Organometallics **2002,** *21,* 3930−3939

Addition of Nucleophiles to Silenes. A Theoretical Study of the Effect of Substituents on Their Kinetic Stability

Michael Bendikov, Sabine Ruth Quadt, Oded Rabin, and Yitzhak Apeloig*

Department of Chemistry and the Lise Meitner-Minerva Center for Computational Quantum Chemistry, Technion-Israel Institute of Technology, Haifa 32000, Israel

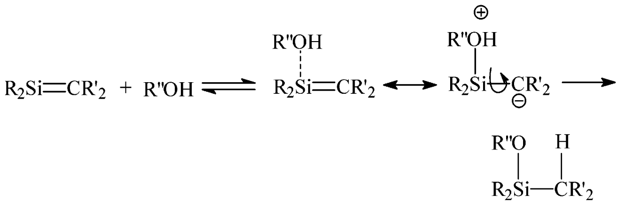
Received April 2, 2002

The addition of water to nine silenes ($H_2Si{=}CH_2$ (**1**), $Me_2Si{=}C(SiH_3)_2$ (**2**), $Cl_2Si{=}CH_2$ (**3**), $Me_2Si{=}CMe_2$ (**4**), $(H_3Si)_2Si{=}CMe_2$ (**5**), $(H_3Si)_2Si{=}C(Me)OSiH_3$ (**6**), $Me_2Si{=}C(SiMe_3)H$ (**7**), Me(HCC)Si$=CH_2$ (**8**), and $Me(Me_3Si)Si{=}CH_2$ (**9**)) was studied with ab initio (MP4/6-31+G(d,p)) and DFT (B3LYP/6-31G(d)) methods. The energy barriers for addition, which denote the kinetic stability of the silene, strongly depend on the substituents. Silenes (**1**−**4**) exhibit low and even negative activation energies (−3 to 8 kcal/mol). Substituents that strongly reduce the polarity of the silene, as in **5** and **6**, increase significantly the activation energy for the nucleophilic addition of H_2O to ca. 16 kcal/mol. The calculated activation energies show a good correlation with Δt (Δt = the difference in the total NBO charge between Si and C), i.e., the higher the polarity of the silene the lower is the activation barrier for water addition.

Introduction

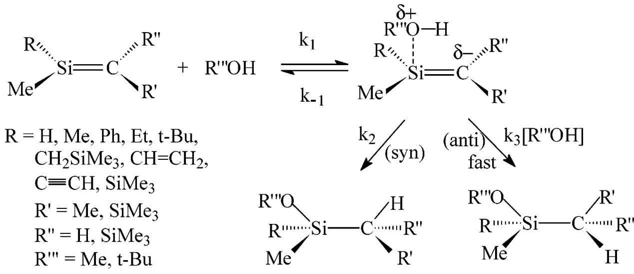
Following the synthesis of the first stable silene in 1981,[1] many reactions of silenes have been reported.[2,3] However, information about the mechanisms of these reactions is still rather limited.[2−4] Among the reactions of silenes the mechanism of the 1,2-addition of nucleophiles is the most studied, but the factors which govern the reactivity of silenes in these reactions are still not fully understood.[2,3,5]

All known silenes undergo nucleophilic addition of water and alcohols relatively easily and this is one of the reactions that complicates their isolation. Several mechanistic studies of the reaction of substituted silenes with water and alcohols were published in recent years.[4−9] Wiberg was the first to propose, on the basis of competition experiments, that addition of alcohols proceeds by a nucleophilic attack at the silicon atom of the silene double bond, involving a reversible formation of a silene−alcohol complex, which further reacts to give the addition product (eq 1).[4] This mechanism is, of course, very different from the usual mechanism of addition to C=C bonds, which generally involves an electrophilic rate-determining step.[10]


(1)

Recently, Leigh and co-workers studied the rates of addition of alcohols to several transient silenes shown in Scheme 1, using nanosecond flash-laser photolysis.[9]

Scheme 1



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* Address correspondence to this author. E-mail: chrapel@techunix.technion.ac.il. Fax: +972-48233735.

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10.1021/om0202571 CCC: $22.00
Publication on Web 08/13/2002

On the basis of these studies they proposed a refined mechanism, shown in Scheme 1, in which a silene–alcohol complex is reversibly formed in the first step of the reaction and proton transfer from the attacking alcohol or from a second alcohol molecule occurs in the second and rate-determining step. Activation parameters for the addition of different alcohols to alkyl-, phenyl-, and silyl-substituted silenes were measured. For all reactions studied $\Delta H^{\#}$ is negative and ranges from -4 to 0 kcal/mol. The negative $\Delta H^{\#}$ values result from the fact that k_2 and k_{-1} have entropies of activation of opposite sign and k_{obs} (k_{obs} is defined as $k_1k_2/(k_2 + k_{-1})$) varies from zero at very high temperatures to k_1 at very low temperatures. This produces a bell-shaped plot of log[k(obs)] vs $1/T$ over an infinitely broad range of temperature. The measured second-order rate constants for the reaction of various silenes with methanol ranged from 1.8×10^8 to 100×10^8 M^{-1} s^{-1}.[9] Note that 100×10^8 M^{-1} s^{-1} is actually a diffusion-controlled reaction rate. The mechanism shown in Scheme 1 explains also the stereochemistry of the addition reaction as proton transfer from the attaching alcohol molecule leads to syn-addition while attack by a second alcohol molecule leads to anti-addition.[5]

Despite all these studies relatively little is yet known on the factors which control the reactivity of silenes. For example, the effect of substituents on the reactivity of silenes is much less explored,[9] compared to alkenes. Answering these questions, in addition to being inherently interesting, is also practically important as it can guide the synthetic efforts toward the preparation of new stable silenes which will be stabilized electronically rather by the traditional use of very bulky substituents.

