ORGANIC LETTERS

2004
Vol. 6, No. 7
1163−1166

Triplet H–C–SiHCl$_2$: Combined Matrix-IR and CCSD(T) Identification, and the Role of the Open-Shell Singlet State

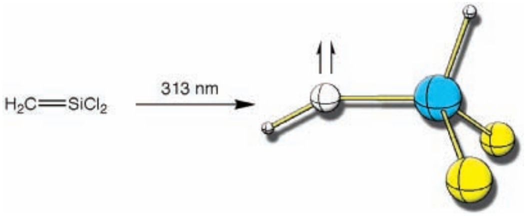
Peter R. Schreiner,*,[§,‡] Hans Peter Reisenauer,[§] Wesley D. Allen,[‡] and Kurt W. Sattelmeyer[‡]

Institute of Organic Chemistry, Justus-Liebig-University, Heinrich-Buff-Ring 58, 35392 Giessen, Germany, and Center for Computational Chemistry, Department of Chemistry, University of Georgia, Athens, Georgia 30605-2525

prs@org.chemie.uni-giessen.de; prs@chem.uga.edu

Received January 27, 2004

ABSTRACT



Triplet carbene H–C–SiHCl$_2$ (1), prepared by a photochemical [1,2]H-shift from 1,1-dichlorosilaethylene, was identified by matching experimental and [CCSD(T)/cc-pVTZ] infrared absorptions. Parts of the potential energy surface were explored utilizing CCSD(T)/cc-pVTZ and B3LYP/6-311+G computations. DFT reproduces the experimental features and CCSD(T) computations for the triplet surface but fails in the description of the open-shell singlet state of 1. We emphasize the notion of electropositive heterosubstitution for the generation of persistent ground-state triplet carbenes.**

Very few electronic ground-state triplet carbenes bearing electropositive elements such as silicon are known,[1] and those species also exhibiting α-hydrogen substituents are prone to rearrangements.[2,3] The only documented confluence of both structural features is $(CH_3)_2HSi-C-H$, whose carbene moiety was deduced from ESR data to be linear.[4] In the prevailing view, bulky substituents are required for sufficient kinetic stabilization of triplet carbenes against external reactions or dimerization,[5−7] although this strategy may operate by thermodynamically destabilizing both singlet and triplet states, with the effect being larger for the singlet.[5] The present communication highlights the key alternative role of electronic stabilization in the design of persistent triplet carbenes. Because valuable magnetic properties may be displayed by open-shell electronic ground-state molecules,[8] organic materials of this type would be particularly useful given the broad arsenal of synthetic organic methods that for the design of complex molecular architectures.

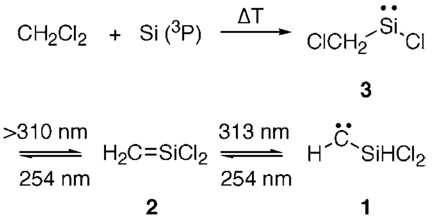
Ground-state triplet ($^3A''$) carbene **1** was prepared[9] by irradiation of 1,1-dichlorosilaethylene **2**[10] with monochromatic light (313 ± 5 nm) in an argon matrix at 10 K (Scheme 1; computed energetics at the CCSD(T) level[11] with the cc-

---

[§] Justus-Liebig-University.
[‡] University of Georgia.
[1] Trommer, M.; Sander, W. *Organometallics* **1996**, *15*, 736−740.
[2] Bourissou, D.; Guerret, O.; Gabbai, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39−91.
[3] Sander, W.; Bucher, G.; Wierlacher, S. *Chem. Rev.* **1993**, *93*, 1583−1621.
[4] Chedekel, M. R.; Skoglund, M.; Kreeger, R. L.; Shechter, H. *J. Am. Chem. Soc.* **1976**, *98*, 7846−7848.
[5] Woodcock, H. L.; Moran, D.; Schleyer, P. v. R.; Schaefer, H. F. *J. Am. Chem. Soc.* **2001**, *123*, 4331−4335.
[6] Tomioka, H.; Watanabe, T.; Hattori, M.; Nomura, N.; Hirai, K. *J. Am. Chem. Soc.* **2002**, *124*, 474−482. Tomioka, H.; Iwamoto, E.; Itakura, H.; Hirai, K. *Nature* **2001**, *412*, 626−628. Hirai, K.; Tomioka, H. *J. Am. Chem. Soc.* **1999**, *121*, 10213−10214.
[7] Tomioka, H. *Acc. Chem. Res.* **1997**, *30*, 315−321.
[8] Zuev, P. S.; Sheridan, R. S. *Tetrahedron* **1995**, *51*, 11337−11341. Nakamura, N.; Inoue, K.; Iwamura, H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 872−873.

