

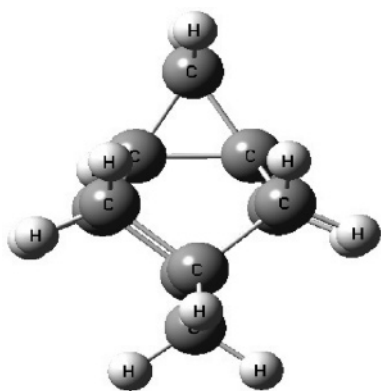
Organic Functionalization of Diamond (100) by Addition Reactions of Carbene, Silylene, and Germylene: A Theoretical Prediction

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

School of Chemistry, Main Building, Cardiff University, Cardiff, CF10 3AT, UK, Department of Chemistry, Fuzhou University, Fuzhou, 350002, China, and State Key Laboratory of Structure Chemistry, Fuzhou, 350002, China

xuy7@cf.ac.uk

Received April 23, 2005



We present a theoretical prediction of the facile cycloadditions of carbene, silylene, and germylene onto the diamond (100) surface, a new type of surface reaction that can be employed to functionalize diamond surface at low temperature. This finding renders the plausibility that the diamond surface can be chemically modified by the well-known carbene addition chemistry, which might introduce new functionalities to the diamond surface for novel applications in a diversity of fields.

Diamond has been attracting tremendous attention as a promising candidate for a wide range of technological applications because of its unique combination of material properties, including high hardness, a large band gap, high saturation carrier velocity, high thermal conductivity, and multispectral optical transparency.^{1–4} The chemical functionalization of the diamond surface might be potentially useful to tailor its properties for specific applications,⁵ for example, surface conductivity, metalization, and electron emission. Hence, it is of paramount interest both fundamentally and technologically to ex-

plore the chemistry of the diamond surface and to seek specific methods of making controlled chemical functionalizations of diamond surfaces. Toward this end, in this letter, we report a theoretical study of the additions of carbene, silylene, and germylene to the C (100)-2×1 surface. Our prediction indicates that the well-known addition reaction of carbenes to olefins in organic chemistry might be a new type of surface reactions that can be employed to functionalize the diamond surface at low temperature. Our results further advance the concept of using organic reactions to modify the solid surface in a controlled fashion.⁶

Indeed, recently, much effort has been made focusing on the chemical modification of the C (100)-2×1 surface both experimentally and theoretically.⁷ For example, it was found that 1,3-dipolar cycloadditions of a series of 1,3-dipolar molecules onto the C (100)-2×1 surface are more favorable over their molecular analogues both thermodynamically and kinetically.^{7a,b} Similarly, another class of Diels–Alder reactions have intensively been studied with regard to the surface dimer of the C (100)-2×1 surface.^{7c,d} More fascinating is the experimental work done at room temperature, reported by Wang et al., that 1,3-butadiene can react with the C (100)-2×1 surface to form a Diels–Alder adduct at room temperature.^{7e} This finding is rather encouraging because it demonstrates the plausibility of functionalizing diamond surfaces by means of synthetic organic chemistry, which might consequently lead to a breakthrough in the fabrication of diamond films at low temperature.

Carbenes have remained a fascinating class of molecules in organic chemistry and been regarded as a highly reactive species.⁸ For instance, methylene (CH₂), the so-called parent carbene, is extremely reactive, and there are few organic compounds able to resist attack by this substance. It is generally deemed that, perhaps, the most

