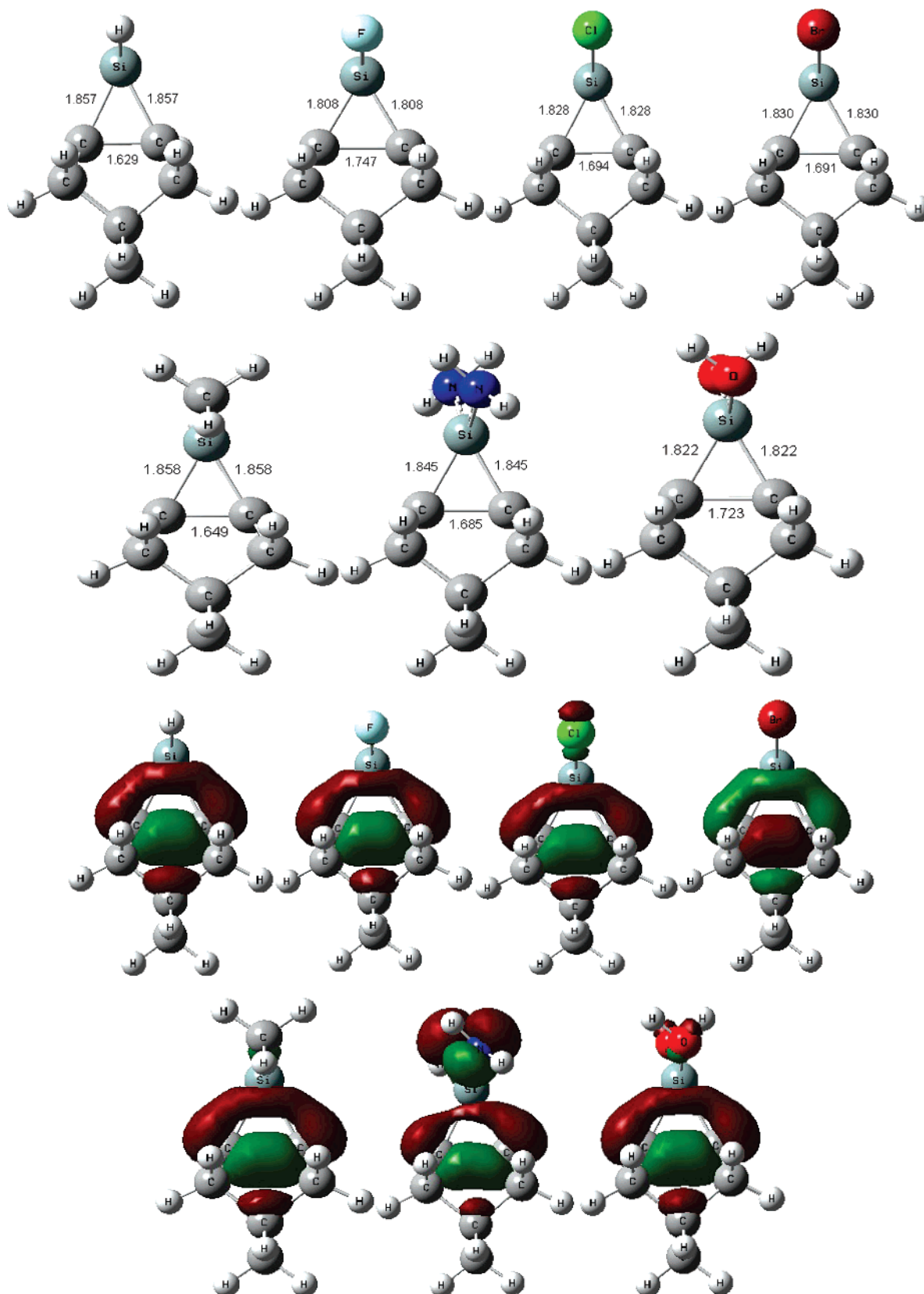
**Figure 2.** B3LYP/6-31G(d) optimized geometries (units in angstroms for bond length) for the additions of various substituted carbenes onto the C (100) surface and the frontier molecular orbitals (FMO) of the products.