Also theoretically not much is known on the factors which govern the reactivity and selectivity of silenes toward nucleophiles. In a previous study Apeloig and Karni[11] predicted, on the basis of qualitative arguments (FMO theory and charge arguments), that substituents which reduce the polarity of silenes are expected to stabilize them kinetically. Similar conclusions were reached later by Nagase et al., again using only qualitative arguments.[12] These authors have also calculated that the barrier for the addition of H_2O to $H_2Si{=}CH_2$ is 8.4 kcal/mol at the MP3/6-31G(d)//RHF/6-31G(d) level.[12] In more recent papers Kira et al.[13,14] calculated for the same reaction a barrier in the range of 1.7–4.1 kcal/mol and for the addition of methanol a barrier in the range of -2.9 to $+0.9$ kcal/mol, depending on the theoretical method used (the methods used were B3LYP/6-311++G(d,p), MP2/6-311++G(d,p), and CBS-Q). Several complexes between the parent silene and water were also located.[14]

In this work we report the first systematic theoretical study of the potential energy surfaces for the addition of water and alcohols (methanol, ethanol, and *tert*-butyl alcohol) to parent and substituted silenes. We have chosen the following representative nine silenes for our study: the parent silene $H_2Si{=}CH_2$ (**1**), $Me_2Si{=}C(SiH_3)_2$ (**2**), $Cl_2Si{=}CH_2$ (**3**), $Me_2Si{=}CMe_2$ (**4**), $(H_3Si)_2Si{=}CMe_2$ (**5**), $(H_3Si)_2Si{=}C(Me)OSiH_3$ (**6**), $Me_2Si{=}C(SiMe_3)H$ (**7**), $Me(HCC)Si{=}CH_2$ (**8**), and $Me(Me_3Si)Si{=}CH_2$ (**9**). **1** and **4** are the most basic and the most intensively studied transient silenes.[2,3] **2**, **5**, and **6** serve as models for known stable silenes, i.e., $Me_2Si{=}C(SiMe_3)SiMe(t\text{-}Bu)_2$ (**10**),[15] (t-BuMe$_2$Si)(Me$_3$Si)Si=(2-Ad) (2-Ad = 2-adamantylidene) (**11**),[16] and $(Me_3Si)_2Si{=}C(OSiMe_3)(1\text{-}Ad)$ (**12**),[1,17] respectively. 1,1-Dichlorosilene **3** is a model for the intensively studied halo-substituted silenes[18] and **7**–**9** are silenes for which the rate constants for the addition of alcohols were measured.[9]

We find that the barrier for nucleophilic addition to silenes, i.e., the silenes' kinetic stability, strongly depends on the substituents so that substituents which strongly reduce the silene polarity increase significantly the activation energy for nucleophilic attack.

Computational Methods

The GAUSSIAN 98[19] series of programs was used for all calculations. All molecules were fully optimized by using the hybrid density functional[20] B3LYP level[21] of theory with the 6-31G(d) basis set. Transition structures were located by using the TS routine of GAUSSIAN 98. Frequency calculations were performed at the same level for all stationary points, to differentiate them as minima or saddle points. In the cases where the direction of the negative eigenvector was not clear, IRC calculation were also performed.[22] The energies for all reactions were evaluated also at the MP4(SDTQ) level of theory[23] with the 6-31+G(d,p) basis set with use of the B3LYP/6-31G(d) optimized geometries (denoted as MP4/6-31+G(d,p)//B3LYP/6-31G(d)). Entropies and Gibbs free energies[24] were also calculated at the B3LYP/6-31G(d) level of theory. Orbital energies, charges fit to the electrostatic potential at points selected according to the CHelpG scheme,[25] charge distribution

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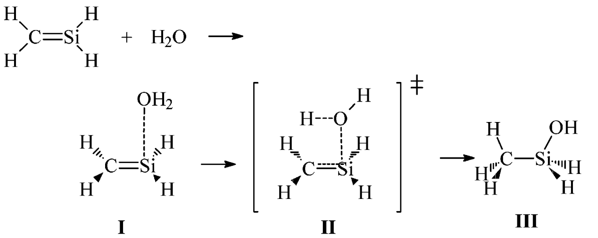
from NBO analysis[26a] (as well as Mülliken population analysis), and NRT (natural resonance theory) weigths[26b] were all calculated at MP2/6-31G(d)//B3LYP/6-31G(d). The pathway of water addition to the parent silene **1** was studied also by using the G2[27] and CBS-Q[28] procedures, and single-point calculations at the MP4, QCISD(T),[29a] and CCSD(T)[29b] levels of theory with use of the 6-311++G(d,p) basis set and MP2 optimized geometry were calculated. The effect of solvent was evaluated by using single-point B3LYP/6-31(d) calculations with the Polarized Continuum model (PCM),[30] using B3LYP/6-31(d) optimized geometries. Basis set superposition errors (BSSE) were estimated by using the counterpoise corrections method.[31] Deuterium isotope effects were calculated with the QUIVER program,[32] using the B3LYP/6-31G(d) calculated force constants.

