Theoretical Studies of the Additions of Germylenes to Ethylene

Ming-Der Su* and San-Yan Chu*

Contribution from the Department of Chemistry, National Tsing Hua University, Hsinchu 30043, Taiwan, R.O.C.

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Abstract: Complete geometry optimizations were carried out using density functional theory to study the potential energy surfaces for cycloaddition of germylene to the C=C double bond of ethylene. The GeX_2 + C_2H_4 (GeX_2 = GeH_2, $Ge(CH_3)_2$, $Ge(NH_2)_2$, $Ge(OH)_2$, GeF_2, $GeCl_2$, $GeBr_2$, and Ge=CH_2) systems are the subject of the present study. All the stationary points were determined at the B3LYP/6-31G* level of theory. The major conclusions that can be drawn from this work are as follows: (i) In contrast to the case of the carbene additions, a π-complex intermediate is formed between germylene and ethylene, which should play a key role in subsequent polymerization. (ii) On the basis of the results of the present study, it is apparent that germylene cycloadditions occur in a concerted, asynchronous manner. (iii) Germacyclopropanes, unlike cyclopropanes, are quite unstable compounds, reverting thermally to their precursors and then polymerizing rapidly, or even reacting with a second molecule of olefin to yield a cyclic compound. (iv) Considering the effect of substitution at the germanium center, our theoretical findings suggest that the cycloaddition of germylene with electropositive and/or bulky substituents is feasible from both a kinetic and a thermodynamic viewpoint. In contrast, germylenes bearing electronegative and/or π-donating substituents will tend not to undergo cycloadditions. Note that this conclusion is based upon the assumption that three-membered-ring germacyclopropane is the unique end product for germylene additions. (v) The cycloadditions of germylenes to alkenes are more endothermic (or less exothermic) than the same reactions of carbenes, reflecting the weaker Ge−C vs C−C bond.

I. Introduction

The divalent carbon compounds known variously as methylene or carbenes (:CH_2) were, and still are, among the most fruitful in organic chemistry from both a mechanistic/theoretical and a preparative viewpoint. Perhaps the most important and characteristic reaction of a carbene is its addition to an olefin to form a cyclopropane. For the understanding of carbene addition reactions, the Skell−Woodworth hypothesis[1,2] has been quite elucidating. Singlet carbenes add to olefins with retention of stereochemistry, whereas a cis/trans mixture follows from addition of triplet carbenes to a sterically uniform olefin, via a biradical.[3,4]

Recently much attention has been directed toward the heavier carbene analogues, such as germylene (:GeX_2).[5,6] In fact, the chemistry of germylene, the third-row counterpart of carbene, has only begun to emerge in the past few years.[7] Although it has become clear that most, if not yet all, reactions of divalent carbon have their counterparts in germylene chemistry, our knowledge of these third-row species remains in a relatively primitive state. A wide variety of germylenes are known, and they display high reactivity toward a variety of organic compounds.[5,6] Unfortunately, the mechanistic basis of germylene chemistry is still poorly understood making many germylene reactions unreliable for synthetic planning, including even the reaction of germylenes with alkenes. For example, one of the best-studied germylenes, $GeCl_2$,[8] reacts with alkenes by an unknown mechanism to give a variety of organogermanium products, including an alkene−germylene copolymer.[9] The same

(1) Skell, P. S.; Woodworth, R. C. *J. Am. Chem. Soc.* **1956,** *78,* 4496.

(2) For reviews and pertinent references see: (a) Kirmse, W. *Carbene Chemistry,* 2nd ed.; Academic Press: New York, 1971. (b) Moss, R. A.; Jones, M., Jr. *Carbenes*; Wiley: New York, 1973; Vol. 1. (c) Jones, M., Jr.; Moss, R. A. *Carbenes*; Wiley: New York, 1975; Vol. 2. (d) Moss, R. A.; Jones, M., Jr. *Reactive Intermediates*; Wiley: New York, 1978; Vol. 1. (e) Moss, R. A.; Jones, M., Jr. *Reactive Intermediates*; Wiley: New York, 1981; Vol. 2. (f) Moss, R. A.; Jones, M., Jr. *Reactive Intermediates*; Wiley: New York, 1985; Vol. 3. (g) Abramovitch, R. A. *Reactive Intermediates*; Plenum: New York, 1980; Vol. 1. (h) Platz, M. S. *Kinetics And Spectroscopy of Carbenes And Biradicals*; Plenum: New York, 1990. (i) Moss, R. A. *Acc. Chem. Res.* **1980,** *13,* 58. (j) Moss, R. A. *Acc. Chem. Res.* **1989,** *22,* 15 and references therein.

(3) Although there is a substantially larger number of examples in which careful work gives results in accord with the Skell−Woodworth hypothesis, there are several examples of failure in the stereochemistry of carbene addition. In fact, the Skell−Woodworth hypothesis should be regarded as reasonable intuition rather than sound theory since there is no firm basis for the presumption that rotation about single bonds will necessarily be much more rapid than spin inversion. Indeed, it has been proved that spin inversion plays a central role in triplet carbene cycloaddition. For details see ref 4.

(4) Su, M.-D. *J. Phys. Chem.* **1996,** *100,* 4339.

(5) (a) Lesbre, M.; Mazerroles, P.; Satgé, J. *The Organic Compounds of Germanium*; Zinatne: Riga, 1990. (b) Lukevics, E.; Gar, T.; Ignatovich, L.; Mironov, B. *Biological Activity of Germanium*; Zinatne: Riga, 1993. (c) Lukevics, E.; Ignatovich, L. *Frontiers of Organogermanium−Tin−Lead Chemistry*; Latvian Institute: Riga, 1993. (d) Patai, S. *The Chemistry of Organin Germanium, Tin, and Lead Compounds*; Wiley: New York, 1995.

(6) (a) Neumann, W. P. *Chem. Rev.* **1991,** *91,* 311. (b) Riviere, P.; Riviere-Baudet, M.; Satgé, J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, U.K., 1982; Vol. 2, Chapter 10. (c) Riviere, P.; Riviere-Baudet, M.; Satgé, J. In *Comprehensive Organometallic Chemistry*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, U.K., 1995; Vol. 2, Chapter 5.

(7) (a) Su, M.-D.; Chu, S.-Y. *J. Am. Chem. Soc.* **1999,** *121,* 4229. (b) Su, M.-D.; Chu, S.-Y. *Inorg. Chem.* **1999,** *38,* 4819.

(8) (a) Hastie, J. W.; Hauge, R. H.; Margrave, J. L. *J. Mol. Spectrosc.* **1969,** *29,* 152. (b) Karolczak, J.; Zhuo, Q.; Clouthier, D. J.; Davis, W. M.; Goddard, J. D. *J. Chem. Phys.* **1993,** *98,* 60.

