Inorg. Chem. **1999,** *38,* 4819−4823 **4819**

Theoretical Study of Reactions of Arduengo-Type Carbene, Silylene, and Germylene with CH_4

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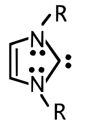
Received April 23, 1999

The potential energy surfaces corresponding to the reaction of cyclic, unsaturated diaminocarbene (DAC), -silylene (DAS), and -germylene (DAG) with methane have been investigated by employing the B3LYP and CCSD(T) levels of theory. Our model calculations demonstrate that the electronic perturbation effect should play a significant role in determining the magnitude of their singlet−triplet splitting. Namely, the singlet−triplet gap of DAC, DAS, and DAG shows the opposite order as the parent compounds (CH_2, SiH_2, and GeH_2), as well as the compounds with π-donor substituents ($C(NH_2)_2$, $Si(NH_2)_2$, and $Ge(NH_2)_2$). Our theoretical investigations suggest that the heavier the X center (X = C, Si, Ge), the larger the insertion barrier, and the less exothermic (or the more endothermic) the insertion reaction. Namely, the chemical reactivity decreases in the order DAC > DAS > DAG. Even so, all the species are predicted to be kinetically stable with respect to insertion reactions with alkanes. Moreover, it is found that a singlet state DAC, DAS, or DAG inserts in a concerted manner, and that the stereochemistry at the X center (X = C, Si, and Ge) is preserved.

I. Introduction

Electron deficient centers which have unsaturated coordination are a source of fascination for any chemist by virtue of their structural, electronic, and reactive novelty. Most familiar are the carbenes, which already have an extensive chemistry as reactive intermediates.[1] In 1991 Arduengo and co-workers reported[2] the isolation of the first stable carbene, 1,3-di(1-adamantyl)imidazol-2-ylidene **1**, which proved to be the prototype for a whole family of stable divalent carbon compounds, even without significant steric crowding.[3] There has been significant synthetic interest in deriving the silylene and germylene analogues of this carbene to look at the effect of substituting silicon and germanium for the carbene carbon.



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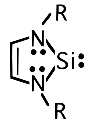

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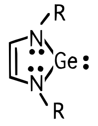

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Following the discovery of stable carbenes by Arduengo and co-workers, the synthesis and characterization of analogous stable silylene **2**[4] and germylene **3**[5] were also reported. In recent years, the large quantity of work that has been devoted to the chemical and physical properties, and reactivity of these stable carbenes and carbene derivatives.[6−10] Of particular interest is the insertion of carbene into alkanes, a reaction which gives the next higher alkane in an almost statistical ratio.[1] In this work, we study the insertion reactions which involve breaking the C−H bond in methane. Moreover, to compare the carbene, silylene, and germylene insertions, the following three reactions

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(4) (a) Denk, M.; Lennon, R.; Hayshi, R.; West, R.; Belyakov, A. V.; Verne, H. P.; Haaland, A.; Wangner, M.; Wetzler, N. *J. Am. Chem. Soc.* **1994**, *116*, 2691. (b) Haaf, M.; Schmiedl, A.; Schmedake, T. A.; Powell, D. R.; Millevolte, A. J.; Denk, M.; West, R. *J. Am. Chem. Soc.* **1998**, *120*, 12714.

(5) (a) Herrmann, W. A.; Denk, M.; Benk, M.; Behm, J.; Scherer, W.; Klingan, F.-R.; Bock, H.; Solouki, B.; Wagner, M. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1485. (b) Arduengo, A. J., III; Dias, H. V. R.; Dixon, D. A.; Harlow, R. L.; Klooster, W. T.; Koetzle, T. F. *J. Am. Chem. Soc.* **1994**, *116*, 6812.

(6) (a) Dixon, D. A.; Arduengo, A. J., III *J. Phys. Chem.* **1991**, *95*, 4180. (b) Heinemann, C.; Thiel, W. *Chem. Phys. Lett.* **1994**, *217*, 11. (c) Closlowski, J. *Int. J. Quantum. Chem., Quantum Chem. Symp.* **1993**, *27*, 309.

