

Organic Functionalization of the Si (100) and Ge (100) Surfaces by Cycloadditions of Carbenes and Nitrenes: A Theoretical Prediction

Yi-Jun Xu,^{*,†} Yong-Fan Zhang,[‡] and Jun-Qian Li[‡]

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

Received: November 7, 2005; In Final Form: December 18, 2005

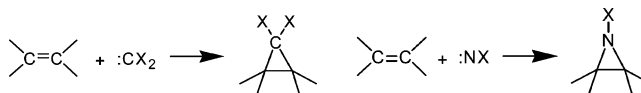
By means of density functional theory (B3LYP/6-31G*) coupled with effective cluster models, we predict that the well-known cycloaddition reactions of carbenes and nitrenes to alkenes in organic chemistry can be employed as a new type of surface reaction to organically functionalize the Si (100) and Ge (100) surfaces at low temperature. The well-established abundance of carbenes and nitrenes addition chemistry in organic chemistry provides versatile flexibility of functionalizing the surfaces of Si (100) and Ge (100), which can potentially impart new organic functionalities to the semiconductors surface for novel applications in a diversity of fields. Our predictions strongly advance the concept of using organic reactions to modify the solid surface in a controlled manner and quite intriguing chemistry can lie in the material featuring the analogous bonding motif. In further perspective, implications for other theoretical work, regarding disilenes, digermenes, silenes, and germenes that all feature the bonding motif similar to alkenes, are also discussed.

1. Introduction

In recent years, considerable growing interest has been focused on the organic functionalization of the surfaces of group IV semiconductors (diamond, silicon, and germanium) owing to its significant potential applications in microelectronics technology.^{1–3} Apart from the fundamental interest, much more important is the promise that the vast range of functions of organic molecules can potentially be incorporated into the surfaces of semiconductors, hence providing versatile flexibility for tailoring the surface properties of semiconductors and creating unique molecular properties by tuning the nature of the attached organic groups.^{1–3} Such a molecular integration of chemical functionalities of organic molecules with the semiconductor surfaces can be very useful for a host of technological applications, including molecular electronics, nonlinear optics, and biological sensors.³ Toward this end, we first predict the viability, by density functional theory calculations, that the famous cycloaddition reactions of carbenes and nitrenes to alkenes in organic chemistry can be used as a new type of surface reaction to functionalize the Si (100) and Ge (100) surfaces.

To date, quite fascinating and plentiful organic-semiconductor surface chemistry has been disclosed, especially on the (100) surfaces of single-crystalline diamond, silicon, and germanium which adopt the 2×1 reconstruction with the first-layer atoms dimerizing to form rows of X–X dimers (X = C, Si, or Ge).³ The chemical bonding in the surface X–X dimers of the X (100)-2×1 surfaces (X = C, Si, or Ge) features a strong σ bond and a much weaker π bond, making them analogous to the C=C double bonds of organic alkenes and thus implying that the chemistry of X (100) might show some similarity to the chemistry of alkenes. Accordingly, the X (100) surface has been found to be subject to 1,3-dipolar cycloaddition with 1,3-dipolar

SCHEME 1: Characteristic Addition of Carbenes and Nitrenes to Alkenes



molecules,⁴ [4+2] cycloaddition (Diels–Alder reaction) with conjugated dienes,⁵ and [2+2] cycloaddition with simple alkenes.⁶ Clearly, many well-known typical reactions with respect to alkenes in organic chemistry have successfully been applied to functionalize the X (100) surfaces due to the structural similarity between them. Indeed, as is often the case with big steps forward in experimental techniques, many old reactions in chemistry can be applicable in a series of novel applications catering to the needs in developing new hybrid material.

Theoretically, computational chemistry can help in the understanding of the reaction mechanisms (including reaction energetics and possible reaction pathways) that occurred on the surface of X (100) combined with today's advanced experimental techniques. Moreover, some unknown given reactions can be predicted by theoretical calculations, thus providing instructive information to experimentalists. In this respect, theoretical and experimental chemistry can aid each other, making it more effective to design novel semiconductor-based material with a clear target. In organic chemistry, carbenes and nitrenes are a fascinating class of highly reactive species.^{7,8} One of the most important and characteristic reactions of carbenes and nitrenes is their cycloaddition to alkenes to form a cyclopropane^{7,9} and aziridine,⁸ respectively (Scheme 1). The as-formed cyclopropane and aziridine can be used as a springboard for further chemical transformations given the well-established ring-opening chemistry of cyclopropane^{7,9,10} and aziridine.^{8,11} However, so far, neither experiment nor theory reports the functionalizations of the Si (100) and Ge (100)-2×1 surfaces by employing the cycloadditions of carbenes and nitrenes.

Analogous addition reactions of carbenes and nitrenes have successfully been reported regarding the functionalization of

* To whom correspondence should be addressed. E-mail: xuy7@cf.ac.uk.

[†] Cardiff University.

[‡] Fuzhou University.

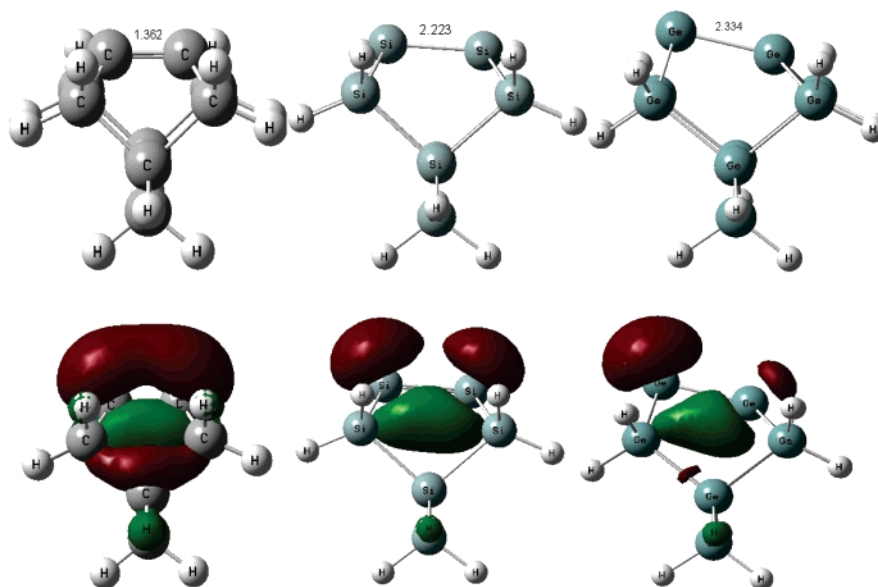


Figure 1. B3LYP/6-31G(d) optimized geometries (units in Å for bond length) of the X_9H_{12} cluster ($X = C, Si, \text{ and } Ge$) and their highest occupied molecular orbitals (HOMOs).

fullerene¹² and single-walled carbon nanotube (SWNCT)¹³ that can both be seen as featuring the bonding motif on the sidewall similar to that of alkenes. More importantly, we have recently predicted, by effective cluster models calculations, that the cycloaddition reactions of carbenes and nitrenes to alkenes in organic chemistry can be used as a new type of surface reaction to modify diamond (100),^{14,15} another allotrope of carbon. Strongly inspired by these pioneering chemical precedents, it is natural to infer that analogous cycloadditions of carbenes and nitrenes can occur on the Si (100) and Ge (100)- 2×1 surfaces.

