subsequent assignment of combination frequencies in the present case is therefore a confirmation of the theoretical origin of such lines.

The multipoint approximation to the electron spin density has failed to describe the hyperfine anisotropy both in magnitude and in direction. A simple dipole–dipole hyperfine calculation based on multipoint electron spin models using the unpaired wave function determined previously[9] either by SCF–$X\alpha$–SW analysis or by approximate EPR parameters underestimated the observed anisotropies by 25–40% and gave angular differences in the maximum hyperfine coupling directions compared to the experimental values by about 40°. The reasons for this are unclear. However, previous analysis of such weak nitrogen couplings required the use of more elaborate molecular orbital hyperfine terms involving near-neighbor atoms to the remote nitrogens.[20,31] These results indicate that the remote nitrogen hyperfine tensor may not be such a sensitive measure of the nature of the unpaired electron wave function on the copper but are instead also reflective of the unpaired spin distributed over the imidazole ring.

The quadrupole parameters were correlated to the molecular bond directions of an imidazole nitrogen for the first time in the solid state. This tensor, rather than the hyperfine interaction, has the potential to be the key identifying factor for the origin of the magnetic coupling in ESEEM studies of more complex models or in metalloproteins. Also, the derived quadrupole parameters were found to be reasonable as compared to those found for the similar amino nitrogen in *N*-benzylimidazole.[35] The results are consistent with the slight electronegativity differences between the $CH_3$ and $CH_2Ph$ groups in these two model systems. The effects of the coordinating copper and the neighboring carbon-bound methyl group in the 1,2-dimethylimidazole system apparently are either small or cancel each other to maintain this predictable trend.

**Acknowledgment.** We would like to thank Dr. J. Cornelius for explaining his angle selection ESEEM simulation program (NANGSEL) and Dr. J. Vitali and Dr. W. B. Mims for helpful discussions. The following grants are acknowledged: U.S.P.H.S. Grants RR-02583 and GM-40168 (to J.P.) and RRO 148601A (to H.J.S.); Grant CHE 84-17548 from the National Science Foundation (to H.J.S.).

**Registry No.** $N_2$, 7727-37-9.

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# Germasilene ($H_2Ge{=}SiH_2$) and Its Isomers Silylgermylene and Germylsilylene: Bond Dissociation Energies, $\pi$-Bond Energies, and Predictions of Isomeric Stability[†]

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**Abstract:** The prototypical Ge=Si doubly bonded molecule germasilene ($H_2Ge{=}SiH_2$) and its valence isomers silylgermylene ($H_3Si{-}GeH$) and germylsilylene ($H_3Ge{-}SiH$) have been investigated in both their ground-state singlet and lowest lying triplet states. All electron ab initio quantum mechanical techniques were employed, including the effects of electron correlation via configuration interaction and coupled cluster methods. Silylgermylene is found to be the lowest lying isomer, about 6 kcal/mol below the trans-bent germasilene minimum. The $\pi$-bond energy of germasilene is predicted to be 25 kcal/mol, essentially identical with those in disilene ($H_2Si{=}SiH_2$) and digermene ($H_2Ge{=}GeH_2$). The bond dissociation energy, however, decreases in the order Si=Si > Si=Ge > Ge=Ge, and in each case is smaller than that required to break the corresponding single bonds in disilane, germylsilane, and digermane. This phenomena is rationalized by consideration of differences in first and second bond dissociation energies in the parent hydrides, Walsh's so-called divalent state stabilization energies (DSSE). Semiquantitative estimates of the relative energies of group 14 doubly bonded compounds and their corresponding divalent isomers can oftentimes be obtained by properly accounting for the DSSE.

## Introduction

In the last 25 years, Si=C, Si=Si, Ge=C, and Ge=Ge doubly bonded molecules have advanced from the status of "nonexistent compounds"[1] to a class of stable molecules with a rapidly developing chemistry.[2] Conspicuous by its absence is any known example of a Ge=Si doubly bonded molecule, as either a stable compound or reactive intermediate, but it is an obvious synthetic target.

Theoretical studies of the $H_2Si{=}CH_2$,[3] $H_2Si{=}SiH_2$,[4] $H_2Ge{=}CH_2$,[5] and $H_2Ge{=}GeH_2$[6,7] multiply bonded parent compounds and their isomers are numerous as well. Attention has focused on the heavy atom–heavy atom bond distances, degree of planarity, double-bond strengths, and relative stabilities of the corresponding carbene, silylene, and germylene isomers and their barriers to interconversion. Indeed, much of what we know of

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these compounds has come from theory. But once again, there have been no theoretical studies of $H_2Ge{=}SiH_2$.

To fill in this information gap, we report here the results of an ab initio theoretical study of the parent Ge=Si doubly bonded compound germasilene ($H_2Ge{=}SiH_2$) and its isomers germylsilylene ($H_3Ge{-}SiH$) and silylgermylene ($H_3Si{-}GeH$) in both their ground-state singlet and lowest lying triplet states. In addition to reporting their equilibrium geometries and relative energies, we also obtain bond dissociation energies (BDE's) for germanium-silicon single and double bonds and compare them to both silicon-silicon and germanium-germanium BDE's. Rationalizations for double-bond BDE's being *smaller* than single-bond BDE's will be presented. In addition, we will show that recognition of differences in first and second M—H BDE's (M = Ge, Si) in the parent hydrides can account for many of the energy differences found between doubly bonded compounds and their divalent isomers.

## Theoretical Methods

All the structures considered here have been precisely optimized within the given symmetry constraints by employment of restricted Hartree-Fock (RHF) self-consistent field (SCF) analytic gradient techniques.[8] Residual Cartesian and internal coordinate gradients are in all cases less than $10^{-5}$ au. Analytic second-derivative methods were used to evaluate the quadratic force constants and resulting harmonic vibrational frequencies.[9] For two states, the twisted singlet diradical states of disilene and digermene (which we will use for comparative purposes to determine $\pi$-bond strengths), the lowest order wave function is a two-configuration SCF (TCSCF). The two orbitals involved in these TCSCF studies are those that correspond to the $\pi$ and $\pi^*$ orbitals of disilene and digermene and are essentially plus and minus combinations of lone-pair orbitals on the two radical centers at the twisted and puckered internal rotation transition states. The structures of these diradical transition states are determined by analytic TCSCF gradient methods,[10] and their nature as true transition states is verified by analytic TCSCF second-derivative matrix[11] and harmonic vibrational frequency determinations.

The basis set used is of double-$\zeta$ plus polarization quality (DZP). Specifically, for silicon and hydrogen the standard Huzinaga-Dunning[12] (11s7p/6s4p) and (4s/2s) are appended with Cartesian polarization functions with exponents $\alpha_d(\mathrm{Si}) = 0.5$ and $\alpha_p(\mathrm{H}) = 0.75$. The germanium basis set is Olbrich's 7s5p3d contraction of Dunning's 13s9p5d primitive set,[13] with an additional 4d polarization function $\alpha_d(\mathrm{Ge}) = 0.25$. Thus, the germanium basis set may be technically designated as (13s9s6d/7s5p4d). This results in a total of 90 contracted functions for $GeSiH_4$.

Electron correlation effects have been included by the method of configuration interaction (CI). Only the valence electrons have been explicitly correlated. Thus, all corelike (Ge, 1s,2s,2p,3s,3p,3d; Si, 1s,2s,2p) orbitals have been omitted from the CI procedure. Otherwise, all single and double excitations from the SCF reference configuration are included (CISD).[14] Improved estimates of the relative energies of the various isomers studied here are obtained by adding on the Davidson correction[15] for unlinked quadruple excitations (CISD+Q). As it is known that optimization at correlated levels of theory is required to obtain accurate structures and relative energies for the planar and trans-bent disilene, trans-bent and planar germasilene have also been optimized at the CISD level of theory by analytic CISD gradient techniques.[16] Otherwise, all correlated energies are determined at the SCF-optimized geometries.

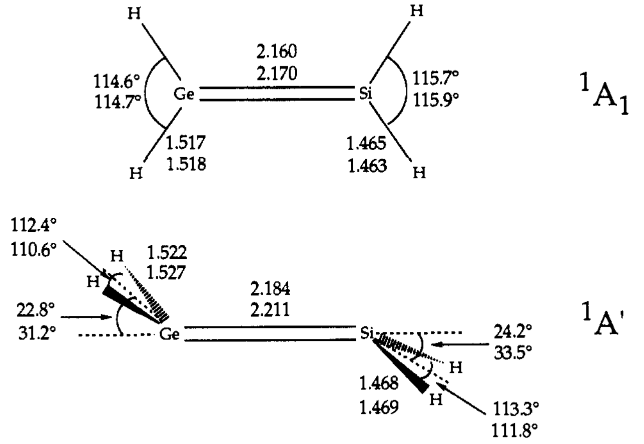

**Figure 1.** Optimized geometries of planar, $C_{2v}$ symmetry, and trans-bent, $C_s$ symmetry, germasilene at both the SCF/DZP and CISD/DZP levels of theory. The CISD parameters are given below the corresponding SCF-optimized values. Bond distances in angstroms.