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(8) (a) Heinemann, C.; Müller, T.; Apeloig, Y.; Schwarz, H. *J. Am. Chem. Soc.* **1996**, *118*, 2023. (b) Boehme, C.; Frenking, G. *J. Am. Chem. Soc.* **1996**, *118*, 2039. (c) Alder, R. W.; Allen, P. R.; Murray, M.; Orpen, G. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1121. (d) Arduengo, A. J., III; Goerlich, J. R.; Marshall, W. J. *J. Am. Chem. Soc.* **1996**, *118*, 11027. (e) Dyer, P.; Baceiredo, A.; Bertrand, G. *Inorg. Chem.* **1996**, *35*, 46. (f) Regitz, M. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 725, 9100.

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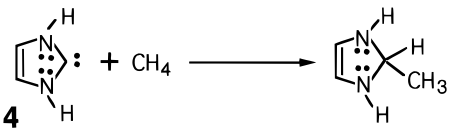
10.1021/ic990442f CCC: $18.00 © 1999 American Chemical Society
Published on Web 09/28/1999

have been investigated with density functional theory (DFT), including corrections for electron correlation: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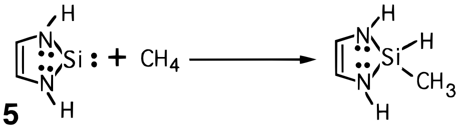
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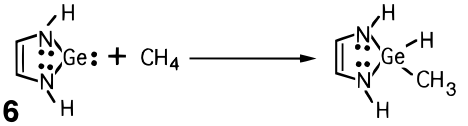
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II. Theoretical Methods

All calculations were carried out using the Gaussian 94 series of programs.[11] The geometries of all species were fully optimized using the hybrid density functional method B3LYP/6-31G* (hereafter designated B3LYP). For triplet states, the UB3LYP/6-31G* calculations were used. Single-point energies were also calculated at CCSD(T)/6-31G**//B3LYP/6-31G* (hereafter designated CCSD(T)), to improve the treatment of electron correlation. Vibrational frequency calculations at the B3LYP/6-31G* level were used to characterize all stationary points as either minimum (the number of imaginary frequencies (NIMAG) = 0) or transition states (NIMAG = 1)).

III. Results and Discussion

The optimized geometries for reactions **4**, **5**, and **6** were calculated at the B3LYP/6-31G* level of theory. The resulting reactants, precursor complexes (**Pcx**), transition states (**TS**), and products (**Pro**) are collected in Figures 1−3. For convenience, we have also given the energies relative to the two reactant molecules in Figures 1−3. Their energy parameters, calculated at the B3LYP and CCSD(T) levels, are summarized in Table 1.

A. Reactants. As one can see in Figures 1−3, the agreement for both bond lengths and bond angles in the rings (**4**, **5**, and **6**) between the B3LYP results and experiments[2,4,5] for the singlet state is quite good, with the bond lengths and angles in agreement to within 0.025 Å and 3.0°, respectively. In addition, our DFT structure for the triplet cyclic carbenes (**4**) is essentially quite similar to that of the ab initio ones.[6] To the best of our knowledge, no experimental or theoretical work on the triplet cyclic silylene (**5**) and germylene (**6**) has been reported so far. In any event, the good agreement between our model calculations and the experimental and theoretical studies available is encouraging. Thus, it is believed that the B3LYP calculations provide an adequate theoretical level for further investigations of molecular geometries, electronic structures, and kinetic features of the reactions.

Moreover, in the case of cyclic carbene reactant (**4**), an interesting trend that can be observed in Figure 1 is the increase in the bond distances (i.e., $C_{2-N1(3)}$ and $N_{1(3)-C5(4)}$) and bond angles (i.e., $\angle N_1C_2N_3$) on going from the singlet to the triplet state. On the other hand, for cyclic silylene (**5**) and germylene (**6**) reactants the triplet state has significantly narrower bond angles ($\angle N_1X_2N_3$) and longer bond distances ($X_{2-N1(3)}$) than the corresponding closed shell singlet state.[6a] The reason for this phenomenon can be understood simply by considering their electronic structures (vide infra).