(5) (a) Miller, J. B.; Brown, D. W. *Langmuir* **1996**, *12*, 5809. (b) Strother, T.; Knickerbocker, T.; Russell, J. N.; Butler, J. E.; Smith, L. M.; Hamers, R. T. *Langmuir* **2002**, *18*, 968. (c) Ida, S.; Tsubota, T.; Tani, S.; Nagata, M.; Matsumoto, Y. *Langmuir* **2003**, *19*, 9693. (d) Potochnik, S. J.; Pehrsson, P. E.; Hsu, D. S.; Calvert, J. M. *Langmuir* **1995**, *11*, 1841. (e) Mackey, B. L.; Russell, J. N., Jr.; Crowell, J. E.; Butler, J. E. *Phys. Rev. B* **1995**, *52*, 17009. (f) Pickett, W. E. *Phys. Rev. Lett.* **1994**, *73*, 1664. (g) Smentkowski, V. S.; Yates, J. T., Jr. *Science* **1996**, *271*, 193. (h) Ida, S.; Tsubota, T.; Hirabayashi, O.; Nagata, M.; Matsumoto, Y.; Fujishima, A. *Diamond Relat. Mater.* **2003**, *12*, 601. (i) Goeting, C. H.; Marken, F.; Gutierrez-Sosa, A.; Compton, R. G.; Foord, J. S. *Diamond Relat. Mater.* **2002**, *9*, 390. (j) Liu, Y.; Gu, Z.; Margrave, J. L.; Khabashesku, V. N. *Chem. Mater.* **2004**, *16*, 3924. (6) (a) Buriak, J. M. *Angew. Chem., Int. Ed.* **2001**, *40*, 532. (b) Hamers, R. J.; Coulter, S. K.; Ellison, M. D.; Hovis, J. S.; Padowitz, D. F.; Schwartz, M. P.; Greenlief, C. M.; Russell, J. N., Jr. *Acc. Chem. Res.* **2000**, *33*, 617.

(7) (a) Lu, X.; Xu, X.; Wang, N.; Zhang, Q. *J. Org. Chem.* **2002**, *67*, 515. (b) Lu, X.; Xu, X.; Wang, N.; Zhang, Q. *J. Phys. Chem. B* **2002**, *106*, 5972. (c) Okamoto, Y. *J. Phys. Chem. B* **2001**, *105*, 1813. (d) Fitzgerald, D. R.; Doren, D. J. *J. Am. Chem. Soc.* **2000**, *122*, 12334. (e) Wang, G. T.; Bent, S. F.; Russell, J. N., Jr.; Butler, J. E.; D'Evelyn, M. P. *J. Am. Chem. Soc.* **2000**, *122*, 744.

(8) (a) Kirmse, W. *Carbene Chemistry*; Academic Press: New York, 1964. (b) Kirmse, W. *Carbene Chemistry*; Academic Press: New York, 1971. (c) Bourissou, D.; Guerret, O.; Gabbai, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39. (d) Herrmann, W. A.; Kücher, C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2162. (e) Cheng, Y.; Meth-Cohn, O. *Chem. Rev.* **2004**, *104*, 2507. (f) Barlugenga, J. *Pure Appl. Chem.* **2002**, *74*, 1317. (g) Wentrup, C. *Science* **2001**, *292*, 1846. (h) Wentrup, C. *Science* **2002**, *295*, 1846.

[†] Cardiff University.

[‡] Fuzhou University and State Key Laboratory of Structure Chemistry.

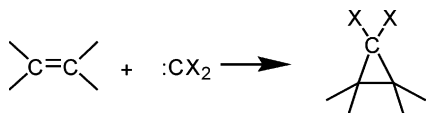
(1) Ashfold, M. N. R.; May, P. W.; Rego, C. A.; Everitt, N. M. *Chem. Soc. Rev.* **1994**, *23*, 21.

(2) Hossain, Z.; Kubo, T.; Aruga, T.; Takag, N.; Tsuno, T.; Fujimori, N.; Nishijima, M. *Jpn. J. Appl. Phys.* **1999**, *38*, 6659.

(3) *The properties of natural and synthetic diamond*; Field, J. E., Ed.; Academic Press: London, 1992.

(4) Wei, J.; Yates, J. T., Jr. *Crit. Rev. Surf. Chem.* **1995**, *5*, 1.