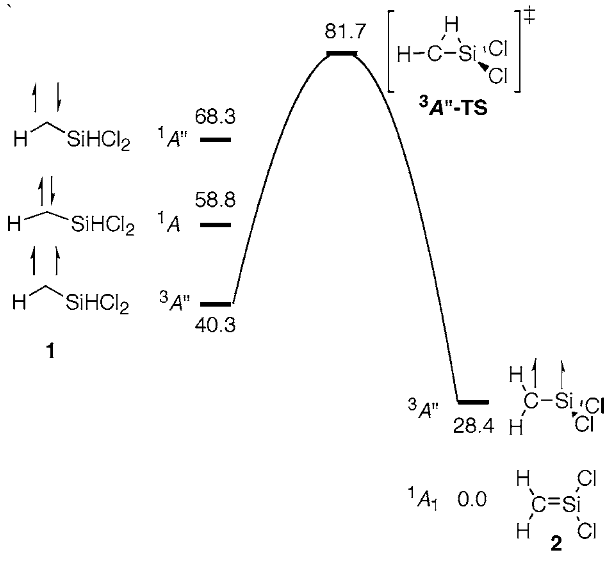
10.1021/ol049842j CCC: $27.50

Scheme 1



pVTZ basis set[12] in Scheme 2). Olefin **2** was generated through the thermal (ΔT) reaction of atomic ground-state triplet silicon atoms (^{3}P) with methylene chloride. The initial chlorosilylene **3** gives **2** upon irradiation with $\lambda > 310$ nm or further thermal reaction. This preparation has the advantage that the desired species is not generated from the diazo or diazirene precursors by photochemical extrusion of N_2, which inevitably gives the singlet ground state from which rearrangements often occur.[13] A full description of this reaction cascade will be described elsewhere.

Scheme 2. Energy Profile in kcal mol^{-1} at CCSD(T)/cc-pVTZ (ROCISD/cc-pVTZ for ^{1}A″-**1**)



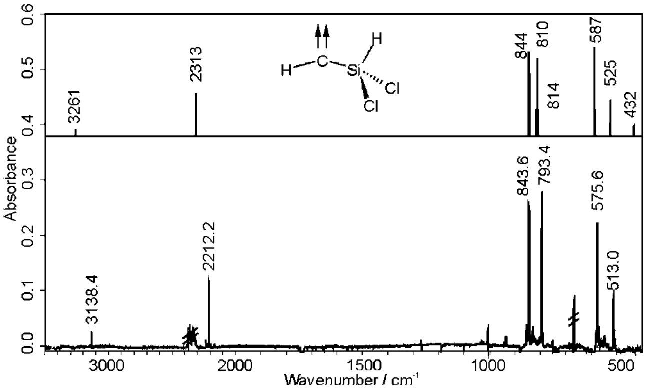


Figure 1. IR spectrum of dichlorosilylcarbene **1**. Top: computed bands [CCSD(T)/cc-pVTZ frequencies with MP2/cc-pVTZ intensities]. Bottom: experimental spectrum, argon matrix, 10 K (positive part of a difference spectrum of the photochemical transformation of silylene **2** into **1** with 313 nm light).