(9) Nefedov, O. M.; Kolesnikov, S. P. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1966,** 201.

phenomenon can also be found in the addition reaction of germylenes to acetylenic derivatives, which usually leads to either dimers or polymers.[10] On the contrary, the three-membered-ring cyclopropane and cyclopropene are the primary products of the carbene addition reactions with olefins and acetylenes, respectively.[2,11] Moreover, no estimates of the absolute activation energies of such additions are as yet available from experiments. The calculations of reaction pathways for germylene cycloadditions and the location and identification of the structures of the transition states is therefore of great theoretical interest. In fact, to our knowledge, until now no theoretical work has been devoted to the study of the reactivity of germylene with alkenes. It is surprising how little is known about the cycloadditions of germylenes to olefins, considering the importance of germylene in synthetic chemistry[5,6] and the extensive research activity on the corresponding carbene species.[2,11]

It is these unsolved problems that arouse our interest. The object of this study is thus to reach a more thorough understanding of germylene chemistry. To this end, we have now undertaken a systematic investigation of the addition reactions of several symmetrically substituted germylenes, GeH_2, $Ge(CH_3)_2$, GeF_2, $GeCl_2$, $GeBr_2$, $Ge(NH_2)_2$, $Ge(OH)_2$, and $GeCH_2$, to ethylene using the density functional theory (DFT). The reason for choosing these molecules as model systems for addition to C_2H_4 is because they have been detected experimentally and most of their spectroscopic and electronic properties have been studied experimentally in some detail.[7] Through this theoretical study, we hope to (a) obtain a detailed understanding of the reactivity of a variety of germylenes toward the C=C double bond of ethylene, (b) investigate the influence of different substituted groups upon the geometries and energies of the intermediates as well as the transition states, (c) predict the trends in activation energies and reaction enthalpies, (d) probe electronic effects on the reactivities in a series of disubstituted germylenes, and (e) highlight the factors which control the activation barrier to germylene cycloadditions.

II. Theoretical Methods

All the calculations reported herein were performed using the Gaussian 94 set of programs.[12] The structures of critical points were located through geometry optimizations at the DFT level using the 6-31G* basis set.[13] The DFT calculations used the Gaussian 94 implementation of Becke's three-term hybrid functional (B3)[14] and the Lee, Yang, and Parr (LYP)[15] correlation functional with nonlocal corrections to both exchange and correlation functionals. The resulting exchange-correlation functionals are referred to in the text as B3LYP, which has been shown to be quite reliable for both geometries and

(10) Satgé, J.; Massol, M.; Riviére, P. *J. Organomet. Chem.* **1973**, *56*, 1 and pertinent references therein.

(11) (a) Zurawski, B.; Kutzelnigg, W. *J. Am. Chem. Soc.* **1978**, *100*, 2654. (b) Rondan, N. G.; Houk, K. N.; Moss, R. A. *J. Am. Chem. Soc.* **1980**, *102*, 1770.

(12) Gaussian 94: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Peterson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian, Inc.: Pittsburgh, PA, 1995.

(13) (a) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257. (b) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

(14) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(15) (a) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785. (b) Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. *Chem. Phys. Lett.* **1989**, *157*, 200.

energies.[16] All geometry optimizations met the default convergence criteria given in Gaussian 94.[12] All DFT calculations were performed using the default grid size given in Gaussian 94.[12] Moreover, all geometries were fully optimized without imposing any symmetry constraints, although in some instances the resulting structure showed various elements of symmetry. The stationary points on the potential energy surface were characterized by calculation of vibrational frequencies at the B3LYP/6-31G* level.

III. The Electronic Structure of X_2Ge: + $H_2C=CH_2$

The vast majority of theoretical studies have been devoted to the analysis of the addition reaction of singlet carbene.[2,11] We shall apply the same theoretical model to the germylenic systems. The addition of a singlet germylene to an ethylene involves simultaneous interactions of the vacant germylenic p orbital (LUMO) with the filled ethylene π orbital (HOMO) and of the filled germylenic σ orbital (HOMO) with the vacant ethylene π^* orbital (LUMO). Although a singlet germylene is inherently both an electrophile and a nucleophile, its behavior here is determined by the electron distribution in the transition state. This, in turn, depends on whether the $LUMO_{germylene}$/$HOMO_{ethylene}$ or $HOMO_{germylene}$/$LUMO_{ethylene}$ interaction is stronger in this state (vide infra). Moreover, according to Hoffmann's work[17] there are two possible routes of approach of a germylene to an olefin as shown in **1** and **2**. The π approach **1** (nonleast motion), with the p orbital of the germylene impinging on the π system of the alkene, has only one plane of symmetry, making this reaction symmetry allowed. On the other hand, **2** gives the most symmetrical transition state and has been called the σ approach (least motion) because the σ orbital of the germylene impinges on the ethylene π system. Hoffmann has pointed out that the σ approach (**2**) is "forbidden" in terms of the conservation of orbital symmetry and is therefore expected to be high in energy.[17] On this basis, the preferred approach should be the π approach (**1**), in which the filled π MO interacts with the empty p orbital of the germylene. Our calculations support this prediction which will be shown in a later section.


(π approach)   (σ approach)
      1   **2**
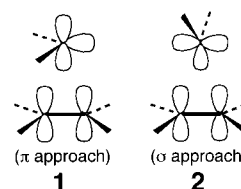
IV. The Geometries and Energetics of X_2Ge: + $H_2C=CH_2$

In this section the results for four regions on the potential energy surfaces will be presented: a disubstituted germylene plus free ethylene, the precursor complex (PC), the transition state (TS), and the cycloaddition product (CP). The fully optimized geometries for those stationary points calculated at the B3LYP/6-31G* level are given in Figures 1−4, respectively. The relative energies at the same level of theory are collected in Table 1.

A. Reactants. By analogy with all known carbenes, there are two low-lying electronic states of germylene. One is the triplet state with one electron in an in-plane σ orbital and one in an orthogonal p orbital. This state is designated $^3A''$. The other is the singlet state with two electrons in a nonbonding σ orbital designated $^1A'$. There is general agreement that ger-