The purpose of this paper is to confirm such an inference by computational studies and prove the viability that the addition reaction of carbenes and nitrenes to alkenes in organic chemistry can be employed as a new kind of surface reaction to functionalize the Si (100) and Ge (100) surfaces, which both feature the bonding motif in the surface dimer similar to that of alkenes, C (100), fullerene, and SWNCT. More importantly, this new type of surface reaction offers another new option for experimentalists to design and construct organic thin films on Si (100) and Ge (100), considering the much higher reactivity of carbenes and nitrenes toward binding to the surface dimer of Si (100) and Ge (100). We believe that the well-established abundance of carbenes and nitrenes addition chemistry, in conjunction with advanced experimental techniques, will provide greater flexibility for functionalizing the surfaces of Si (100) and Ge (100) in a controlled manner, therefore contributing to design the new semiconductor-based microelectronics hybrid material. Our theoretical predictions strongly reinforce the concept that similar intriguing chemistry can exist in the material featuring an analogous bonding motif.^{3–6,14,15}

2. Computational Details and Models

As previously done,^{4,5a,b,d,h,l,m,6a,b} we used Si_9H_{12} and Ge_9H_{12} clusters (as shown in Figure 1) to model a dimer site of the Si (100) and Ge (100)- 2×1 surface, respectively. This one-dimer cluster consists of two surface silicon or germanium atoms representing the surface dimer and seven atoms representing three layers of subsurface bulk atoms. The dangling bonds of the subsurface atoms are terminated by a total of 12 hydrogen atoms. The hybrid density functional method B3LYP,¹⁶ i.e., Becke's three-parameter nonlocal-exchange functional with the

correlation functional of Lee–Yang–Parr, together with the standard all-electron split-valence basis set 6-31G(d) was employed. In principle, cluster 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, allowing one to treat problems occurring on a solid surface with the typical language of chemistry, the language of orbitals.¹⁷ 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.¹⁷ On the other hand, because the surface dimer can be regarded as the most reactive site on the X (100) surface, it is reasonable to adopt such simple Si_9H_{12} and Ge_9H_{12} cluster models to qualitatively predict whether the additions of carbenes and nitrenes in organic chemistry can be applied to functionalize the Si (100) and Ge (100) surfaces. As a matter of fact, despite their simplicity, these cluster models along with the B3LYP/6-31G(d) level of theory have been widely employed in previous investigations on the chemistry of X (100) surfaces ($X = C, Si, \text{ and } Ge$) and have proved to be effective and reliable in describing the surface reaction energetics and mechanisms on X (100) surfaces, and in particular, they are very useful in qualitatively predicting the possibility of a given reaction on the X (100) surface.^{4,5a,b,d,h,l,m,6a,b} For example, Xu and co-workers have used such a simple Si_9H_{12} cluster model to comprehensively investigate the detailed mechanisms for the complete decomposition of NH_3 to NH_x ($x = 0–2$) on the Si (100)- 2×1 surface.¹⁸ Employing the same X_9H_{12} cluster models, the interesting diradical mechanisms for the cycloaddition chemistry of ethylene on X (100) surfaces ($X = C, Si, \text{ and } Ge$) have been systematically reported.^{6a,b} In addition, such effective X_9H_{12} cluster models were also used to theoretically predict other reactions, e.g. 1,3-dipolar cycloadditions,⁴ Diels–Alder cycloadditions,⁵ and hydroboration reaction.¹⁹

Theoretically, Si_9H_{12} and Ge_9H_{12} cluster models fulfill the requirements of stoichiometry principle, neutrality principle, and coordination principle, and they can be concluded as good models of choice.²⁰ Furthermore, cluster models present the

advantage in terms of a compromise between accuracy and computational cost if clusters are properly selected.^{17,20,21} A similar C₉H₁₂ cluster coupled with the B3LYP/6-31G(d) level of theory was successfully used regarding the addition of carbenes and nitrenes onto the diamond (100) surface.^{14,15} Besides, calculations with larger cluster models Si₁₅H₁₆ and Ge₁₅H₁₆ have confirmed the predictions by means of small Si₉H₁₂ and Ge₉H₁₂ clusters, suggesting that the predicted qualitative conclusion is insensitive to cluster size, which is consistent with that on the C (100) surface^{14,15} and faithfully reinforces the effectiveness of using such a model scheme to theoretically predict the possibility of a given reaction.^{4,6,18,19}

Geometry optimizations without constrained degrees of freedom were carried out with use of analytical gradients and the Berny algorithm. No geometry constraint was imposed on the clusters. Harmonic vibrational frequencies were calculated to confirm that the optimized products are truly local minima, i.e., the stationary points were positively identified as minima without imaginary frequencies (NIMAG = 0). Reported energies were zero-point vibrational energy corrected. Single-point calculations were done, using the 6-311G(2d,2p), to investigate the basis set effect on the reaction energetics although our main interest is in qualitative trends of surface reactions, not in absolute energetics values. At the B3LYP/6-31G(d) level of theory, geometry optimizations reveal that the X = X dimers in the Si₉H₁₂ and Ge₉H₁₂ clusters are asymmetric, whereas the one in the C₉H₁₂ cluster is symmetric as can be clearly seen from the optimized geometry and the highest occupied molecular orbital (HOMO) (as shown in Figure 1). The predicted buckling angle of the Ge=Ge dimer and Si=Si dimer is about 15.7° and 1.7°, respectively. The results are in qualitative agreement with the experimental observation that at low temperatures dimers on Ge (100) and Si (100) surfaces are buckled, whereas those on the C (100) surface are symmetric.^{3h} All the calculations were performed with the Gaussian-98 program.²²

To confirm our inference that the additions of carbenes and nitrenes to alkenes in organic chemistry can be employed as a new type of surface reaction to functionalize the Si (100) and Ge (100) surfaces at low temperature, the following were selected as testing model molecules, i.e., singlet carbene (CH₂), dichlorocarbene (CCl₂), silylene (SiH₂), dichlorosilylene (SiCl₂), germylene (GeH₂), and dichlorogermylene (GeCl₂) were adopted to theoretically predict the additions of carbenes onto Si (100) and Ge (100), and singlet nitrene (NH), aminonitrene (NNH₂), and oxycarbonylnitrene (NCOOCH₃) were used to predict the additions of nitrenes onto Si (100) and Ge (100). Such a choice is based on two main reasons. First, these model molecules, except dichlorocarbene, dichlorosilylene, and dichlorogermylene, were used in our recent theoretical predictions regarding the cycloadditions of carbenes and nitrenes onto diamond (100).^{14,15} From the standpoint of experimental technology, simple reagents, e.g., CH₂, SiH₂, and GeH₂, are generally highly active, far from those ordinary reagents (for example, CCl₂ and oxycarbonylnitrene that have been experimentally reported with respect to functionalization of SWNCT and fullerene^{12,13}). Thus, it is necessary to carry on these additional [2+1] cycloaddition calculations, using CCl₂, SiCl₂, and GeCl₂ as model molecules, so as to strongly suggest the feasibility that the famous addition reactions of carbenes and nitrenes to alkenes can be used as a new type of surface reaction to modify the Si (100) and Ge (100) surfaces with the help of synthetic organic chemistry and today's advanced surface science. Second, these model molecules were also used to theoretically study the sidewall functionalization of SWNCT by the additions of carbenes and

TABLE 1: Calculated Reaction Energies (ΔE_r , in kcal/mol) for the Addition Reactions of Carbene (CH₂), Silylene (SiH₂), Germylene (GeH₂), Dichlorocarbene (CCl₂), Dichlorosilylene (SiCl₂), and Dichlorogermylene (GeCl₂) onto the Si (100) and Ge (100)-2×1 Surfaces

system	method	ΔE_r
CH ₂ + Si ₉ H ₁₂	B3LYP/6-31G(d)	-123.7
	B3LYP/6-311G(2d,2p)	-120.8
SiH ₂ + Si ₉ H ₁₂	B3LYP/6-31G(d)	-71.1
	B3LYP/6-311G(2d,2p)	-69.0
GeH ₂ + Si ₉ H ₁₂	B3LYP/6-31G(d)	-67.2
	B3LYP/6-311G(2d,2p)	-56.5
CH ₂ + Ge ₉ H ₁₂	B3LYP/6-31G(d)	-115.1
	B3LYP/6-311G(2d,2p)	-101.3
SiH ₂ + Ge ₉ H ₁₂	B3LYP/6-31G(d)	-76.6
	B3LYP/6-311G(2d,2p)	-60.6
GeH ₂ + Ge ₉ H ₁₂	B3LYP/6-31G(d)	-75.6
	B3LYP/6-311G(2d,2p)	-47.3
CCl ₂ + Si ₉ H ₁₂	B3LYP/6-31G(d)	-70.9
	B3LYP/6-311G(2d,2p)	-68.5
SiCl ₂ + Si ₉ H ₁₂	B3LYP/6-31G(d)	-46.4
	B3LYP/6-311G(2d,2p)	-42.7
GeCl ₂ + Si ₉ H ₁₂	B3LYP/6-31G(d)	-41.8
	B3LYP/6-311G(2d,2p)	-28.8
CCl ₂ + Ge ₉ H ₁₂	B3LYP/6-31G(d)	-70.5
	B3LYP/6-311G(2d,2p)	-53.6
SiCl ₂ + Ge ₉ H ₁₂	B3LYP/6-31G(d)	-52.4
	B3LYP/6-311G(2d,2p)	-34.9
GeCl ₂ + Ge ₉ H ₁₂	B3LYP/6-31G(d)	-51.8
	B3LYP/6-311G(2d,2p)	-28.8

nitrenes.²³ By comparison, the interesting analogy and difference among them can be obtained, which will add much to the richness and diversity of solid surface and organic chemistry, and also provide beneficial indications for further theoretical work.