(ZPVE) corrected. Geometry optimization shows that the C=C dimer in the C<sub>9</sub>H<sub>12</sub> cluster is symmetric as can be clearly seen from the optimized geometry and the highest occupied molecular orbital (HOMO) in Figure 1. This is in good agreement with the experimental observation.<sup>12</sup> All of the calculations were carried out with the Gaussian 98 program.<sup>13</sup>

### 3. Results and Discussion

Table 1 summarizes the reaction energies for the additions of various substituted singlet carbenes, silylenes, and germylenes onto the C (100) surface. Clearly, all of these addition reactions are exothermic, suggesting that the additions of carbenes, silylenes, and germylenes onto C (100) are quite thermodynami-

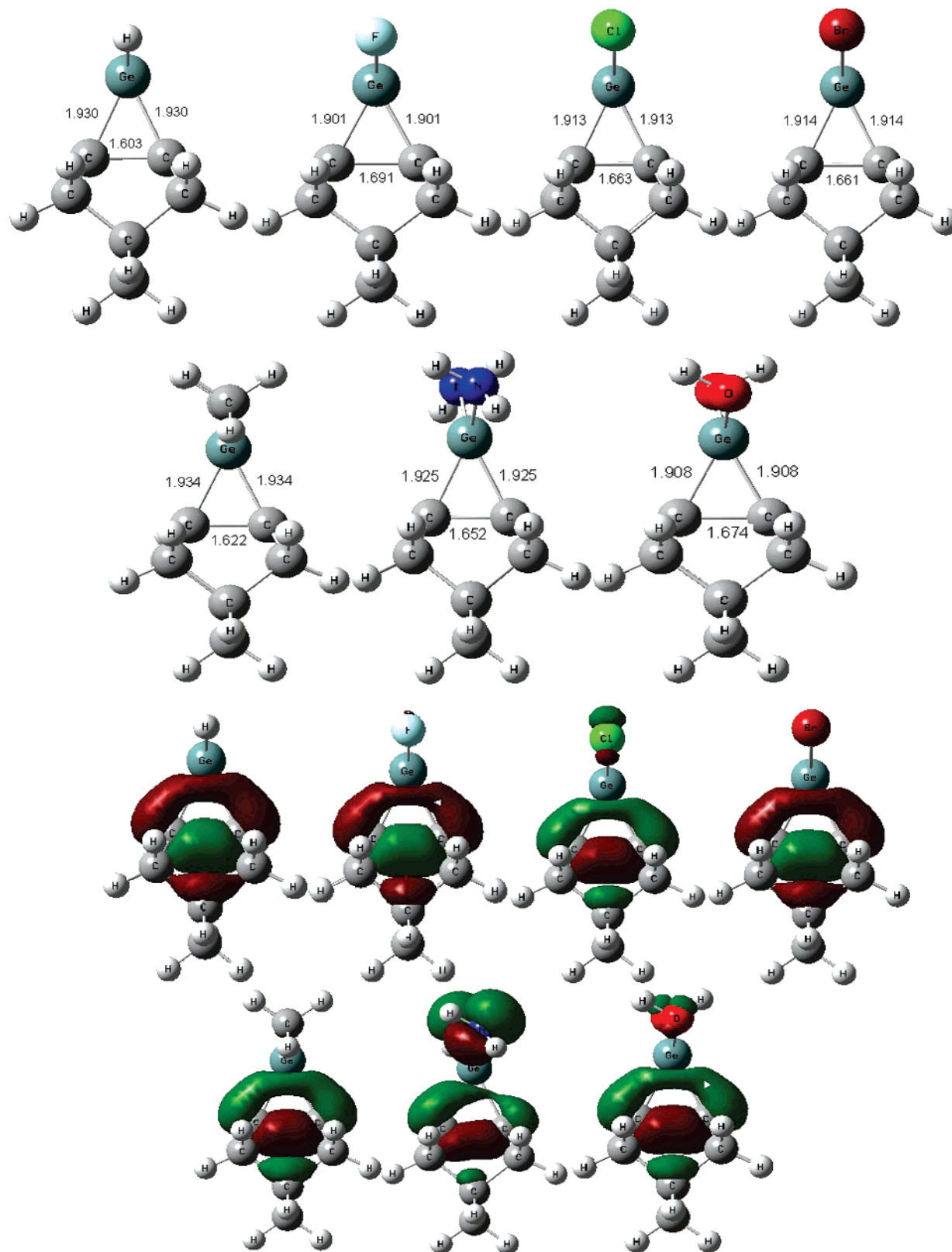




**Figure 3.** B3LYP/6-31G(d) optimized geometries (units in angstroms for bond length) for the additions of various substituted silylenes onto the C (100) surface and the frontier molecular orbitals (FMO) of the products.