(16) (a) Su, M.-D.; Chu, S.-Y. *J. Phys. Chem.* In press, and references therein. (b) Lin, C.-L.; Su, M.-D.; Chu, S.-Y. *Chem. Commun.* **1999**, 2383.
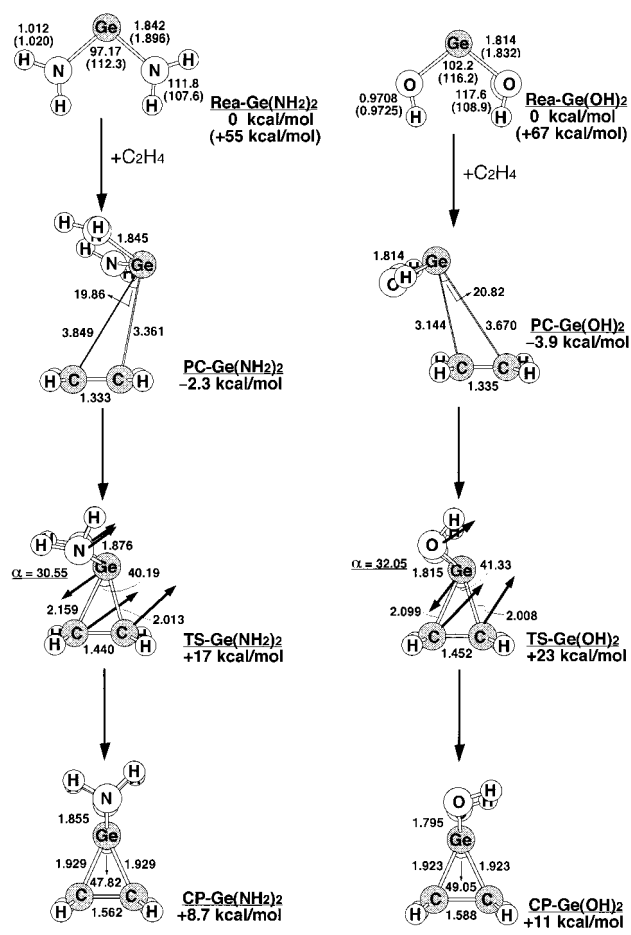
(17) Hoffmann, R. *J. Am. Chem. Soc.* **1968**, *90*, 1475.
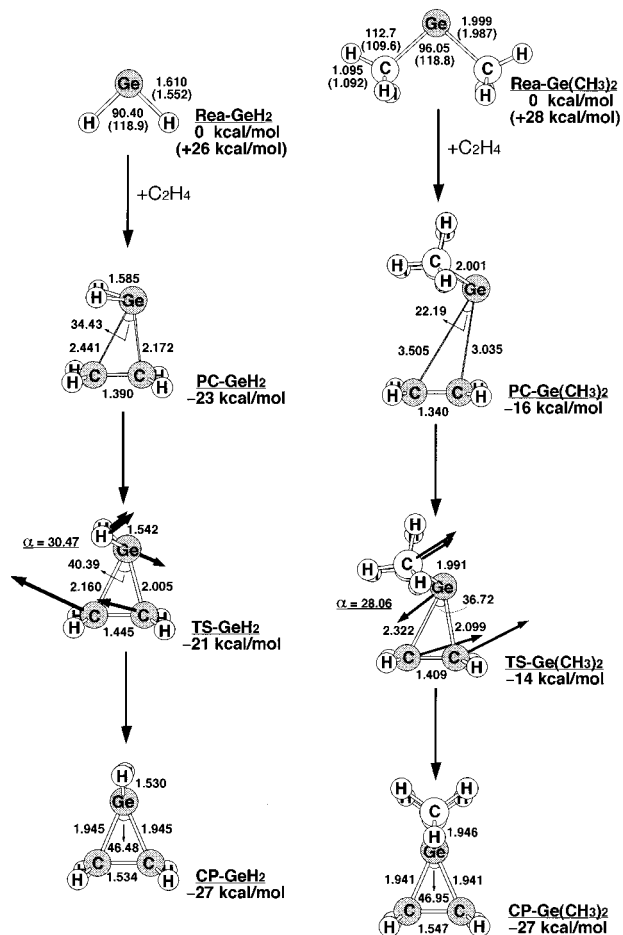
Figure 1. B3LYP/6-31G* optimized geometries (in Å and deg) of the reactants (singlet and triplet), precursor complexes (PC), transition states (TS), and cycloaddition products (CP) of GeH_2 and $Ge(CH_3)_2$. Values in parentheses are at the triplet state. For the definition of α see the text. The heavy arrows indicate the main atomic motions in the transition state eigenvector.

Figure 2. B3LYP/6-31G* optimized geometries (in Å and deg) of the reactants (singlet and triplet), precursor complexes (PC), transition states (TS), and cycloaddition products (CP) of $Ge(NH_2)_2$ and $Ge(OH)_2$. Values in parentheses are at the triplet state. For the definition of α see the text. The heavy arrows indicate the main atomic motions in the transition state eigenvector.

mylenes, unlike most carbenes, will have singlet ground states.[7,18] Indeed, our DFT calculations suggest that for the germylenes studied in this work the singlet $^1A'$ state is much more stable in energy than the triplet $^3A''$ state by 26−82 kcal/mol. This implies that addition will probably proceed with retention of stereochemistry as it does for singlet carbenes (vide infra).

As can be seen in Figures 1−4, theoretical investigation of the substituted germylenes (GeX_2) shows that the equilibrium value of the bond angle (∠XGeX) is much larger in the excited $^3A''$ state than in the $^1A'$ state. This result is in good accord with our previous theoretical findings.[7] Moreover, one of the germylene properties that has attracted a great deal of experimental and theoretical interest is its singlet−triplet separation. Perusal of the data in Table 1 reveals several interesting trends. The most obvious trend is that electropositive, π-accepting or bulky substituents lower the singlet−triplet energy gap, whereas strongly electron-withdrawing or π-donating substituents raise this energy gap. In addition, there is a very clear trend toward increasing singlet−triplet splitting as substituents go from left to right along a given row. For instance, the singlet−triplet energy gap increases in the following order: $Ge(CH_3)_2$ (28 kcal/mol) < $Ge(NH_2)_2$ (55 kcal/mol) < $Ge(OH)_2$ (67 kcal/mol) <

GeF_2 (82 kcal/mol). Additionally, as in the case of the carbene species, the singlet−triplet splitting increases as the electronegativity of the substituents is increased. For example, GeF_2 (82 kcal/mol) > $GeCl_2$ (63 kcal/mol) > $GeBr_2$ (56 kcal/mol). In the case of germylidene ($GeCH_2$), the simplest unsaturated germylene, the B3LYP/6-31G* theory finds that its $^1A'$ state is lower in energy than the $^3A''$ state by 57 kcal/mol,[19] which is in good agreement with our previous work.[7]

Finally, as discussed above, the aforementioned eight germylenes all possess singlet states with large singlet−triplet energy gaps (ca. 26−82 kcal/mol). This suggests that the size of the singlet−triplet energy separation renders the production of the first excited triplet state practically impossible under the experimental conditions. Thus, only the reactions of the singlet state are considered throughout this work.

B. Precursor Complexes. The geometries and energies of complexation of germylene with ethylene, i.e., **PC−GeH₂**, **PC−Ge(CH₃)₂**, **PC−Ge(NH₂)₂**, **PC−Ge(OH)₂**, **PC−GeF₂**, **PC−GeCl₂**, **PC−GeBr₂**, and **PC−GeCH₂**, were also calculated. The optimized geometries are shown in Figures 1−4. For convenience, the energies are given relative to the reactant molecules (GeX_2 + C_2H_4) which are also listed in Table 1.

Calculated vibrational frequencies for the precursor complexes reveal that these structures are true minima on the potential

(18) Köcher, J.; Lehnig, M.; Neumann, W. P. *Organometallics* **1988**, *7*, 1201.