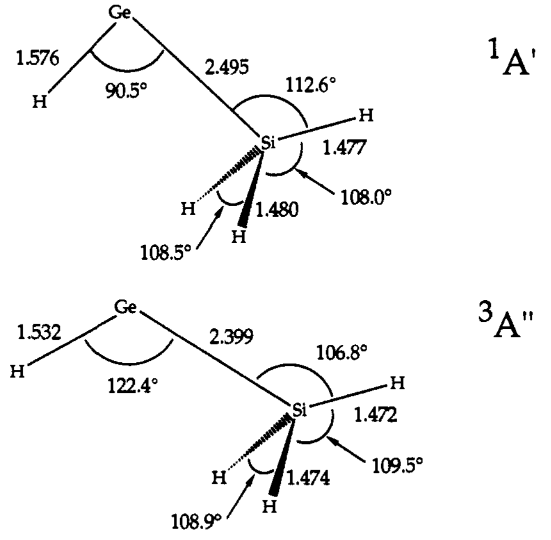

**Figure 2.** SCF/DZP-optimized geometries of the $^1A'$ and $^3A''$ states of silylgermylene in $C_s$ symmetry. Bond distances in angstroms.

To include the effects of electron correlation in estimates of the bond dissociation energies of germasilene, disilene ($H_2Si{=}SiH_2$), digermene ($H_2Ge{=}GeH_2$), germylsilane ($H_3Ge{-}SiH_3$), disilane ($H_3Si{-}SiH_3$), digermane ($H_3Ge{-}GeH_3$), and also the simple hydrides $H_3Ge{-}H$, $H_2Ge{-}H$, $H_3Si{-}H$, and $H_2Si{-}H$, we have employed the size-extensive coupled cluster singles and doubles method (CCSD).[17] For two crucial open-shell molecules, $GeH_3$ and $SiH_3$, the CCSD energies have been determined by use of a program recently developed by Scuseria for open-shell CCSD wave functions based on an RHF reference.[18] The resulting correlated energies do not include any spin contamination. As with the CISD energies, the CCSD energies are determined at the SCF-optimized geometries by use of the frozen-core approximation. To assess the reliability of the CISD relative energies for the germasilene isomers, the singlet-state energies of germylsilylene and silylgermylene have also been obtained with the more rigorous CCSD method.

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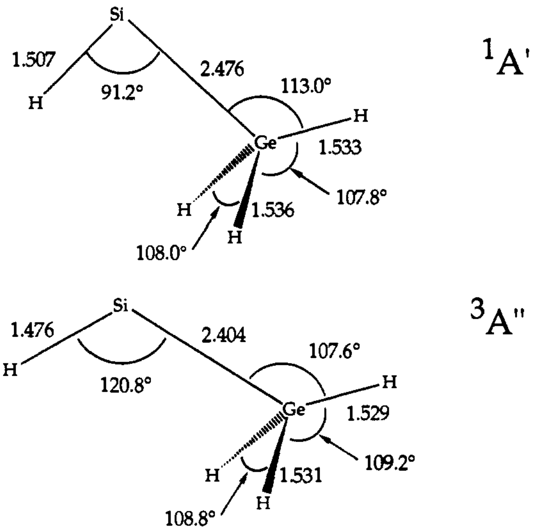

**Figure 3.** SCF/DZP-optimized geometries of the $^1A'$ and $^3A''$ states of germylsilylene in $C_s$ symmetry. Bond distances in angstroms.

For the doubly bonded species, the BDE's are determined directly from the reaction

$$H_2M{=}M'H_2 \rightarrow H_2M + M'H_2$$

For $H_3Ge—H$ and $H_3Si—H$, we have used a scheme analogous to that of Pople et al.[19] in their study of first- and second-row $AH_n$ molecules, which employs isogryic reactions to minimize differential electron-correlation effects. An isogyric reaction is one that conserves the number of unpaired spins and consequently the number of electron pairs. The previous reaction is already isogyric as the products are ground-state singlets, and the simple bond-cleavage reactions of germyl and silyl radicals are isogyric as well. The reaction

$$H_3M—H \rightarrow H_3M + H$$

is, however, not isogyric, and direct determination of the BDE's will be less accurate as a consequence. To alleviate this problem, an appropriate number of hydrogen atoms and molecules is added to each side of the reaction to yield an overall isogyric process. The reaction energy for the isogyric process is then determined from the CCSD total energies, and the BDE's are determined relative to the exact dissociation energy ($D_e$) for the hydrogen molecule, 109.48 kcal/mol. For example, the previous reaction now becomes

$$H_3M—H + H \rightarrow H_3M + H_2$$

and in the case of M = Ge the energy of this process (from Table I) is −0.031 55 hartree (or 19.8 kcal/mol). Using the exact $D_e$ for $H_2$, we determine $D_e$ of $H_3Ge—H$ to be 89.7 kcal/mol. The BDE, technically labeled $D_0$, but abbreviated throughout the rest of the paper as $D$, is then obtained by adding in differences in zero-point vibrational energies (Table I), which we scale by 0.9 to account for known theoretical deficiencies. The result is $D(H_3Ge—H)$ = 84.0 kcal/mol. Similar schemes are used for determining the BDE's of germylsilane, disilane, and digermane.

The optimized geometries of the various $GeSiH_4$ isomers are shown in Figures 1–3 and the top of Figure 4. Other structures employed in the present research for comparative purposes and for the determination of BDE's are given in Figures 4–7. Total energies are given in Table I for all molecules in the present study. Unless otherwise stated, all the relative energies quoted throughout the paper are those obtained at the highest level of theory routinely used in this study, namely CISD+Q.

## Structures and Relative Energies

As in the case of the corresponding homonuclear doubly bonded molecules disilene[4] and digermene,[6,7] planar germasilene (shown at the top of Figure 1, with SCF values given above the corresponding CISD-optimized parameters) has a single imaginary frequency leading to the trans-bent isomer shown at the bottom of Figure 1. The pyramidalization at the Ge and Si centers is accompanied by a lengthening of the Ge=Si double-bond length from 2.160 to 2.184 Å at the SCF level of theory, a slight lengthening of the bond lengths to the hydrogen atoms and a

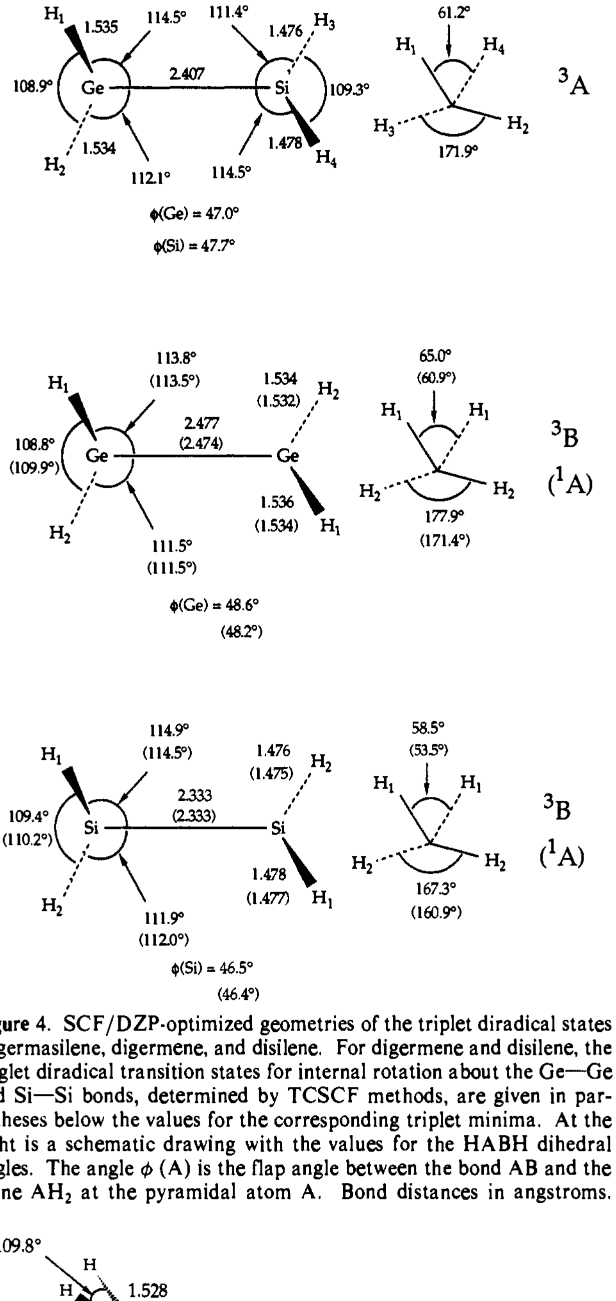

**Figure 4.** SCF/DZP-optimized geometries of the triplet diradical states of germasilene, digermene, and disilene. For digermene and disilene, the singlet diradical transition states for internal rotation about the Ge—Ge and Si—Si bonds, determined by TCSCF methods, are given in parentheses below the values for the corresponding triplet minima. At the right is a schematic drawing with the values for the HABH dihedral angles. The angle ϕ (A) is the flap angle between the bond AB and the plane $AH_2$ at the pyramidal atom A. Bond distances in angstroms.