3. Results and Discussion

A. Addition of Carbene, Dichlorocarbene, Silylene, Dichlorosilylene, Germylene, and Dichlorogermylene. Table 1 and Figure 2 summarize the calculated reaction energies and optimized geometries for the additions of carbene (CH₂), dichlorocarbene (CCl₂), silylene (SiH₂), dichlorosilylene (SiCl₂), germylene (GeH₂), and dichlorogermylene (GeCl₂) onto the Si (100) and Ge (100)-2×1 surfaces. All these [2+1] additions onto the Si (100) and Ge (100) surfaces are highly exothermic, indicating these surface reactions are thermodynamically favorable. For the addition of prototype carbene, CH₂, onto Si (100), the reaction energy predicted at the B3LYP/6-31G(d) level is -123.7 kcal/mol. The reaction energy predicted at the same theoretical level for the addition of SiH₂ and GeH₂ onto Si (100) is -71.1 and -67.2 kcal/mol, respectively. This suggests higher exothermicity for the addition of CH₂ onto Si (100) than that of SiH₂ and GeH₂, which can be ascribed to the weakness of Si-Si and Ge-Si bonds as compared to C-Si bonds. The same reactivity trend has also been observed for the addition reaction of CH₂, SiH₂, and GeH₂ onto the surface dimer of diamond (100)¹⁴ and the sidewall of SWNCT.^{23a,b} For instance, Lu et al. used the two-layered ONIOM (B3LYP/6-31G*: AM1) theoretical method to investigate the addition of SiH₂ and GeH₂ onto the sidewall of SWNCT, for which it was predicted to be exothermic by -20.7 and -8.5 kcal/mol, respectively.^{23a} Su and co-workers reported another theoretical exploration of the mechanism of the cycloadditions of CH₂, SiH₂, and GeH₂ onto the sidewall of SWNCT employing a two-layered ONIOM (B3LYP/6-311G*: PM3) approach, wherein they found that the greater the atomic number of the carbene center, the larger the activation energy and the less exothermic the cycloaddition

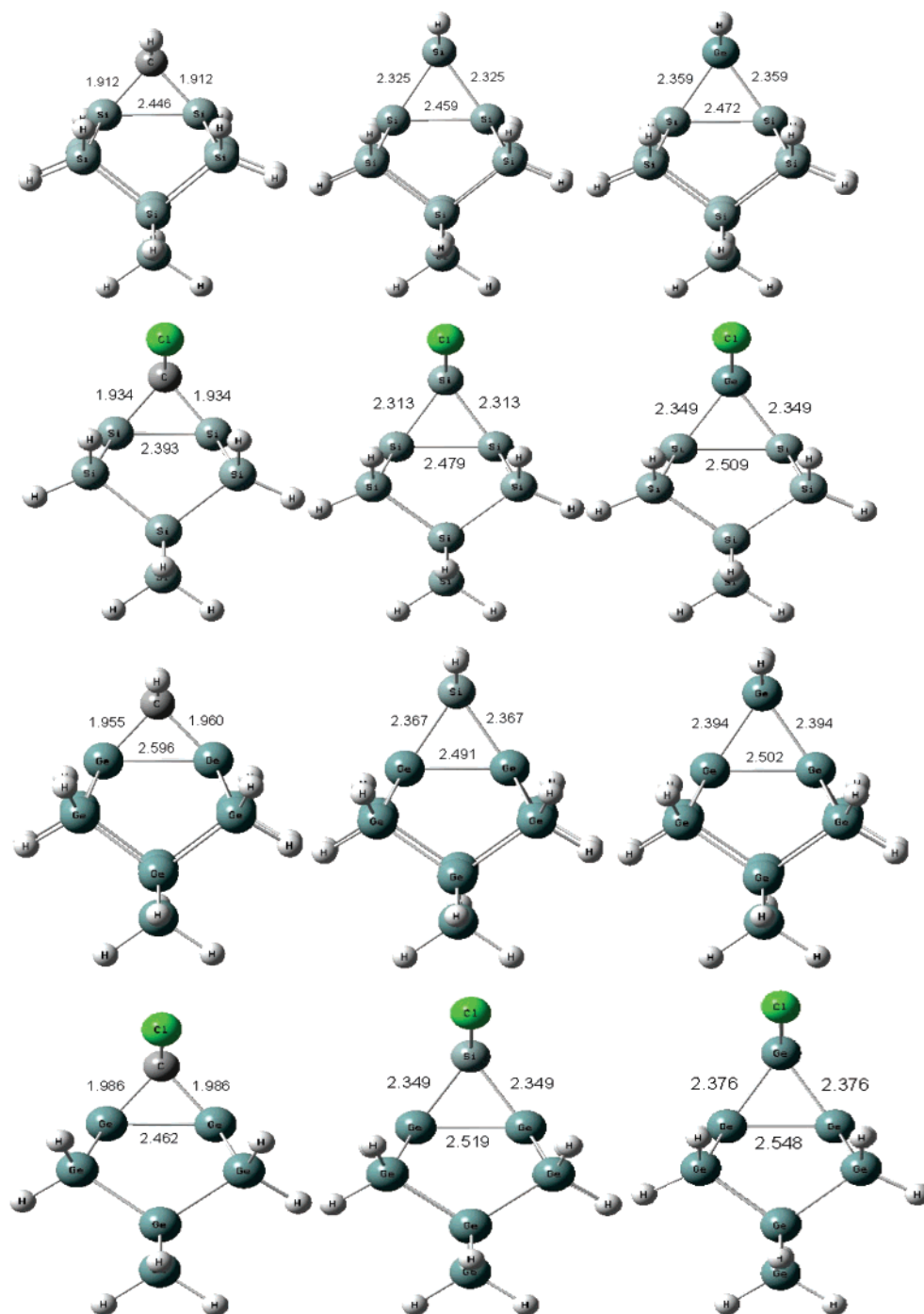


Figure 2. B3LYP/6-31G(d) optimized geometries (units in Å for bond length) for the additions of carbene, dichlorocarbene, silylene, dichlorosilylene, germylene, and dichlorogermene onto the Si (100) and Ge (100) surfaces.

reaction.^{23b} It should be particularly noted that Su's^{23b} and Chen's^{13e} studies consistently suggest that SWNCT with CH₂, SiH₂, and GeH₂ adds favor opened structures rather than three-membered rings reported by Lu and co-workers,^{23a} strongly underlining the need for careful validation of the chosen ONIOM approach for studying given reactions on SWNCT. However, the predicted trend of surface reactivity for the additions of CH₂, SiH₂, and GeH₂ onto the sidewall of SWNCT is consistent, i.e., the reactivity follows the order CH₂ > SiH₂ > GeH₂.^{23a,b}