Results and Discussions

(I) The Parent Silene. (1) Selection of the Theoretical Model. The simplest model reaction that we have studied is the addition of water to the parent silene **1**. The addition of water to $H_2Si{=}CH_2$ is believed to proceed via the formation of a weakly bound silene–water complex **I**, followed by transition state **II** which leads to the product silanol **III** as shown in eq 2.[33]



(2)

Being the prototype reaction we have studied eq 2 using a wide variety of theoretical levels to evaluate their reliability, so that we can choose the method that can be applied with confidence to larger systems for which the application of the most sophisticated methods is prohibitive. Our findings are as follows: (a) the effect of the theoretical method on the calculated geometry of TS **II** is small (Table 1). In particular, the calculated geometry of TS **II** optimized with the B3LYP level of theory is as good as the corresponding MP2 optimized geometry. (b) The effect of increasing the size of the basis-set on the relative energies of complex **I** and of TS **II** is smaller than 5.2 kcal/mol (Table 2), while the basis-set effect on the relative energy of product **III** is more significant, about 10 kcal/mol. (c) The calculated activation energies are almost the same with the MP4, CISD(T), and CCSD(T) methods (Table 2) and within 3–4 kcal/mol they are also consistent with the G2 and CBS-Q results (Table 2). (d) The B3LYP/6-31G(d) and MP2/cc-pVTZ methods are the only methods which predict negative activation energies, in contrast to all other methods which predict positive activation energies. On the basis of the comparisons in Table 2 we have chosen the MP4/6-31+G(d,p)//B3LYP/6-31G(d) level of theory as a compromise that will allow us to study relatively large substituted systems while still applying a highly reliable and accurate level of theory. We have tried to apply the counterpoise correction method for estimating basis set superposition errors (BSSE) which may result from the incompleteness of the basis sets we use. We find that BSSE significantly overestimate the relative barriers for nucleophilic addition compared to the G2, CBS-Q, or MP2/cc-pVTZ results (Table 2). For example, the BSSE for eq 2 is 5.89 kcal/mol, leading to an activation barrier of 10.65 kcal/mol at MP4/6-31+G(d,p)//B3LYP/6-31G(d) + BSSE, which is certainly too high (based on other calculations as well as on experiment[9]). Previous experience has also shown that use of the counterpoise method[31] for calculating basis set superposition errors sometimes does not improve systematically the calculated relative energies.[34]

Table 1. Comparison of the Si···O Bond Length (Å) and the C–Si–O Bond Angle (deg) in Transition State II at Different Levels of Theory

method	Si···O	∠C–Si–O
B3LYP/6-31G(d)	1.970	89.2
B3LYP/6-31+G(d)	1.953	88.3
B3LYP/6-31G(d,p)	1.970	89.0
B3LYP/6-311++G(d,p)	1.940	87.8
MP2/6-31G(d)	1.963	88.8
MP2/6-31+G(d)	1.945	88.1
MP2/6-31G(d,p)	1.973	88.5
MP2/6-311++G(d,p)	1.931	87.8
MP2/cc-pVTZ	1.941	90.0

The effect of solvent on the parent reaction was estimated for the two most popular solvents for addition of nucleophiles to silenes: toluene and THF (using the PCM model,[30] PCM/B3LYP/6-31G(d), at the B3LYP/6-31G(d) optimized structures). Using toluene as a solvent results in the reaction barrier of 3.4 kcal/mol and the complex is by 1.2 kcal/mol lower than reactants. With the more polar solvent, THF, the barrier increased further, to 9.5 kcal/mol, and the complex is calculated to have even a positive energy of formation (4.6 kcal/mol). The energy difference between the complex and the TS is essentially the same for gas-phase calculations and for calculations with a solvation model. However, the absolute value of the activation energy is higher in the condensed phase than in the gas phase. This can be understood considering the fact that the parent silene is a very polar molecule and it is more strongly stabilized by a polar environment than the less polar complex or TS. These differences in polarity result in higher activation energy toward nucleophilic addition and the silene–water complex disappears from the PES. Our solvent effect calculations are in line with recent

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[33] Our calculation shows that the "abnormal" addition of water, i.e., oxygen attacks the silene's carbon, is much higher in energy and for any of silenes **1**–**9** it cannot compete with the "normal" addition. Apeloig, Y.; Bendikov, M. To be submitted for publication.