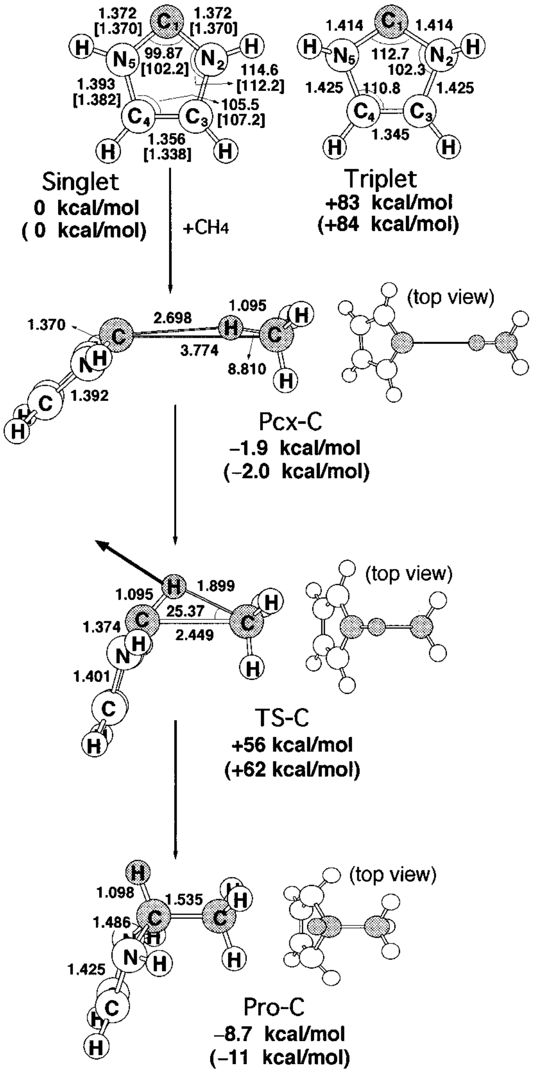

Figure 1. B3LYP/6-31G* optimized geometries (in Å and deg) for stationary points of the cyclic carbene **4** + CH_4 reaction system. The heavy arrows indicate the main atomic motions in the transition state eigenvector. The parameters from experiments (see ref 6) are given in brackets [ ], those obtained by the B3LYP level are given without enclosure, and energies by the CCSD(T) level are given in parentheses ( ).

Figure 4 is an MO correlation diagram of valence orbitals for **4**, **5**, and **6**. The substitution of a single carbon atom at the carbene center by silicon or germanium pushes the π_3 and π_4 orbitals up in energy. Additionally, this substitution also decreases the energies of the σ and π_5 orbitals. These two effects lead to a smaller HOMO−LUMO energy difference for cyclic silylene (**5**) and germylene (**6**). Note that the nature of the HOMO and the LUMO in **4**−**6** is quite different from that encountered in most group 4B divalent compounds. Here, the HOMO and the LUMO are essentially nonbonding σ and p-π orbitals, respectively.[1] For example, the HOMO of the cyclic carbene (**4**) is an essentially nonbonding σ orbital based on C_2, and the LUMO is an antibonding π orbital with the carbene

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[11] 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 94*; Gaussian, Inc.: Pittsburgh, PA, 1995.