cally favorable. On the other hand, it should be noted that the reaction energies of the additions of silylenes and germynes onto the C (100) surface are much lower than those of carbenes, which can be attributed to the weakness of Si–C bonds and Ge–C bonds as compared to C–C bonds. Detailed inspection of the reaction energies makes us find that, regarding the

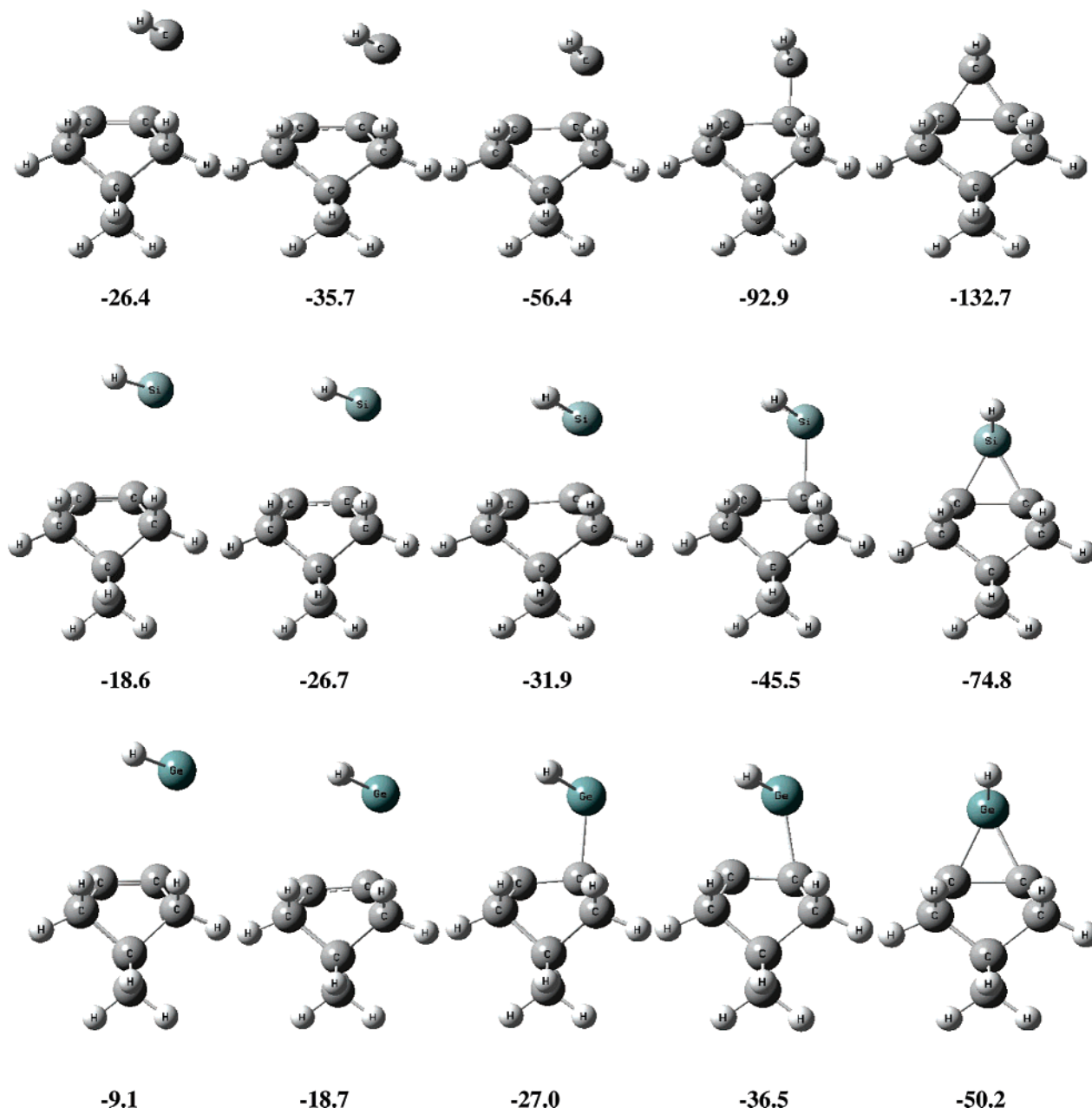
additions of carbenes onto C (100), the exothermicity roughly follows the order  $\text{CH}_2$  (−132.7 kcal/mol) >  $\text{C}(\text{CH}_3)_2$  (−109.5 kcal/mol) >  $\text{CBr}_2$  (−92.5 kcal/mol) >  $\text{CCl}_2$  (−90.4 kcal/mol) >  $\text{CF}_2$  (−78.6 kcal/mol) >  $\text{C}(\text{OH})_2$  (−66.4 kcal/mol) >  $\text{C}(\text{NH}_2)_2$  (−47.2 kcal/mol). An analogous reactivity trend is also observed for the additions of silylenes and germynes onto the



