and the 1-adamantyl carbonium ion heat of formation has been estimated by several methods.[44,45]

McKervey and Mackle et al.[43] have determined the heats of formation of nine bridged-ring hydrocarbons and critically compared the values they obtained to previous measurements and EFF calculations. The values that they present are summarized in Table IV. From the data in Table IV, it seems most reasonable to choose ΔH_f°[adamantane] = −31.6 ± 0.6 kcal/mol.

Of the published values for ΔH_f°[II], one[44] requires the estimation of ΔH_f°[1-adamantyl bromide] and another[45] requires the estimation of both ΔH_f°[1-adamantyl bromide] and ΔH_f°[1-adamantyl chloride] by group methods. Benson's group method fails for adamantane, giving ΔH_f°[adamantane] = −36.52 kcal/mol.[46] This is not surprising since a substantial amount of strain energy in the adamantane ring system is predicted by EFF calculations.[14] On this basis, there is no reason to expect that the group method can be applied successfully to calculations of the heats of formation of 1-chloro- and 1-bromo-adamantane. Hence, estimates of ΔH_f°[II] calculated from estimated heats of formation of the 1-halo-adamantanes must be regarded with suspicion.

A reliable estimate of ΔH_f°[II] can be derived from a photoionization appearance potential measurement of II from adamantane.[47] The appearance potential obtained, 10.6 eV, yields ΔH_f°[II] = 160 kcal/mol. This value should be a good estimate since 1,2-hydride shifts are not allowed in II,[48] and Schwarz[49] has shown that loss of hydrogen occurs exclusively at the bridgehead sites in electron impact ionization of adamantane, so that II should be the only ion formed by the loss of hydrogen from the parent adamantyl radical ion. Comparison of this absolute value for ΔH_f°[II] to the values for the relative hydride affinity of II from the gas-phase equilibrium studies presented in Table X is made difficult by uncertainty in the value for $\Delta H_f^\circ[(CH_3)_3C\cdot]$,[50] which leads to uncertainty in the value for $\Delta H_f^\circ[(CH_3)_3C^+]$. Choosing $\Delta H_f^\circ[(CH_3)_3C\cdot]$ = 10.3 ± kcal/mol gives $\Delta H_f^\circ[(CH_3)_3C^+]$ = 165 kcal/mol.[51] Then, from Kebarle and Sharma's measurement of ΔH for reaction 1, with ΔH_f°[adamantane] and ΔH_f°[isobutane], ΔH_f°[II] is calculated to be 158 ± 3 kcal/mol, in good agreement with the value calculated from the ionization potential measurement mentioned above.

Clearly, the measurement of ΔH° for reaction 1 by high-pressure mass spectrometry equilibrium experiments is the most precise, and it is this value that was used to calculate the difference in tertiary bond energies between adamantane and isobutane. It should be stressed that this difference is known to a precision of ±1 kcal/mol, but the final assignment of absolute bond energies must await agreement on a value for $\Delta H_f^\circ[(CH_3)_3C\cdot]$.

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Structures and Energies of Singlet Silacyclopropenylidene and 14 Higher Lying C_2SiH_2 Isomers

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Abstract: The closed-shell molecular structures and relative energies of 15 different isomers of the formula C_2SiH_2 have been investigated via nonempirical molecular electronic structure theory. Eight structures were found to be minima on the self-consistent-field potential energy hypersurface by using a double-ζ (DZ) basis set. The three lowest lying isomers have further been optimized with the DZ basis set augmented by polarization functions (DZ+P), and vibrational frequencies and IR intensities were obtained at this level of theory by using analytical gradients and second derivatives. Correlation energies have been predicted at the DZ+P level via configuration interaction including all single and double excitations of the valence orbitals (DZ+P CI). 3-Silacyclopropenylidene (**1**) has clearly been found to be the global minimum on the singlet C_2SiH_2 potential energy hypersurface. Vinylidenesilene (**2**) and silylenylacetylene (**3**) are 17 and 22 kcal/mol higher in energy, respectively (DZ+P CI). While **1**, **2**, and **3** might experimentally be observed, the other isomers are higher in energy. and it is less likely that they will soon be identified.