Excellent matching (Figure 1) of measured fundamental and unscaled theoretical harmonic IR absorption frequencies and intensities unequivocally identifies and characterizes $^3A''$-**1**, which is indefinitely stable under these conditions. If the CCSD(T)/cc-pVTZ harmonic C−H stretching frequency (3261 cm^{-1}) of $^3A''$-**1** is appended with the mean anharmonicity (−123 cm^{-1}) of the ν_1 and ν_3 fundamentals of $^3B_1$ methylene,[14] the carbene bond stretch of $HCSiHCl_2$ is computed to occur at 3138 cm^{-1}, exactly where the absorption is measured! In contrast, the same theoretical scheme for closed-shell singlet **1** yields $\nu_1 = 2905$ cm^{-1}, below the experimental value by 233 cm^{-1}.

The assigned C−H stretching frequency of $^3A''$-**1** is in full accord with the CCSD(T)/cc-pVTZ structure, which exhibits a short, strong C−H bond ($r_e = 1.079$ Å) and a wide H−C−Si angle ($\theta_e = 152.4°$) significantly deviating from linearity. The analogous parameters for triplet methylene are $r_e = 1.075$ Å and 133.9°.[14,15] The IR absorption at 2212 cm^{-1} (computed: $\omega_2 = 2313$ cm^{-1} with anticipated anharmonicity[16] of about −80 cm^{-1}) can be assigned to the Si−H bond stretch; the C−Si vibration appears at 844 cm^{-1} (computed 844 cm^{-1}; modest coupling with the C−Si−H bend). For additional proof of structure, we also prepared dideutero-$^3A''$-**1** (D−C−$SiDCl_2$, Figure 2) by the same method starting from D_2CCl_2 + Si. The vibrational matching is equally good and further confirms our structural assignment. A full normal coordinate analysis of the vibrations of both isotopomers of

---

(9) Matrix Experiments. A stream of silicon atoms evaporating from a resistively heated silicon rod at ca. 1380 °C was cocondensed with a gaseous mixture of dichloromethane in argon onto the surface of a CsI window at 10 K. The matrices thus formed were probed by FTIR and UV/vis spectroscopy. Photochemical transformations were initiated by irradiation of the matrices with light from a mercury high-pressure lamp in combination with a long pass filter ($\lambda > 310$ nm) or a monochromator, from a mercury low-pressure lamp (254 nm) or from a KrF excimer laser (248 nm). Differences of spectra were used to evaluate spectral changes.

(10) Maier, G.; Mihm, G.; Reisenauer, H. P.; Littmann, D. *Chem. Ber.* **1984**, *117*, 2369−2381. Maier, G.; Mihm, G.; Reisenauer, H. P. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 597−598. Maier, G.; Mihm, G.; Reisenauer, H. P. *Chem. Ber.* **1984**, *117*, 2351−2368.

(11) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett.* **1989**, *157*, 479−483. Lee, T. J.; Scuseria, G. E. In *Quantum Mechanical Electronic Structure Calculations with Chemical Accuracy*; Langhoff, S. R., Ed.; Kluwer: Dordrecht, 1995; pp 47−108.

(12) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007−1023. Dunning, T. H., Jr.; Peterson, K. A.; Woon, D. E. In *The Encyclopedia of Computational Chemistry*; Schleyer, P. v. R., Allinger, N. L., Clark, T., Gasteiger, J., Kollman, P. A., Schaefer, H. F., Schreiner, P. R., Eds.; John Wiley & Sons: Chichester, 1998; Vol. 1, pp 88−115.

(13) Platz, M. S.; Huang, H. Y.; Ford, F.; Toscano, J. *Pure Appl. Chem.* **1997**, *69*, 803−807. Platz, M. S., Ed.; *Kinetics and Spectroscopy of Carbenes and Diradicals*; Plenum: New York, 1990.

(14) Császár, A. G.; Leininger, M. L.; Szalay, V. *J. Chem. Phys.* **2003**, *118*, 10631−10641.

(15) Petek, H.; Nesbitt, D. J.; Darwin, D. C.; Ogilby, P. R.; Moore, C. B.; Ramsay, D. A. *J. Chem. Phys.* **1989**, *91*, 6566−6578.

(16) Wang, X.-G.; Sibert, E. L., III. *J. Chem. Phys.* **2000**, *113*, 5384−5400.