**Figure 4.** B3LYP/6-31G(d) optimized geometries (units in angstroms for bond length) for the additions of various substituted germylenes onto the C (100) surface and the frontier molecular orbitals (FMO) of the products.

C (100) surface. Hence, these lead us to conclude that, irrespective of carbenes, silylenes, and germylenes, the cycloadditions of those with the more electropositive substituents are much more exothermic than those with electronegative and  $\pi$ -donating substituents. Carbenes, silylenes, and germylenes with electronegative and  $\pi$ -donating substituents can be regarded as less electrophilic as compared to those with the more

electropositive substituents. As a result, the additions of carbenes, silylenes, and germylenes with electronegative and  $\pi$ -donating substituents onto the nucleophilic surface C=C dimer are less favorable than those with the more electropositive substituents. The calculated results using larger clusters  $C_{15}H_{16}$  and  $C_{21}H_{20}$  indicate that the size of cluster plays a minor effect on the calculated reaction energetics, which is in faithful



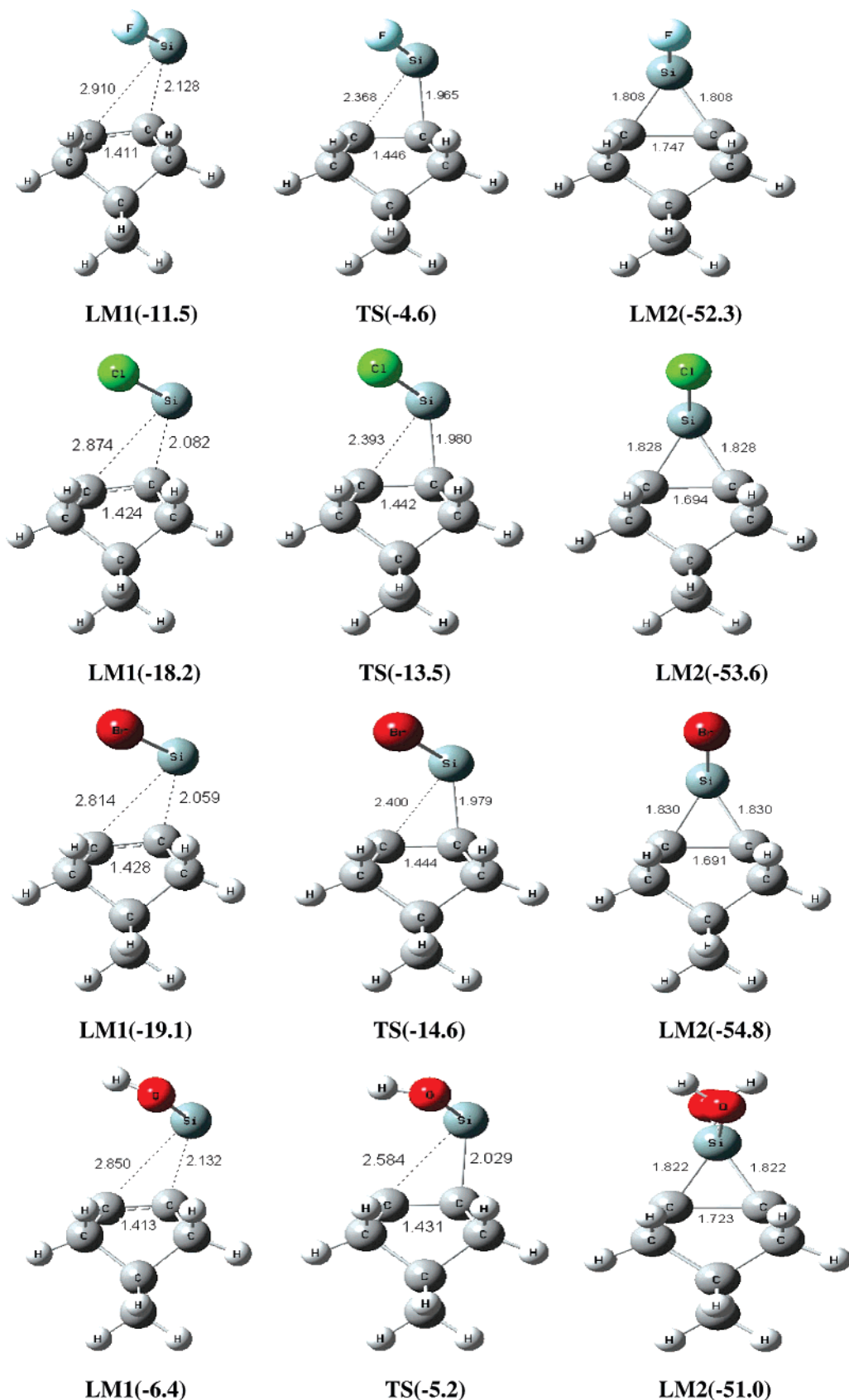
**Figure 5.** A series of geometries on the reaction path for the additions of prototype carbene ( $\text{CH}_2$ ), silylene ( $\text{SiH}_2$ ), and germylene ( $\text{GeH}_2$ ) onto the C (100) surface. Energies relative to free reactants are given in kcal/mol.