Theoretical[1] and experimental[2] studies of triatomic SiC_2 structures have shown perhaps surprisingly that the cyclic singlet isomer with a CC triple bond is the global minimum of the SiC_2 potential energy hypersurface. By comparison, the C_3 molecule has a linear ${}^1\Sigma_g{}^+$ ground state.[3] In addition the related Si_2C molecule has recently been predicted to have a nonlinear energy minimum.[4] Thus, the substitution of carbon by silicon may result in very different structures for the lowest lying isomers of simple

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Table I. Total (Hartrees) and Relative (kcal/mol) Energies of the Optimized Structures of C_2SiH_2[a]

	DZ SCF			DZ+P SCF			DZ+P(CI)		DZ+P(CI) + Davidson corr	
	E_{tot}	E_{rel}	EV[b]	E_{tot}	E_{rel}	EV[b]	E_{tot}	E_{rel}	E_{tot}	E_{rel}
1	−365.674 02	0.0	(+)	−365.745 38	0.0	(+)	−366.061 38	0.0	−366.098 72	0.0
2	−365.663 26	6.8	(+)	−365.713 46	20.0	(+)	−366.031 00	19.1	−366.071 55	17.0
3	−365.655 69	11.5	(+)	−365.713 88	19.8	(+)	−366.025 14	22.7	−366.063 08	22.4
4	−365.585 03	55.8	(+)							
5	−365.488 11	116.7	(+)							
6	−365.535 83	86.7	(−)							
7	−365.468 07[c]	129.2	(−)							
10s	−365.604 51	43.6	(+)							
10a	−365.599 46	46.8	(+)							
12s	−365.409 78	165.8	(+)							

[a] All results reported here are based on the single-configuration SCF method. The CI results involve all single and double excitations relative to one reference configuration. For higher level theoretical predictions, see text. [b] Eigenvalues of the Hessian matrix; a (+) sign means only positive eigenvalues (minimum); a (−) sign indicates that one negative eigenvalue has been found (transition state). [c] The C–Si–C angle was enforced at 180° along the optimization.

Chart I

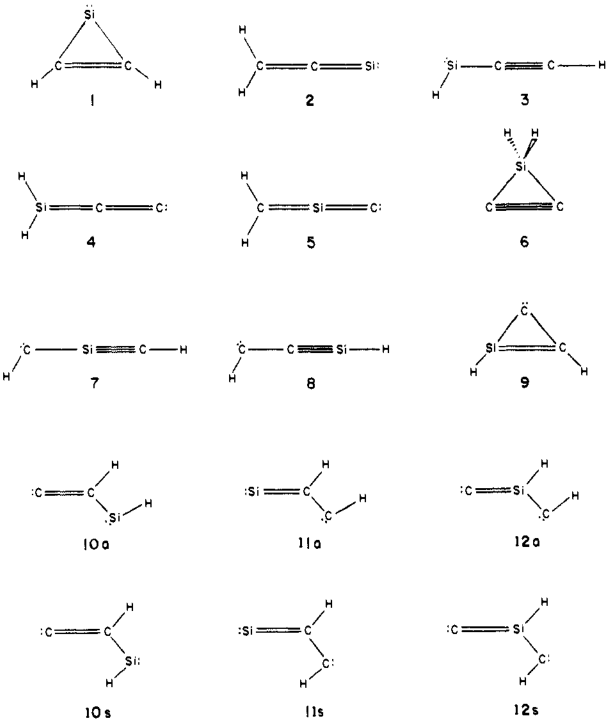

Table II. Mulliken Population Data for Structures **1**, **2**, and **3** at the DZ+P SCF Level of Theory[a]

	1	**2**	**3**
P_{CC}	0.32	0.45	0.84
P_{CSi}	0.22	0.46	0.15
$P(\pi)_{CSi}$	0.06	0.05[b]	0.03[b]
P_{CH}	0.40	0.42	0.39
P_{SiH}			0.32
$q_C{}^1$	−0.40	−0.18	−0.32
$q_C{}^2$	−0.40	−0.53	−0.25
q_{Si}	+0.56	+0.48	+0.63
$\rho(\pi)_{Si}$	0.26	0.11[b]	0.08[b]
$q_H{}^1$	+0.12	+0.12	+0.16
$q_H{}^2$	+0.12	+0.12	−0.21