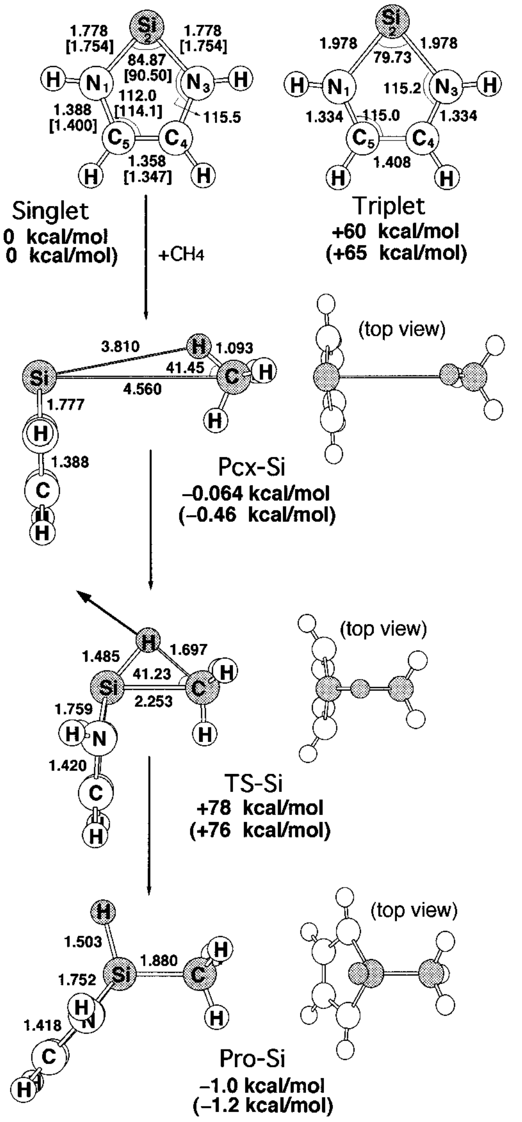

Figure 2. B3LYP/6-31G* optimized geometries (in Å and deg) for stationary points of the cyclic silylene **5** + CH_4 reaction system. The heavy arrows indicate the main atomic motions in the transition state eigenvector. The parameters from experiments (see ref 4) are given in brackets [ ], those obtained by the B3LYP level are given without enclosure, and energies by the CCSD(T) level are given in parentheses ( ).

center (i.e., C_2) lying along the nodal plane (i.e., the π_4 orbital). In contrast to the cyclic carbene, the HOMO and LUMO for cyclic silylene (**5**) are π_3 and π_5 orbitals, respectively. The same phenomenon is also found in the cyclic germylene (**6**) as demonstrated in Figure 4. As a result, in the triplet state of **4** one electron is situated in the π_4 orbital, in which the unpaired electron is distributed over just four centers. Our DFT results of Figure 1 suggest that the distances $C_{2-N1(3)}$ and $N_{1(3)-C5(4)}$, and the angle $\angle N_1C_2N_3$ should be larger for the triplet compared to the singlet. This is largely a σ effect based on rehybridization of the atoms in the ring system. The nonplanar structure of the triplet places more p-orbital character in the σ bonds hence they are longer in the triplet.[12] Similarly, in the triplet state of **5** and **6**, one electron is situated in the π_5 orbital, in which there are antibonding interactions between the X center, nitrogen, and carbon atoms. This orbital is empty in the singlet state. The additional occupation of π_5 therefore leads to a weakening of bonds $X_{2-N1(3)}$ and a narrowing of the angle $\angle N_1C_2N_3$. These qualitative arguments agree with our computational results obtained at the B3LYP level of theory as given in Figures 2 and 3.

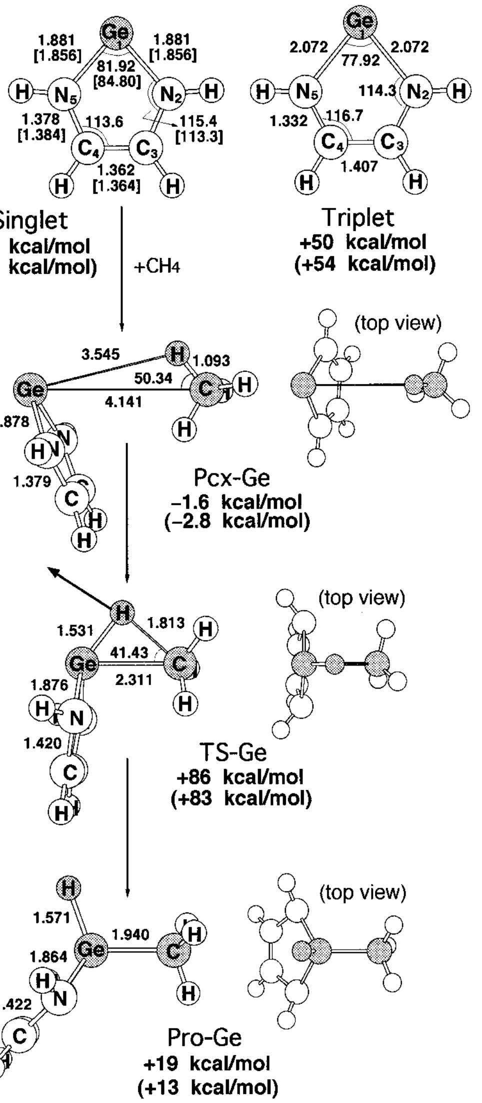

Figure 3. B3LYP/6-31G* optimized geometries (in Å and deg) for stationary points of the cyclic germylene **6** + CH_4 reaction system. The heavy arrows indicate the main atomic motions in the transition state eigenvector. The parameters from experiments (see ref 5) are given in brackets [ ], those obtained by the B3LYP level are given without enclosure, and energies by the CCSD(T) level are given in parentheses ( ).