agreement with previous theoretical studies.<sup>6a–d,7–9</sup> These strongly suggest the reliability of using such an effective  $\text{C}_9\text{H}_{12}$  cluster to study of the additions of carbenes, silylenes, and germylenes onto the C (100)- $2 \times 1$  surface dimer. The additions of carbenes, silylenes, and germylenes onto C (100) belong to a rather localized process at low coverage.

Figures 2–4 depict the optimized geometries and the frontier molecular orbitals (FMO) of the final product. As a result of the additions of carbenes, silylenes, and germylenes onto the C (100) surface, the bond length of  $\text{C}=\text{C}$  dimer is elongated by 0.2–0.4 Å as compared to 1.362 Å in the free  $\text{C}_9\text{H}_{12}$  cluster. The pictures of frontier molecular orbitals correspond to the highest occupied molecular orbitals except for those of  $\text{GeCl}_2$  and  $\text{Ge}(\text{CH}_3)_2$  that correspond to the HOMO–1 orbitals. These frontier molecular orbitals clearly suggest that the chemical bonding has formed between the surface dimer and the oncoming carbenes, silylenes, and germylenes. Noteworthy, the as-formed surface products feature a three-membered cyclopropane-like structure, which would be subject to further chemical

manipulations, such as ring opening accompanied by the attachment of other chemical functional groups.<sup>7,14,15</sup>

Previously, an analogous reactivity trend for the cycloadditions of  $\text{CH}_2$ ,  $\text{SiH}_2$ , and  $\text{GeH}_2$  onto the sidewall of SWNCT has been theoretically reported by means of the two-layered ONIOM approach.<sup>14</sup> For example, using a two-layered ONIOM (B3LYP/6-31G\*: AM1) approach, Lu et al. also reported the exothermicity of the addition of  $\text{SiH}_2$  onto the sidewall of SWNCT is  $-20.7$  kcal/mol, which is much higher than  $-8.5$  kcal/mol for that of  $\text{GeH}_2$ .<sup>14a</sup> By means of a two-layered ONIOM (B3LYP/6-31G\*: PM3) method, Su et al. investigated the mechanism of the cycloadditions of  $\text{CH}_2$ ,  $\text{SiH}_2$ , and  $\text{GeH}_2$  onto the sidewall of SWNCT.<sup>14b</sup> They found that the greater is the atomic number of the carbene center, the larger is the activation energy and the less exothermic is the cycloaddition reaction. However, it should be mentioned that the predicted reaction pathways by Su et al. are different from those reported by Lu et al. For example, a transition state is found for the addition of  $\text{SiH}_2$  onto the sidewall of SWNCT, whereas no