[a] P_{AB} are the bond orders of the AB bond, and $P(\pi)$ shows the out-of-plane π-contribution. q_A is the atomic net charge on atom A, and $\rho(\pi)_A$ gives the orbital charge in the out-of-plane p-AO of atom A. [b] Only the out-of-plane component has been considered.

molecules. In light of these results we were interested in investigating the structures and energies of small silahydrocarbons, i.e., to see what happens when silacarbon clusters such as SiC_2 are hydrogenated. Here we report the results of our theoretical investigation on the singlet structures of 15 different isomers of the formula C_2SiH_2 shown in Chart I. While C_2SiH_4 has been the subject of a systematic *ab initio* theoretical study,[5] relatively little seems to be known about the simpler C_2SiH_2 molecule.

Theoretical Approach. We started our investigation by geometry optimization of all 15 different isomers shown in Chart I at the self-consistent-field (SCF) level of theory by using the standard Huzinaga–Dunning[6,7] double-ζ (DZ) basis set, designated Si(11s7p/6s4p), C(9s5p/4s2p), and H(4s/2s). Isomers **1**, **2**, **4**, **5**, and **6** were constrained to have C_{2v} symmetry, and C_s symmetry was enforced for the remaining structures. The optimization was carried out with analytical first[8] and numerical second derivative methods. The resulting stationary point structures were characterized by their harmonic vibrational frequencies as minima, saddle points, or higher extrema, by using analytical second derivative techniques.[9] The three lowest lying isomers **1**, **2**, and **3** have been further optimized by employing the DZ basis set augmented by polarization functions (DZ+P) with orbital exponents $\alpha_d(Si) = 0.5$, $\alpha_d(C) = 0.75$, and $\alpha_p(H) = 0.75$. To furnish a more reliable assessment of the global minimum for the singlet C_2SiH_2 potential energy hypersurface, single-point configuration interaction (CI)[10] wave functions have been determined with the DZ+P basis set for **1**, **2**, and **3**, including all single and double excitations (SD) of the valence orbitals relative to the Hartree–Fock reference configuration. This amounts to 13 805, 14 061, and 27 426 configurations for **1**, **2**, and **3**, respectively. Vibrational frequencies and IR intensities[11] were determined for these isomers at the DZ+P SCF level of theory.

It should be emphasized that the present theoretical study is in the nature of a survey. The research covers no less than 15 isomers of C_2SiH_2, with geometrical optimizations carried out for each. Moreover, this work is by no means the "final word" on every aspect of the C_2SiH_2 problem. We have only considered structures for which a closed-shell singlet valence representation is reasonable. It is possible that some of the higher energy isomers (perhaps **10**–**12**) might have triplet electronic ground states. However, such triplets are not likely to be candidates for the global minimum. Singlet silylenes and methylenes are more properly described in zeroth order by two-configuration SCF wave functions,[12] and this is undoubtedly true of the 15 structures considered