SCHEME 1. Addition of Carbenes to Alkenes



important and characteristic reaction of a carbene is its addition to an olefin to form a cyclopropane (Scheme 1).^{8,9}

Meanwhile, note that single state carbenes are in general highly electrophilic species⁸ and therefore can be used as an excellent model molecules to test whether the C (100)-2×1 surface can be functionalized by the addition reaction of carbenes toward the surface C=C double bond, hence providing much valuable and instructive information to experiments. Furthermore, note that analogous carbene addition reactions were reported with fullerene and single wall carbon nanotube.^{10,11} Strongly inspired by these chemical precedents, we naturally infer that a similar process should proceed on the C (100)-2×1 surface. The present theoretical calculations reported herein are to confirm this inference.

As previously done, a C₉H₁₂ cluster model (Figure 1) was employed to represent a dimer site on the C (100) surface. This surface model has been used previously in the theoretical studies of the 1,3-polar cycloadditions and the Diels–Alder reactions on the C (100)-2×1 surface.^{7a–d} The hybrid density functional B3LYP method and the standard 6-31G(d) basis sets were employed.¹³ It has been shown previously that this theoretical method can provide a reliable description of surface reaction mechanism on the C (100)-2×1 surface.^{7a–d} Furthermore, it has been shown that the optimized geometries and calculated reaction energetics are almost independent of cluster sizes. That is, the dimer–dimer interaction does not play much effect on the predicted conclusions.^{7a–d} More importantly, it is worthwhile to note that the difference in the reaction energetics predicted by the B3LYP method and the much higher level but more expensive G3(MP2) approach, is marginal.^{7c} Hence, these reinforce the validity of study using the B3LYP/6-31G(d) theoretical method together with a C₉H₁₂ cluster model. In addition, cluster

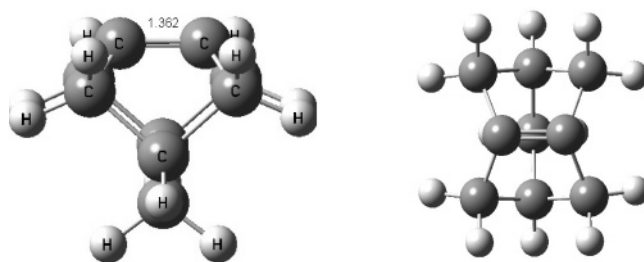


FIGURE 1. Side view and top view of a C₉H₁₂ cluster model.

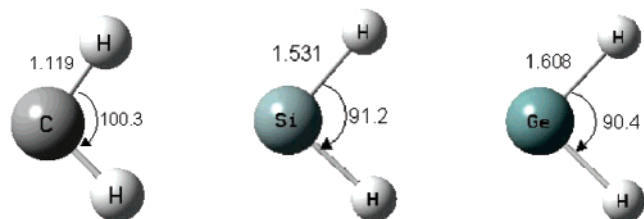


FIGURE 2. B3LYP/6-31G(d) optimized geometries (units in Å for bond length and deg for angle) of singlet carbene (CH₂), silylene (SiH₂), and germylene (GeH₂).

TABLE 1. Calculated Reaction Energies (with/without zero-point vibrational energy corrected) (ΔE_r , in kcal/mol) for the Addition Reactions of Singlet Carbene, Silylene, and Germylene to the C (100)-2×1 Surface and Ethylene at the B3LYP/6-31G(d) Level

reaction system	ΔE_r	ΔE_r (+ZPVE) ^a
CH ₂ +C ₉ H ₁₂	-142.4	-134.0
CH ₂ +C ₁₅ H ₁₆	-141.5	-133.3
CH ₂ +C ₂₁ H ₂₀	-141.6	-133.4
SiH ₂ +C ₉ H ₁₂	-79.6	-75.2
SiH ₂ +C ₁₅ H ₁₆	-78.7	-74.4
SiH ₂ +C ₂₁ H ₂₀	-78.7	-74.5
GeH ₂ +C ₉ H ₁₂	-68.2	-64.1
GeH ₂ +C ₁₅ H ₁₆	-68.6	-64.6
GeH ₂ +C ₂₁ H ₂₀	-68.7	-64.5
CH ₂ +ethylene	-112.6	-103.8
SiH ₂ +ethylene	-43.0	-38.7
GeH ₂ +ethylene	-27.4	-23.4

^a Reaction energies with zero-point vibrational energy corrected.