(19) Harper, W. W.; Ferrall, E. A.; Hilliard, R. K.; Stogner, S. M.; Grev, R. S.; Clouthier, D. J. *J. Am. Chem. Soc.* **1997**, *119*, 8361.
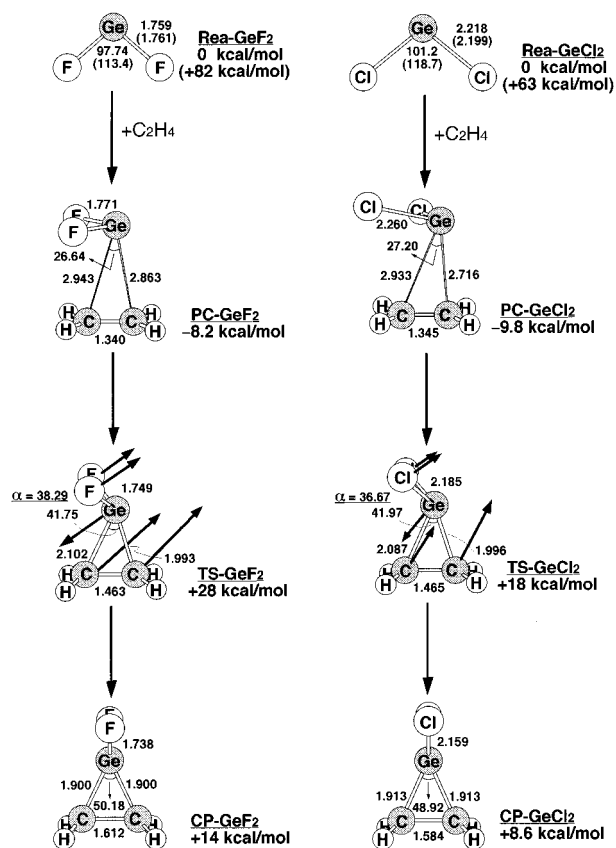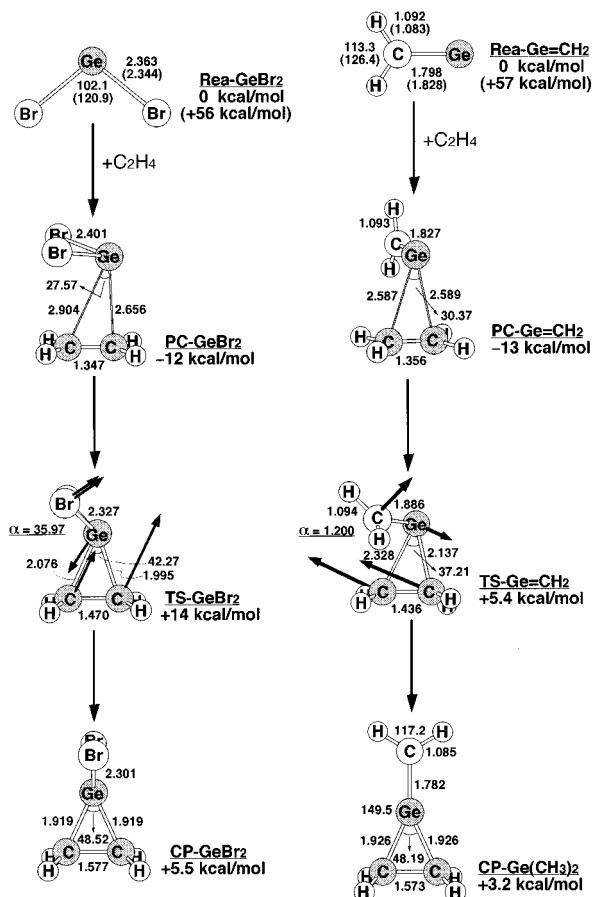
Figure 3. B3LYP/6-31G* optimized geometries (in Å and deg) of the reactants (singlet and triplet), precursor complexes (PC), transition states (TS), and cycloaddition products (CP) of GeF_2 and $GeCl_2$. Values in parentheses are at the triplet state. For the definition of α see the text. The heavy arrows indicate the main atomic motions in the transition state eigenvector.

energy surface. Since the germylene plus ethylene reaction leads to a three-membered-ring product as expected for a 1,2-addition, it is reasonable to assume a parallel plane approach of germylene to ethylene in the formation of the π-complex. As will be shown below, the parallel plane orientation of the reacting molecules is maintained along this reaction coordinate.

As one can see from Figures 1−4, each complex consists of a slightly distorted germylene arranged in a plane approximately parallel to that of the essentially undistorted ethylene. Additionally, the calculations indicate that the germylene approach to ethylene is off-center. The substituents of germylene are oriented in such a way that they point outward across the ethylene face. In all of the precursor complexes, germylene (GeX_2) is not disposed symmetrically with respect to the ethylene molecule, having two different Ge−C bond distances (i.e., one longer and one shorter, see below). It should be noted that the average Ge−C distances in the π-complex are calculated to be ∼2.2− 3.8 Å, which are, in turn, reflected in the calculated complexation energy. Namely, the longer the Ge−C distances, the smaller the binding energy of the π-complex. For instance, the DFT results predict that the Ge−C distance increases in the following order: **PC−GeH₂** (∼2.3 Å) < **PC−GeF₂** (∼2.9 Å) < **PC−Ge(OH)₂** (∼3.4 Å) < **PC−Ge(NH₂)₂** (∼3.6 Å). The binding energies relative to their corresponding reactants follow the same trend as the Ge−C distance described above: **PC− GeH₂** (−23 kcal/mol) < **PC−GeF₂** (−8.2 kcal/mol) < **PC− Ge(OH)₂** (−3.9 kcal/mol) < **PC−Ge(NH₂)₂** (−2.3 kcal/mol).

Furthermore, of the eight precursor complexes, **PC−GeH₂** is the most stable, being calculated as 23 kcal/mol lower in

Figure 4. B3LYP/6-31G* optimized geometries (in Å and deg) of the reactants (singlet and triplet), precursor complexes (PC), transition states (TS), and cycloaddition products (CP) of $GeBr_2$ and $Ge=CH_2$. Values in parentheses are at the triplet state. For the definition of α see the text. The heavy arrows indicate the main atomic motions in the transition state eigenvector.