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Table 2. Relative Energy and Activation Barrier for the Addition of Water to $H_2Si{=}CH_2$ (eq 2) at Different Levels of Theory (kcal/mol)[a]

method	complex **I**	TS **II**	product **III**
B3LYP/6-31G(d)//B3LYP/6-31G(d)	−5.76	−1.73	−77.30
BSSE[b] (B3LYP/6-31G(d))	4.05	5.78	
B3LYP/6-311++G(d,p)//B3LYP/6-311++G(d,p)	−2.78	3.49	68.12
MP2/6-31G(d)//MP2/6-31G(d)	−4.87	0.87	−78.56
MP4/6-311++G(d,p)//MP2/6-311++G(d,p)	−3.36	4.47	−68.87
QCISD(T)/6-311++G(d,p)//MP2/6-311++G(d,p)	−3.16	5.33	−67.95
CCSD(T)/6-311++G(d,p)//MP2/6-311++G(d,p)	−3.15	5.39	−67.98
MP2/cc-pVTZ//MP2/cc-pVTZ	−5.03	−2.71	
CBS-Q	−0.61	0.72	
G2	−0.64	1.99	
MP4/6-31+G(d,p)//B3LYP/6-31G(d)	−2.17	4.76	−70.75
BSSE[b] (MP4/6-31+G(d,p)/B3LYP/6-31G(d))	2.43	5.89	

[a] All energies are relative to the infinitively separated reactants: $H_2Si{=}CH_2 + H_2O$. [b] Basis-set superposition error.

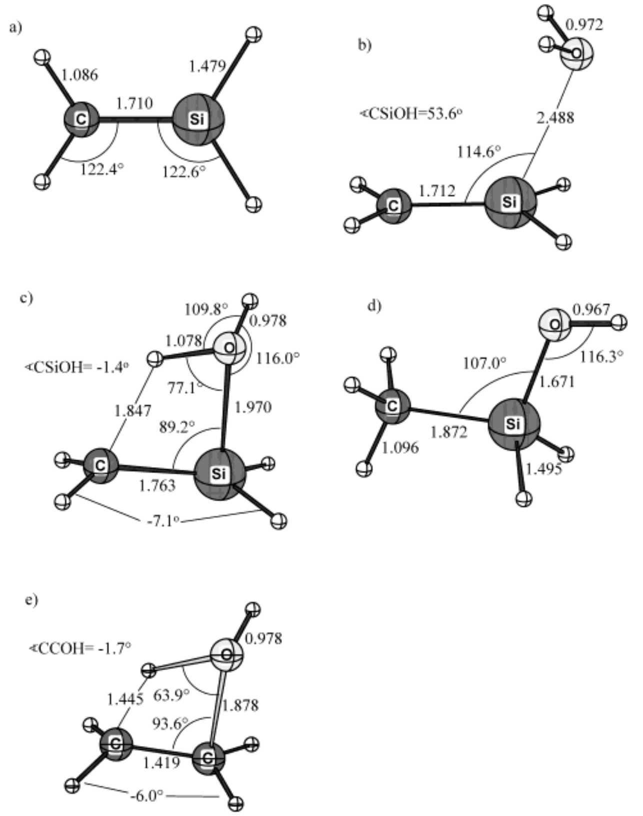

Figure 1. Optimized structures at B3LYP/6-31G(d) of (a) the parent silene **1**, (b) its complex with water (**I**), (c) the TS for the addition of water to **1** (**II**), (d) product of the addition of water to **1** (**III**), and (e) transition structure (at B3LYP/6-31G(d)) for the addition of water to ethylene. Bond lengths are in Å and bond angles in deg.

Table 3. Calculated Free Energies (at 298 K) for the Addition of Water to $H_2Si{=}CH_2$ (eq 2) at Several Levels of Theory (kcal/mol)[a]

method	complex **I**	TS **II**
B3LYP/6-31G(d)//B3LYP/6-31G(d)	3.63	8.66
MP2/cc-pVTZ//MP2/cc-pVTZ	4.71	7.80
CBS-Q	5.63	10.57
G2	4.88	11.89

[a] All energies are relative to the infinitively separated reactants: $H_2Si{=}CH_2 + H_2O$.

experimental finding of Leigh and Li, who found reduced rate for addition of alcohols to silenes in THF compared to hydrocarbon or acetonitrile solutions.[9h]

(2) The Parent Reaction. The parent silene is highly polar[11] and this is one of the reasons for its very high reactivity toward polar reagents, such as water. Another reason for the very low activation barrier for water addition might be the high exothermicity of this reaction of about −70 kcal/mol (Table 2). The high exothermicity results from the fact that the weak Si=C π-bond is traded for a new extremely strong Si−O bond. The calculated structures of the silene−water complex **I**, the transition state (TS) **II**, and the product **III** of the addition of water to the parent silene are shown in Figure 1.