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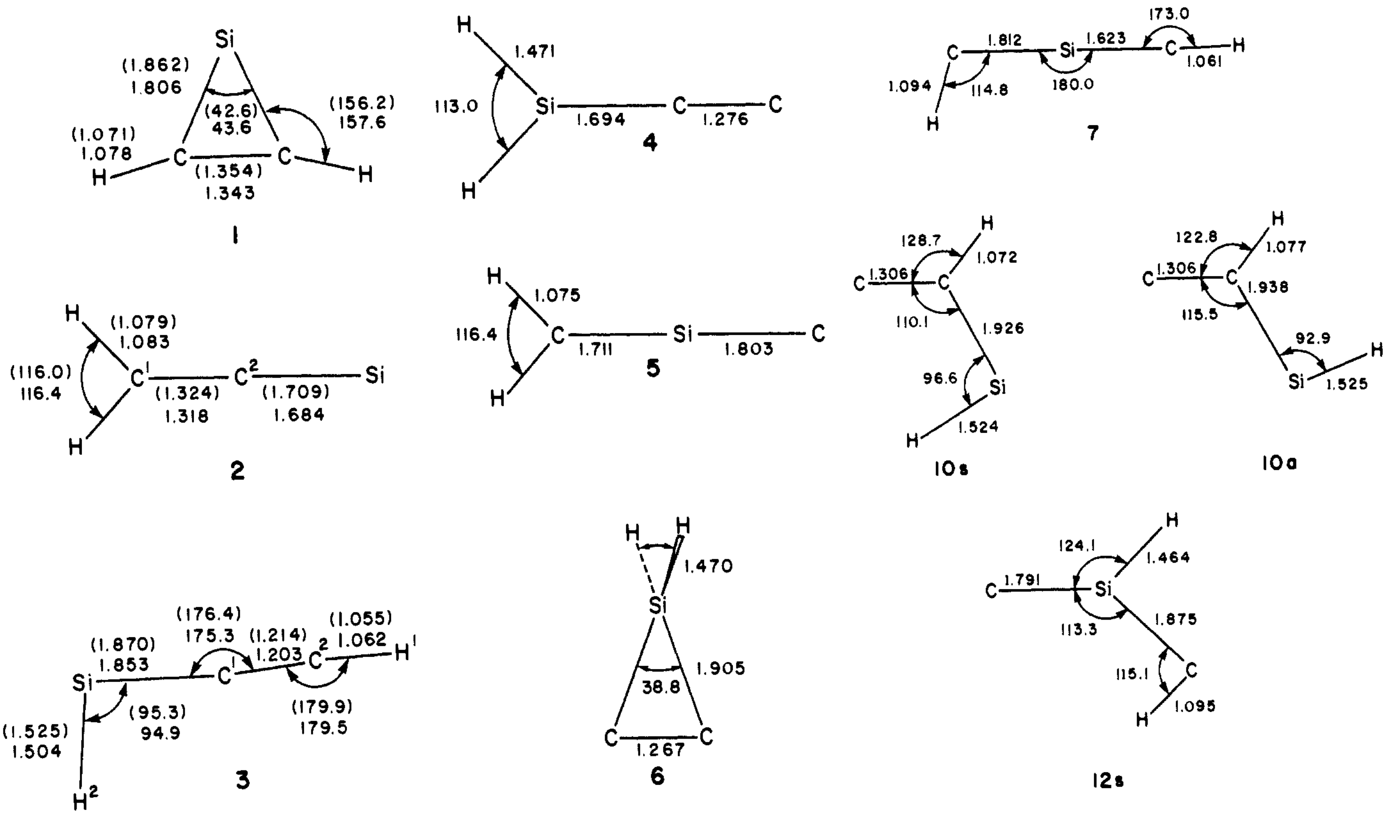

Figure 1. Optimized geometries for structures **1**–**12**. Bond lengths are given in Å, bond angles in degree. For **1**–**3**, the values in parentheses are the results of optimization at the DZ SCF level, while the parameters appearing first arise from the DZ+P SCF optimization. Structures **4**–**12** were optimized only at the DZ SCF level of theory.

Table III. Theoretically Determined Vibrational Frequencies and IR Intensities at the DZ+P Level for Structures **1**, **2**, and **3**[a]

	3-silacyclopropenylidene (**1**)			vinylidenesilene (**2**)			silylenylacetylene (**3**)		
	freq	intens[b]	mode	freq	intens[b]	mode	freq	intens[b]	mode
1	3378 (3374)	0.74 (0.10)	CH stretch asym	3341 (3340)	0.18 (0.19)	CH stretch asym	3619 (3620)	1.05 (1.02)	CH stretch
2	3356 (3352)	0.30 (0.12)	CH stretch sym	3264 (3264)	0.89 (0.89)	CH stretch sym	2239 (2248)	1.95 (1.86)	CC stretch
3	1569 (1564)	0.00 (0.00)	CC stretch	1859 (1865)	1.39 (1.08)	CC stretch	2188 (2186)	5.96 (5.91)	SiH stretch
4	1233 (1239)	1.08 (1.06)	CH rock asym	1539 (1539)	0.09 (0.06)	CH_2 scissor	910 (905)	3.50 (3.46)	HSiC bend
5	1061 (1070)	0.00 (0.00)	CH wag asym	1129 (1124)	0.50 (0.52)	CH_2 wag	885 (877)	0.72 (0.75)	CH wag
6	976 (977)	0.38 (0.47)	CH rock sym	1111 (1110)	0.31 (0.30)	CH_2 rock	751 (759)	1.56 (1.53)	CH rock
7	849 (853)	1.23 (1.46)	SiC stretch	810 (809)	0.56 (0.52)	SiC stretch	633 (631)	2.35 (2.34)	SiC stretch
8	749 (748)	2.16 (2.27)	CH wag sym	314 (318)	1.05 (1.08)	CCSi bend	297 (296)	0.24 (0.27)	CC rock
9	729 (715)	0.93 (1.15)	ring def	256 (256)	0.38 (0.43)	CCSi wag	245 (246)	0.25 (0.28)	CC wag