More interestingly, regarding the additions of CH₂, SiH₂, and GeH₂ onto the surface dimer of Si (100) and Ge (100), no transition states have been located in our theoretical calculations. This is not surprising at all considering the reaction profiles of

additions of CH₂, SiH₂, and GeH₂ to ethylene²⁴ and diamond (100).¹⁴ Previous ab initio and density functional theoretical calculations consistently disclosed that the overall reaction is barrierless for the addition of CH₂, SiH₂, and GeH₂ to ethylene, respectively.²⁴ Similar additions of CH₂, SiH₂, and GeH₂ onto diamond (100) were also predicted to have no energy barrier by means of density functional cluster models calculations.¹⁴ Note that the surface dimer π -bond strength is 5–10 kcal/mol for Si (100) and Ge (100),²⁵ much smaller than the π -bond strength of 56 kcal/mol in ethylene^{6b} and ~28 kcal/mol for diamond (100).²⁶ Indeed, singlet CH₂, SiH₂, and GeH₂ are extremely reactive species in organic chemistry and can be seen as high electrophiles, whereas the surface Si=Si dimer and Ge=Ge dimer of Si (100) and Ge (100) can be viewed as high

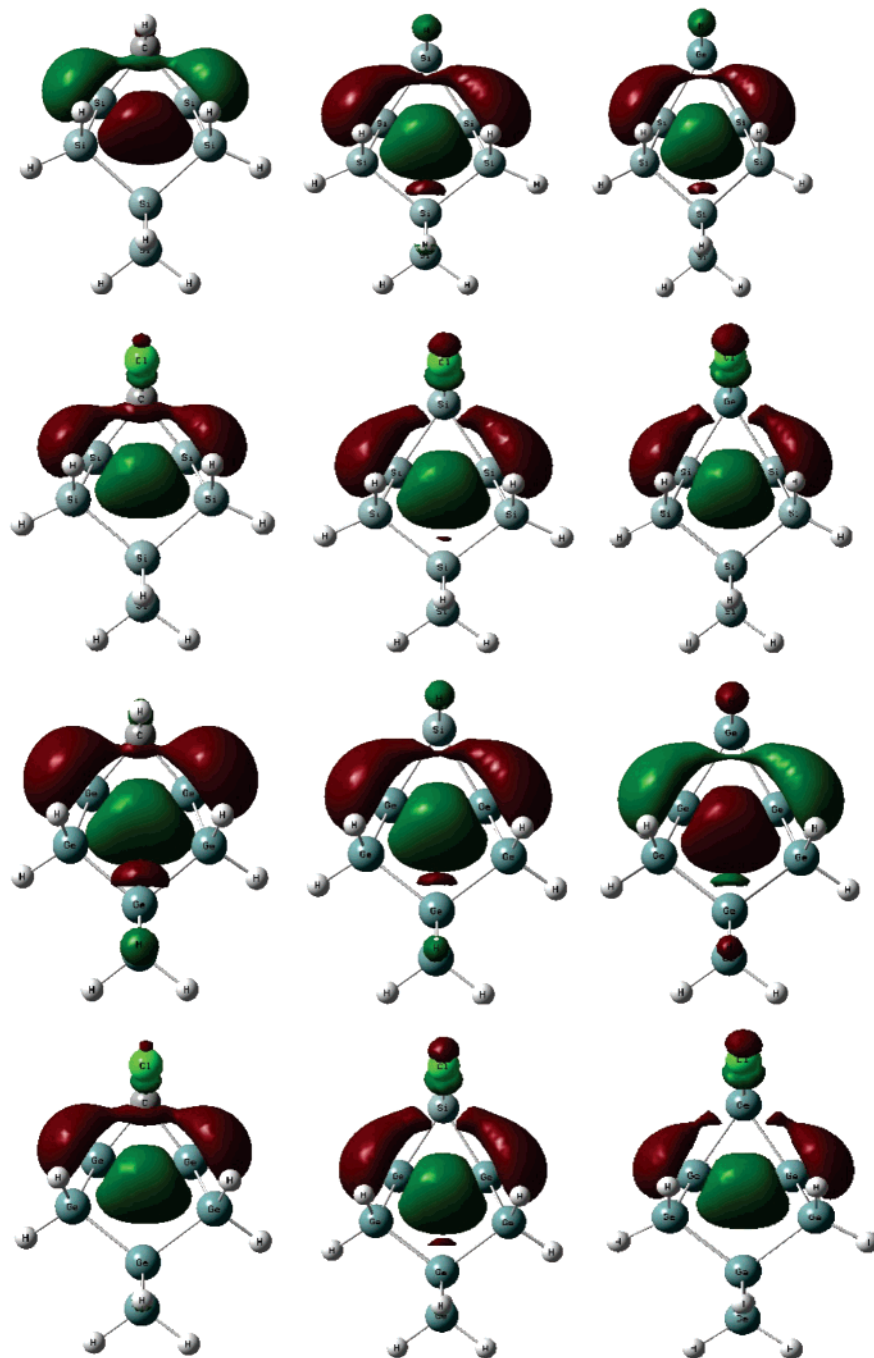


Figure 3. The highest occupied molecular orbitals (HOMOs) for the additions of carbene, dichlorocarbene, silylene, dichlorosilylene, germylene, and dichlorogermylene onto the Si (100) and Ge (100) surfaces.

nucleophiles. Hence, the facileness of the additions of carbene, silylene, and germylene onto Si (100) and Ge (100) should be expected. It is the high reactivity of carbene, silylene, and germylene and the surface dimer of Si (100) and Ge (100) that leads to the addition reaction proceeding without energy barrier. A similar barrierless process also has been observed for the hydroboration of Si (100) and Ge (100) with borane, a strongly Lewis acid.¹⁹ However, similar addition reactions on the sidewall of SWNCT need to surmount a given energy barrier,^{23a,b} which can be ascribed to the high π -conjugating bonding character of the sidewall of SWNCT.

Experimentally, simple reagents, CH_2 , SiH_2 , and GeH_2 , are generally highly reactive and often produced in situ conditions, far from those ordinary reagents (for example, CCl_2 , which has been used experimentally in the functionalization of SWNCT

and fullerene).^{12a,13} Thus, we have also used CCl_2 , SiCl_2 , and GeCl_2 as model molecules to perform the additional [2+1] cycloaddition calculations. As seen from Table 1, the additions of dichlorocarbene (CCl_2), dichlorosilylene (SiCl_2), and dichlorogermylene (GeCl_2) onto Si (100) and Ge (100) are still highly exothermic. Interestingly, these addition reactions also have no energy barrier. However, analogous [2+1] cycloaddition of CCl_2 onto the 1,2-pari site of SWNCT was predicted to have an energy barrier of 14.0 kcal/mol, using a two-layered ONIOM approach.^{23a} More importantly, our theoretical predictions significantly suggest the feasibility that the well-known addition reaction of carbenes to alkenes can be employed as a new type of surface reaction to organically functionalize the Si (100) and Ge (100) surfaces. In practice, carbenes (silylenes and germynes) can be produced via the process of photolysis and

thermolysis at moderate temperature⁷ and therefore introduced onto the Si (100) and Ge (100) surfaces. For example, carbenes can be generated by photolyzing dazoalkanes and diazirines,^{7c} and silylenes can be generated by photolyzing trisilanes.²⁷ In addition, note that the additions of CCl₂, SiCl₂, and GeCl₂ onto Si (100) and Ge (100) are less exothermic than that of CH₂, SiH₂, and GeH₂, suggesting the substituents should play an important effect on the profile of addition reactions with respect to various substituted carbenes, silylenes, and germynes.