The activation energies for reaction 2 are calculated to be negative[35a] with some of the theoretical methods and the relative energies of the complexes are always negative (Table 2). The free energies of activation (at 298 K) and the free energies of complexation are positive in all cases[35b] and the free energies of the complexes are lower than the free energies of the transition states (Table 3). This means that in all cases the dissociation of the complexes back to the reactants is faster than the reaction forward to give the products. Thus, on the ΔG potential energy surface (PES) the second step is the rate-determining step. The entropy of activation is about −40 eu, and this contribution increases the free energy of the transition state by ca. 12 kcal/mol at 298 K. The addition of zero-point energy corrections changes the energies only slightly, by ca. 1 kcal/mol.

In the first step of the addition reaction the 2p lone pair on the oxygen interacts with the silene's LUMO (which is mostly located on silicon) to form a weak silene−water complex **I** (Figure 1b). The binding energy of the water molecule to the silene is small, in the range of −0.6 to −5.8 kcal/mol depending on the theoretical method used (Table 2). The weak complexation is evident also in the calculated geometry of the complex (Figure 1b). Thus, the Si=C bond is elongated by only ca. 0.002 Å; relative to the isolated silene, the Si atom is only slightly pyramidalized and the C atom remains planar (the sum of the angles around Si and C is 358.0° and 359.8°, respectively). The complex has C_s symmetry at B3LYP/6-31G(d), MP2/6-31G(d), MP2/6-311G(d), and MP2/6-311+G(d,p) or C_1 symmetry, but with a CSiOH

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[35] (a) For discussion of negative activation energies see: Apeloig, Y.; Sklenak, S. *Can. J. Chem.* **2000**, 78, 1496. (b) The fact that the free energy of the complex is higher than that of the reactants arises from the contribution of entropy (Table 9). On the ΔH surface the complex is lower in energy than the reactants. Thus, no TS is expected between reactants and the complex.

Table 4. Calculated Energies (kcal/mol) for the Addition of Water to Ethylene and to 1,1-Dicyanoethylene[a]

	TS	product
$H_2C{=}CH_2$	56.59 (48.29)	−15.45 (−23.47)
$H_2C{=}C(CN)_2$[b]	45.93 (37.46)	−11.46 (−16.39)
$H_2C{=}C(CN)_2$, abnormal[c]	61.13 (56.54)	−11.67 (−15.33)

[a] At MP4/6-31+G(d,p)//B3LYP/6-31G(d). Energies at B3LYP/6-31G(d) are given in parentheses. All energies are relative to the reactants. [b] Attack of oxygen at CH_2. [c] Attack of oxygen at $C(CN)_2$.

dihedral angle close to 0°, at B3LYP/6-31+G(d), B3LYP/6-311G(d), and B3LYP/6-311++G(d,p) as well as MP2/6-31+G(d).

In the second and rate-determining step of the reaction an electrophilic addition of the hydrogen to the carbon atom occurs (Figure 1c) leading to the formation of the product. In TS **II** (C_1 symmetry) the silene moiety remains nearly planar, but now the C atom is more strongly pyramidalized than the Si atom (the sum of the angles around Si and C is 356.9° and 351.8°, respectively). The Si−O distance in the TS is relatively long (1.970 Å, relative to 1.671 Å in the product silanol) and the Si−C bond is still relatively short (1.763 Å in **II**, and 1.710 Å in **1** and 1.872 Å in **III**). According to NBO-NRT analysis the bond order of the forming Si···O bond in TS **II** is very small (0.121). All these parameters indicate that TS **II** can be characterized as being early TS along the reaction coordinate. The negative eigenvector which characterizes this TS indicates that the rate-determining step in this reaction is the proton transfer from the water oxygen to the silene's carbon atom. The calculated kinetic isotope effect, KIE (using B3LYP/6-31G(d) force constants), is 1.69, consistent with an early transition state.

(3) Comparison between the Addition of Water to Silene 1 and to Alkenes. The energies calculated for the addition of water to ethylene and to 1,1-dicyanoethylene are given in Table 4.

A complex between ethylene and water could not be located, which is not surprising considering the nonpolar nature of the C═C bond and its high bond energy. The barrier for addition of water to ethylene is very high (56.6 kcal/mol), which is consistent with the fact that this reaction is symmetry forbidden.[10,36] Indeed the addition of water to alkenes occurs only in strong acidic or basic media.[36] The calculated TS for this addition reaction (Figure 1e) occurs relatively late (the C═C bond length in the TS is 1.416 Å relative to 1.331 Å in ethylene) and it shows both electrophilic and nucleophilic contributions from the water molecule, for example, the O−H bond length of 1.252 Å is considerably elongated (0.969 Å in water). According to NBO-NRT analysis in the TS the bond order of the forming C···O bond is relatively high, 0.651, compared to a bond order of only 0.121 of the forming Si···O bond in **II**.

Addition of water to a polar alkene, $H_2C{=}C(CN)_2$, was calculated to provide a better comparison with the polar silenes, e.g., **1**. Two pathways for the addition of water were considered: "normal" where the oxygen attacks the more electrophilic CH_2 group and "abnormal" (or "inverted") where the oxygen attacks the $C(CN)_2$ carbon.