[a] Two-configuration SCF predictions obtained with the DZ+P basis set are given in parentheses. [b] 1 $(D/A)^2$/amu = 42.25 km/mol.

here. However, the CI and Davidson-corrected results demonstrate for the three lowest lying structures (**1**–**3**) that the single configuration SCF description is qualitatively acceptable.

Predictions for Silacyclopropenylidene (1). The total and relative energies of the optimized structures are given in Table I. Figure 1 gives the predicted geometries, while the results of Mulliken population analyses[13] for several of the structures are given in Table II. The theoretically determined vibrational frequencies are listed in Table III.

While structures **1**, **2**, and **3** were all found to be low-lying energetically at the DZ SCF level of theory, the results at the higher level leave no doubt that 3-silacyclopropenylidene (**1**) is the global minimum on the singlet C_2SiH_2 potential energy hypersurface. The energy difference with respect to the next most stable isomer, i.e., vinylidenesilene (**2**) is only 6.8 kcal/mol at the DZ SCF level of theory. However, the addition of polarization functions preferentially favors the cyclic structure, a result which is only slightly affected when the correlation energy is considered.

The C–C bond distance in **1** (1.343 Å at DZ+P) corresponds to a normal C=C double bond (1.35 Å in ethylene), but multiple bonds in small cyclic molecules tend to be shorter with respect to standard acyclic structures. For example, the C=C double bond in cyclopropene at a comparable level of theory (6-31G*) is 1.276 Å.[14] In the parent hydrocarbon cyclopropenylidene, the C=C bond distance at the DZ+P level was predicted to be 1.314 Å.[15] Thus, the C–C bond in **1** may be considered a relatively weak double bond. On the other hand, the C–Si bond distance of 1.806 Å in **1** is intermediate between standard values for single and double bonds (1.92 and 1.71 Å, respectively)[5,16] and may be compared to the cyclic SiC_2 structure, which has a C–Si bond distance of 1.835 Å (DZ+P).[1]

These data indicate substantial delocalization of the C=C double bond into the formally empty 3p AO of silicon, weakening the C–C and enforcing the C–Si bond. This conclusion is supported by the results of the Mulliken analysis of the wave function for **1**. Although there is a strong charge polarization in 3-silacyclopropenylidene in the expected direction C(δ−), Si(δ+), π-donation into the $3p_z$ AO of silicon by carbon amounts to 0.26 Mulliken electrons. Also, the C–Si bond order is made up by

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roughly 25% π-contribution. Thus, stronger delocalization of the π-bond into the ring of 3-silacyclopropenylidene is found compared to the CC triple bond in cyclic SiC_2.[1] Without this delocalization the carbon–silicon bond is much longer: in 1-silacyclopropanylidene the C–Si distance at the 3-21G SCF level of theory is 1.947 Å.[5] By comparison, the C–Si distance in 3-silylcyclopropane at 3-21G was found to be 1.869 Å,[5] similar to the DZ value for **1**. These conclusions regarding the nature of the C═C and C—Si bonds in **1** are in several ways similar to those drawn earlier by Gordon[17] in his theoretical study of silacyclopropene.