Figure 2 displays the optimized geometries of the product for the additions of CH₂, SiH₂, GeH₂, CCl₂, SiCl₂, and GeCl₂ onto the surface dimer of Si (100) and Ge (100). As a result of the additions onto the Si (100) and Ge (100) surface, the bond length of Si=Si dimer and the Ge=Ge dimer is elongated by 0.2–0.3 Å. The HOMO pictures shown in Figure 3 suggest that the chemical bonding has formed between the surface dimer and the oncoming carbenes, silylenes, and germynes. Interestingly, the as-formed surface products have the three-membered cyclopropane-like structure, which would be subject to further chemical manipulations, such as ring-opening^{7,9,10} accompanied by the attachment of other functional inorganic/organic groups. In this regard, the well-established ring-opening chemistry of cyclopropane can be flexibly used.^{7,9,10}

It was suggested that the B3LYP/6-31G(d) level of theory tends to overestimate the Ge–C bond strength and, as a result, the reaction energies will be overestimated although the predicted trend including possible reaction mechanism remains unchanged.^{6b} In view of this, we have carried out single-point energy calculations using the higher basis set 6-311G(2d,2p) to improve the accuracy of reaction energies, and to see how much effect the basis set plays on our predicted reaction energies. As seen from Table 1, with regard to the additions of CH₂, SiH₂, CCl₂, and SiCl₂ onto Si (100), and CCl₂ onto Ge (100), the reaction energies calculated with the higher basis set 6-311G(2d,2p) are nearly comparable to those with the standard 6-31G(d) basis set that has been used widely in theoretical studies concerning the reaction on the (100) surfaces of diamond, Si, and Ge,^{6a,b} whereas for the additions of GeH₂, GeCl₂, SiCl₂, and GeCl₂ onto Si (100), and CH₂, SiH₂, GeH₂, SiCl₂, and GeCl₂ onto Ge (100), the calculated reaction energies using the basis set 6-31G(d) are overestimated to some extent, as compared to those using the higher basis set 6-311G(2d,2p). For example, the reaction energies calculated at the B3LYP/6-31G(d) level are overestimated by about 10 kcal/mol as compared to those at the B3LYP/6-311G(2d,2p) level, for the additions of CH₂ and SiH₂ onto the Ge (100) surface. Meanwhile, the error induced by using different basis sets is different with respect to various substituted carbenes, silylenes, and germynes. These clearly suggests that single-point energy calculations employing a larger basis set or a high theoretical level are necessary, particularly when one's primary theoretical interest aims to accurately address the reaction energetics values or to compare to the available experimental data. Nevertheless, it should be worthwhile to emphasize that the qualitatively predicted conclusion is consistent, i.e., the addition reactions of CH₂, CCl₂, SiH₂, SiCl₂, GeH₂, and GeCl₂ onto the surface dimer of Si (100) and Ge (100) are favorable both thermodynamically and kinetically. More significantly, our predictions shown above strongly suggest the viability that the well-known addition reaction of carbenes to alkenes in organic chemistry can be employed as a new type of surface reaction to functionalize the Si (100) and Ge (100) surfaces. Such a new type of reaction coupled with the enrichment of carbene chemistry would be remarkably useful in the functionalization of semiconductor surfaces, given the

TABLE 2: Calculated Reaction Energies (ΔE_r , in kcal/mol) for the Addition Reactions of Nitrene (CH₂), Aminonitrene (NNH₂), and Oxycarbonylnitrene (NCOOCH₃) onto the Si (100) and Ge (100)-2×1 Surfaces

system	method	ΔE_r
NH + Si ₉ H ₁₂	B3LYP/6-31G(d)	−153.2
	B3LYP/6-311G(2d,2p)	−155.6
NNH ₂ + Si ₉ H ₁₂	B3LYP/6-31G(d)	−55.6
	B3LYP/6-311G(2d,2p)	−58.4
NCOOCH ₃ + Si ₉ H ₁₂	B3LYP/6-31G(d)	−117.5
	B3LYP/6-311G(2d,2p)	−119.3
NH + Ge ₉ H ₁₂	B3LYP/6-31G(d)	−134.5
	B3LYP/6-311G(2d,2p)	−128.8
NNH ₂ + Ge ₉ H ₁₂	B3LYP/6-31G(d)	−40.3
	B3LYP/6-311G(2d,2p)	−29.4
NCOOCH ₃ + Ge ₉ H ₁₂	B3LYP/6-31G(d)	−105.3
	B3LYP/6-311G(2d,2p)	−91.8

well-known abundance of carbenes addition chemistry in modern organic chemistry.^{7,9}

B. Addition of Nitrene, Aminonitrene, and Oxycarbonylnitrene. Apart from carbenes in organic chemistry, nitrenes are another class of fascinating and highly reactive species.⁸ Similar to the case of carbenes, the addition of nitrenes to alkenes is one of the most important reactions associated with nitrenes, and the as-formed aziridine is quite versatile for further chemical transformations.^{8,11} Experimentally, this famous addition reaction in organic chemistry has successfully been applied to functionalize the sidewall of SWNCT/fullerene and produce oxycarbonylaziridino-SWNCT/fullerene.^{12,13d} The surface dimer of Si (100) and Ge (100) features the bonding motif similar to that of alkenes, diamond (100), fullerene, and SWNCT. Moreover, the π -bond strength of the surface dimer of Si (100) and Ge (100) is much weaker, giving rise to the higher reactivity toward the attack of nitrenes. Hence, the addition of nitrenes onto the surface dimer of Si (100) and Ge (100) should be naturally expected.

As seen from Table 2, the addition of nitrene, NH, onto the surface dimer of Si (100) is predicted to be highly exothermic by −153.2 kcal/mol at the B3LYP/6-31G(d) level. The higher exothermicity for the addition of NH onto Si (100) is similar to that of CH₂. Besides, the addition of NH onto Si (100) has no activation energy barrier that is exactly the same as that of NH addition to ethylene²⁸ and diamond (100),¹⁵ respectively. Indeed, the additions of aminonitrene and oxycarbonylnitrene onto Si (100) and Ge (100) are also barrierless, that is, no transition states are located. It is the high reactivity of both the Si (100) and Ge (100) surfaces and nitrenes that leads to the addition reaction proceeding without energy barrier. The same barrierless process was also predicted to occur on diamond (100),¹⁵ using density functional cluster model calculations. Among these three kinds of nitrenes, the exothermicity for the addition of aminonitrene onto Si (100) and Ge (100) is the lowest, indicating that substituents play an important effect on the reaction profile, similar to that of carbenes.

Theoretically, analogous cycloadditions of oxycarbonylnitrene onto fullerene and SWNCT have been reported.²³ The addition of oxycarbonylnitrene onto fullerene was predicted to have an activation energy barrier of 3.6 kcal/mol with use of the ONIOM (B3LYP/6-31G**:: AM1) approach,^{23c} whereas an activation energy barrier of 7.2 kcal/mol was predicted for the addition of oxycarbonylnitrene onto the sidewall of (5,5)-SWNCT with use of the ONIOM (B3LYP/6-31G*:: AM1) approach.^{23a} Although it is not reasonable to compare the absolute values calculated with different methods, it can be qualitatively concluded that the same nitrenes addition reactions are more facile on Si (100) and Ge (100) than those on fullerene and SWNCT. Indeed, the