Table 1. Relative Energies (kcal/mol) for Singlet and Triplet GeX_2 Species and for the Process $GeX_2 + H_2C=CH_2 \rightarrow$ Precursor Complex $\rightarrow$ Transition State $\rightarrow$ Product[a,b]

system	ΔE_{st}[c]	reactants	ΔE_{cpx}[d]	$\Delta E^{\ddagger}$[e]	ΔH[f]
GeH_2	+26.4	0	−23.5	−21.5	−27.4
$Ge(CH_3)_2$	+28.6	0	−15.6	−14.2	−27.3
$Ge(NH_2)_2$	+55.8	0	−2.34	+16.8	+8.67
$Ge(OH)_2$	+67.4	0	−3.89	+23.3	+11.4
GeF_2	+82.4	0	−8.15	+27.9	+13.8
$GeCl_2$	+62.6	0	−9.82	+18.2	+8.57
$GeBr_2$	+55.8	0	−11.8	+13.5	+5.51
$GeCH_2$	+57.5	0	−12.6	+5.44	+3.19

[a] At the B3LYP/6-31G* level. [b] All optimized geometries can be found in Figures 1−4. [c] A positive value indicates a singlet ground state. [d] The stabilization energy of the precursor complex, relative to its corresponding reactants. [e] The activation energy of the transition state, relative to its corresponding reactants. [f] The reaction enthalpy of the product, relative to its corresponding reactants.

energy than the corresponding reactants, followed by **PC− Ge(CH₃)₂** and **PC−GeCH₂** with the complexation energies of 16 and 13 kcal/mol, respectively. However, their activation energy (relative to its corresponding precursor complex) for the process is GeH₂ (2.0 kcal/mol) < Ge(CH₃)₂ (1.4 kcal/mol) < GeCH₂ (18 kcal/mol). Both **PC−Ge(OH)₂** and **PC−Ge(NH₂)₂** complexes reside in fairly shallow minima as shown by complexation energies of 2.3 and 3.9 kcal/mol, and activation energies of the cycloaddition of 27 and 19 kcal/mol, respectively. According to these theoretical results, it is therefore anticipated

that experimental observations of these GeX_2 π-complexes formed during the reactions should be very difficult, since the interaction between the substituted germylene and ethylene is very weak, giving loosely bound π-complex.

On the other hand, as demonstrated in Table 1, the energetic ordering of the addition of halogen-substituted germylene to ethylene shows that the activation energy (relative to its corresponding precursor complex) for the process is $GeBr_2$ (25 kcal/mol) < $GeCl_2$ (28 kcal/mol) < GeF_2 (36 kcal/mol). In addition, the stabilization energy of the precursor complex decreases in the following order: $GeBr_2$ (12 kcal/mol) > $GeCl_2$ (10 kcal/mol) > GeF_2 (8.1 kcal/mol). From these theoretical results, it seems possible to conclude that halogened substituents on the germylene lead to a weakly bound germylene−alkene complex, and that the π-complex might be observable in gas-phase germylene/ethylene reaction mixtures at low temperature. This phenomenon of germylene additions is different from that in the corresponding carbene additions, in which stable carbene−alkene complexes, in particular complexes between CCl_2 and ethylene and tetramethylethylene, do not exist.[20]

C. Transition States. We have located the transition state for each substituted germylene (**TS−GeH₂**, **TS−Ge(CH₃)₂**, **TS−Ge(NH₂)₂**, **TS−Ge(OH)₂**, **TS−GeF₂**, **TS−GeCl₂**, **TS−GeBr₂**, and **TS−GeCH₂**) at the B3LYP/6-31G* level of theory. The optimized geometries of the eight transition states can be found in Figures 1−4, respectively, along with the imaginary frequency eigenvector. One can observe that the main components of the transition vector correspond to the displacement of the germylene toward the alkene, whose eigenvalue gives an imaginary frequency of 349i (**TS−GeH₂**), 178i (**TS−Ge(CH₃)₂**), 241i (**TS−Ge(NH₂)₂**), 324i (**TS−Ge(OH)₂**), 425i (**TS−GeF₂**), 299i (**TS−GeCl₂**), 252i (**TS−GeBr₂**), and 402i cm⁻¹ (**TS−GeCH₂**). Also, as one can observe in Figures 1−4, the approach between the two reactants is accompanied by a progressive rotation of germylene. As indicated by components of the transition vectors, germylene has already begun to rotate to adopt the position it has in the cycloaddition product.

Moreover, the transition states of all the reactions investigated, shown in Figures 1−4, have a common structure, in which germylene is slightly off-center. For convenience, we define the geometrical variables as indicated in **3** in our study of the cycloadditions of substituted germylenes. From Figures 1−4, it is readily seen that, in all of the TS structures, the germanium atom in germylene is initially bonded to only one of the carbon atoms in ethylene, i.e., $r_1 \neq r_2$. This means that the mechanism of the singlet germylene addition to ethylene is the asynchronous one. A similar asynchronous approach had previously been found for the addition to ethylene in free methylene.[11]

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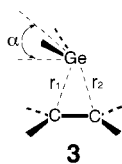
In addition, a characteristic of the transition states of the reaction involving addition to an ethylene, which might be sensitive to the "philicity" of the germylene, is the angle of inclination of the germylene plane relative to the plane of the

double bond (see **3**). According to Moss, Houk, and co-workers,[2i,j] one can assume that germylenes for which the angle α is less than 45° in the transition states of the reaction involving addition to ethylene are electrophilic. The angles $\alpha > 50°$ correspond to nucleophilic germylenes. The range $45° < \alpha < 50°$ corresponds to ambiphilic germylenes. In the extreme, the angle α would be expected to be 0° for a pure electrophilic interaction (π approach, **1**) and 90° for a pure nucleophilic interaction (σ approach, **2**). The B3LYP calculations demonstrate that all the TSs studied in this work have α of less than 45° ($\sim$1.2−38°) as shown in Figures 1−4. This suggests that singlet germylenes exhibit electrophilic character in the addition reactions with an alkene, and that the internal pathway in the mutual approach of the reactants is predominantly a π approach. Thus, our calculations support the predictions, as mentioned earlier, that the germylene avoids forbiddenness by a π approach, rather than by a σ approach.