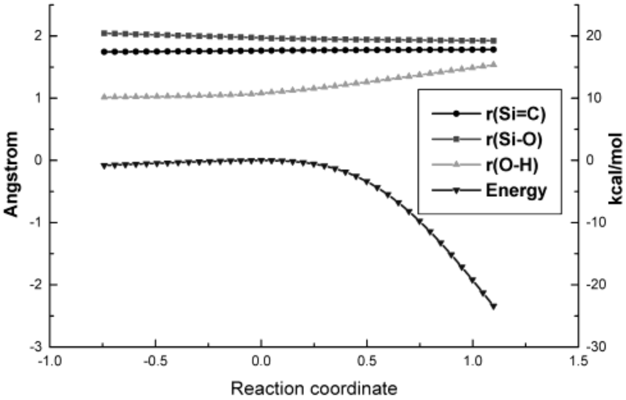

Figure 2. IRC calculations (at B3LYP/6−31(G)) for transition state **II**. A positive reaction coordinate corresponds to the path leading to the product.

Also in these cases alkene−water complexes were not found. We find that two cyano groups reduce the barrier for water addition by ca. 10 kcal/mol. The "abnormal" pathway is by 15 kcal/mol higher in energy than the "normal" addition and it actually requires 5−6 kcal/mol more energy than the addition to ethylene itself.

(4) Is the Addition of Water to the Parent Silene Electrophilic or Nucleophilic? The calculated NBO charges for the TSs for the addition of water to silene (and ethylene) and for silene−water complex) are given in Table 5. The charge on the H_2O molecule in the silene−water complex **I** is slightly positive (0.07 e), indicating the nucleophilic role of the water molecule in the formation of **I**. In the TS this charge is nearly zero, i.e., charge flows back from the silene to water. This indicates that in the TS region the silene changes its role from being an electrophile in the complex to a nucleophile in the TS. However, the overall charge shifts are relatively small.

The main geometrical change that occurs in the TS region is in the O−H bond length, i.e., the H atom shifts from the oxygen toward the carbon. This is consistent with the direction of the negative eigenvector calculated in TS **II**. However, this is accompanied by only a small charge transfer from the attacking H_2O to the silene (Table 5). The main change that occurs in the TS is charge polarization within the silene, in which the SiH_2 and CH_2 fragments become more highly charged in the TS than in the isolated silene (Table 5).

To follow the geometrical and energetic changes which occur in the region of the TS, we performed a detailed intrinsic reaction coordinate (IRC) calculation for TS **II** and the results are presented in Figure 2. There are very small changes in the Si−O and O−H bond lengths before the TS is reached. After the TS is traversed the O−H bond elongates very fast. It can therefore be concluded that before the TS is reached the attack of water has both nucleophilic (Si−O distance shortening) and electrophilic (O−H bond elongation) in character. After the TS is traversed the reaction is mostly electrophilic in character.

(5) Addition of Alcohols to $H_2Si{=}CH_2$. To investigate the effect of the attacking nucleophile we have studied also the addition of methanol, ethanol, and *tert*-butyl alcohol to $H_2Si{=}CH_2$ (**1**). The relative energies calculated at MP4/6-31+G(d,p)//B3LYP/6-31G(d) are

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(36) March, J. *Advanced Organic Chemistry*, 3rd ed.; John Wiley & Sons: New York, 1985.

Table 5. Calculated NBO Charges in the Addition of Water to Ethylene and to $H_2Si{=}CH_2$ (at MP2/6-31G(d)//B3LYP/6-31G(d))[a]

	C	CH_2	E^b	$EH_2{}^b$	H_2O
silene **1**	−1.08	−0.58 (−0.19) [−0.26]	0.94	0.58 (0.19) [0.26]	
silene complex **I**	−1.20	−0.71	1.03	0.64	0.07
silene TS **II**	−1.37	−0.86 (−0.45) [−0.52]	1.27	0.85 (0.39) [0.39]	0.01 (0.06) [0.13]
ethylene	−0.42	0.00	−0.42	0.00	
ethylene TS	−0.81	−0.33	−0.18	0.29	0.05

[a] With NBO analysis. Mülliken charges are given in parentheses and CHelpG charges are given in square brackets. [b] E = C for ethylene, E = Si for silene.

Table 6. Calculated Energies in the Addition of Alcohols to $H_2Si{=}CH_2$ and Gas-Phase Acidity of the Corresponding Alcohols (kcal/mol)[a,b]

nucleophile	complex	TS	product	acidity[c]
water	−2.17 (−5.76)	4.76 (−1.73) [6.24] *0.87*	−70.75 (−77.30)	390.8 (0.0)
methanol	−4.46 (−2.25)	0.34 (0.86) [2.56] *−1.66*	−72.34 (−73.77)	379.2 (−11.6)
ethanol	−4.75 (−2.44)	−0.14 (0.80) [2.12]	−69.50 (−70.50)	376.1 (−14.7)
tert-butyl alcohol	−5.13 (−1.22)	−0.42 (2.71)	−68.28 (−67.88)	373.3 (−17.5)