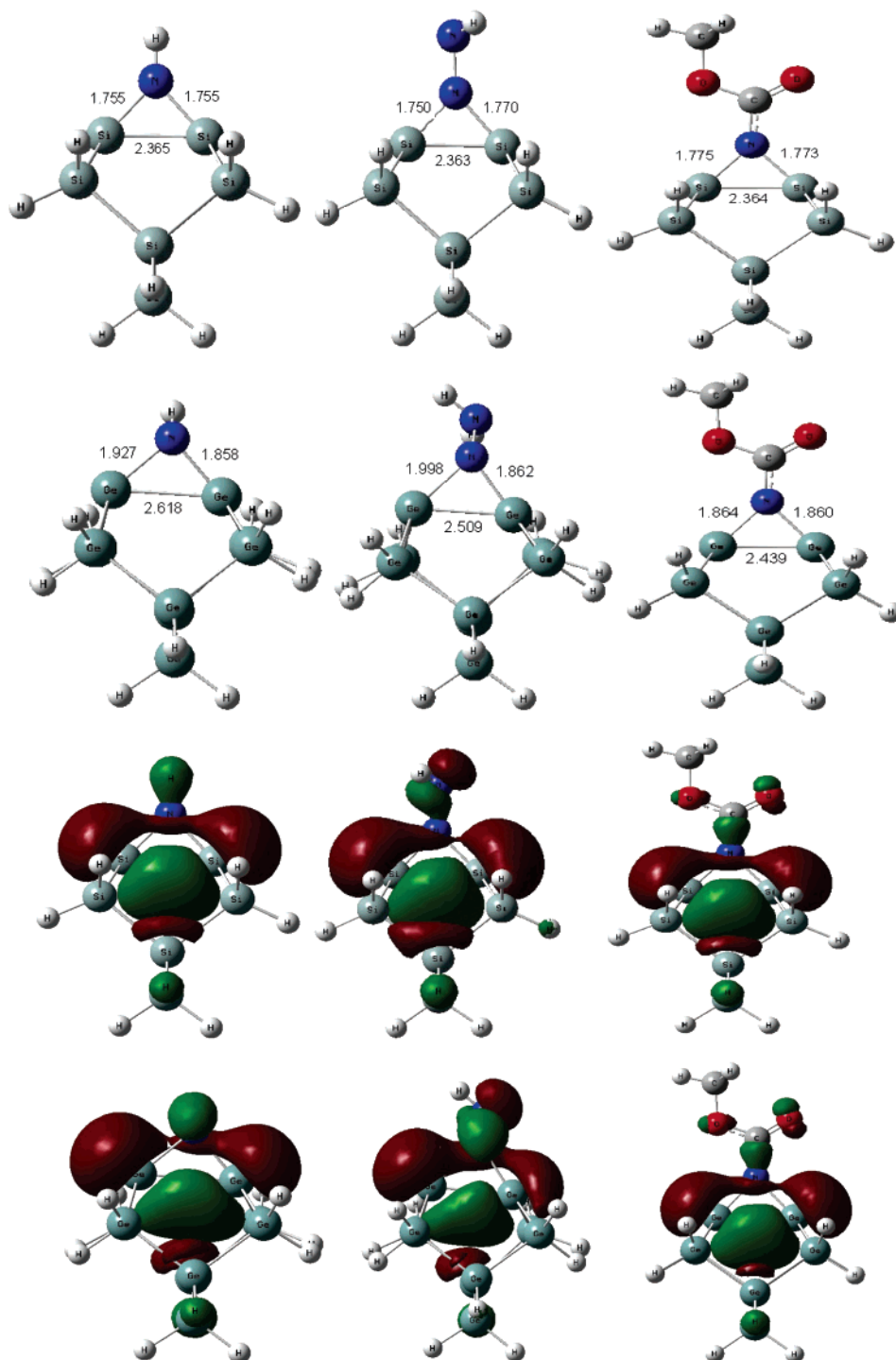


Figure 4. B3LYP/6-31G(d) optimized geometries (units in Å for bond length) for the additions of nitrene, aminonitrene, and oxycarbonylnitrene onto the Si (100) and Ge (100)-2 × 1 surfaces and their corresponding highest occupied molecular orbitals (HOMOs).

cycloaddition of nitrene, aminonitrene, and oxycarbonylnitrene onto diamond (100) has also been predicted to have no energy barrier.¹⁵ Single-point energy calculations using the higher basis set 6-311G(2d,2p) show that the basis set plays a minor effect on the calculated reaction energies for the additions of nitrene, aminonitrene, and oxycarbonylnitrene onto the Si (100) surface, whereas the error of ca. 6–13 kcal/mol exists in the calculated reaction energies for the additions onto Ge (100).

Figure 4 displays the optimized geometries of the products and their corresponding HOMOs. The HOMOs suggest the formation of chemical bonding between the nitrenes and the surface dimer. Noteworthy, the as-formed products have a three-membered aziridine-like structure that could be used as a

starting point for further chemical functionalizations, for example, by ring-opening with nucleophiles, elimination, or rearrangement.^{8,11} In this regard, the well-established synthetic methods for aziridine ring-opening can be adopted.¹¹ In addition, via the addition of nitrenes, a variety of different groups can also possibly be introduced which may lead to other new property profiles. For example, sidewall functionalizations of SWNCT by the addition of oxycarbonylnitrene allow for the covalent binding of many different functional groups, such as alkyl chains, aromatic groups, dendrimers, crown ethers, and oligoethylene glycol units. If a similar process could be experimentally achieved with regard to the Si (100) and Ge (100) surfaces, it would be quite interesting to construct organic/

inorganic films on the Si (100) and Ge (100) surfaces. In practice, nitrenes can be generated via the process of photolysis and thermolysis at moderate temperature.⁸ For instance, oxycarbonylnitrenes produced by the thermal decomposition of alkyl azidoformate precursors were successfully applied to the sidewall functionalization of SWNCT.^{13d}

The discussions shown above significantly suggest the feasibility that the famous addition reaction of carbenes and nitrenes to alkenes in organic chemistry can be employed as a new type of reaction to functionalize the Si (100) and Ge (100) surfaces. Owing to the high reactivity of carbenes, nitrenes, and the surface dimer of Si (100) and Ge (100), these surface reactions are predicted to be rather facile. So far, we are not aware of any experimental or theoretical work prior to the present one with regard to this type of reaction on the Si (100) and Ge (100) surfaces.

C. Implications for Other Theoretical Work. Alkenes, fullerene, SWNCT, and the (100) surfaces of diamond, Si, and Ge share the analogous bonding motif that can be depicted with a strong σ -bond and a weak π -bond and, accordingly, they show some similarity in chemistry. With the help of today's advanced experimental techniques, many old typical addition reactions with respect to alkenes in organic chemistry have successfully been realized regarding the functionalization of these solid material.^{3–6} Theoretically, motivated by this structure similarity in the chemical bonding motif, many predictions have been reported and some of them have been confirmed in subsequent experiments. These active promotions between experiment and theory strongly propel the rapid progress of current chemistry including developing new material to fulfill the specific purpose.

Note that disilenes, digermenes, silenes, and germenes²⁹ can also be seen as featuring the bonding motif analogous to that of alkenes, fullerene, SWNCT, and (100) of group IV semiconductors. However, analogous addition reactions of carbenes and nitrenes to alkenes have not been reported with regard to disilenes, digermenes, silenes, and germenes although it has been well-known that they are much more reactive than alkenes. Meanwhile, different from the planar structure of ethylene, disilenes, digermenes, silenes, and germenes have the trans-bending structure, making the detailed reaction mechanism different from that of alkenes for some well-known reactions.³⁰ In this respect, it is worthwhile to carry on theoretical work regarding the additions of carbenes and nitrenes to disilenes, digermenes, silenes, and germenes. This will certainly contribute to the richness of organosilicon and organogermanium chemistry and the understanding of the various facets of heavier molecular analogues of alkenes.³⁰ Theoretical predictions in this regard not only help us construct a logic framework to view factors determining the fundamental chemical properties of disilenes, digermenes, silenes, and germenes, but also provide the instructive information to experimentalists. Such a "bridged-like" theoretical study will result in abundant and interesting chemistry both in the theoretical domain and the experimental arena.

4. Concluding Remarks

In summary, we have predicted the viability that the well-known additions of carbenes and nitrenes to alkenes in organic chemistry can be employed as a new type of surface reaction to functionalize the Si (100) and Ge (100) surfaces. The as-formed cyclopropane-like or aziridine-like surface species would be subject to further chemical manipulations given the well-established cyclopropane or aziridine ring-opening chemistry. Our theoretical work provides another example that the surface of group IV semiconductors can be functionalized by synthetic

organic chemistry. This new type of surface reaction in combination with a wide variety of carbenes and nitrenes would offer versatile flexibility of constructing organic films on the Si (100) and Ge (100) surfaces at low temperature. To this end, further theoretical and experimental efforts are needed. Our theoretical predictions may open a new branch of chemistry in organic functionalizations of Si (100) and Ge (100). In broader perspective, this type of reaction can also be extended to react with the heavier molecular analogues of alkenes because disilenes, digermenes, silenes, and germenes feature the bonding motif similar to that of alkenes. Theoretical predictions in this regard will certainly enrich organosilicon and organogermanium chemistry.

Furthermore, our theoretical work significantly advances the concept of using organic reactions to functionalize the solid surface in a controlled manner and similar intriguing chemistry can exist in the material featuring an analogous bonding motif. We look forward to the experimental realization of the predictions herein as well as to the potential applications of as-functionalized semiconductor surfaces.

Acknowledgment. The support of the Natural Science Foundation of China is gratefully acknowledged.