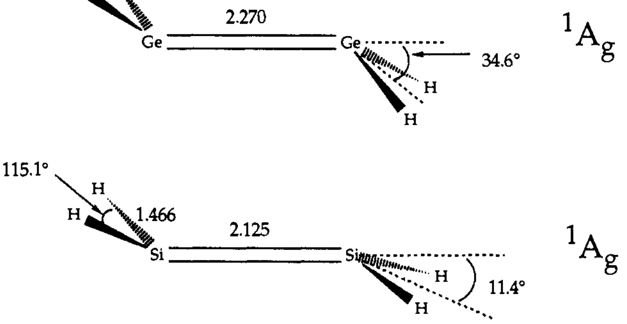

**Figure 5.** SCF/DZP-optimized geometries of trans-bent digermene and disilene in $C_{2h}$ symmetry. Bond distances in angstroms.

decrease of the H—Ge—H and H—Si—H angles. All of these effects are accentuated at the CISD level of theory, and the trends are consistent with the notion[6a] that the bonding in the limiting case is that of a germylene and silylene donor–acceptor complex. That is, the internal $GeH_2$ and $SiH_2$ coordinates tend toward those of free ground-state $^1A_1$ $GeH_2$ and $SiH_2$, shown in Figure 7. One curious feature is that the bonding is slightly more pyramidalized (by about 2°) about the silicon atom than the germanium atom

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**Table I.** Total Energies of All the Molecules Investigated (Hartrees) and Unscaled Zero-Point Vibrational Energies (kcal/mol) (Number of Imaginary Vibrational Frequencies in Parentheses after the ZPVE, Evaluated at the SCF Level of Theory)

| molecule | symmetry | electronic state | $E_{SCF}$ | $E_{CISD}$ | $E_{CISD+Q}$ | $E_{CCSD}$ | ZPVE |
|---|---|---|---|---|---|---|---|
| $H_2Ge{=}SiH_2$ | $C_{2v}$ | $^1A_1$ | −2365.88447 | −2366.09747 | −2366.12132 | −2366.11915 | 20.09 (1) |
| $H_2Ge{=}SiH_2$ | $C_s$ | $^1A'$ | −2365.88488 | −2366.09886 | −2366.12335 | −2366.12118 | 20.24 |
| $H_2Ge{-}SiH_2$ | $C_1$ | $^3A$ | −2365.88113 | −2366.07401 | −2366.09247 | | 19.75 |
| $H_3Si{-}GeH$ | $C_s$ | $^1A'$ | −2365.90623 | −2366.11161 | −2366.13329 | −2366.13160 | 20.13 |
| $H_3Si{-}GeH$ | $C_s$ | $^3A''$ | −2365.89834 | −2366.09119 | −2366.10953 | | 20.71 |
| $H_3Ge{-}SiH$ | $C_s$ | $^1A'$ | −2365.88014 | −2366.08544 | −2366.10742 | −2366.10573 | 19.61 |
| $H_3Ge{-}SiH$ | $C_s$ | $^3A''$ | −2365.87889 | −2366.06991 | −2366.08809 | | 20.06 |
| $H_3Ge{-}GeH_3$ | $D_{3d}$ | $^1A_{1g}$ | −4152.89803 | | | −4153.15572 | 30.81 |
| $H_3Ge{-}SiH_3$ | $C_{3v}$ | $^1A_1$ | −2367.10721 | | | −2367.36606 | 31.77 |
| $H_3Si{-}SiH_3$ | $D_{3d}$ | $^1A_{1g}$ | −581.31673 | | | −581.57613 | 32.85 |
| $H_2Ge{=}GeH_2$ | $C_{2h}$ | $^1A_g$ | −4151.68419 | −4151.89769 | −4151.92275 | −4151.92049 | 19.45 |
| $H_2Ge{-}GeH_2$ | $C_2$ | $^3B$ | −4151.68179 | −4151.87394 | −4151.89260 | | 19.05 |
| $H_2Ge{-}GeH_2$ | $C_2$ | $^1A$ | −4151.67689 | −4151.86948 | −4151.88839 | | 18.73 (1) |
| $H_2Si{=}SiH_2$ | $C_{2h}$ | $^1A_g$ | −580.08533 | −580.29868 | −580.32254 | −580.32052 | 20.85 |
| $H_2Si{-}SiH_2$ | $C_2$ | $^3B$ | −580.08080 | −580.27376 | −580.29183 | | 20.52 |
| $H_2Si{-}SiH_2$ | $C_2$ | $^1A$ | −580.07641 | −580.26994 | −580.28827 | | 20.17 (1) |
| $H_4Ge$ | $T_d$ | $^1A_1$ | −2077.01887 | | | −2077.16291 | 19.79 |
| $H_3Ge$ | $C_{3v}$ | $^2A_1$ | −2076.40655 | | | −2076.52544 | 13.52 |
| $H_2Ge$ | $C_{2v}$ | $^1A_1$ | −2075.81690 | −2075.92320 | −2075.93064 | −2075.92750 | 7.41 |
| $H_2Ge$ | $C_{2v}$ | $^3B_1$ | −2075.79868 | −2075.88893 | −2075.89377 | | 7.72 |
| $H_4Si$ | $T_d$ | $^1A_1$ | −291.23469 | | | −291.37962 | 20.87 |
| $H_3Si$ | $C_{3v}$ | $^2A_1$ | −290.61190 | | | −290.73119 | 14.26 |
| $H_2Si$ | $C_{2v}$ | $^1A_1$ | −290.00467 | −290.11080 | −290.11812 | −290.11514 | 7.84 |
| $H_2Si$ | $C_{2v}$ | $^3B_1$ | −289.99563 | −290.08474 | −290.08921 | | 8.14 |
| $H_2$ | $D_{\infty h}$ | $^1\Sigma_g$ | −1.13109 | −1.16666 | −1.16666 | −1.16666 | 6.64 |
| H | $K_h$ | $^2S_g$ | −0.49764 | −0.49764 | −0.49764 | −0.49764 | 0.00 |

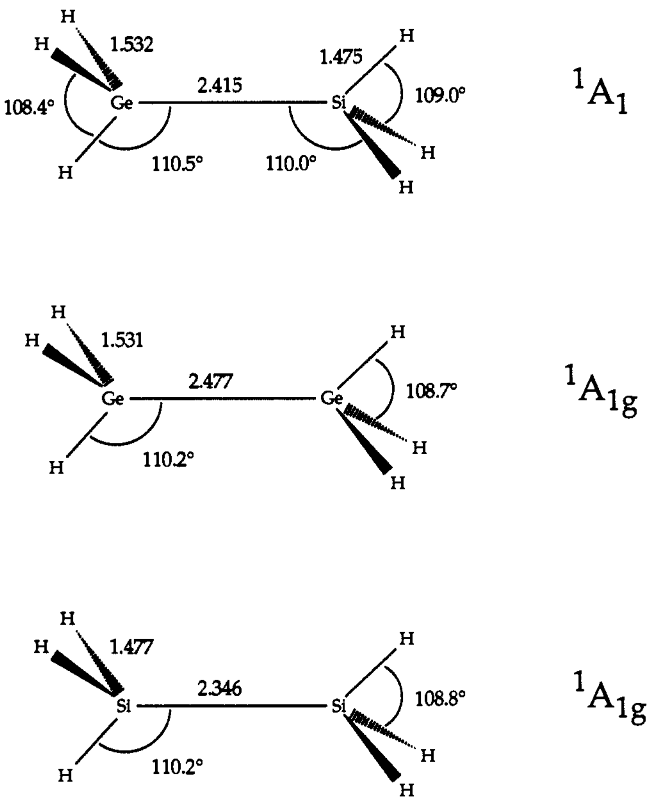

Figure 6. SCF/DZP-optimized geometries of germylsilane, digermane, and disilane. Bond distances in angstroms.

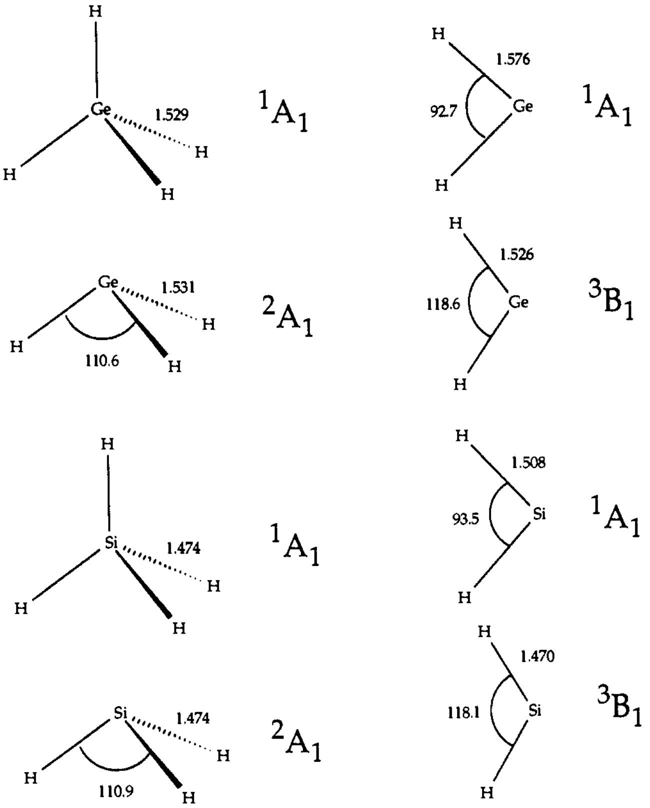

Figure 7. SCF/DZP-optimized geometries of the parent hydrides $GeH_n$ and $SiH_n$ ($n$ = 2–4). Optimized geometries for germylene, $GeH_2$, and silylene, $SiH_2$, are given for both the ground-state singlet and lowest lying triplet states. Bond distances in angstroms.

in trans-bent germasilene, whereas digermene is distinctly more trans-bent than disilene (Figure 5). At the SCF level of theory, the trans-bent minimum lies only 0.3 kcal/mol below the planar structure (see Table II for relative energies). Single-point CISD energies raise this to 0.9 kcal/mol, and appending the Davidson correction (CISD+Q) gives 1.3 kcal/mol (Table II). At the CISD-optimized geometries, the CISD and CISD+Q relative energies are raised slightly to 1.1 and 1.8 kcal/mol, respectively. Conversion of the energy differences to 0 K enthalpy differences ($\Delta H$) by including differences in zero-point vibrational energies (scaled by 0.9) lowers these values by only 0.1 kcal/mol.