(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) Rondan, 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) (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.; Urey, 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) Lu, X.; Tian, F.; Zhang, Q. *J. Phys. Chem. B* **2003**, *107*, 8388. (f) Chu, Y. Y.; Su, M. D. *Chem. Phys. Lett.* **2004**, *394*, 231. (g) Chen, Z.; Nagase, S.; Hirsh, A.; Haddon, R. C.; Thiel, W.; von Schleyler, P. R. *Angew. Chem., Int. Ed.* **2004**, *43*, 1552.

(11) Hirsch, A. *The chemistry of fullerenes*; Thieme: Stuttgart, 1994. (12) (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. *J. Chem. Phys.* **2004**, *120*, 8753. (c) Xu, Y. J.; Li, J. Q. *Chem. Phys. Lett.* **2004**, *400*, 406. (d) Xu, X.; Nakatsui, H.; Lu, X.; Ehara, M.; Cai, Y.; Wang, N.; Zhang, Q. *Theor. Chem. Acc.* **1999**, *172*, 170. (e) Xu, Y. J.; Li, J. Q.; Zhang, Y. F.; Chen, W. K. *Surf. Sci.* **2003**, *525*, 13. (f) Fu, G.; Xu, X.; Lu, X.; Wang, H. *J. Am. Chem. Soc.* **2005**, *127*, 3989.

(13) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. A* **1988**, *37*, 785.

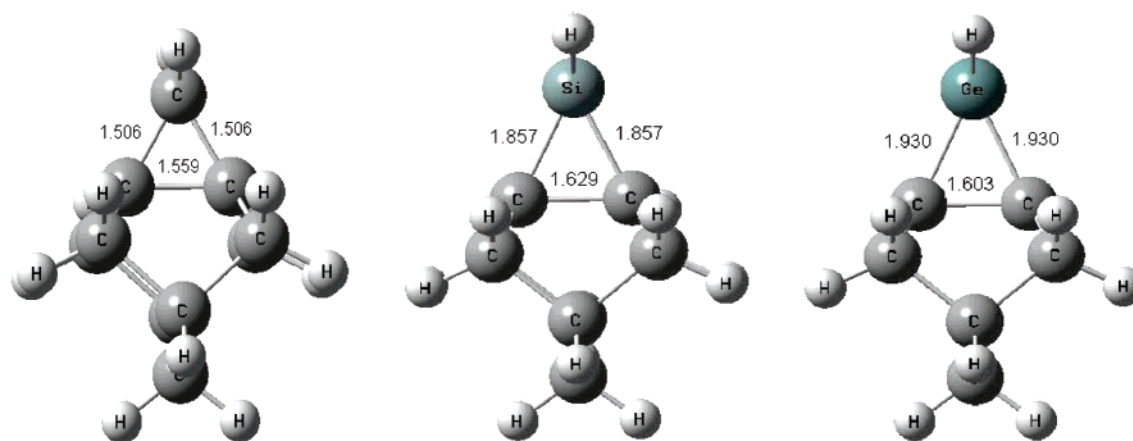


FIGURE 3. B3LYP/6-31G(d) optimized geometries (units in Å for bond length) of the additions of singlet carbene, silylene, and germylene to the C (100)-2×1 surface using a C₉H₁₂ cluster.

analogue in previous studies.^{10e,f,14} All of the calculations were performed with the Gaussian 98 program.¹⁵