The other striking feature is the singlet−triplet splittings ($\Delta E_{st} = E_{triplet} - E_{singlet}$).[6a] Our DFT and CCSD(T) (in parentheses) calculations indicate that the singlet−triplet splittings for carbene (**4**), silylene (**5**), and germylene (**6**) are 82 (84), 60 (65), and 50 (54) kcal/mol, respectively, i.e., the ΔE_{st} decreases in the order **4** > **5** > **6**. On the other hand, the singlet−triplet energy gaps in the parent molecules, CH_2, SiH_2, and GeH_2, have been shown to increase down group 4B. Namely, CH_2 (−9.0 kcal/mol) < SiH_2 (21 kcal/mol) < GeH_2 (23 kcal/mol) (a positive value indicates a singlet state).[13−15] Also, the B3LYP/6-31G* results indicate that the ΔE_{st} increases in the order $C(NH_2)_2$ (51 kcal/

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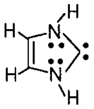
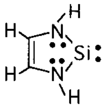
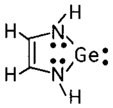
(12) (a) Herrmann, W.; Kocher, C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2163 and references therein. (b) We thank referee A for bringing this paper to our attention.

(13) (a) Jensen, P.; Bunker, P. R. *J. Chem. Phys.* **1988**, *89*, 1327. (b) Berkowitz, J.; Greene, J. P.; Cho, H.; Ruscic, B. *J. Chem. Phys.* **1987**, *86*, 1235.

Table 1. Relative Energies (in kcal/mol) for Singlet and Triplet Cyclic Carbene (**4**), Silylene (**5**), and Germylene (**6**), and for the Process **4** (**5** and **6**) + H−CH_3 → Precursor Complex → Transition State → Product[a]

		ΔE_{st}[b]	ΔE_{cpx}[c]	$\Delta E^{\ddagger}$[d]	ΔH[e]
4		+82.66	−1.952	+56.38	−8.689
		(+84.58)	(−2.000)	(+62.23)	(−10.72)
5		+59.71	−0.0644	+77.79	−1.040
		(+65.34)	(−0.457)	(+75.76)	(−1.161)
6		+50.44	−1.625	+86.52	+19.38
		(+53.98)	(−2.847)	(+82.94)	(+12.96)

[a] At the B3LYP/6-31G* and CCSD(T)/6-31G**//B3LYP/6-31G* (in parentheses) levels. [b] Energy relative to the corresponding singlet state. A positive value means the singlet is the ground-state. [c] The stabilization energy of the precursor complex, relative to the corresponding reactants. [d] The activation energy of the transition state, relative to the corresponding reactants. [e] The exothermicity of the product, relative to the corresponding reactants.

mol) < $Si(NH_2)_2$ (55 kcal/mol) < $Ge(NH_2)_2$ (56 kcal/mol) (after considering the zero point energy corrections). In other words, the singlet−triplet gap of **4**−**6** shows the opposite order as the parent compounds (CH_2, SiH_2, and GeH_2), as well as the compounds with π-donor substituents ($C(NH_2)_2$, $Si(NH_2)_2$, and $Ge(NH_2)_2$). As already discussed, the reason for such a difference in the singlet−triplet splitting can be traced directly to electronic factors. From Figure 4, it is apparent that the magnitude of the energy difference between HOMO and LUMO for cyclic systems becomes smaller as one proceeds along the series from C to Ge. In contrast, the difference in ΔE_{st} between CH_2, SiH_2, and GeH_2 is linked to the general observation that the heavier the element, the larger the energy difference between singlet and triplet states. It was found that the pronounced singlet stability of the higher element homologues of methylene is due to the stronger contracted valence s orbitals as compared with the corresponding valence p orbital.[16] This also appears in the geometries of the singlet CH_2 ($\angle HCH = 102°$) > SiH_2 ($\angle HSiH = 92.1°$) > GeH_2 ($\angle HGeH = 91.4°$).[17] Accordingly, our theoretical findings indicate that the electronic perturbation effect, where the symmetry of frontier orbitals changes, should play a significant role in determining the energy ordering of the frontier orbitals. This, in turn, can affect the magnitude of the singlet−triplet splitting for such cyclic divalent molecules.

Finally, as seen from Table 1, all the five-membered ring systems (**4**, **5**, and **6**) are predicted to have singlet ground states according to both DFT and CCSD(T) computational results. This strongly implies that all three reactions (eqs 1−3) should proceed on the singlet surface. We shall thus focus on the singlet surface from now on.