The SCF-optimized geometries of the $^1A'$ and $^3A''$ electronic states ($C_s$ symmetry) of the silylgermylene isomer ($H_3SiGeH$) are shown in Figure 2. As is typical of divalent Ge compounds (see, e.g., Figure 7), the singlet states have bond angles near 90° with elongated bonds (compare Figures 7 and 6) whereas the triplet states have bond angles near 120° with shorter bonds than in normal saturated germanium compounds. The Ge—Si bond

**Table II.** Relative Energies (kcal/mol) of the Isomers of $GeSiH_4$ at the SCF, CISD, CISD+Q, and CCSD Levels of Theory and 0 K Enthalpy Differences at the CISD+Q Level of Theory (with Use of Scaled SCF Harmonic Vibrational Frequencies), All Obtained with a DZP Basis Set

| molecule | symmetry | electronic state | $\Delta E_{SCF}$ | $\Delta E_{CISD}$ | $\Delta E_{CISD+Q}$ | $\Delta E_{CCSD}$ | $\Delta H_{CISD+Q}$ |
|---|---|---|---|---|---|---|---|
| $H_2Ge{=}SiH_2$ | $C_{2v}$ | $^1A_1$ | 13.7 | 8.9 | 7.5 | 7.8 | 7.5 |
| $H_2Ge{=}SiH_2$ | $C_s$ | $^1A'$ | 13.4 | 8.0 | 6.2 | 6.5 | 6.3 |
| $H_2Ge{-}SiH_2$ | $C_1$ | $^3A$ | 15.8 | 23.6 | 25.6 | | 25.2 |
| $H_3Si{-}GeH$ | $C_s$ | $^1A'$ | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| $H_3Si{-}GeH$ | $C_s$ | $^3A''$ | 5.0 | 12.8 | 14.9 | | 14.4 |
| $H_3Ge{-}SiH$ | $C_s$ | $^1A'$ | 16.4 | 16.4 | 16.2 | 16.2 | 15.7 |
| $H_3Ge{-}SiH$ | $C_s$ | $^3A''$ | 17.1 | 26.2 | 28.4 | | 28.3 |

distances are particularly striking, being nearly 0.1 Å shorter in the triplet state than in the singlet state. This may be at least partly ascribed to negative hyperconjugation, i.e., germanium $\pi$ to Si—H $\sigma^*$ electron donation in the triplet state. A second consequences of this negative hyperconjugative stabilization in the triplet state is a reduced singlet–triplet splitting in silylgermylene (14.9 kcal/mol CISD+Q) compared to $GeH_2$ (23.1 kcal/mol), although at least some of this difference may be attributed to inductive destabilization of the germanium lone pair in the singlet by the relatively electropositive silyl group. The singlet state of silylgermylene lies 6.2 kcal/mol below trans-bent germasilene and is the lowest lying isomer of $GeSiH_4$.

The singlet and triplet states of germylsilylene ($H_3GeSiH$) shown in Figure 3 exhibit the same relative structural trends as silylgermylene discussed previously, although the bond distance variations between the $^1A'$ and $^3A''$ states are less than those found above. This might have been predicted from a comparison of the parent compounds $SiH_2$ and $GeH_2$ (Figure 7) where similar behavior is found. This, for example, while the Ge—H bond distances in $GeH_2$ differ by 0.050 Å between the singlet and triplet states, the corresponding distances in $SiH_2$ differ by only 0.038 Å, and similarly the Ge—Si distances in singlet and triplet germylsilylene differ by 0.072 Å compared to 0.096 Å in silylgermylene. The singlet–triplet splitting in $H_3GeSiH$ is 12.2 kcal/mol, compared to 18.1 kcal/mol in $SiH_2$ at the same level of theory. That germyl substitution in silylenes has a smaller effect (5.9 kcal/mol) on the singlet–triplet splitting than silyl substitution in germylenes (8.2 kcal/mol from above) may be traced to germanium's slightly greater electronegativity than silicon, the result being a smaller predicted inductive destabilization of the lone pair in the singlet state and smaller negative-hyperconjugative stabilization of the triplet state in the silylene than the germylene. The singlet state of germylsilylene is predicted to lie 16.2 kcal/mol above the ground-state silylgermylene isomer.

One final isomer, about which we will say much more in the next section, is the triplet state of the germasilene linkage isomer ($H_2GeSiH_2$), shown at the top of Figure 4. The optimized geometry of this state has no elements of symmetry (i.e., it belongs to the $C_1$ point group) and is consistent with a description as linked germyl and silyl radical centers. Compare, for example, the geometry of this isomer with those of the parent germyl and silyl radicals in Figure 7. The Ge—H and Si—H bond distances and the H—Ge—H and H—Si—H bond angles are all only slightly perturbed from those in the parent radicals. The triplet state is predicted to be 19.4 kcal/mol above singlet trans-bent germasilene and 25.6 kcal/mol above the lowest lying silylgermylene isomer.

In summary, the lowest lying isomer of $GeSiH_4$ is singlet silylgermylene (top of Figure 2). Next is the doubly bonded trans-bent germasilene isomer (Figure 1), predicted to be 6.2 kcal/mol above silylgermylene and 1.3 kcal/mol below the planar germasilene transition state. The triplet state of silylgermylene (bottom of Figure 2) and the singlet state of germylsilylene (top of Figure 3) appear next but are only about 1 kcal/mol apart, predicted to lie 14.9 and 16.2 kcal/mol above the ground state, respectively. The relative ordering of these two states could easily change with larger basis sets or more extensive electron correlation methods. The triplet state of the germasilene linkage isomer (top of Figure 4) is the next most stable isomer, 25.6 kcal/mol above silylgermylene. Finally, the $^3A''$ state of germylsilylene, shown at the bottom of Figure 3, is predicted to be the highest lying isomer, 28.4 kcal/mol above the ground state. Also listed in Table II are relative energies of the various singlet isomers determined with the more theoretically complete CCSD method. In all cases these are nearly identical with the CISD+Q results, as expected for single-reference-dominated systems with only a few (12) electrons being correlated.

Finally, a note about the likely accuracy of our theoretically predicted isomeric energy differences. Studies by Bauschlicher and Taylor[20] have shown that CISD+Q relative energies for singlet–triplet splittings ($\Delta E_{ST}$) in $CH_2$ and $SiH_2$ are within 1 kcal/mol of the full CI results with a DZP basis set and that the remaining errors are thus due to basis set limitations. Balasumbramanian and McLean,[21] using large basis sets and multireference CI wave functions (MRCI), obtain $\Delta E_{ST}(SiH_2)$ = 19.6 kcal/mol, compared to the value 18.1 kcal/mol found here, but argue that the final value will be 21.0 ± 1.0 kcal/mol. Thus, the actual singlet–triplet splitting in germysilylene may be a few kilocalories per mole higher than that found here. Confusing this issue somewhat, however, is our result $\Delta E_{ST}(GeH_2)$ = 23.1 kcal/mol, which is identical with large basis set MRCI results.[22] In the end, we estimate that all our CISD+Q relative energies are accurate to within about ±4 kcal/mol.

## $\pi$-Bond Energies

As a matter of general interest, and great utility, we determined an estimate of the Ge=Si $\pi$-bond energy from the rotational barrier. Other definitions of $\pi$-bond energy are possible, such as those from heats of hydrogenation or disproportionation, but the results are usually similar. A technical problem associated with the lack of symmetry in the rotational transition state of germasilene prevents a trivial determination of the actual transition state on the open-shell singlet surface, so we will use instead the triplet-state energy and carefully calibrate the result by comparison with disilene and digermene, for which we may compare the triplet energy with that of the actual transition state on the singlet surface.

The triplet state of germasilene is shown in the top of Figure 4, and given below it are the triplet and rotated singlet states of both digermene and disilene, the singlet states having been determined with two-configuration SCF methods. Generally speaking, the minimum in the triplet surface of doubly bonded species is quite close to the rotated singlet transition states, and that is what we found here as well. Schmidt et al.[23] have demonstrated this to be a wide-ranging phenomena, although they noted that disilene was a bit of an exception, as they found a significant difference in the degree of pyramidalization at the silicon in the singlet transition state and triplet minimum. The energetic consequence was nonetheless very small, with less than 0.3 kcal/mol separating the two structures.