Table 1 and Figure 3 list the reaction energies and optimized geometries respectively predicted at the B3LYP/6-31G(d) theoretical level for the addition reactions of carbene, silylene, and germylene to the C (100)-2×1 surface. Clearly, the calculated reaction energy is −134.0 kcal/mol for the addition reaction of the prototype carbene, CH₂, onto the C (100) surface, indicating that this surface reaction is quite highly exothermic. As compared to that of ethylene molecular analogue in the gas phase, the exothermicity for the addition of carbene to the C (100) surface is significantly increased, that is, more than 30 kcal/mol higher than that of the gas-phase addition reaction of CH₂+C₂H₄, suggesting the reactivity of the C=C bond dimer of the C (100)-2×1 surface is much higher than ethylene. This remarkable enhancement of the reactivity was also found in previous studies regarding the 1,3-dipolar additions^{7a,b} and Diels–Alder additions^{7c,d} onto the C (100) surface, which can be ascribed to the reduced overlap between the p orbitals of the surface C=C dimer.⁷ In analogy, our calculations predicted an exothermicity of −75.2 and −64.1 kcal/mol regarding the addition reactions of silylene and germylene onto the C (100)-2×1 surface, respectively, which is much higher than that of ethylene molecular analogue in the gas phase (as shown in Table 1).^{10e,f,14} Noteworthy, the reaction energies of the addition of silylene and germylene to the C (100)-2×1 surface are much lower

than that of carbene. This can be attributed to the weakness of Ge–C and Si–C bonds as compared to C–C bonds.^{10e} Alternatively, it can be understood on the basis of a configuration mixing model.^{10f,16} The calculated results using larger clusters (see Table 1 and Supporting Information) show that the calculated geometries and reaction energies are insensitive to the size of clusters, which are in faithful accordance with previous theoretical predictions.^{7a–d}

More interestingly, these surface reactions are unactivated; that is, no transition states have been located with regard to the additions of carbene, silylene, and germylene to the C (100)-2×1 surface. This is not surprising at all considering the gas-phase reaction profile of the additions of carbene, silylene, and germylene to ethylene, respectively. Regarding the addition of silylene to ethylene (SiH₂+C₂H₄), the overall reaction is barrierless predicted by ab initio calculations^{14a–c} and density functional calculations.^{10f} For the reaction of the additions of carbene to ethylene (CH₂+C₂H₄) and germylene to ethylene (GeH₂+C₂H₄), previous theoretical calculations predicted that the overall additions of carbene and germylene to ethylene have no activation energy barrier, although a rather weak π-complex precursor and a transition state are identified, but both lower than free reactants in energy.^{10f,14d} As is well known, due to the reduced overlap between the p orbitals of the surface C=C dimer, the π-bonding in the surface C=C dimer is weaker than that in ethylene, giving rise to higher reactivity on the surface dimer of the C (100)-2×1 surface.^{6,7a–d} Hence, the additions of carbene, silylene, and germylene to the C (100)-2×1 surface should be much more favorable both thermodynamically and kinetically as compared to their molecular analogues. Our theoretical calculations have apparently confirmed this inference. More significantly, our results strongly suggest that this kind of addition reactions can be used as a new type of surface reactions to functionalize the diamond surface. In practice, carbenes (or silylenes and germylenes) can be produced via the process of photolysis and thermolysis at moderate temperature.⁸ For example, carbenes can be generated by photolyzing dizealkanes

(14) (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.; Boganov, S. E.; Egorov, M. P.; Faustov, V. E.; Promyslov, V. M.; Nefedov, O. M.; Walsh, R. *Phys. Chem. Chem. Phys.* **2002**, *4*, 5079.

(15) 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.