[a] All energies are relative to the infinitively separated reactants. [b] At MP4/6-31+G(d,p)//B3LYP/6-31G(d). Values in parentheses are at B3LYP/6-31G(d). Values in square parenthesis are at CCSD(T)/6-31G(d)/B3LYP/6-31G(d). Values in italics are at MP2/6-31G(d). [c] Experimental values in the gas phase; values in parentheses are relative to water.[10]

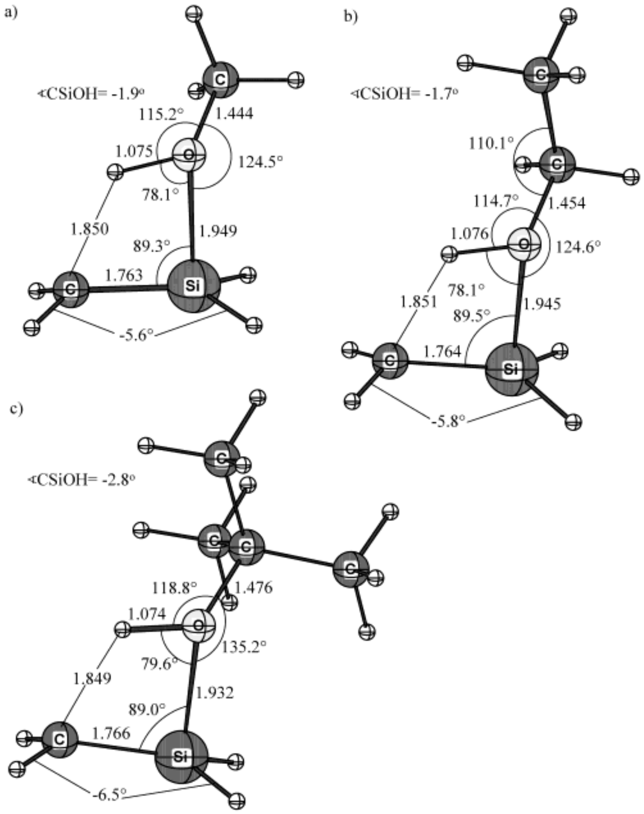

Figure 3. Optimized transition state structures (at B3LYP/6-31G(d)) for the addition to $H_2Si{=}CH_2$ of (a) methanol, (b) ethanol, and (c) *tert*-butyl alcohol. Bond lengths are in Å and bond angles in deg.

given in Table 6 and the calculated geometries of the transition states are shown in Figure 3.

The activation energies for the addition of all the alcohols studied to **1** are very small, in the range of −2 to +6 kcal/mol, regardless of the computational method used. The activation energy decreases slightly along the series H_2O > MeOH > EtOH > *t*-BuOH. This order follows the gas-phase acidity of the nucleophile (Table 6), so that the higher the alcohol acidity the lower is the activation energy (calculated at MP4/6-31+G(d,p)//B3LYP/6-31G(d)).[37]

The activation energy for the addition of *tert*-butyl alcohol to **1** follows its higher gas-phase acidity and it is the lowest among the alcohols studied. This shows that in the addition to **1** *tert*-butyl alcohol does not exert a significant steric effect. However, the size of the *tert*-butyl group probably becomes significant in the addition to substituted silenes.

The transition state structures for the addition of the three alcohols to silene **1** are very similar (Figure 3). Yet, a small gradual change toward a later TS is observed along the series H_2O, MeOH, EtOH, *t*-BuOH, i.e., $r(\mathrm{Si}\cdots\mathrm{O})$ = 1.970, 1.949, 1.945, 1.932 Å, respectively, and $r(\mathrm{Si}{=}\mathrm{C})$ = 1.763, 1.763, 1.764, 1.766 Å, respectively (compare Figure 1c and Figure 3).

The calculated KIE also increases gradually along this series, from 1.69 for water to 2.28 for MeOH and to 2.64 for *t*-BuOH. The calculated KIE for methanol addition is somewhat larger than that reported experimentally (k_H/k_D = 1.3−1.9) for several alkyl- and phenyl-substituted silenes.[9] The calculated isotope effect thus supports the conclusion that the TS changes to a later TS along the series water, methanol, ethanol, *tert*-butyl alcohol. The NBO charge distribution in the TS remains nearly unchanged along the series and it is very similar to that in the addition of water to $H_2Si{=}CH_2$.

(II) The Effect of Substituents on the Kinetic Stability of Silenes. To explore the influence of substituents on the reactivity of silenes we studied the addition of water to the substituted silenes **2**−**9**.[33] The choice of these particular silenes was dictated by our attempts to model known experimental data, as mentioned in the Introduction. For example, silene **5** is a

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(37) B3LYP/6-31G(d) energies predict the opposite trend in the activation energies. However, as calculations using the more sophisticated CCSD(T)/6-31G(d)//B3LYP/6-31G(d) and MP2/6-31G(d)//MP2/6-31G(d) methods show the same trend as the MP4/6-31+G(d, p)//B3LYP/6-31G(d) calculations (Table 6), we conclude that in this case the B3LYP method fails to predict the correct energy trend, although the optimized geometries are very similar to the ones calculated with the other methods.[38]

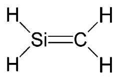
(38) For similar failures of the B3LYP method see: (a) Martin, J. M. L.; El-Yazal, J.; François, J.-P. *Mol. Phys.* **1995**, *86*, 1437. (b) Johnson, B. J.; Gonzales, C. A.; Gill, P. M. W.; Pople, J. A. *Chem. Phys. Lett.* **1994**, *221*, 100. (c) Ventura, O. N.; Kieninger, M.; Irving, K. *Adv. Quantum Chem.* **1997**, *28*, 293.