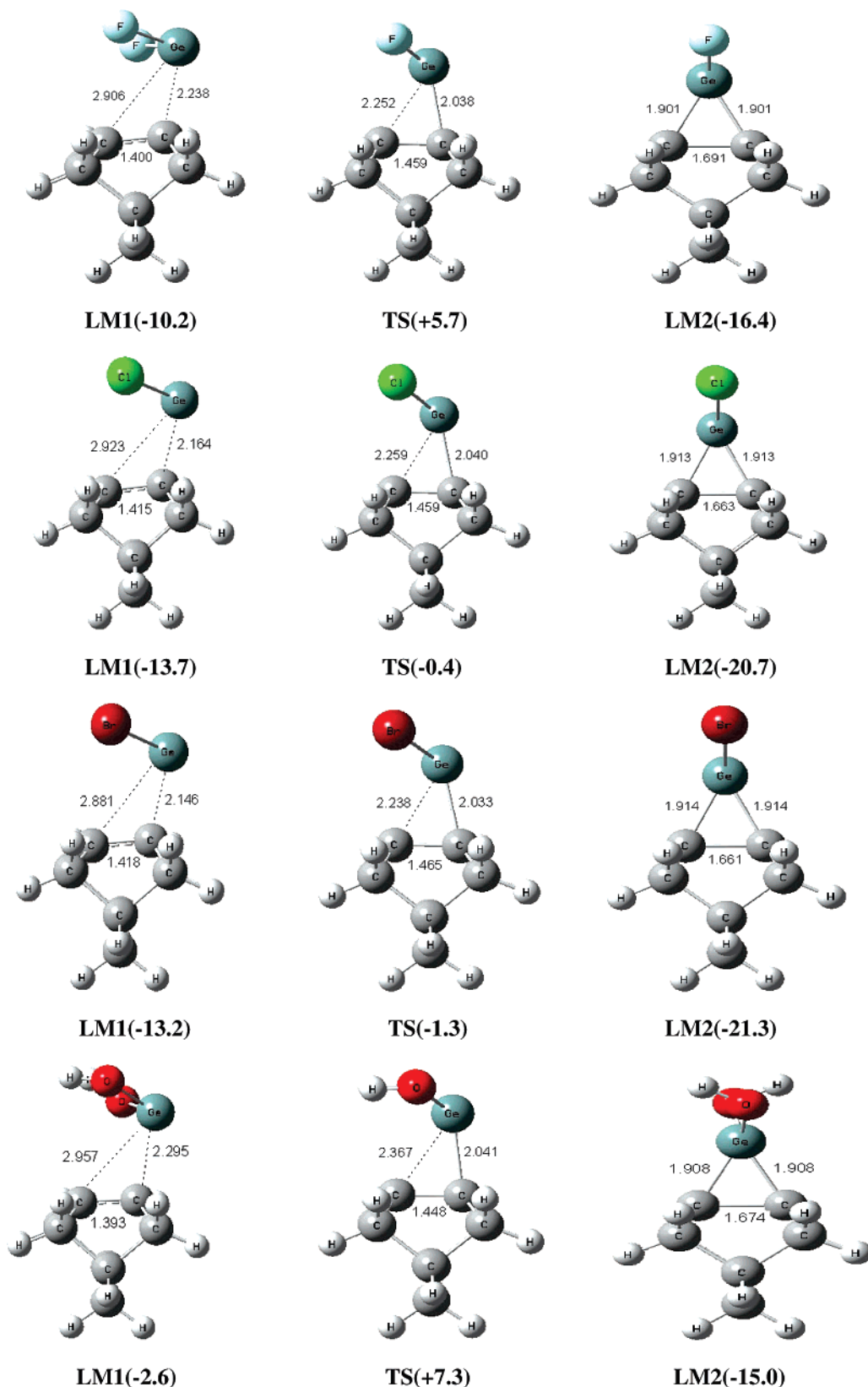


**Figure 6.** B3LYP/6-31G(d) optimized geometries (units in angstroms for bond length) of the intermediate, transition state, and product for the additions of  $\text{SiF}_2$ ,  $\text{SiCl}_2$ ,  $\text{SiBr}_2$ , and  $\text{Si(OH)}_2$  onto the C (100) surface. Energies (units in kcal/mol) relative to free reactants are given in parentheses.