Vinylidenesilene (2) and Silylenylacetylene (3). While the unsubstituted linear and cyclic SiC_2 singlet structures have nearly the same energy (at the DZ+P SCF level, the linear isomer is misleadingly found to be 5.1 kcal/mol more stable than the cyclic molecule[1]), the 3,3- and 1,3-dihydrogenated species **2** and **3** lie 17.0 and 22.4 kcal/mol higher in energy than **1** (DZ+P CI). The energy difference between **1** and **2** is in the same range as was found for the analogous C_3H_2 isomers, i.e., cyclopropenylidene is 18.0 kcal/mol lower in energy than vinylidenecarbene (6-31G*SCF).[14] The C–C and C–Si bonds in **2** are both slightly shorter than the respective standard values for a double bond (1.35 Å for C═C and 1.71 Å for C═Si).[16] The partial triple-bond character of the carbon–silicon bond in **2** is reflected in the small (0.048) contribution of the out-of-plane orbitals to the C–Si total bond order.

At the DZ+P CI level, silylenylacetylene (**3**) is 5.3 kcal/mol higher in energy than structure **2** (the analogous C_3H_2 isomer propargylene is 12.2 kcal/mol less stable than propadienylidene at the DZ+P SCF level).[18] Moreover, some π-conjugation is found leading to a slightly longer C–C triple and shorter C–Si single bond similar to silylacetylene.[5] A slight trans-bent geometry was found for the C–C triple-bonded isomer **3**. Unless the barriers for hydrogen and silicon rearrangement in **2** and **3** are very low, all three isomers **1**, **2**, and **3** should be experimentally observable. The theoretical IR frequencies and intensities shown in Table III indicate characteristic differences and may be helpful in identifying the different C_2SiH_2 structures.

Higher Energy C_2SiH_2 Isomers. Permutation of silicon and carbon atoms in **2** leads to structures **4** (1-silapropenylidene) and **5** (2-silapropenylidene). Although both isomers were found to be minima on the DZ SCF potential energy hypersurface, they are rather high in energy compared to **1**–**3**. The main reason for the energetic destabilization of **4** compared to **3** can be found in the (weaker) Si–H bonds of the former relative to the C–H bonds of **3**. The average bond strength for a carbon–hydrogen bond is 99 kcal/mol, while that for a silicon–hydrogen bond is 77 kcal/mol.[19] The difference between the two bond energies nearly matches the stability difference between **3** and **4**, although such a quantitative agreement is fortuitous since the difference between the silicon and carbon lone-pair electrons has not been considered.

Structure **5** is very high in energy. The H_2C–SiC bond corresponds to a double bond, but the H_2CSi–C bond is only intermediate between single and double bonds. It is not very likely that **5** will be observed experimentally in the near future.

1-Silapropenylidene (**4**) is the ring-opened form of 3-silacyclopropyne (**6**); which is found to be a transition state and not a minimum on the (DZ SCF) C_2SiH_2 energy hypersurface. However, while **6** is 30.9 kcal/mol higher in energy than **4**, cyclopropyne was predicted to lie 59.8 kcal/mol above propenylidene at the same level of theory.[20] Thus, the substitution of a carbon atom by silicon favors the cyclic structure in SiC_2 vs. C_3 as well as C_2SiH_2 vs. C_3H_2, and in both cases a stabilization of ~30 kcal/mol is found.[1]

Permutation of silicon and carbon atoms in structure **3** leads to the isomers **7** and **8**, which have silicon–carbon triple bonds. Previous theoretical work on the prototype for a Si–C triply bonded molecule, i.e., silaacetylene HSiCH, showed that only after inclusion of correlation effects[21] was a barrier found for rearrangement to the more stable silylidene (57.7 kcal/mol lower than silaacetylene at the DZ+d SCF level of theory)[22] isomer. For **7** and **8**, even lower lying isomers are available. At the DZ SCF level, **7** rearranges to the global singlet minimum **1**, while optimization of **8** yields only the valence tautomer **3**. Partial geometry optimization of **7** at the DZ level with enforced linearity of the C–Si–C entity demonstrates that this structure is 129.2 kcal/mol higher in energy than **1**, and the Hessian matrix has one negative eigenvalue. Neither **7** nor **8** are stable structures at the DZ SCF level, and we do not think that this result will change at higher levels of theory.