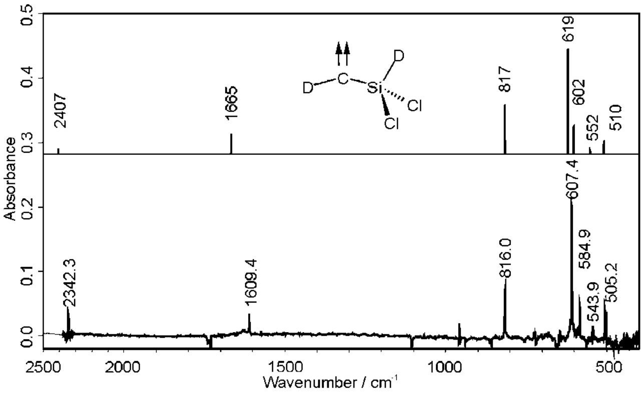
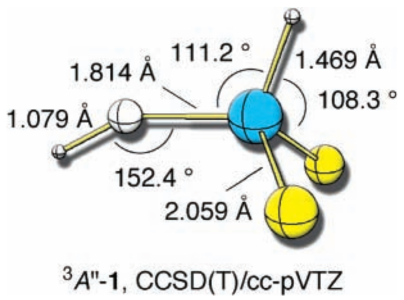


Figure 2. IR spectrum of dideuteriodichlorosilylcarbene **1**-d_2. Top: computed bands [CCSD(T)/cc-pVTZ frequencies with MP2/cc-pVTZ intensities]. Bottom: argon matrix, 10 K (positive part of a difference spectrum of the photochemical transformation of silylene **2**-d_2 into **1**-d_2 with 313 nm light).

$^3A''$-**1**, including total energy distributions (TEDs) from theory, is given in Supporting Information.



The closed- and open-shell singlet states of $HCSiHCl_2$ were carefully examined to exclude their appearance in the matrix-IR experiments on **1**. The open-shell singlet is often neglected in carbene studies with the tacit assumption that it is much higher in energy than the other two states. The B3LYP/6-311+G** density functional method[17] paints an entirely different picture, placing open-shell $^1A''$-**1** 9.6 kcal mol^{-1} *below* closed-shell $^1A'$-**1**! However, more rigorous ab initio computations completely invalidate this result.

At the CCSD(T)/cc-pVTZ level, closed-shell $^1A'$-**1** optimizes in C_s symmetry to a structure with a trans H−C−Si−H framework, a long C−H distance of 1.106 Å, and an H−C−Si angle of 105.9°, lying 18.5 kcal mol^{-1} above $^3A''$-**1**. The $^1A'$ structure of **1** has an a'' vibrational mode of imaginary frequency (186i cm^{-1}) leading to a C_1 conformation (^1A) 0.9 kcal mol^{-1} lower in energy, wherein one of the chlorines has migrated to an unusual partial bridging position to donate σ(SiCl) electron density into the empty carbene p orbital.

To reliably describe the open-shell singlet state, configuration interaction singles and doubles theory was invoked with a proper restricted Hartree−Fock reference wave function (ROCISD).[18] At the ROCISD/cc-pVTZ level, $^1A''$-**1** has a C_s minimum with a trans H−C−Si−H framework, a very short C−H distance of 1.065 Å, and an very wide H−C−Si angle of 175.0°. By means of an equivalent and balanced correlation treatment of the open-shell singlet/triplet pair of states, this theoretical method places $^1A''$-**1** 28.0 kcal mol^{-1} above $^3A''$-**1**. Conjoining the cc-pVTZ ROCISD ($^1A''$, $^3A''$) and CCSD(T) (^1A, $^3A''$) energy separations yields the profile of Scheme 2, wherein the open-shell singlet of **1** lies *above* its closed-shell singlet counterpart by about 10 kcal mol^{-1}. Thus, the ROCISD/cc-pVTZ computations preclude the possibility that the $^1A''$ state of **1** is the species identified in the matrix isolation experiments, not only on energetic grounds but also on the basis of a predicted open-shell singlet C−H stretching frequency 90 cm^{-1} (ROHF/cc-pVTZ) higher than the triplet absorption at 3138 cm^{-1}. Closed-shell ^1A-**1** is likewise eliminated on both accounts by the CCSD(T)/cc-pVTZ results discussed above.