The activation barriers for the addition reactions are presented in Table 1. It is clear that the transition structures for **TS−GeH₂** and **TS−Ge(CH₃)₂** cycloadditions are lower in energy than the energy of the reactants. Thus, no net barrier to reaction exists, and a "negative" activation energy is predicted at the DFT level. In contrast, it was found that electronegative and/or π-donating substitution has a large effect on the addition barriers. For instance, the energy of the transition state relative to its corresponding reactants, at B3LYP/6-311G*, is predicted to be the following (kcal/mol): 17, 23, 28, 18, 13, and 5.4 for **TS−Ge(NH₂)₂**, **TS−GeF₂**, **TS−GeCl₂**, **TS−GeBr₂**, and **TS−GeCH₂**, respectively, and −21 and −14 for **TS−GeH₂** and **TS−Ge(CH₃)₂**, respectively. In other words, GeH_2 and $Ge(CH_3)_2$ species may readily undergo addition reactions with alkenes, while others may not have enough energy to overcome the barrier to cycloaddition. In fact, in the literature there exist a number of examples of "negative" avtivation energies in organic as well as organometallic reactions.[21,22] The previous theoretical findings suggest that it might be the depth of the precursor complex potential well that determines whether the barrier lies above or below the reactant threshold. Deepening the well of the π-complex can lower the barrier to reaction to below the energy of the reactants.[23] This is what we observed for GeH_2 and $Ge(CH_3)_2$ additions, in which the stable complexes with substantial binding energies (−23 and −16 kcal/mol, respectively) are predicted, leading to a so-called "negative" activation energy. Consequently, it is reasonable to conclude that electron-withdrawing groups (or π-donating groups) on the germylene increase the activation barrier of addition, whereas electron-donating groups (or π-accepting groups) on the germylene accelerate the addition reaction.
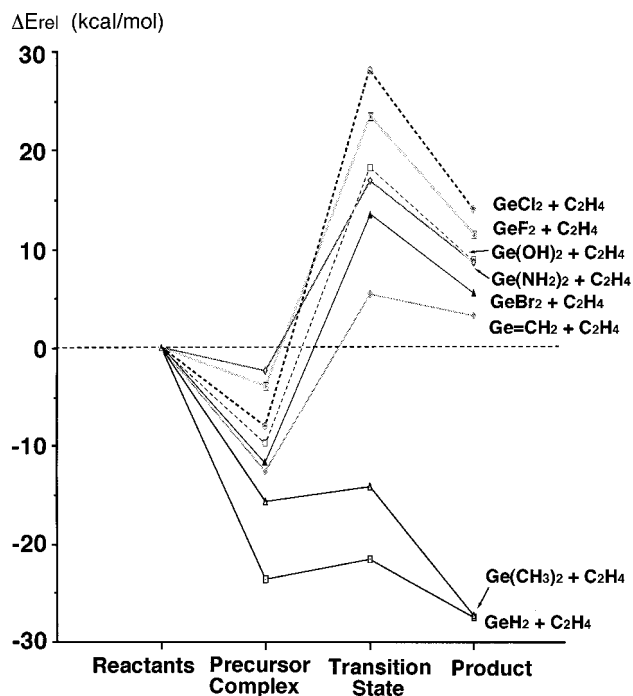
D. Cycloaddition Products. The B3LYP/6-31G* geometries of the cycloaddition products (**CP−GeH₂**, **CP−Ge(CH₃)₂**, **CP−Ge(NH₂)₂**, **CP−Ge(OH)₂**, **CP−GeF₂**, **CP−GeCl₂**, **CP−GeBr₂**, and **CP−GeCH₂**) considered in this work are displayed in Figures 1−4, respectively. To simplify comparisons and to emphasize the trends, the calculated reaction enthalpies for addition are also collected in Table 1. The results for the

(20) (a) Houk, K. N.; Rondan, N. G.; Mareda, J. *Tetrahedron* **1985**, *41*, 1555. (b) Houk, K. N.; Rondan, N. G.; Mareda, J. *J. Am. Chem. Soc.* **1984**, *106*, 4291. (c) Blake, J. F.; Wierschke, S. G.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1989**, *111*, 1919. (d) Keating, A. E.; Garcia-Garibay, M. A.; Houk, K. N. *J. Am. Chem. Soc.* **1997**, *119*, 10805. (e) Moss, R. A.; Yan, S.; Krogh-Jespersen, K. *J. Am. Chem. Soc.* **1998**, *120*, 1088.

(21) Isaacs, N. S. *Physical Organic Chemistry*; Wiley: New York, 1995.
(22) (a) Crabtree, R. H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 789. (b) Schroder, D.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1937. (c) Amdtsen, B. A.; Bergman, R. G.; Mobley, T. A.; Peterson, T. H. *Acc. Chem. Res.* **1995**, *28*, 154. (d) Su, M.-D.; Chu, S.-Y. *J. Am. Chem. Soc.* **1997**, *119*, 10178. (e) Su, M.-D.; Chu, S.-Y. *Chem. Eur. J.* **1999**, *5*, 198. (f) Su, M.-D.; Chu, S.-Y. *J. Am. Chem. Soc.* **1999**, *121*, 1045.

(23) Nevertheless, in this respect the theoretical studies of Houk et al. are of interest. Using an ab initio technique these workers have found that for certain systems, interaction of carbene and alkene is sufficiently strong so that there is no enthalpic barrier to product formation, and that no potential energy minimum exists for a complex. For details see ref 17.

ΔE_rel (kcal/mol)

Figure 5. Potential energy surfaces for the cycloadditions of various germylenes to ethylene. The relative energies are taken from the B3LYP/6-31G* level as given in Table 1. For the B3LYP optimized structures of the stationary points see Figures 1–4.

cycloaddition products of the germylene addition might perhaps be one of the most interesting results of the present study since very little is known about their geometrical and energetic properties.

The expected products of the addition reactions of germylenes with ethylene are the three-membered ring germacyclopropanes, the heavier analogues of cyclopropane. Experimental structures for those cyclic compounds are not to our knowledge known. Our theoretical estimates of the Ge–C bond length lie in the range of 1.90–1.94 Å, which is somwhat shorter than that of other Ge–C bonds (1.98 Å) in the crystal structure of Me₃Ge–CH₃.[6b]

A particularly noticeable feature of germacyclopropane is its position on the reaction path. For the addition reactions of germylene bearing electron-withdrawing substituents, the activation barrier and the energy difference between reactants and products is 13–28 and 5.5–14 kcal/mol, respectively, as determined using the B3LYP/6-31G* calculations. This indicates that this type of reaction is energetically very unfavorable and would be quite endothermic. In the case of germylidene, the addition barrier and the energy difference between reactants and product are 5.4 and 3.2 kcal/mol, respectively, again indicating this addition reaction is kinetically unstable, and that, if it did occur, the reaction would be endothermic as opposed to the exothermic results for GeH₂ and Ge(CH₃)₂ species (vide infra). Unlike the carbene addition reaction, whose primary product is cyclopropane, the high endothermicity of germacyclopropane on the surface is certainly related to its structural rigidity. Germacyclopropane possesses a rigid, planar three-membered ring, exhibiting a high ring strain.[24] Besides this, the extreme difference between the atomic radius of carbon and that of germanium is reflected in a longer bond length and a lower bond strength for the Ge–C bond than for the C–C bond. Both of these effects tend to make it difficult for such germylene

additions to produce the germacyclopropane. Moreover, the inverse of the germylene addition reaction, the elimination of germylene from germacyclopropane (right to left in Figure 5), is endothermic by 8.1, 12, 14, 9.7, 8.0, and 2.2 kcal/mol for Ge(NH₂)₂, Ge(OH)₂, GeF₂, GeCl₂, GeBr₂, and GeCH₂, respectively. Accordingly, although it seems likely that the three-membered germacyclopropanes are the end products of these addition reactions, they ought to be too unstable to be characterized experimentally. Our theoretical findings are consistent with the experimental observations.[6,9,10,25] Experimental studies which have previously relied on end product analysis techniques indicate that the product germacyclopropanes have not yet been detected either in gas phase or in solution (vide infra).

On the other hand, at the B3LYP/6-31G* level, all the stationary points (PC, TS, and CP) for both GeH₂ and Ge(CH₃)₂ cycloadditions have energies that are lower than those of the reactants. This indicates both GeH₂ and Ge(CH₃)₂ add to the C=C double bond of ethylene to give the π-complex and germacyclopropane in a reversible reaction (see **4**). In other words, there exists an equilibrium between the π-complex and heterocyclic product for both GeH₂ and Ge(CH₃)₂ additions. It has to be emphasized again that, as noted earlier, all the π-complex intermediates have one longer (weaker) and one shorter (stronger) Ge–C bond distance.