transition state is located for that of  $\text{GeH}_2$  in Lu's study.<sup>14a</sup> However, transition states have been located for all of the additions of  $\text{CH}_2$ ,  $\text{SiH}_2$ , and  $\text{GeH}_2$  onto the sidewall of SWCNT in Su's work.<sup>14b</sup> Furthermore, Chen et al.<sup>14c</sup> and Su et al.<sup>14b</sup>

consistently suggest that SWCNT with  $\text{CH}_2$ ,  $\text{SiH}_2$ , and  $\text{GeH}_2$  favor opened structures rather than three-membered rings reported by Lu et al., hence strongly underlying the need for careful validation of the chosen ONIOM approach for studying





**Figure 7.** B3LYP/6-31G(d) optimized geometries (units in angstroms for bond length) of the intermediate, transition state, and product for the additions of GeF<sub>2</sub>, GeCl<sub>2</sub>, GeBr<sub>2</sub>, and Ge(OH)<sub>2</sub> onto the C (100) surface. Energies (units in kcal/mol) relative to free reactants are given in parentheses.

reactions on SWNCT.<sup>14c</sup> Although it is not reasonable to compare the absolute reaction energies for analogous addition reactions on SWNCT with those on C (100) because different theoretical methods were used, it can be qualitatively concluded that the reactivity of the surface C=C dimer of C (100) is much

higher than that of SWNCT, which can be attributed to the high  $\pi$ -conjugating bond character of the sidewall of SWNCT.

Our calculations of exploring the reaction pathways reveal that no intermediates and transition states are located except for the additions of SiF<sub>2</sub>, SiCl<sub>2</sub>, SiBr<sub>2</sub>, Si(OH)<sub>2</sub>, GeF<sub>2</sub>, GeCl<sub>2</sub>,



GeBr<sub>2</sub>, and Ge(OH)<sub>2</sub> onto the C (100) surface, strongly suggesting that the additions of these substituted carbenes, silylenes, and germynes onto C (100) are kinetically favorable. For example, regarding the additions of prototype carbene (CH<sub>2</sub>), silylene (SiH<sub>2</sub>), and germylene (GeH<sub>2</sub>) onto C (100), persistent searches for the transition states have yielded only structures with energies below the energy of free reactants. Detailed potential energy scans (PES) reinforce that such addition reactions are indeed barrierless (see Figure 5). This is quite reasonable considering the gas-phase reaction profile of the additions of CH<sub>2</sub>, SiH<sub>2</sub>, and GeH<sub>2</sub> to ethylene.<sup>16</sup> Previous theoretical calculations predicted that the overall additions of CH<sub>2</sub>, SiH<sub>2</sub>, and GeH<sub>2</sub> to ethylene are all barrierless.<sup>16</sup> As is well known, the surface C=C dimer of C (100) has higher reactivity than ethylene due to the reduced overlap between the p orbitals of the surface C=C dimer.<sup>7-9</sup> Thus, the additions of CH<sub>2</sub>, SiH<sub>2</sub>, and GeH<sub>2</sub> onto the C (100) surface should be much more favorable as compared to their ethylene molecular analogues, which has been confirmed by our previous theoretical study.<sup>7</sup>