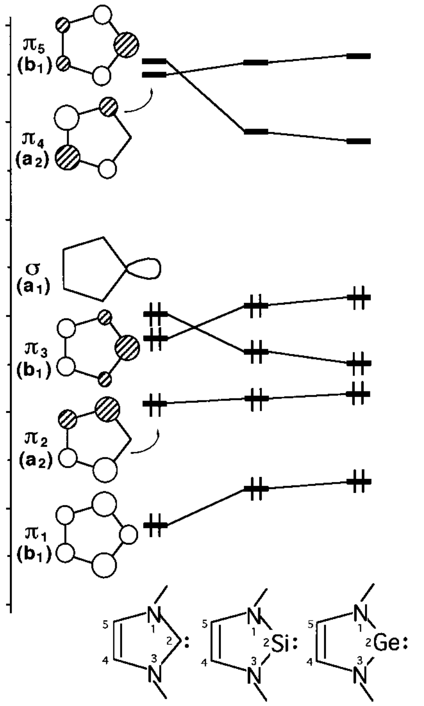


Figure 4. Schematic representation of the relative energies (au) for frontier orbitals of cyclic carbene (**4**), silylene (**5**), and germylene (**6**) based on the B3LYP/6-31G* calculations.

B. Precursor Complexes. The structures of precursor complexes (**Pcx-C**, **Pcx-Si**, and **Pcx-Ge**) optimized at the B3LYP level are shown in Figures 1−3, respectively. All the precursor complexes displays similar X- - -(CH_4) bonding characteristics (X = C, Si, Ge). The methane ligand is coordinated to the X center in an η^2 fashion via one C−H σ bond with the X−C−H plane nearly orthogonal to the cyclic compound coordination plane. Compared to the structures of the isolated reactants, both cyclic reactant (**4**, **5**, and **6**) and methane geometries in the precursor complexes are essentially unperturbed. As shown in Figures 1−3, the X−C distances to CH_4 in the precursor complexes **Pcx-C**, **Pcx-Si**, and **Pcx-Ge** are 3.77, 4.56, 4.14 Å, respectively. Such large bond distances between cyclic carbene (silylene and germylene) and methane is expected to be reflected in small values for the complex stabilization energy. Indeed, it was estimated that the energy of the precursor complex relative to its corresponding reactants is less than 3.0 kcal/mol as shown in Table 1. This suggests that the experimental detection of such complexes will be difficult.

C. Transition States. The optimized transition state structures (**TS−C**, **TS−Si**, and **TS−Ge**) together with arrows indicating the main atom motion in the transition state eigenvector are shown in Figures 1−3, respectively. All three transition state structures show the same three-center pattern involving X (X = C, Si, Ge), carbon and hydrogen atoms.[18] The transition state vectors represented by the heavy arrows in **TS−C**, **TS−Si**, and **TS−Ge** all are in accordance with the insertion process, primarily the C−H bond stretching with a hydrogen migrating

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(14) (a) Shavitt, I. *Tetrahedron* **1985**, *41*, 1531. (b) Goddard, W. A., III. *Science* **1985**, *227*, 917. (c) Schaefer, H. F., III. *Science* **1986**, *231*, 1100. (d) Bauschlicher, C. W., Jr.; Langhoff, S. R. *J. Chem. Phys.* **1987**, *87*, 387.

(15) Su, M.-D.; Chu, S.-Y. *J. Am. Chem. Soc.* **1999**, *121*, 4229 and earlier references therein.

(16) (a) Kutzelnigg, W. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 272. (b) Magnusson, E. *J. Am. Chem. Soc.* **1984**, *106*, 1177, 1185. (c) We thank referee B for bringing these papers to our attention.

(17) Selmani, A.; Salahub, D. R. *J. Chem. Phys.* **1988**, *89*, 1529 and references therein.