4
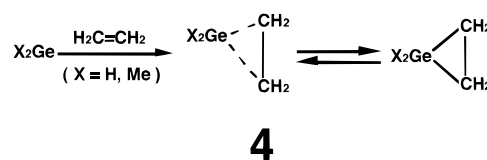
The supporting evidence comes from the fact that free Ge(CH₃)₂ gives cycloaddition with 2 mol of α-substituted styrene. A two-step mechanism involving 1:1 adduct, as indicated in **5**, was postulated by Neumann and Köcher.[26] They suggested that it should have one stronger Ge–C bond, the Ge–CH₂ bond, and one weaker, the Ge–benzyl bond, ready for the insertion of the second molecule of olefin, thus causing the regiospecificity of the overall reaction. In addition, no acyclic diradical intermediates have been observed. As a consequence, our theoretical results provide strong support for the existence of π-complex intermediate, which intervenes in the cyclo-addition process before the full Ge–C bond formation occurs.


5
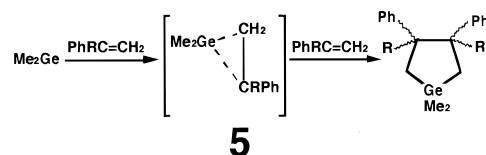
For clarity, the potential energy profiles based on the data in Table 1 are summarized in Figure 5. As seen in Figure 5, our DFT calculations suggest that no stable three-membered ger-macyclopropanes are formed between alkene and germylenes, in agreement with the experimental findings,[9] while a potential energy minimum may exist for a π-complex. This strongly implies that the existence of the π-complex should play a key role in such germylene additions. In fact, it was experimentally found that germylenes react with ethylene and various substi-tuted ethylenic compounds with the formation of organoger-manium polymers. For instance, interaction of GeCl₂ with CH₂=CHCl and CH₂=CCl₂ gave exclusively polymers of the

(24) Isaacs, N. S. *Physical Organic Chemistry*; Wiley: New York, 1995; p 346.

(25) Becerra, R.; Boganov, S. E.; Egorov, M. P.; Lee, V. Y.; Nefedov, O. M.; Walsh, R. *Chem. Phys. Lett.* **1996**, *250*, 111.

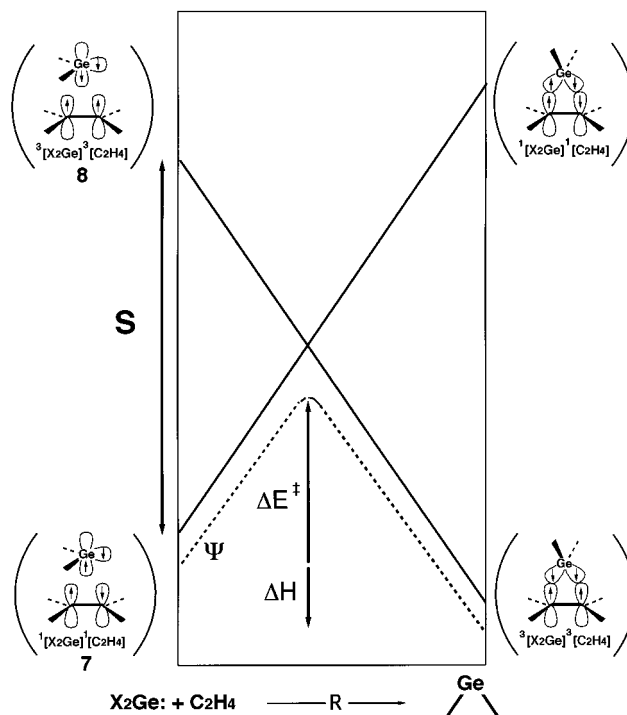(26) Köcher, J.; Neumann, N. P. *Organometallics* **1985**, *4*, 400.

structure $[(CH_2CHR)_mGeCl_2]_n$, where R = H or Cl and $m \approx$ 2.[10] Also, $GeBr_2$ formed a polymer $[CH_2CH_2GeBr_2]_n$, with $CH_2=CH_2$.[10] Many interesting examples can be found in refs 6 and 10. According to our theoretical results, these reactions may be rationalized in terms of initial formation of a weakly bound π-complex, which polymerizes. Indeed, the structure of the π-complex implies that the longer Ge−C bond of the incipient three-membered ring can break when the intermediate rearranges to an acyclic polymer. See **6**. Certainly, to obtain a better understanding of mechanisms of such a germylene/alkene polymerization requires further computational studies as well as experiments. Such studies, however, are beyond the scope of the present work.

R = H, Cl, CH₂Cl, CH₂OH, (CH₂)₃Me
X = F, Cl, Br, Ph, Me

6
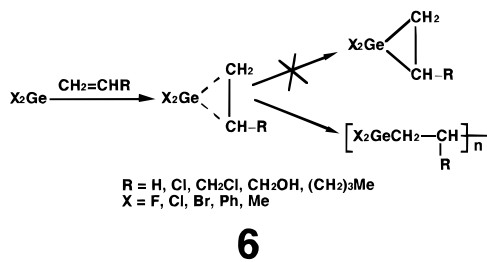
Furthermore, it is reasonable to extend these explanations to the addition reactions of germylenes to acetylene. Namely, the addition of germylenes to acetylene usually leads to polymers,[10,27] via initial formation of the three-membered π-complex. Although we have not carried out such calculations, the fact that the germacyclopropenes are unstable compounds[28] shows that the π-complex intermediate must also play a role in addition reactions of germylenes with acetylene.

E. The Origin of the Barrier and the Reaction Enthalpy for Cycloaddition of Germylenes. Through the elegant studies performed by Pross and Shaik,[29,30] it was found that the configuration mixing (CM) model can successfully explain the origin of barrier heights for carbene addition reactions.[31] Since germylene is one of the heavier analogues of carbene, it is in principle conceivable that the same predictions could also be applied to organogermanic systems.[7]

In this approach, it was suggested that the barrier for the reaction between germylene and ethylene is a result of a crossing between two surfaces, one associated with the reactant spin-coupling (A_R, **7**) and the other with the product spin-coupling (A_P, **8**). In other words, configuration A_R (**7**), labeled $^1[X_2Ge]^1$-$[C_2H_4]$, is termed the reactant configuration, in which the two electrons on the X_2Ge moiety are spin-paired to form the lone pair, while the two electrons on the C_2H_4 moiety are spin-paired to form a C=C π bond. On the other hand, configuration **8** is the product configuration. Note that the spin arrangement is now different. The electron pairs are coupled to allow formation of both Ge−C bonds and simultaneous C=C π bond breaking. To obtain this configuration from the reactant configuration **7**, each of the two original electron pairs needs to be uncoupled. Namely, those two electron pairs require excitation from the singlet state to the triplet state. Hence, this configuration is labeled $^3[X_2Ge]^3[C_2H_4]$. It should be noted that there is no actual spin change here because, despite the fact that $^3[X_2Ge]^3[C_2H_4]$

(27) Krebs, A.; Berndt, J. *Tetrahedron Lett.* **1983**, *24*, 4083.