The triplet state of germasilene, as noted in the previous section, lies 19.4 kcal/mol above the trans-bent doubly bonded structure. The triplet-state minima of disilene and digermene are very similar, being 19.3 and 18.9 kcal/mol above their respective doubly bonded trans-bent structures at the CISD+Q level of theory. The actual singlet transition state is only slightly higher, 21.5 kcal/mol for disilene and 21.6 kcal/mol for digermene. In reality, however,

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**Table III.** Bond Dissociation Energies and π-Bond Strengths (kcal/mol)

| bond | $D$ | π bond | $D$ |
|---|---|---|---|
| $H_3Ge—H$ | 84.0 | Ge=Ge | 25 |
| $H_2Ge—H$ | 57.4 | Ge=Si | 25 |
| $H_3Si—H$ | 90.6 | Si=Si | 25 |
| $H_2Si—H$ | 68.5 | Ge=C | 31[c] |
| $H_3C—H$ | 104.6[a] | Si=C | 38[d] |
| $H_2C—H$ | 111.2[a] | Si=N | 36[d] |
| $H_2N—H$ | 107.2[a] | Si=O | 50[d] |
| HO—H | 117.9[a] | Si=P | 29[d] |
| $H_2P—H$ | 81.4[a] | | |
| $H_3Ge—GeH_3$ | 64.3 | | |
| $H_3Ge—SiH_3$ | 67.0 | | |
| $H_3Si—SiH_3$ | 69.4 | | |
| $H_3Si—CH_3$ | 88.2[b] | | |
| $H_2Ge=GeH_2$ | 36.9 | | |
| $H_2Ge=SiH_2$ | 44.8 | | |
| $H_2Si=SiH_2$ | 52.0 | | |

[a] Reference 19. [b] Reference 26. [c] Reference 24. [d] Reference 23.

this comparison is slightly biased toward the transition state, as it is being described by a TCSCF reference, and the trans-bent minima, which can be smoothly connected to the transition state along a $C_2$ symmetry path, are being described with only a single-configuration reference. To account for this bias, we have determined the two-reference CISD+Q energies of disilene and digermene at their SCF-optimized geometries. This raises the π-bond energy estimate of disilene and digermene to 23.8 and 24.3 kcal/mol, respectively. Assuming this would be raised by another kilocalorie per mole or so if the energies of the trans-bent structures were determined at TCSCF-optimized geometries instead of being obtained by single-point energies at the SCF-optimized geometries, we would arrive at an estimate of about 25 kcal/mol for the π-bond energies of both disilene and digermene; and since their triplet energies are nearly identical with that of germasilene, we must assume that germasilene, too, has a π-bond energy of about 25 kcal/mol.

The Si=Si π-bond energy determined above, 25 kcal/mol, is identical with that recommended by Schmidt et al.[23] It is surprising that the Ge=Ge and Ge=Si π-bond energies should be nearly identical with this. Dobbs and Hehre[24] have reported π-bond energies for X=C bonds (X = C, Si, Ge, Sn), and they found Ge=C π bonds to be 4 kcal/mol weaker than Si=C (31 vs 35 kcal/mol). Trinquier et al.[5b] found a slightly smaller value for the Ge=C π-bond energy, 28.7 kcal/mol, which might be partially attributed to their determination of the singlet diradical energy at the triplet geometry. It may be that larger basis sets will uncover some differences in Si=Si, Ge=Si, and Ge=Ge π-bond energies, but it appears likely that they will remain close to one another.

## Bond Dissociation Energies

The bond dissociation energies determined by the procedure outlined in Theoretical Methods are given in Table III. Many of these have been previously determined with larger basis sets theoretically, or by experiment. For example Pople et al.[19] have determined BDE's of $SiH_n$ by ab initio quantum mechanical methods, as have Ho et al.[25] and Walsh[26] has determined the sequential BDE's of silane experimentally as well. Walsh and co-workers have also determined $D(H_3Si—SiH_3)$[26] and the Ge—Ge BDE in $Ge_2H_6$, as well as the first BDE in $GeH_4$.[27] While we were writing up the results of the present work, two studies on $GeH_n$ appeared, one experimental[28] and one theoretical,[29] that determined the sequential bond dissociation energies of $GeH_4$. The results obtained here differ from those reported by these other researchers by a few kilocalories per mole at most. The largest discrepancy, where comparison can be made, is for the Si—Si single bond in disilane where we predict 69.4 kcal/mol and Walsh obtains 73.6 kcal/mol. We have no reason to suspect that Walsh's number is wrong, and if we used a larger basis set, the value we predict could very well squeeze into the experimental error bars given by Walsh as 2 kcal/mol. In the discussion that follows, however, we will employ the values determined in this work for the germanium and silicon compounds for internal consistency, even though a better set might be chosen. This choice will not alter any of our conclusions in a significant manner. Included in Table III are a number of BDE's and π-bond energies (which we will make use of later) that do not derive from this work, and these are referenced in the table. Except for $D(H_3Si—CH_3)$, which is an experimental value due to Walsh,[26] all of the BDE's and π-bond energies reported there are determined from theoretical studies.

One feature of silicon (and germanium) BDE's that deserves special comment is the relationship between the first and second bond dissociation energies. In his extensive studies of silicon thermochemistry, Walsh[26,30-33] has observed that the second bond dissociation energy in $SiX_4$ compounds is invariably lower than the first. He has defined this difference to be the divalent-state stabilization energy and takes it as evidence of a lone-pair stabilizing effect in $SiX_2$ species. Correlations between the electronegativity of X and the value of the DSSE have been noted[33] and rationalized as a deshielding effect. That is, the more electronegative is X, the more the bonding electrons are pulled toward it, which increases the attraction of the silicon nucleus for the lone-pair (mainly s-type) electrons, yielding a larger DSSE. Walsh has determined values of the DSSE for $SiX_2$ compounds with X = H, Me, F, Cl, Br, and I. In addition, Walsh has determined values of the first and second Si—H BDE's in $H_3CSiH_3$ and $Si_2H_6$, thus providing values of the DSSE for $H_3CSiH$ and $H_3SiSiH$.[26] Curiously, neither of the latter two compounds fit the original definition of DSSE given by Walsh[30] as they are not of the $SiX_4$ type; i.e., they do not have four equivalent substituents. The following question arises: Is the DSSE a property of $SiX_4$, or of the silylene, $SiX_2$, only? Clearly, if it is a property of the silylene itself, as Walsh assumes, it acquires much greater utility. If, for example, the DSSE of $SiH_2$, which we determine to be 22.1 kcal/mol (Walsh finds 19.4, Pople et al. 24.9, and Ho et al. 19.3 kcal/mol), is a property only of $SiH_2$, then knowledge of $D(H_2YSi—Y)$ is sufficient to determine $D(H_2Si—Y)$ as well, for any Y.

Thermochemical data to test the hypothesis of the dependence of DSSE only on the silylene are unfortunately quite scarce. One source is the extensive theoretical study of Ho et al.,[25] in which they determined heats of formation of all the $SiH_nCl_m$ compounds. Using their data, we can compare DSSE's obtained for $SiH_2$, SiHCl, and $SiCl_2$ by breaking either a pair of H bonds or Cl bonds from the appropriate silane. In each case the agreement is very good, even though the individual Si—H and Si—Cl BDE's are themselves quite different. For example, the DSSE of $SiH_2$ determined from $SiH_4$ is 19.1 kcal/mol (=90.0 kcal/mol for the first Si—H BDE minus 70.9 kcal/mol for the second Si—H BDE) whereas that from $SiH_2Cl_2$ is 22.1 kcal/mol (=110.2 − 88.1). For $SiCl_2$, DSSE = 43.5 kcal/mol (=90.7 − 47.2) from $SiCl_2H_2$ and 43.1 kcal/mol (=110.2 − 67.1) from $SiCl_4$. Finally, for SiHCl, one finds DSSE = 30.8 kcal/mol (=90.5 − 59.7) from $SiClH_3$ and 31.8 kcal/mol (=111.0 − 79.2) from $SiHCl_3$. Thus, Walsh's assumption that the DSSE depends only on the resuling silylene appears reasonable from this limited data.

Assuming that the DSSE is, in general, a function only of the resulting divalent silylene and is a feature of germanium chemistry as well, we are in a position to explain the curious fact that disilene,

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digermene, and germasilene all require *less* energy to break their double bonds than their corresponding single bonds. For example, from Table III we see that $D(\mathrm{H_3Si{-}SiH_3}) = 69.4$ kcal/mol but that $D(\mathrm{H_2Si{=}SiH_2}) = 52.0$ kcal/mol and that Ge—Ge and Ge—Si single bonds also have larger BDE's than their corresponding double bonds. These results can be predicted as follows. Starting with disilene, we first break the double bond by rotating it. As we determined in the last section, and in agreement with previous studies,[23] this requires 25 kcal/mol and leaves the molecule in the rotated singlet diradical state. Assuming that the $\mathrm{SiH_2}$ radical attached to each other has the same electronic effects as an $\mathrm{SiH_3}$ group, breaking the remaining Si—Si bond will require the same energy as that required to break the single bond in $\mathrm{H_3Si{-}SiH_3}$, 69.4 kcal/mol (Table III), *minus* 2 times the DSSE of $\mathrm{SiH_2}$, 22.1 kcal/mol, as we have now produced two silylenes. That is, we predict $D(\mathrm{H_2Si{=}SiH_2}) = 25.0 + 69.4 - 2(22.1) = 50.2$ kcal/mol, in excellent agreement with the value, 52.0 kcal/mol, given in Table III. This procedure is summarized as follows

$$\mathrm{H_2M{=}M'H_2} \rightarrow \mathrm{H_2M{-}M'H_2} \qquad \Delta E = D_\pi$$

$$\mathrm{H_2M{-}M'H_2} \rightarrow \mathrm{MH_2} + \mathrm{M'H_2}$$

$$\Delta E = \mathrm{D}_\sigma - \mathrm{DSSE(MH_2)} - \mathrm{DSSE(M'H_2)}$$

which yields

$$\mathrm{H_2M{=}M'H_2} \rightarrow \mathrm{MH_2} + \mathrm{M'H_2}$$

$$\Delta E = D_\pi + D_\sigma - \mathrm{DSSE(MH_2)} - \mathrm{DSSE(M'H_2)} \qquad (1)$$

By use of eq 1 with $\mathrm{DSSE(GeH_2)} = 26.6$ kcal/mol (obtained from the data in Table III) along with the values for Ge—Si and Ge—Ge single-bond BDE's and the $\pi$-bond energies obtained earlier, analogous predictions of $D(\mathrm{H_2Ge{=}GeH_2})$ and $D(\mathrm{H_2Ge{=}SiH_2})$ may be obtained as

$$D(\mathrm{H_2Ge{=}GeH_2}) = 25.0 + 64.3 - 2(26.6) = 36.1 \text{ kcal/mol}$$

$$D(\mathrm{H_2Ge{=}SiH_2}) = 25.0 + 67.0 - 26.6 - 22.1 = 43.3 \text{ kcal/mol}$$

both in excellent agreement with the values predicted directly from theory in Table III.