References and Notes

- (1) (a) Cui, Y.; Wei, Q.; Park, H.; Lieber, C. M. *Science* **2001**, 293, 1289. (b) Yates, J. T., Jr. *Science* **1998**, 279, 335.
- (2) (a) Meyer zu Heringdorf, F. J.; Reuter, M. C.; Tromp, R. M. *Nature* **2001**, 412, 517. (b) Hamers, R. J. *Nature* **2001**, 412, 489. (c) Lopinski, G. P.; Wayner, D. D. M.; Wolkow, R. A. *Nature* **2000**, 406, 48. (d) Piva, P. G.; Dilabio, G. A.; Pitters, J. L.; Zikovsky, J.; Rezeq, M.; Dogel, S.; Hofer, W. A.; Wolkow, R. A. *Nature* **2005**, 435, 658.
- (3) For recent reviews, see: (a) Bent, S. F. *J. Phys. Chem. B* **2002**, 106, 2830. (b) Filler, M. A.; Bent, S. F. *Prof. Surf. Sci.* **2003**, 73, 1. (c) Bent, S. F. *Surf. Sci.* **2002**, 500, 879. (d) Waltenburg, H. N.; Yates, J. T., Jr. *Chem. Rev.* **1995**, 95, 1589. (e) Buriak, J. M. *Chem. Rev.* **2002**, 102, 1271. (f) Duke, C. B. *Chem. Rev.* **1996**, 96, 1237. (g) Hamers, R. J.; Wang, Y. *Chem. Rev.* **1996**, 96, 1261. (h) Hamers, R. J.; Coulter, S. K.; Ellison, M. D.; Hovis, J. S.; Padowitz, D. F.; Schwartz, M. P.; Greenlief, C. S.; Russell, J. N., Jr. *Acc. Chem. Res.* **2000**, 33, 617. (i) Wolkow, R. A. *Annu. Rev. Phys. Chem.* **1999**, 50, 413. (j) Buriak, J. M. *Chem. Commun.* **1999**, 1051. (k) Lu, X.; Lin, M. C. *Int. Rev. Phys. Chem.* **2002**, 21, 137. (l) Yoshinobu, J. *Prof. Surf. Sci.* **2004**, 77, 37. (m) Tao, F.; Xu, G. Q. *Acc. Chem. Res.* **2004**, 37, 882.
- (4) For example, see: (a) Barriocanal, J. A.; Doren, D. J. *J. Phys. Chem. B* **2000**, 104, 12269. (b) Lu, X.; Xu, X.; Wang, N.; Zhang, Q. *J. Phys. Chem. B* **2002**, 106, 5972. (c) Lu, X.; Xu, X.; Wang, N.; Zhang, Q. *J. Org. Chem.* **2002**, 67, 515. (d) Lu, X.; Fu, G.; Wang, N.; Zhang, Q.; Lin, M. C. *Chem. Phys. Lett.* **2003**, 371, 172. (e) Lu, X.; Fu, G.; Wang, N.; Zhang, Q.; Lin, M. C. *Chem. Phys. Lett.* **2001**, 343, 212. (f) Barriocanal, J. A.; Doren, D. J. *J. Vac. Sci. Technol. A* **2000**, 18, 1959.
- (5) For example, see: (a) Fitzgerald, D. R.; Doren, D. J. *J. Am. Chem. Soc.* **2000**, 122, 12334. (b) Okamoto, Y. *J. Phys. Chem. B* **2001**, 105, 1813. (c) Wang, G. T.; Bent, S. F.; Russell, J. N., Jr.; Butler, J. E.; D'Evelyn, M. P. *J. Am. Chem. Soc.* **2000**, 122, 744. (d) Konecny, R.; Doren, D. J. *J. Am. Chem. Soc.* **1997**, 119, 11098. (e) Teplyakov, A. V.; Kong, M. J.; Bent, S. F. *J. Am. Chem. Soc.* **1997**, 119, 11100. (f) Hovis, J. S.; Liu, H. B.; Hamers, R. J. *J. Phys. Chem. B* **1998**, 102, 6873. (g) Choi, C. H.; Gorden, M. S. *J. Am. Chem. Soc.* **1999**, 121, 11311. (h) Lu, X.; Xu, X.; Wang, N.; Zhang, Q.; Liu, M. C. *J. Phys. Chem. B* **2001**, 105, 10069. (i) Fink, A.; Menzel, D.; Widdra, W. *J. Phys. Chem. B* **2001**, 105, 3828. (j) Mui, C.; Bent, S. F.; Musgrave, C. B. *J. Phys. Chem. A* **2000**, 104, 2457. (k) Lee, S. W.; Nelen, L. N.; Ihm, H.; Scoggins, T.; Greenlief, C. M. *Surf. Sci.* **1998**, 410, L773. (l) Lu, X.; Zhu, M.; Wang, X.; Zhang, Q. *J. Phys. Chem. B* **2004**, 108, 4478. (m) Lu, X.; Wang, X.; Yuan, Q.; Zhang, Q. *J. Am. Chem. Soc.* **2003**, 125, 7923.
- (6) For example, see: (a) Lu, X. *J. Am. Chem. Soc.* **2003**, 125, 6384. (b) Lu, X.; Zhu, M.; Wang, X. *J. Phys. Chem. B* **2004**, 108, 7359. (c) Hovis, J. S.; Coulter, S. K.; Hamers, R. J.; D'Evelyn, M. P.; Russell, J. N.; Bulter, J. E. *J. Am. Chem. Soc.* **2000**, 122, 732. (d) Cho, J. H.; Kleinman, L. *Phys. Rev. B* **2003**, 67, 115314. (e) Liu, H.; Hamers, R. J. *J. Am. Chem. Soc.* **1997**, 119, 7593. (f) Miotto, R.; Ferraz, A. C.; Srivastava, G. P. *Surf. Sci.* **2002**, 507–510, 12. (g) Lopinski, G. P.; Moffatt, D. J.; Wayner, D. D. M.; Wolkow, R. A. *J. Am. Chem. Soc.* **2000**, 122, 3548. (h) Cho, J. H.; Kleinman, L. *Phys. Rev. B* **2001**, 64, 235420. (i) Lal, P.; Teplyakov, A. V.; Noah, Y.; Kong, M. J.; Wang, G. T.; Bent, S. F. *J. Chem. Phys.* **1999**, 110,