(28) Su, M.-D.; Chu, S.-Y. Manuscript in preparation.

(29) (a) Shaik, S.; Schlegel, H. B.; Wolfe, S. *Theoretical Aspects of Physical Organic Chemistry*; John Wiley & Sons Inc.: New York, 1992. (b) Pross, A. *Theoretical and Physical principles of Organic Reactivity*; John Wiley & Sons Inc.: New York, 1995.

(30) Su, M.-D. *Inorg. Chem.* **1995**, *34*, 3829.

(31) Pross, A.; Moss, R. A. *Tetrahedron Lett.* **1990**, *31*, 4553.

Figure 6. Energy diagram for an addation reaction showing the formation of a state curve (Ψ) by mixing two configurations: the reactant configuration (A_R) and the product configuration (A_P). In the reactants, they are separated by an energy gap S. $S = \Delta E_{st}$ (i.e., the germylene singlet−triplet splitting) + $\Delta E_{\pi\pi^*}$ (i.e., the π(C=C) → π^*(C=C) triplet excitation energy for ethylene). Configuration mixing near the crossing point causes an avoided crossing (dotted line).
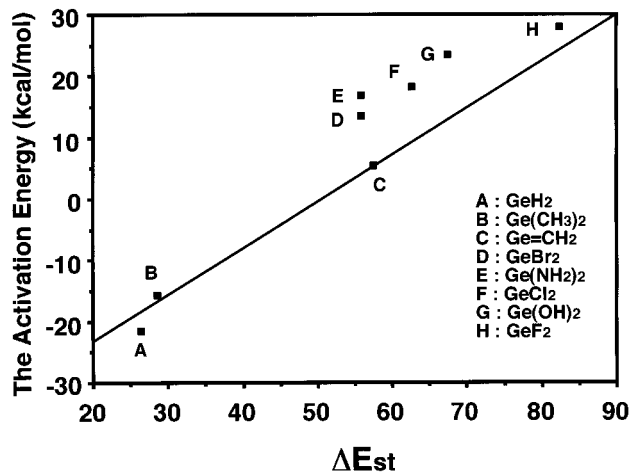
Figure 7. ΔE_{st} ($= E_{triplet} - E_{singlet}$) for germylenes (see the second column in Table 1) vs the activation energy for cycloaddition of germylenes to ethylene (see the fifth column in Table 1). The linear regression equation is $\Delta E^{\ddagger} = 0.921\Delta E_{st} - 41.7$, with a correlation coefficient $R^2 = 0.926$. All values were calculated at the B3LYP/6-31G* level. See the text.

appears to contain two triplet pairs, the overall spin state of $^3[X_2Ge]^3[C_2H_4]$ remains a singlet. Moreover, it is a doubly excited configuration only in the reactant geometry. In terms of the product geometry, it is not an excited configuration at all, just the configuration that describes the ground-state cyclopropane products. Consequently, it is the avoided crossing of these two configurations that leads to the simplest description of the ground-state energy profiles for the germylene cycloadditions. As demonstrated in Figure 7, the barrier height ($\Delta E^{\ddagger}$) and the reaction enthalpy (ΔH) are therefore determined by two

important factors: ΔE_{st} (i.e., the germylene singlet−triplet splitting) and $\Delta E_{\pi\pi*}$ (i.e., the $\pi(C=C) \rightarrow \pi*(C=C)$ triplet excitation energy for ethylene). In consequence, if $\Delta E_{\pi\pi*}$ is a constant and ΔE_{st} is reduced, then curve crossing occurs at a lower energy, leading to a lower barrier and a larger exothermicity.

$^1[X_2Ge]^1[C_2H_4]$ $^3[X_2Ge]^3[C_2H_4]$
7 **8**
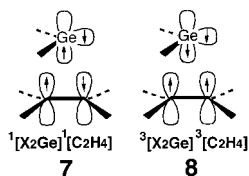
Our computational results support the above prediction. For the B3LYP/6-31G* calculations on the aforementioned eight systems studied here, a plot of activation barrier versus ΔE_{st} is given in Figure 7: the best fit is $\Delta E^{\ddagger} = 0.921\Delta E_{st} - 41.7$.[32a] Likewise, suppose that germacyclopropane is the unique end-product for germylene additions, then a linear correlation between ΔE_{st} and the reaction enthalpy (ΔH) is also obtained at the same level of theory: $\Delta H = 0.848\Delta E_{st} - 46.7$.[32b] As a consequence, the singlet−triplet splitting of germylene can be used as a guide to predict the reactivities of various germylenes toward cycloadditions to olefins. Thus, our model calculations suggest that electron-withdrawing and/or π-donating substituents (such as halogen, alkoxy, and amido groups) on germylene will result in a larger ΔE_{st} and then may hinder the cycloaddition with alkene. In contrast, electronpositive and/or bulky substituents (such as hydrogen and alkyl groups) on germylene will lead to a smaller ΔE_{st} and, in turn, will facilitate the cycloaddition with olefin.

IV. Conclusion

In the present paper, we describe the results of our studies on the reactivity of a series of substituted germylenes toward an ethylene. In particular, this work enables one to reach a theoretical interpretation of the experimental behavior of the addition reaction of germylene to olefins (or even to acetylenes). Despite the fact that the estimated magnitude of the barrier and the predicted geometry of the transition state for such reactions appear to be dependent on the level of calculation applied, our qualitative predictions are in agreement with the calculated

results presented here as well as the available experimental observations.

Taking all aforementioned eight reactions ($GeX_2 + C_2H_4$) studied in this paper together, one can draw the following conclusions:

(1) In contrast to the case of the carbene additions, an interesting observation regarding the mechanism of germylene addition is the initial formation of a germylene−ethylene π-complex, which should play a key role in any subsequent polymerization.

(2) Considering the effect of substitution at the germanium center, our theoretical findings suggest that the cycloaddition of germylene with electropositive and/or bulky substituents is energetically feasible from both a kinetic and a thermodynamic viewpoint. On the contrary, electron-withdrawing groups on the germylene hinder the cycloaddition. It should be noted that this conclusion is based upon the assumption that three-membered-ring germacyclopropane is the unique end-product for germylene additions.

(3) Germacyclopropanes, unlike cyclopropanes, are quite unstable compounds, reverting thermally to their precursors and then polymerizing rapidly, or then even reacting with the second molecule of olefin to yield a cyclic compound.

(4) The cycloadditions of germylenes to alkenes are more endothermic (or less exothermic) than the same reactions of carbenes,[2,11] reflecting the weaker Ge−C vs C−C bond.

(5) If the three-membered-ring germacyclopropane is the primary product for germylene cycloadditions to an olefin, then the singlet−triplet splitting of germylene can be used as a diagnostic tool to predict the reactivities of various germylenes.[7]

It is hoped that our study will stimulate further research into the subject.

Supporting Information Available: A full set of parameters, encompassing all the compounds addressed in this work, along with molecular structures (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA990954T

(32) (a) The correlation coefficient is $R^2 = 0.926$. (b) The correlation coefficient is $R^2 = 0.891$.