Permutation of silicon and carbon atoms in the ring structure of **1** gives 1-silacyclopropenylidene (**9**). However, with the DZ basis set **9** was found not to be a minimum on the SCF potential energy hypersurface but rather leads to the ring-opened isomer **10**, 3-silapropenediylidene. This result is somewhat surprising since on the C_2SiH_4 potential energy hypersurface, 1-silacyclopropene is clearly a minimum at 3-21G.[5] Two minima were found for **10**, the syn conformer **10s**, and the anti form **10a** which is slightly less stable. Permutation of silicon and carbon atoms in structure **10** leads to the isomers **11** and **12**. Only the syn conformer of **12** is a minimum, albeit a very high lying one. **12a** rearranges without barrier to **10**, and both conformers of **11** fall away to the global minimum **1**. Due to its very high energy, **12a** is unlikely to be observed experimentally, and **10s** and **10a** may also rearrange readily to the more stable C_2SiH_2 species.

Higher Levels of Theory—TCSCF and TC-CISD. As noted in the section Theoretical Approach, singlet silylenes are more properly described in zeroth order by two-configuration self-consistent-field (TCSCF) wave functions. For this reason the three lowest energy structures silacyclopropenylidene (**1**), vinylidenesilene (**2**), and silylenylacetylene (**3**) were examined at this higher level of theory. All three structures were completely reoptimized at the DZ+P TCSCF level of theory.

For silacyclopropenylidene the lowest energy TCSCF wave function has the form

$$\Phi = C_1\ 5a_1^2 3b_2^2 6a_1^2 7a_1^2 2b_1^2 4b_2^2 8a_1^2 + C_2\ 5a_1^2 3b_2^2 6a_1^2 7a_1^2 2b_1^2 4b_2^2 5b_2^2 \tag{1}$$

At the DZ+P TCSCF equilibrium geometry for silacyclopropenylidene, $C_1 = 0.993$ and $C_2 = 0.117$, and the TCSCF energy is 0.01028 hartrees below the analogous single configuration SCF energy. The DZ+P TCSCF equilibrium geometry of **1** is very similar to the DZ+P single configuration SCF structure seen in Figure 1. For example, the Si–C distance is 1.805 Å, vs. 1.806 Å in Figure 1. TCSCF vibrational frequencies and intensities are reported in parentheses in Table III. Although the SCF and TCSCF frequencies are nearly identical, some of the intensities show a greater spread between the two levels of theory. Most notably the asymmetric C–H stretch is of medium-to-low intensity at the SCF level of theory but of very low intensity from TCSCF predictions. Finally, the DZ+P TCSCF dipole moment of **1** is 0.80 debye, less than one-quarter the value for the parent hydrocarbon cyclopropenylidene.[15]

The lowest energy TCSCF wave function for vinylidenesilene (**2**) is of the form

$$\Phi = C_1\ 6a_1^2 7a_1^2 8a_1^2 2b_2^2 2b_1^2 3b_2^2 9a_1^2 + C_2\ 6a_1^2 7a_1^2 8a_1^2 2b_2^2 2b_1^2 3b_2^2 3b_1^2 \tag{2}$$

At the DZ+P TCSCF equilibrium geometry for **2**, $C_1 = 0.986$ and $C_2 = 0.166$, and the TCSCF energy is 0.01608 hartrees below the analogous single configuration SCF energy. The SCF and TCSCF equilibrium geometries are essentially superposable, with the Si═C distances, for example, being 1.6840 Å (SCF) and 1.6855 Å (TCSCF). The predicted TCSCF vibrational fre-

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quencies and infrared intensities are very similar to the ordinary SCF results, while the TCSCF dipole moment for vinylidenesilene is 0.77 debye.

For silylenylaetylene (**3**) the lowest energy TCSCF wave function has the form

$$\Psi = C_1\ 7a'^2 8a'^2 9a'^2 10a'^2 2a''^2 11a'^2 12a'^2 + C_2\ 7a'^2 8a'^2 9a'^2 10a'^2 2a''^2 11a'^2 3a''^2 \quad (3)$$

At the DZ+P TCSCF equilibrium geometry of silylenylacetylene, $C_1 = 0.982$ and $C_2 = 0.187$, and the TCSCF energy is 0.017 47 hartrees below the analogous single configuration SCF energy. For the parent silylene (SiH_2), the TCSCF/SCF energy difference is about 0.02 hartrees. On this basis we see that the TCSCF treatment is less essential for all three structures **1**, **2**, and **3** considered here than for the parent, unsubstituted SiH_2. For silylenylacetylene we see the largest TCSCF/SCF structural difference encountered in this research, for the Si–C distance. There we predict r_e(Si–C, SCF) = 1.853 Å and r_e(Si–C, TCSCF) = 1.856 Å, still a difference of only 0.0034 Å. Like the other principal species (**1** and **2**) studied here, **3** has a moderate dipole moment: 0.63 debye at the TCSCF level of theory.