With respect to the additions of SiF<sub>2</sub>, SiCl<sub>2</sub>, SiBr<sub>2</sub>, Si(OH)<sub>2</sub>, GeF<sub>2</sub>, GeCl<sub>2</sub>, GeBr<sub>2</sub>, and Ge(OH)<sub>2</sub> onto the C (100) surface, the optimized geometries of the intermediate (LM1) and product (LM2) are depicted in Figures 6 and 7, along with the transition state (TS) that connects the intermediate and the product. Obviously, both the intermediate and the transition state are lower in energy than the free reactants for the additions of SiF<sub>2</sub>, SiCl<sub>2</sub>, SiBr<sub>2</sub>, Si(OH)<sub>2</sub>, GeCl<sub>2</sub>, and GeBr<sub>2</sub> onto C (100). For instance, regarding the case of SiF<sub>2</sub>, the precursor complex LM1 is -11.5 kcal/mol lower in energy than the reactants. The transition state TS is 6.9 kcal/mol higher in energy than the intermediate LM1, but is -4.6 kcal/mol lower in energy than the reactants. Hence, the overall reaction is barrierless. For the cases of GeF<sub>2</sub> and Ge(OH)<sub>2</sub>, the predicted transition states are only +5.7 and +7.3 kcal/mol higher in energy than the free reactants, respectively, illustrating the overall additions are also kinetically favorable. As such, our theoretical calculations strongly suggest that the additions of carbenes, silylenes, and germynes onto the C (100) surface are much favorable both thermodynamically and kinetically, and the famous addition reactions of carbenes to alkenes in organic chemistry can potentially be employed as a new type of surface to functionalize the diamond (100) surface. It is the high reactivity of the surface C=C dimer of C (100) and carbenes, silylenes, and germynes that leads to the easiness of the addition reactions.<sup>7</sup> Analogous barrierless processes were observed for the hydroboration of C (100) with borane,<sup>17</sup> and the epoxidation of C (100) with dioxirane.<sup>9</sup>

In broad perspective, we believe that this type of surface organic reaction can also be extended to modify disilenes, digermenes, silenes, germenes, Si (100), Ge (100), fullerene, and SWNCT because all of these substances feature an analogous bonding motif.<sup>7-9,10a,18-20</sup> That is, the bonding motif of all of these substances can be typically depicted by a strong  $\sigma$  bond and a weak  $\pi$  bond, hence implying that similar chemistry might exist among them. On the other hand, it should be mentioned that no systematic theoretical work has been reported concerning the effect of substituents on the reaction profiles for the additions of carbenes, silylenes, and germynes onto SWNCT, fullerene, disilenes, digermenes, silenes, germenes, Si (100), and Ge (100). To address these issues and understand the underlying reaction mechanisms would certainly be interesting both from a fundamental viewpoint and for potential technological applications. Theoretical explorations in this regard

would add much to the richness of chemistry of solid surface and organic/inorganic chemistry.

Meanwhile, it should be noted that the results predicted herein only pertain to the low coverage limit due to the use of size-selected cluster models. In the case of high coverage, some steric repulsion of the adsorbed species would be expected, particularly for the species with larger substituents. Further theoretical investigation should be pursued by means of a slab model to unravel the effect of coverage on the addition profiles of these substituted carbenes, silylenes, and germynes onto the diamond (100) surface.

#### 4. Concluding Remarks

In conclusion, we have explored the cycloadditions of various substituted carbenes, silylenes, and germynes onto the C (100) surface by means of effective cluster models calculations. The results reveal that the substituents do play an important effect on the reaction energetics and the detailed reaction pathways. It was found that, regardless of carbenes, silylenes, and germynes, the cycloadditions of those with electropositive substituents (H and CH<sub>3</sub>) are much more favorable than those with electronegative and  $\pi$ -donating substituents (such as F, OH, and NH<sub>2</sub>) from both a thermodynamic and a kinetic viewpoint. Only for the additions of SiF<sub>2</sub>, SiCl<sub>2</sub>, SiBr<sub>2</sub>, Si(OH)<sub>2</sub>, GeF<sub>2</sub>, GeCl<sub>2</sub>, GeBr<sub>2</sub>, and Ge(OH)<sub>2</sub> onto C (100) have the precursor intermediate and transition state been located. Nevertheless, the overall addition reactions are either barrierless or have a very low activation energy barrier. Our results strongly suggest the feasibility that the additions of carbenes to alkenes in organic chemistry can potentially be employed as a new type of surface reaction to modify the diamond (100) surface at low temperature. Interestingly, the as-formed product has the three-membered cyclopropane structure, which would be subject to further transformations, for example, ring opening accompanied by attaching other chemical functional groups.

In broad perspective, we believe that this type of surface organic reaction can be extended to functionalize disilenes, digermenes, silenes, germenes, Si (100) and Ge (100), fullerene, and SWNCT because all of them feature a bonding motif analogous to that of C (100). By comparison, the analogy and difference among them can be found, therefore contributing much to the richness and diversity of solid surface chemistry and organosilicon/organogermanium chemistry. Finally, our results strongly advance the concept of using organic reactions to modify solid surface, and quite intriguing chemistry can exist in the material featuring an analogous bonding motif.

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