Unusually small double-bond BDE's, particularly that in $\mathrm{F_2C{=}CF_2}$, have recently been discussed by Carter and Goddard.[34] They have argued that small double-bond BDE's are associated with fragments that have singlet ground states, as opposed to triplets. For example, the bond dissociation energy (at 298 K) of ethylene is 172.2 ± 2.1 kcal/mol and dissociates to ground-state triplet (methylene) fragments, whereas tetrafluoroethylene, which dissociates to ground-state singlet $\mathrm{CF_2}$ fragments, has an empirically determined bond dissociation somewhere in the range of 53–76 kcal/mol, depending on which value of the heat of formation of $\mathrm{CF_2}$ one uses. In a later publication,[35] Carter and Goddard determined the BDE of tetrafluoroethylene to be 64.5 kcal/mol by quantum mechanical methods. Carter and Goddard have further proposed[34] that the difference between the "intrinsic" double-bond energy, chosen to be that in ethylene, and the actual double-bond BDE is just the sum of the singlet–triplet splittings in the fragments, if the singlet is the most stable. That is, if CXY and CX′Y′ have singlet ground states, then

$$D(\mathrm{XYC{=}CX'Y'}) = D_{\mathrm{int}}(\mathrm{C{=}C}) - [\Delta E_{\mathrm{ST}}(\mathrm{CXY}) + \Delta E_{\mathrm{ST}}(\mathrm{CX'Y'})]$$

A second prediction of Carter and Goddard[34] is that the singlet–triplet splitting in a ground-state singlet carbene (CXY) may be approximated by the difference in the sum of the first and second C—H BDE's in $\mathrm{CH_4}$ and $\mathrm{XYCH_2}$. That is

$$\Delta E_{\mathrm{ST}} = D_{12}(\mathrm{H_2C;\, H,H}) - D_{12}(\mathrm{XYC;\, H,H})$$

where $D_{12}(\mathrm{XYC;\, H,H}) = D(\mathrm{XYHC{-}H}) + D(\mathrm{XYC{-}H})$. Thus, for example, using the value for the singlet–triplet splitting in $\mathrm{CF_2}$ of 57.5 kcal/mol obtained in their MRCI studies[36] and experimental values for $D_{12}(\mathrm{H_2C;\, H,H}) = 214.2$ kcal/mol and $D_{12}(\mathrm{F_2C;\, H,H}) = 168.0$ kcal/mol (which also depends on which value one uses for $\Delta H_f(\mathrm{CF_2})$), Carter and Goddard[36] note that

$$D(\mathrm{F_2C{=}CF_2}) = 172.2 - 2(57.5) = 57.2 \text{ kcal/mol}$$

in good agreement with their theoretically determined value of 64.5 kcal/mol.[35] Furthermore, they predict[34] that

$$\Delta E_{\mathrm{ST}}(\mathrm{CF_2}) = 214.2 - 168.0 = 46.2 \text{ kcal/mol}$$

from empirically determined values of $D_{12}(\mathrm{F_2C;\, H,H})$ and $D_{12}(\mathrm{H_2C;\, H,H})$, in reasonable agreement with their accurate MRCI value of 57.5 kcal/mol. In some cases agreement is less satisfactory. For example, CHF, for which huge atomic natural-orbital MRCI studies[37] and experiment[38] find $\Delta E_{S}T(\mathrm{CHF}) = 11.4$ kcal/mol (in contrast, ref 36 finds $\Delta E = 17.7$ kcal/mol; note, however, that the experiments[38] cannot exclude the possibility that the origin is 1 quantum on either side of their observed peak, i.e., the value may be 14.7 or 8.1 kcal/mol), the Carter–Goddard scheme predicts $D(\mathrm{FHC{=}CHF}) = 172.2 - 2(11.4) = 149.4$ kcal/mol, compared to 122.0 ± 6 kcal/mol for experimental heats of formation.[36] Carter and Goddard's basic premise that the dominant effect in bond energy trends in $\mathrm{CXYH_2}$ and substituted olefins is the singlet–triplet splitting in CXY has been extended by Trinquier and Malrieu[39] to rationalize cases of double-bond bending as well.

We point out that our analysis, summarized by eq 1, yields equally good predictions for $D(\mathrm{F_2C{=}CF_2})$. From experimental heats of formation at 0 K,[40] the first and second BDE's of $\mathrm{CF_4}$ are found to be 128.3 and 86.6 kcal/mol, respectively, yielding $\mathrm{DSSE(CF_2)} = 41.7$ kcal/mol. Thus, from eq 1, and taking the C—C $\sigma$- and $\pi$-bond energies to be their standard values of 88[40] and 65 kcal/mol,[23] we obtain

$$D(\mathrm{F_2C{=}CF_2}) = 65 + 88 - 2(41.7) = 69.6 \text{ kcal/mol}$$

compared to Carter and Goddard's theoretically determined value of 64.5 kcal/mol.[35] We should emphasize the difference between the two approaches. Carter and Goddard assume that the BDE in $\mathrm{F_2C{=}CF_2}$ is lower than that in ethylene by twice the singlet–triplet splitting in $\mathrm{CF_2}$, which they equate with the difference between the *sum* of the first and second C—H BDE's in $\mathrm{CH_4}$ and $\mathrm{CF_2H_2}$, whereas we have determined $D(\mathrm{F_2C{=}CF_2})$ as the sum of standard $\sigma$- and $\pi$-bond strengths in the parent hydrocarbons (which is *not* the same as $D(\mathrm{H_2C{=}CH_2})$, see the following text) minus twice the *difference* in the first and second BDE's in $\mathrm{CF_4}$ (i.e., the DSSE of $\mathrm{CF_2}$), which is assumed to be a property of $\mathrm{CF_2}$ itself.

It is worth noting that $D(\mathrm{H_2C{=}CH_2})$ can be prediced from $D(\mathrm{H_3C{-}CH_3})$ and the sequential BDE's of $\mathrm{CH_4}$ in the same way that $D(\mathrm{H_2Si{=}SiH_2})$, $D(\mathrm{H_2Ge{=}GeH_2})$, and $D(\mathrm{H_2Ge{=}SiH_2})$ were predicted previously from $D(\mathrm{H_3Si{-}SiH_3})$, $D(\mathrm{H_3Ge{-}GeH_3})$, $D(\mathrm{H_3Ge{-}SiH_3})$ and the sequential BDE's of $\mathrm{SiH_4}$ and $\mathrm{GeH_4}$. Thus, using eq 1 and standard values of 88[40] and 65 kcal/mol[23] for C–C single- and double-bond energies along with the sequential BDE's in methane (Table III) of 104.6 and 111.2 kcal/mol from Pople et al.,[19] we predict

$$D(\mathrm{H_2C{=}CH_2}) = 65 + 88 - 2(-6.6) = 166.2 \text{ kcal/mol}$$

compared to the value, 169.9 kcal/mol, determined from 0 K heats of formation.[40] The qualitative difference in the relationship between single- and double-bond BDE's in C—C-bonded molecules, on the one hand, and Si—Si, Ge—Ge, and Ge—Si compounds, on the other hand, can therefore be related to properties

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of the parent hydrides. That is, whereas for silicon and germanium compounds the second BDE is much smaller than the first (DSSE is larger and positive), in the hydrocarbons the second BDE is larger than the first (DSSE is negative).

The second BDE in methane being larger than the first is well-known and mentioned in virtually every standard organic chemistry text, with the traditional explanation being that the methyl radical ($CH_3$) is planar and involves stronger $sp^2$-hybridized C—H bonds. The analysis above, then, is equivalent to the assumption that the $C_{sp^2}$—$C_{sp^2}$ bond in the twisted diradical state of ethylene is stronger than a normal $C_{sp^3}$—$C_{sp^3}$ single bond by twice the amount that the $C_{sp^2}$—H bond in the methyl radical is stronger than the $C_{sp^3}$—H bond in methane. At the risk of being too quantitative, we might note that the small difference between the predicted and experimental values of $D(H_2C{=}CH_2)$ may be related to the well-known stabilization of primary methyl radicals compared to $CH_3$, generally attributed to hyperconjugation. Regardless, it is clear that the principal difference between the actual BDE in ethylene and the sum of standard $\sigma$- and $\pi$-bond strengths can be related to the properties of methane itself, namely its first and second C—H BDE's.

While we cannot advocate the use of DSSE as a quantitative measure of singlet–triplet splittings in carbenes, silylenes, or germylenes, in many ways it is superior to Carter and Goddard's measures. For example, DSSE is not required to be positive, whereas Carter and Goddard[34] predict that the sum of the first two C—H BDE's is independent of substitution in a $CXYH_2$ compound unless CXY has a ground-state singlet. In fact, the DSSE of $CH_2$, −6.6 kcal/mol, is within a few kilocalories per mole of the actual singlet–triplet splitting of methylene, found to be −9.0 kcal/mol.[41] Carter and Goddard's scheme trivially yields the singlet–triplet splitting in $SiH_2$, as it is defined in such a way as to guarantee it,[34] but the DSSE's of $SiH_2$, and $GeH_2$ are, by themselves, both within a few kilocalories per mole of their singlet–triplet splittings.