10545. (j) Lee, S. W.; Hovis, J. S.; Coulter, S. K.; Hamers, R. J.; Greenlief, C. M. *Surf. Sci.* **2000**, *464*, 6. (k) Fink, A.; Huber, R.; Widdra, W. J. *J. Chem. Phys.* **2001**, *115*, 2768. (l) Cho, J. H.; Kleinman, L. *Phys. Rev. B* **2003**, *68*, 195413.
- (7) (a) Wentrup, C. *Science* **2001**, *292*, 1846. (b) Wentrup, C. *Science* **2002**, *295*, 1846. (c) Kirmse, W. *Carbene Chemistry*; Academic Press: New York, 1971. (d) Bourissou, D.; Guerret, O.; Gabbai, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39. (e) Herrmann, W. A.; Köcher, C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2162. (f) Cheng, Y.; Meth-Cohn, O. *Chem. Rev.* **2004**, *104*, 2507. (g) Barlugenga, J. *Pure Appl. Chem.* **2002**, *74*, 1317.
- (8) (a) *Nitrenes*; Lwowski, W., Ed.; Wiley-Interscience: New York, 1970. (b) *Azides and Nitrenes*; Scriven, E. F. V. Ed.; Academic Press: New York, 1974. (c) Wentrup, C. *Reactive Intermediates*; Wiley: New York, 1984. (d) *Reactive Intermediate Chemistry*; Moss, R. A.; Platz, M. S.; Jones, M., Jr., Eds.; Wiley: New York, 2003.
- (9) (a) Krogh-Jespersen, K.; Yang, S.; Moss, R. A. *J. Am. Chem. Soc.* **1999**, *121*, 6269. (b) Moss, R. A. *Acc. Chem. Res.* **1980**, *13*, 58. (c) Moss, R. A. *Acc. Chem. Res.* **1989**, *22*, 15. (d) Hoffmann, R. *J. Am. Chem. Soc.* **1968**, *90*, 1475. (e) Rondon, N. G.; Houk, K. N.; Moss, R. A. *J. Am. Chem. Soc.* **1980**, *102*, 1770. (f) Doering, W. v. E.; Hoffmann, A. K. *J. Am. Chem. Soc.* **1954**, *76*, 6162. (g) Goumri-Magnet, S.; Kato, T.; Gornitzka, H.; Baceiredo, A.; Bertrand, G. *J. Am. Chem. Soc.* **2000**, *122*, 4464.
- (10) For reviews about cyclopropane chemistry, see: (a) Franz, A. K.; Woerpel, K. A. *Acc. Chem. Res.* **2000**, *33*, 813 and references therein. (b) de Meijere, A. *Chem. Rev.* **2003**, *103*, 931.
- (11) For reviews about aziridine chemistry, see: (a) Tanner, D. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 599. (b) Sweeney, *Chem. Soc. Rev.* **2002**, *31*, 247. (c) Muller, P.; Fruit, C. *Chem. Rev.* **2003**, *103*, 2905.
- (12) (a) Hirsch, A. *The chemistry of fullerenes*; Thieme: Stuttgart, Germany, 1994. (b) Holzinger, M.; Vostrowsky, O.; Hirsch, A.; Hennrich, F.; Kappes, M.; Weiss, R.; Jellen, F. *Angew. Chem., Int. Ed.* **2001**, *40*, 4002. (c) Diederich, F.; Issacs, L.; Philip, D. *Chem. Soc. Rev.* **1994**, *243*. (d) Smith, A. B., III; Tokuyama, H. *Tetrahedron* **1996**, *52*, 5257.
- (13) (a) Chen, J.; Hamon, M. A.; Hu, H.; Chen, Y.; Rao, A. M.; Eklund, P. C.; Haddon, R. C. *Science* **1998**, *282*, 95. (b) Kamaras, K.; Itkis, M. E.; Hu, H.; Zhao, B.; Haddon, R. C. *Science* **2003**, *301*, 1501. (c) Strano, M. S.; Dyke, C. A.; Usrey, M. L.; Barone, P. W.; Allen, M. J.; Shan, H.; Kittrell, C.; Hauge, R. H.; Tour, J. M.; Smalley, R. E. *Science* **2003**, *301*, 1519. (d) Hu, H.; Zhao, B.; Hamon, M. A.; Kamaras, K.; Itkis, M. E.; Haddon, R. C. *J. Am. Chem. Soc.* **2003**, *125*, 14893. (e) Chen, Z.; Nagase, S.; Hirsch, A.; Haddon, R. C.; Thiel, W.; Schleyer, P. v. R. *Angew. Chem., Int. Ed.* **2004**, *43*, 1552.
- (14) Xu, Y. J.; Zhang, Y. F.; Li, J. Q. *J. Org. Chem.* **2005**, *70*, 6089.
- (15) Xu, Y. J.; Zhang, Y. F.; Li, J. Q. *J. Org. Chem.* **2005**, *70*, 7773.
- (16) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. A* **1988**, *37*, 785.
- (17) (a) Pacchioni, G. *Surf. Rev. Lett.* **2000**, *7*, 277. (b) Xu, Y. J.; Li, J. Q.; Zhang, Y. F.; Chen, W. K. *J. Chem. Phys.* **2004**, *120*, 8753.
- (18) (a) Xu, X.; Kang, S. Y.; Yamabe, T. *Phys. Rev. Lett.* **2002**, *88*, 076106. (b) Xu, X.; Kang, S. Y.; Yamabe, T. *Chem. Eur. J.* **2002**, *8*, 5351.
- (19) (a) Konecny, R.; Doren, D. J. *J. Phys. Chem. B* **1997**, *101*, 10983. (b) Xu, Y. J.; Li, J. Q. *Appl. Surf. Sci.* **2005**, Sep. 8th web-online.
- (20) (a) Xu, X.; Nakatsuji, H.; Lu, X.; Ehara, M.; Cai, Y.; Wang, N. Q.; Zhang, Q. E. *Theor. Chem. Acc.* **1999**, *172*, 170. (b) Fu, G.; Xu, X.; Lu, X.; Wan, H. L. *J. Am. Chem. Soc.* **2005**, *127*, 3989.
- (21) (a) Xu, Y. J.; Li, J. Q. *Chem. Phys. Lett.* **2005**, *406*, 249. (b) Xu, Y. J.; Li, J. Q.; Zhang, Y. F.; Chen, W. K. *Surf. Sci.* **2003**, *525*, 13. (c) Xu, Y. J.; Li, J. Q. *Chem. Phys. Lett.* **2005**, *412*, 439. (d) Xu, Y. J.; Li, J. Q. *Chem. Phys. Lett.* **2004**, *400*, 406. (e) Xu, Y. J.; Li, J. Q.; Zhang, Y. F. *Surf. Rev. Lett.* **2003**, *10*, 691. (f) Xu, Y. J.; Zhang, Y. F.; Li, J. Q. *Chem. Phys.* **2005**, *315*, 267.
- (22) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*; Gaussian, Inc.: Pittsburgh, PA, 1998.
- (23) (a) Lu, X.; Tian, F.; Zhang, Q. *J. Phys. Chem. B* **2003**, *107*, 8388. (b) Chu, Y. Y.; Su, M. D. *Chem. Phys. Lett.* **2004**, *394*, 231. (c) Cases, M.; Duran, M.; Solá, M. *J. Mol. Model.* **2000**, *6*, 205.
- (24) (a) Al-Rubaiey, N.; Walsh, R. *J. Phys. Chem.* **1994**, *98*, 5303. (b) Sengupta, D.; Nguyen, M. T. *Mol. Phys.* **1996**, *89*, 1567. (c) Skancke, P. N.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1997**, *119*, 8012. (d) Becerra, R.; Bogdanov, S. E.; Egorov, M. P.; Faustov, V. E.; Promyslov, V. M.; Nefedov, O. M.; Walsh, R. *Phys. Chem. Chem. Phys.* **2002**, *4*, 5079.
- (25) (a) D'Evelyn, M. P.; Cohen, S. M.; Rouchouze, E.; Yang, Y. L. *J. Chem. Phys.* **1993**, *98*, 3560. (b) Doren, D. J. *Adv. Chem. Phys.* **1996**, *95*, 1.
- (26) Hukka, T. I.; Pakkanen, T. A.; D'Evelyn, M. P. *J. Phys. Chem.* **1994**, *98*, 12420.
- (27) Gasper, P. P.; Holten, D.; Konieczny, S.; Corey, J. Y. *Acc. Chem. Res.* **1987**, *20*, 329.
- (28) Zurawski, B.; Kutzelnigg, W. *J. Am. Chem. Soc.* **1978**, *100*, 2654.
- (29) For reviews about the heavier molecular analogues of alkenes, see: (a) Kira, M. *J. Organomet. Chem.* **2004**, *689*, 4475. (b) Raabe, G.; Michl, J. *Chem. Rev.* **1985**, *85*, 419. (c) West, R. *Pure Appl. Chem.* **1984**, *56*, 163. (d) Cowley, A. H.; Norman, N. C. *Prog. Inorg. Chem.* **1986**, *34*, 1. (e) Grev, R. S. *Adv. Organomet. Chem.* **1991**, *33*, 125. (f) Weidenburch, M. *Coord. Chem. Rev.* **1994**, *130*, 275. (g) Kira, M. *Pure Appl. Chem.* **2000**, *72*, 2333. (h) Power, P. P. *Chem. Rev.* **1999**, *99*, 3463. (i) Kira, M.; Iwamoto, T. *J. Organomet. Chem.* **2000**, *610*, 236.
- (30) For example, see: (a) Mosey, N. J.; Baines, K. M.; Woo, T. K. *J. Am. Chem. Soc.* **2002**, *124*, 13306. (b) Su, M. D. *J. Phys. Chem. A* **2004**, *108*, 823. (c) Su, M. D. *Inorg. Chem.* **2004**, *43*, 4846. (d) Kira, M.; Ishima, T.; Iwamoto, T.; Ichinohe, M. *J. Am. Chem. Soc.* **2001**, *123*, 1676.