The essential structural and energetic features of the ground-state triplet and closed-shell singlet states of **1** are accurately recovered by B3LYP/6-311+G**, which reproduces the CCSD(T)/cc-pVTZ benchmark (^1A, $^3A''$) energy separation to within 1 kcal mol^{-1}. The failure of the density functional method lies exclusively in its treatment of the open-shell singlet, presumably because the zeroth-order wave function of this state cannot be represented by a single Slater determinant.

Although $^3A''$-**1** truly is a triplet methylene derivative displaying close to tetrahedral bond angles within the $SiHCl_2$ moiety (only one conformer was located) as well as typical Si−H and Si−Cl bond lengths, halogen substitution has an appreciable effect in the stabilization relative to the respective silene, because the parent carbene H−C−SiH_3 lies 46.2 kcal mol^{-1} above silaethylene (vide infra).[19] Providing further

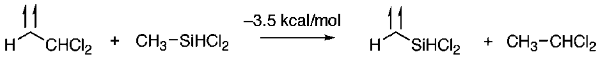
---

[17] All DFT structures were optimized and characterized with Gaussian 98 (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) using the B3LYP functional (A. D. Becke, *J. Chem. Phys.* 1993, *98*, 5648−5652. Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785−789) and a 6-311+G** basis set. This level of theory gives reasonably accurate carbene singlet−triplet energy separations (Schreiner, P. R.; Karney, W. L.; Schleyer, P. v. R.; Borden, W. T.; Hamilton, T. P.; Schaefer, H. F. *J. Org. Chem.* **1996**, *61*, 7030−7039. Das, D.; Whittenburg, S. L. *J. Mol. Struct. (THEOCHEM)* **1999**, *492*, 175−186); systematic errors are on the order of about 2−4 kcal mol^{-1} disfavoring the singlet states.

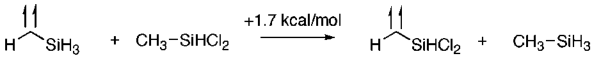
[18] Open-shell singlet CISD energy and gradient computations were performed with PSI 2.0.8 (Janssen, C. L.; Seidl, E. T.; Scuseria, G. E.; Hamilton, T. P.; Yamaguchi, Y.; Remington, R. B.; Xie, Y.; Vacek, G.; Sherrill, C. D.; Crawford, T. D.; Fermann, J. T.; Allen, W. D.; Brooks, B. R.; Fitzgerald, G. B.; Fox, D. J.; Gaw, J. F.; Handy, N. C.; Laidig, W. D.; Lee, T. J.; Pitzer, R. M.; Rice, J. E.; Saxe, P.; Scheiner, A. C.; Schaefer, H. F.; PSITECH, Inc.: Watkinsville, GA, 1995). For background theory, see: Roothaan, C. C. J. *Rev. Mod. Phys.* **1960**, *32*, 179−185. Handy, N. C.; Goddard, J. D.; Schaefer, H. F., III. *J. Chem. Phys.* **1979**, *71*, 426−435. Yamaguchi, Y.; Osamura, Y.; Goddard, J. D.; Schaefer, H. F., III. *A New Dimension to Quantum Chemistry. Analytic Derivative Methods in Ab Initio Molecular Electronic Structure Theory*; Oxford Press: New York, 1994.

[19] Maier, G.; Reisenauer, H. P.; Glatthaar, J. *Chem. Eur. J.* **2002**, *8*, 4383−4391.

support for this point, halogen-substitution groups also stabilize aromatic triplet carbenes.[20] The triplet stabilization effect of the entire $SiHCl_2$ substituent was evaluated (at B3LYP/6-311+G**) relative to its carbon analogue by means of isodesmic eq 1.



(1)



(2)

The stabilizing effect in **1** is seen to be sizable considering the singlet–triplet energy separations of methylene (about 9 kcal mol^{-1}) or even the more comparable ethylidene (about 5 kcal mol^{-1}).[21] Although there is no *direct* stabilizing effect of the chlorine substituents for the carbene **1** (eq 2), chlorine substitution significantly (almost 10 kcal mol^{-1}) decreases the stability of silene **2**, as evident from the singlet–triplet energy separations (B3LYP/6-311+G**) of $H_2C{=}SiH_2$ (35.1 kcal mol^{-1}) and $H_2C{=}SiCl_2$ (25.8 kcal mol^{-1}).