With its built-in zero as the singlet–triplet splitting of $SiH_2$, it is not surprising that Carter and Goddard's scheme does reasonably well in predicting singlet–triplet splittings for substituted silylenes for which the substituents have small electronic effects. Two examples are $H_3CSiH$ and $Si(CH_3)_2$, for which quantum mechanical studies[42,43] predict singlet–triplet splittings about 5–10 kcal/mol larger than that in $SiH_2$, in agreement with predictions from Carter and Goddard's scheme employing experimental values for the sequential BDE's determined by Walsh.[26] But the DSSE accurately predicts that the singlet–triplet splittings in those cases are slightly larger than that in $SiH_2$ without any built-in knowledge. For the case of silylsilylene ($H_3SiSiH$) Carter and Goddard's method incorrectly predicts (using Walsh's data[26]) that the singlet–triplet splitting should be larger than that in $SiH_2$, while theoretical studies find it to be about 6 kcal/mol lower,[42] a trend quantitatively predicted by DSSE.[26] Again, however, we note that both DSSE and the method proposed by Carter and Goddard compare less well with good theoretical and experimental values for singlet–triplet splittings in halogen-substituted carbenes and silylenes.

Experimentally, it is found that germylenes ($R_2Ge$) are monomeric if R is an N-, O-, S-, or halogen-centered ligand.[44] This can be understood from eq 1, Walsh's tables of DSSE for halogenated silylenes,[31-33] and the qualitative (sometimes quantitative) relationship between DSSE and singlet–triplet splittings of divalent carbon, silicon, and, we assume, germanium compounds (also see ref 7). Specifically, Walsh finds DSSE($SiF_2$) = 49 ± 10 kcal/mol, DSSE($SiCl_2$) = 38 ± 4 kcal/mol, DSSE($SiBr_2$) = 34 ± 12 kcal/mol, and DSSE($SiI_2$) = 32 ± 13 kcal/mol, all (ignoring error bars) significantly larger than DSSE($SiH_2$), which Walsh determines to be 19.4 ± 2 kcal/mol.[33] Assuming that this trend holds for germanium as well, the DSSE($GeX_2$) should all be larger than DSSE($GeH_2$) by similar amounts. Thus, using eq 1 with DSSE($MH_2$) replaced by DSSE($GeX_2$), we predict that any $X_2Ge{=}GeX_2$ compound for which DSSE($GeX_2$) is more than 18 kcal/mol greater than DSSE($GeH_2$), the double-bond BDE will be negative, and thus will not be stable. Fluorine and chlorine appear to satisfy this criteria for instability, while bromine and iodine seem to fall a bit shy. Nonetheless, for cases in which $D(X_2Ge{=}GeX_2)$ is small, less than about 20 kcal/mol, intermolecular forces can easily lead to structures more stable than the doubly bonded dimer. Quantum mechanical studies show, in fact, that dibridged $XM(\mu\text{-}X_2)MX$ structures are significantly more stable than doubly bonded $X_2M{=}MX_2$ for M = Ge, X Cl, Br, and for M=Si with X = F, Cl, Br.[45,46] Exploiting the relationship between DSSE and singlet–triplet splittings noted previously, it is easy to predict that N-, O-, and S-centered ligands should also increase DSSE($GeR_2$), as both lone-pair donation from the ligand to the formally empty germanium $\pi$-type orbital of the germylene singlet state and electronegativity induced s-pair contraction should lead to a larger singlet-triplet splitting and, hence, a larger DSSE, leading (through eq 1) to small double-bond BDE's and potentially monomeric structures.

The two digermenes for which crystal structures have been determined provide an interesting comparison. The first is tetrakis[bis(trimethylsilyl)methyl]digermene ($R_2Ge{=}GeR_2$ with R = $CH(SiMe_3)_2$), which is stable in the solid phase[7,47] but is monomeric $R_2Ge$ in the liquid and gas phases.[48,49] The bond distance in the dimer is $r$(Ge=Ge) = 2.347 Å. By contrast, if R = 2,6-diethylphenyl, the digermene retains its structural integrity in solution[50] and has a much shorter bond distance in the crystal $r$(Ge=Ge) = 2.213 Å. The unusual behavior in the case of R = $CH(SiMe_3)_2$ can be rationalized by noting that bis(trimethylsilyl)methyl should stabilize the singlet state of $R_2Ge$ relative to the triplet by the well-known silicon $\beta$ effect[51] and, thus, we postulate, lead to a larger DSSE($R_2Ge$), resulting in a small $D(R_2Ge{=}GeR_2)$. According to this model, digermenes should be stabilized by choosing silicon-based substituents ($SiR_3$) provided they can be made sufficiently bulky, as they are known to decrease the DSSE.[26]

## Predictions of Isomeric Energy Differences

It is well-known that accurate predictions of thermochemical properties can often be made by summing up contributions from the various atoms, bonds, groups, or components and their possible interactions in a molecule.[52] This requires, however, that accurate thermochemical information for a moderately extensive list of model compounds be known in advance. This is largely the case for significant classes of organic compounds. For silicon and germanium, however, the same cannot be said. The basic thermodynamic data for more than the simplest classes of silicon and germanium compounds just do not exist. Nonetheless, we will show in this section that fairly accurate predictions of relative

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**Table IV.** Comparison of Predicted and Theoretically Determined Isomeric 0 K Enthalpy Differences

| reaction $H_nM{=}M'H_{n'} \rightarrow H_{n+1}M{-}M'H_{n'-1}$ | $D_\pi + D_2(M'{-}H) - D_1(M{-}H) = \Delta H_{\text{predict}}$ | $\Delta H_{\text{ab initio}}$ |
|---|---|---|
| $H_2Ge{=}SiH_2 \rightarrow H_3Ge{-}SiH$ | 25 + 68.5 - 84.0 = 9.5 | 9.4 |
| $H_2Ge{=}SiH_2 \rightarrow HGe{-}SiH_3$ | 25 + 57.4 - 90.6 = -8.2 | -6.3 |
| $H_2Ge{=}GeH_2 \rightarrow H_3Ge{-}GeH$ | 25 + 57.4 - 84.0 = -1.6 | -2.0[a] |
| $H_2Si{=}SiH_2 \rightarrow H_3Si{-}SiH$ | 25 + 68.5 - 90.6 = 2.9 | 6.4[b] |
| $H_2Si{=}CH_2 \rightarrow H_3Si{-}CH$ | 38 + 111.2 - 90.6 = 58.6 | 45.2[c] |
| $H_2Si{=}CH_2 \rightarrow HSi{-}CH_3$ | 38 + 68.5 - 104.6 = 1.9 | 3.6[d] |
| $H_2Ge{=}CH_2 \rightarrow HGe{-}CH_3$ | 31 + 57.4 - 104.6 = -16.2 | -17.6[e,f] |
| $H_2Si{=}PH \rightarrow HSi{-}PH_2$ | 29 + 68.5 - 84.0 = 16.1 | 13.1[e,g] |
| $H_2Si{=}NH \rightarrow HSi{-}NH_2$ | 36 + 68.5 - 107.2 = -2.7 | -17.9[e,h] |
| $H_2Si{=}O \rightarrow HSi{-}OH$ | 50 + 68.5 - 117.9 = 0.6 | 4.6[c] |

[a] Grev, R. S.; Schaefer, H. F. Unpublished research. [b] Reference 56. [c] Reference 42. [d] Reference 55. [e] These values are $\Delta E$; i.e., they are not corrected for zero-point vibrational energies. [f] Reference 5c. [g] Reference 58. [h] Reference 57.

energies for the most studied (by theory) class of isomers can be made from published theoretical data on $\pi$-bond energies and sequential BDE's for the parent hydrides. Specifically, we will show that the relative energies of the various doubly bonded compounds ($H_2Si{=}MH_n$) and their corresponding silylene isomers ($HSi{-}MH_{n+1}$) are largely predictable. In addition, for three cases (Ge=Ge, Ge=Si, Ge=C) for which germanium $\pi$-bond energies are known, the $H_2Ge{=}MH_n$ and $HGe{-}MH_{n+1}$ isomeric energy differences will be shown to be in good agreement with the best theoretical predictions.

The reactions investigated, predicted isomeric energy differences, and best available theoretically determined isomeric energy differences are shown in Table IV with use of the data from Table III on $\pi$-bond energies and BDE's of the parent hydrides, determined either in this work of from other theoretical studies referenced in Table III. As examples of how the predictions in Table IV are determined, we will explicitly work out the predicted isomeric energy differences of germasilene, germylsilylene, and silylgermylene, presented earlier in this work. For the germasilene–germylsilylene system, we start out with germasilene and first imagine breaking the $\pi$ bond, which we found to have an energy of 25 kcal/mol. Next, we break the Si—H bond, whose energy we take to be equal to the second BDE in silane, i.e., 68.5 kcal/mol (Table III). Finally, we form the Ge—H bond, whose energy is taken to be that of the first BDE in germane, 84.0 kcal/mol. Thus, we predict the isomerization reaction to require 25 + 68.5 - 84.0 = 9.5 kcal/mol, in excellent agreement with the value, 9.4 kcal/mol, determined for the 0 K enthalpy difference from Table II. This procedure may be summarized as follows:

$$H_2Ge{=}SiH_2 \rightarrow H_2Ge{-}SiH_2 \qquad \Delta H = 25 \text{ kcal/mol}$$

$$H_2Ge{-}SiH_2 \rightarrow H_2Ge{-}SiH + H \qquad \Delta H = 68.5 \text{ kcal/mol}$$

$$H_2Ge{-}SiH + H \rightarrow H_3Ge{-}SiH \qquad \Delta H = -84.0 \text{ kcal/mol}$$

$$H_2Ge{=}SiH_2 \rightarrow H_3Ge{-}SiH \qquad \Delta H = 25 + 68.5 - 84.0 = 9.5 \text{ kcal/mol}$$

For the germasilene–silylgermylene isomerization, one finds

$$H_2Ge{=}SiH_2 \rightarrow H_2Ge{-}SiH_2 \qquad \Delta H = 25 \text{ kcal/mol}$$

$$H_2Ge{-}SiH_2 \rightarrow HGe{-}SiH_2 + H \qquad \Delta H = 57.4 \text{ kcal/mol}$$

$$HGe{-}SiH_2 + H \rightarrow HGe{-}SiH_3 \qquad \Delta H = -90.6 \text{ kcal/mol}$$

$$H_2Ge{=}SiH_2 \rightarrow HGe{-}SiH_3 \qquad \Delta H = 25 + 57.4 - 90.6 = -8.2 \text{ kcal/mol}$$

once again in good agreement with the value, -6.3 kcal/mol, obtained directly in the current study.