(18) Such characteristic three-center transition states are in accordance with mechanisms postulated by Bach and co-workers, see: (a) Bach, R. D.; Andres, J. L.; Su, M.-D.; McDouall, J. J. W. *J. Am. Chem. Soc.* **1993**, *115*, 5768. (b) Bach, R. D.; Su, M.-D.; Aldabagh, E.; Andres, J. L.; Schlegel, H. B. *J. Am. Chem. Soc.* **1993**, *115*, 10237. (c) Bach, R. D.; Su, M.-D. *J. Am. Chem. Soc.* **1994**, *116*, 10103.

to the X center. The B3LYP frequency calculations for the transition states **TS−C**, **TS−Si**, and **TS−Ge** predict the unique imaginary frequency values of 1106i, 1343i, and 1245i, respectively. In addition, the X−H bond formation distances are between 1.09 Å in **TS−C** and 1.53 Å in **TS−Ge**. If one considers the Hammond postulate,[19] which predicts structural and energetic relationships between transition states, reactants, and products on the potential energy surface, then the relative position of the transition states **TS−C**, **TS−Si**, and **TS−Ge** with regard to the precursor complexes can be estimated. Considering only the X−H bond distance in formation, it is apparent that the **TS−Ge** is closest to the precursor complex, while **TS−C** is the most advanced transition state structure. According to the Hammond postulate,[19] the **TS−C** should have the smallest and **TS−Ge** the highest activation barrier. This was fully confirmed by our theoretical calculations. As shown in Table 1, the barrier height (CCSD(T)) for the insertion reaction increases in the order **TS−C** (62 kcal/mol) < **TS−Si** (76 kcal/mol) < **TS−Ge** (83 kcal/mol). In other words, the greater the atomic number of the X center, the higher the insertion barrier.

D. Products. The structures of the insertion products (**Pro-C**, **Pro-Si**, and **Pro-Ge**) generated at the B3LYP level of theory are also illustrated in Figures 1−3. It should be noted that the newly formed X−C bonds (X = C, Si, Ge) in the TS are stretched by 59%, 20%, and 19% relative to their final equilibrium values in cyclic carbene (**4**), silylene (**5**), and germylene (**6**) insertions, respectively. Again, these features indicate that the cyclic carbene insertion reaction reaches the TS relatively early, whereas the cyclic silylene and germylene insertion arrives at the TS relatively late. One may therefore anticipate that the cyclic carbene insertion reaction is more exothermic, which is confirmed by our B3LYP and CCSD(T) calculations. The present calculations predict that the enthalpies for the insertion reactions of cyclic carbene (**4**), silylene (**5**), and germylene (**6**) with methane are −10.7, −1.16, and 13.0 kcal/mol, respectively. Namely, the **4** + CH_4 reaction is calculated to be 10 and 24 kcal/mol more exothermic than reactions **5** + CH_4 and **6** + CH_4, respectively. In consequence, due to the large activation barrier and the strongly endothermic reaction energy for the cyclic germylene (**6**) reaction compared to the cyclic carbene (**4**) and silylene (**5**) cases, the former should have considerable stability toward the C−H bond attack.

In summary, from our study of the insertion reactions (eqs 1−3), we come to the following conclusions:

(a) Since the qualitative features of the potential energy profiles of the B3LYP and CCSD(T) levels are quite similar to each other, the use of the former is sufficient to provide qualitatively correct results.

(b) The present study demonstrates that in the cyclic carbene (**4**), silylene (**5**), and germylene (**6**) species, the electronic perturbation effect should be directly related to the energy ordering of the frontier orbitals and, in turn, the magnitude of their singlet−triplet splitting.

(c) Our theoretical findings suggest that a singlet state cyclic carbene (**4**), silylene (**5**), or germylene (**6**) inserts in a concerted manner via a three-center transition state, and that the stereochemistry at the X center (X = C, Si, Ge) is preserved. However, the calculated barrier heights are sizable (62, 76, 83 kcal/mol for **4**, **5**, and **6** insertions, respectively), suggesting that cyclic diaminocarbene (**4**), -silylene (**5**), or -germylene (**6**) are kinetically stable to the insertion reactions with alkanes, especially in the case of **6**. Our theoretical results are consistent with experimental practices of handling cyclic diaminocarbenes in ether and aromatic solvents.[12(a)]

(d) Considering both the activation barrier and the energy obtained from the model calculations presented here, we conclude that the greater the atomic number of the X center, the larger the activation energy, the less exothermic (or the more endothermic) the insertion reaction, and, therefore, the more difficult is its insertion into the C−H bond of methane.

Acknowledgment. We are very thankful to the National Center for High-Performance Computing of Taiwan and the Computing Center at Tsing Hua University for generous amounts of computing time. We also thank the National Science Council of Taiwan for their financial support. We wish to thank Professor H. B. Schlegel for providing useful software. We express our gratitude to the referees for their valuable comments.

IC990442F

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[19] Hammond, G. S. *J. Am. Chem. Soc.* **1954**, *77*, 334.