The assumption that only triplet carbene ground states with bulky substituents will be stable derives from the observation that π-donor substituents inevitably stabilize the singlet state more than the triplet state through effective p-π overlap (lone pairs from heteroatoms or conjugated double bonds).[2,7] But even electron-deficient π- as well as σ-donor heteroatom (e.g., BR_2)-substituted carbenes are predicted to have nearly linear singlet ground states.[22] Hence, only a mild σ-electron donor (and poor π-donor) will aid in stabilizing the triplet by increasing the s-orbital contribution at the carbene center:[23] The $SiHCl_2$ group serves this purpose well.

For kinetic stability, the barrier for the thermal rearrangement of a carbene to the respective olefin (in the same electronic state) must be sufficiently high. We compute a more than adequate 41.4 kcal mol^{-1} barrier for the rearrangement of $^3A''$-**1** to $^3A''$-**2** (Scheme 2). This large barrier should allow the spectroscopic identification of $^3A''$-**1** even at much higher temperatures (which are not available under matrix conditions). The alternative migration of a chlorine atom to the carbene center is partially attenuated by the "chlorophilic" nature of silicon. Chlorine substituents are known to destabilize Si═C double bonds, as is also evident from the low-lying (28.4 kcal mol^{-1}) triplet state of **2**.[24]

In summary, we report and assign the first infrared spectrum of a silicon-subsituted triplet carbene bearing an α-hydrogen. The assignment of $^3A''$-**1** based on the matching of measured and ab initio theoretical IR absorptions is unequivocal. The closed- and open-shell singlet states of **1** lie above the triplet ground state by substantial amounts, 19 and 28 kcal mol^{-1}, respectively. A large barrier of about 41 kcal mol^{-1} blocks rearrangement of carbene **1** to olefin **2** on the triplet surface, although there is likely an intersystem crossing mechanism which would become operative at lower energies. With regard to preparing triplet ground-state carbenes that would have a significant lifetime (say 1 h)[7] at ambient temperatures, steric and electronic effects should *both* be considered. Hence, the attachment of a bulky group with a silicon atom (also to avoid dimerization) to the carbene center may be a good strategy to prepare these elusive targets. Computational as well as experimental studies along this route are well underway.

Acknowledgment. This work was supported by the Fonds der Chemischen Industrie. We are obliged to Y. Yamaguchi for his help with the CISD computations. We thank H. F. Bettinger, A. A. Fokin, J. Glatthaar, B. C. Rinderspacher, and W. Sander for helpful comments.

Supporting Information Available: Tables of electronic total energies, cartesian coordinates, and vibrational frequencies of all optimized species; internal coordinate quadratic force field of $^3A''$-**1**, and analysis of the normal modes of vibration of the parent and deuterated isotopomers. This material is available free of charge via the Internet at http://pubs.acs.org.

OL049842J

---

(20) Enyo, T.; Nicolaides, A.; Tomioka, H. *J. Org. Chem.* **2002**, *67*, 5578–5587.

(21) Bettinger, H. F.; Schreiner, P. R.; Schleyer, P. v. R.; Schaefer, H. F., III. In *The Encyclopedia of Computational Chemistry*; Schleyer, P. v. R., Allinger, N. L., Clark, T., Gasteiger, J., Kollman, P. A., Schaefer, H. F., Schreiner, P. R., Eds.; John Wiley & Sons: Chichester, 1998; pp 183–196.

(22) Irikura, K. K.; Goddard, W. A.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 48–51.

(23) Pauling, L. *J. Chem. Soc., Chem. Commun.* **1980**, 688–689. Schoeller, W. W. *J. Chem. Soc., Chem. Commun.* **1980**, 124–125.

(24) Allendorf, M. D.; Melius, C. F. *J. Phys. Chem.* **1993**, *97*, 720–728.