For two of the isomerization reactions listed in Table IV, thermochemical data do exist to allow a more rigorous determination of the reaction enthalpy, as has already been done by Walsh.[53,54] These are the silaethylene–methylsilylene[53] and disilene–silylsilylene[54] systems, for which $D(H_3SiSiH_2{-}H)$, $D(H_3SiSiH{-}H)$, $D(H_3CSiH_2{-}H)$, and $D(H_3CSiH{-}H)$ have all been experimentally determined, and $D(H_3SiCH_2{-}H)$ can be approximated by the value measured for $D[(H_3C)_3SiCH_2{-}H)]$. In the case of the silaethylene–methylsilylene system, the results do not change very much, mainly due to a cancellation of errors in the present study. Specifically, this results from the fact that both the first C—H BDE (approximated) and the second Si—H BDE in $H_3SiCH_3$ are lower than the values in the parent compounds, $SiH_4$ and $CH_4$, by about 4 or 5 kcal/mol. Thus, employing Walsh's values for these quantities[26] and using $D_\pi(Si{=}C) = 38$ kcal/mol leads to an improved estimate of $\Delta H$ for silaethylene–methysilylene of 4.3 kcal/mol (instead of 1.9 kcal/mol predicted here) in excellent agreement with the value, 3.6 kcal/mol, obtained from high-level theoretical results.[55] For the disilene–silylsilylene isomerization reaction, Walsh's data predict $\Delta H = 12.1$ kcal/mol, substantially greater than the value predicted here, 2.9 kcal/mol, and the value determined from theory, 6.4 kcal/mol.[56] The principal difference between our simple prediction and that obtained from Walsh's data[26] arises from the fact that $D(H_3SiSiH_2{-}H)$ is found to be about 4 kcal/mol lower and $D(H_3SiSiH{-}H)$ is near 3 kcal/mol higher, respectively, than those in $SiH_4$.

The largest discrepancy between the isomerization enthalpies predicted here with bond energies for the parent hydrides and those determined from theoretical studies occurs for the silanimine–aminosilylene system. In this case, there is abundant evidence to suggest that the principal error results from the assumption that the second Si—H BDE in $H_2NSiH_3$ is equal to that in $SiH_4$. In particular, Truong and Gordon[57] have shown that the barrier to internal rotation about the Si—N bond in aminosilylene ($HSi{-}NH_2$) is a whopping 28 kcal/mol. Coupled with a planar $H_2{-}N{-}Si$ framework, and a shorter than normal Si—N bond distance, this suggests a very strong stabilization of the silicon empty p-orbital by the nitrogen lone pair,[57] which should show up as a substantial increase in the DSSE($H_2N{-}SiH$) as well. For the $H_2Si{=}PH$, $HSi{-}PH_2$ system, isoovalent with silanimine, the good agreement between predicted and theoretically determined isomerization energies[58] is related to results of Schade and Schleyer's study of vinylphosphane.[59] These authors found that the large barrier to planarity in phosphines is effectively insurmountable by $\pi$-type interactions (which are *not*, surprisingly, inherently smaller than those involving nitrogen), leading to a phosphorus lone pair that is too bent away from any possible interaction site to provide significant perturbations.

Despite the fact that the overall good agreement between these predictions and results from quantum mechanical studies may result from a fortuitous cancellation of errors in some cases, the central theme of this study is nonetheless valid, namely, that *proper recognition of the differences between first and second bond dissociation energies goes a long way toward explaining isomeric energy differences and double-bond dissociation energies.* To drive home this point, we provide the following examples. If, instead of using actual first and second M—H BDE's, one uses average M—H bond energies, both disilene and digermene would be predicted to be 25 kcal/mol (the $\pi$-bond energy) more stable than their silylsilylene and germylgermylene isomers, when, in fact, their energies are fairly close to one another. The difference between prediction and reality can, in these cases, be directly identified with their respective DSSE's. For the germasilene–germylsilylene isomers, germasilene is more stable because the second Si—H BDE in $SiH_4$ is not sufficiently different from the first Ge—H BDE in $GeH_4$ to overcome the $\pi$-bond energy,

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whereas for the germasilene–silylgermylene isomers, the lower lying $H_3Si$—GeH isomers results from the much greater difference between the second Ge—H BDE in $GeH_4$ and the first Si—H BDE in $SiH_4$.

## Making $R_2Ge{=}SiR_2$

There are two widely used methods for forming stable Si=Si and Ge=Ge doubly bonded compounds. The first is via dimerization of divalent metallylene species ($MR_2$) generated either by chemical means or photolysis. The chemical route was employed to make the first stable solid digermene, whose crystal structure was reported by Hitchcock et al.,[47] whereas the photochemical route was used by West et al. to prepare the first stable disilene.[60] Photolytic generation of germylenes with subsequent dimerization to digermenes has also been widely observed.[61–63] Thus, one obvious route to form a germasilene would be to photolyze a mixture of silylene and germylene precursors and obtain a mixture of disilenes, digermenes, and germasilenes, which one might then hope to separate. This procedure has been attempted by West et al., but it failed to yield the desired product, possibly as a result of kinetic problems.[64]

The other widely used route to doubly bonded group 14 compounds is by photolysis of the appropriate three-membered ring (3MR) compound, which generates both the desired doubly bonded compound directly and a divalent silylene or germylene that can provide additional product through dimerization. Masamune and his co-workers have pioneered the use of this technique, and it has yielded both disilenes,[65] from cyclotrisilanes, and digermenes,[50] from cyclotrigermanes. Thus, another obvious method for forming a germasilene is by photolysis of an appropriate 3MR. The problem is the question of which three-membered ring should one start with, an Si—Si—Ge 3MR or an Si—Ge—Ge 3MR. *If* the answer to this question can be provided from purely thermodynamic considerations, the data from Table III are sufficient to provide an answer. That is, for an Si—Si—Ge 3MR, two possible results are extrusion of a silylene with formation of a germasilene and extrusion of a germylene with concomitant production of a disilene. In this case, the energetically lowest lying products are disilene + germylene, 7.2 kcal/mol lower than germasilene + silylene (just the difference between $D(H_2Si{=}SiH_2)$ and $D(H_2Ge{=}SiH_2)$). On the other hand, for an Si—Ge—Ge ring the two possible outcomes are production of silylene + digermene or germylene + germasilene, and in this case the desired result, production of the germasilene, is thermodynamically favored by 7.9 kcal/mol. Thus, on purely thermodynamic grounds, a three-membered Si—Ge—Ge ring is the best candidate as a precursor for the desired germasilene. This approach is currently being investigated in the laboratory of K.M.B. in London, Ontario.

## Conclusions

By ab initio quantum mechanical studies, we have found that the lowest lying isomer of $GeSiH_4$ is silylgermylene ($H_3SiGeH$), about 6 kcal/mol more stable than the trans-bent doubly bonded germasilene isomer ($H_2Ge{=}SiH_2$). The $\pi$-bond energies of germasilene, disilene, and digermene have all been found to be about 25 kcal/mol, although the double-bond dissociation energies are found to decrease from 52 (Si=Si) to 45 (Ge=Si) to 37 kcal/mol (Ge=Ge) with increasing germanium substitution. This effect is attributed to properties of the parent hydrides $SiH_n$ and $GeH_n$. Specifically, it is related to the increased divalent state stabilization energy[26,30–33] of germanium compounds relative to silicon. We have shown that the DSSE, which is assumed to be a property only of the divalent state ($MR_2$), can be used to rationalize other cases of unusually small double-bond dissociation energies, such as that in $F_2C{=}CF_2$, as well as those in cases such as ethylene, where the dissociation energy is larger than the sum of standard single- and double-bond energies. In this sense, it is more general than the model recently proposed by Carter and Goddard,[34] which emphasizes ground-state singlet $MR_2$ fragments as the source of double-bond instability. The DSSE does, however, bear some resemblance to singlet–triplet splittings, although as a quantitative measure it fails for strongly electronegative substituents. Finally, we have shown that many of the energy differences between group 14 doubly bonded molecules and their divalent isomers can be predicted reasonably well from bond dissociation energies in the parent hydrides and tabulated values of $\pi$-bond energies *provided* that proper recognition is given to differences between first and second bond dissociation energies.

**Acknowledgment.** The research carried out at the University of Georgia was supported by a grant from the National Science Foundation, Grant CHE-8718469. K.M.B. thanks the Natural Sciences and Engineering Research Council of Canada and the University of Western Ontario for financial support. We also thank Professor Gustavo Scuseria at Rice University for determining the open-shell CCSD energies reported in this research. Helpful discussions with Tony Millevolte, Brian Shephard, and Bob West at the University of Wisconsin are also gratefully acknowledged.

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