For our final large basis set predictions of the relative energies of **1**, **2**, and **3**, CI with all single and double excitations was carried out with respect to both TCSCF reference functions (see wave functions (1), (2), and (3), respectively). With the restrictions discussed earlier, there are totals of 27 083 (**1**), 26 988 (**2**), and 52 714 (**3**) configurations included. DZ+P TC-CISD total energies are −366.064 47, −366.036 50, and −366.031 21 hartrees, respectively. These total energies place vinylidenesilene 17.6 kcal above **1** and silylenylacetylene 20.9 kcal above **1**. With the TCSCF-CISD Davidson correction,[26] **2** falls to within 16.4 kcal of **1**, and **3** lies 21.6 kcal above **1**. These results, of course, are qualitatively similar to our one reference CI predictions.

Conclusions

The global minimum on the C_2SiH_2 singlet potential energy hypersurface is 3-silacyclopropenylidene (**1**) which has a relatively short carbon–silicon bond.

It is appropriate to note at this point that the analogous hydrocarbon compound cyclopropenylidene has recently been synthesized by the group of Maier and Hoffmann.[24] Cyclopropenylidene was identified with the help of theoretical predictions[15] of the vibrational frequencies and IR intensites, much like those reported here for the sila-substituted **1**. We note in this regard that DZ+P SCF vibrational frequencies (such as those reported in Table III) are typically ~10% higher than the observed fundamentals.[25]

After structure **1** come vinylidenesilene **2** and silylenylacetylene **3**, which are 17 and 22 kcal/mol higher in energy at the DZ+P CI level of theory. Five more minima have been identified theoretically, but they are all much higher in energy, and it will be difficult to identify them experimentally. It is hoped that the theoretically determined vibrational frequencies and IR intensities will help in identifying the three C_2SiH_2 low-lying isomers.

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Registry No. **1**, 100899-98-7; **2**, 100909-38-4; **3**, 99278-14-5.

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Theoretical Study of the Conformation of Cis Carbene–Olefin–Transition Metal Complexes: Back-Donation vs. Ligand–Ligand Interaction

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Abstract: The conformation of several cis carbene–olefin–transition metal complexes (d^6 octahedral, d^4 pseudooctahedral, and d^8 trigonal-bipyramidal) have been studied by means of Extended Hückel calculations. In the case of d^6 tungsten octahedral complexes, it is shown that the two main factors which determine the optimal conformations are metal-to-ligand back-donation and direct ligand–ligand interaction. The relative amounts of both factors depend strongly on the electronic nature of the ligands at the metal. When they are innocent ligands with no π acceptor properties, maximization of the back-donation from the metal to the carbene and the olefin determines the best conformations. This is obtained when the two π acceptor orbitals overlap with two different d nonbonding orbitals. Four-electron repulsion between the occupied nonbonding orbitals and the occupied ligand orbitals then distinguishes between the conformations which have an equivalent amount of back-donation. When the ligands are π acceptor ligands (such as CO), ligand–ligand interaction takes a determining influence. This interaction is optimal when the π systems of the carbene and olefin are coplanar (that is when back-donation is minimized). The introduction of the π donor group on the carbene carbon increases also the importance of the ligand–ligand interaction. The structures of d^4 pseudooctahedral tantalum and d^8 trigonal-bipyramid carbene–olefin complexes are also discussed.

Cis metal–carbene–olefin complexes have been proposed as key intermediates in the olefin metathesis,[1] cyclopropanation of alkenes,[2] and the Ziegler–Natta polymerization of alkenes.[3] Considerable effort has been spent in the isolation and charac-

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