(16) Pross, A. *Theoretical and physical principles of organic reactivity*; Wiley: New York, 1995.

and diazirines. In addition, the as-formed cyclopropane-like surface species would be subject to further chemical manipulations, such as ring opening accompanied by the attachment of other chemical functional groups,¹⁷ therefore possibly imparting other new functionalities to the diamond surface.

In summary, we have predicted the viability of the additions of parent carbene, silylene, and germylene to the diamond (100)-2×1 surface, which is much more favorable over their molecular analogues and is as well in complete accordance with previous studies regarding the modification of the diamond (100) surface using other organic reactions, 1,3-dipolar additions and Diels–Alder reactions. More significantly, the facileness of this new type of surface reactions demonstrates that the well-known addition reactions of carbenes to alkenes in organic chemistry can be applied to functionalize the diamond surface at low temperature, and in addition the as-formed cyclopropane-like surface species would undergo further chemical modifications, hence imparting other new functionalities to the diamond surface, which might lead to novel potential applications of diamond films. Our results strongly advance the concept of using organic reactions to modify the solid surface, particularly to modify the diamond (100) surface because it behaves very much like molecular olefins.^{6,7} In a broader perspective, this new type of surface reaction in combination with the wide variety of carbenes, silylenes, and germylenes would provide high flexibility of functionalizing and fabricating the diamond films at low temperature. More detailed work is underway to investigate in what manner the reaction profile (including reaction energetics and reaction paths) regarding the additions of various sub-

(17) Franz, A. K.; Woerpel, K. A. *Acc. Chem. Res.* **2000**, *33*, 813 and references therein.

stituted carbenes,⁸ silylenes,¹⁸ and germylenes¹⁹ to the C (100)-2×1 surface would change, given the well-known abundance of the chemistry of carbenes, silylenes, and germylenes.^{8,18,19}

What is more, this kind of surface organic reactions can also be extended to modify the Si (100) and Ge (100) surfaces, which feature the bonding motif in the surface dimer analogous to that of the C (100) surface.^{6,7,20} In the meantime, we look forward to experimental realization of the reaction reported herein and hope that our study stimulates further research into this subject.

Acknowledgment. The support of the Natural Science Foundation of China and the Foundation of State Key Laboratory of Structure Chemistry is gratefully acknowledged.

Supporting Information Available: Cartesian coordinates and calculated frequencies of the optimized products, and optimized geometries using larger clusters C₁₅H₁₆ and C₂₁H₂₀. This material is available free of charge via the Internet at <http://pubs.acs.org>.

JO050823C

(18) (a) Bourissou, D.; Guerret, O.; Gabbai, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39. (b) Jasinsk, J. M.; Meyerson, B. S.; Scott, B. A. *Annu. Rev. Phys. Chem.* **1987**, *38*, 109. (c) Weidenbruch, M. *Coord. Chem. Rev.* **1994**, *130*, 275. (d) Tokitoh, N.; Okazaki, R. *Coord. Chem. Rev.* **2000**, *210*, 251.

(19) (a) Neumann, W. P. *Chem. Rev.* **1991**, *91*, 311. (b) Lesbire, M.; Mazerroles, P.; Satgé, J. *The organic compounds of germanium*; Zinatne: Riga, 1990. (c) Su, M. D.; Chu, S. Y. *J. Am. Chem. Soc.* **1999**, *121*, 4229. (d) Su, M. D.; Chu, S. Y. *J. Am. Chem. Soc.* **1999**, *121*, 11478.

(20) (a) Buriak, J. M. *Chem. Rev.* **2002**, *102*, 1271. (b) Lu, X.; Lin, M. C. *Int. Rev. Phys. Chem.* **2002**, *21*, 137. (c) Wolkow, R. A. *Annu. Rev. Phys. Chem.* **1999**, *50*, 413. (d) Bent, S. F. *J. Phys. Chem. B* **2002**, *106*, 2830. (e) Waltenburg, H. N.; Yates, J. T., Jr. *Chem. Rev.* **1995**, *95*, 1589.