Table 7. Total and π-Mülliken Charges and NBO Charges on the Multiply Bonded Silicon and Carbon Atoms in Silenes 1−9

	Mülliken charges						NBO charges		
silene	π(Si)	π(C)	$\Delta\pi$[a,b]	t(Si)[c]	t(C)[c]	$\Delta(t)$[a,c]	t(Si)[c]	t(C)[c]	$\Delta(t)$[a,c]
$H_2Si{=}CH_2$ (**1**)	0.13	−0.11	0.24	0.32	−0.56	0.88	0.94	−1.08	2.02
$Me_2Si{=}C(SiH_3)_2$ (**2**)	0.30	−0.17	0.47	0.65	−0.67	1.32	1.71	−1.76	2.47
$Cl_2Si{=}CH_2$ (**3**)	0.11	−0.20	0.31	0.59	−0.58	1.17	1.37	−1.21	2.58
$Me_2Si{=}CMe_2$ (**4**)	0.10	−0.08	0.18	0.52	−0.11	0.63	1.50	−0.68	2.18
$(H_3Si)_2Si{=}CMe_2$ (**5**)	0.01	−0.03	0.04	−0.01	−0.06	0.05	0.45	−0.53	0.98
$(H_3Si)_2Si{=}C(Me)OSiH_3$ (**6**)	−0.05	0.01	−0.06	−0.06	0.20	−0.26	0.35	−0.14	0.49
$Me_2Si{=}C(SiMe_3)H$ (**7**)	0.22	−0.14	0.36	0.60	−0.61	1.21	1.61	−1.50	3.11
$Me(HCC)Si{=}CH_2$ (**8**)	0.13	−0.15	0.28	0.46	−0.56	1.02	1.48	−1.13	2.61
$Me(Me_3Si)Si{=}CH_2$ (**9**)	0.12	−0.11	0.23	0.29	−0.54	0.83	0.98	−1.09	2.07

[a] Δ = the charge on the silicon atom minus the charge on the carbon atom. [b] π = π-charge. [c] t = total charge.

model for the stable silene (t-$BuMe_2Si)(Me_3Si)Si{=}(2$-Ad) (**11**) synthesized by our group.[16]



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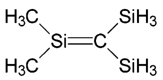

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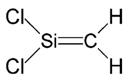

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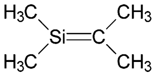

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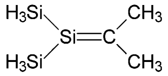

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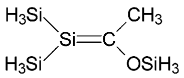

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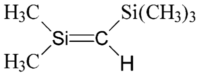

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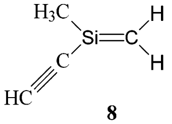

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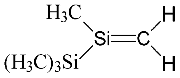

9

(1) Charge Distribution and Bond Orders in Silenes 1−9. Let us first examine the charge distribution in the reactant silenes. The effect of the substituents on the charge distribution is very large (Table 7), as pointed out previously by Apeloig and Karni.[11] According to the calculations, $Me_2Si{=}C(SiH_3)_2$, $Cl_2Si{=}CH_2$, and $Me_2Si{=}C(SiMe_3)H$ are the most polar silenes among the silenes studied, with the silicon atom being strongly positively charged. $(H_3Si)_2Si{=}CMe_2$ and $(H_3Si)_2Si{=}C(Me)OSiH_3$ are the least polar silenes. The total NBO polarity, $\Delta(t)$, i.e., the charge on the silicon atom minus the charge on the carbon atom, increases in the following order: **6** < **5** < **1** < **9** < **4** < **2** < **3** < **8** < **7**. The trends observed in the NBO and Mülliken charges as a function of the substituents are similar, although some small differences between the two methods are found (Table 7).

The parent silene **1** is a very polar molecule. Tetramethyl silene **4** has a similar degree of polarity. In silenes **2** and **3** the polarity increases by ca. 0.4−0.5 e compared to silenes **1** and **4**. On the other hand, in silene **6** the overall polarity (Δt(NBO)) of ca. 0.5 e is much lower than that in the parent silene, where Δt(NBO) = 2.0 e. In **6** the Me and $OSiH_3$ substitution at carbon reduces the negative charge at the sp^2 carbon and the silyl substituents reduce the positive charge at the sp^2 silicon, reducing the overall polarity in **6** relative to **1**. In all silenes studied the carbon atom is the nucleophilic site of the Si=C bond, except probably **6**, where according to the total Mülliken charges the silicon atom is calculated to be the slightly more nucleophilic site of the double bond. However, according to the NBO charges, even in **6**, the silicon atom is still the most electrophilic site.

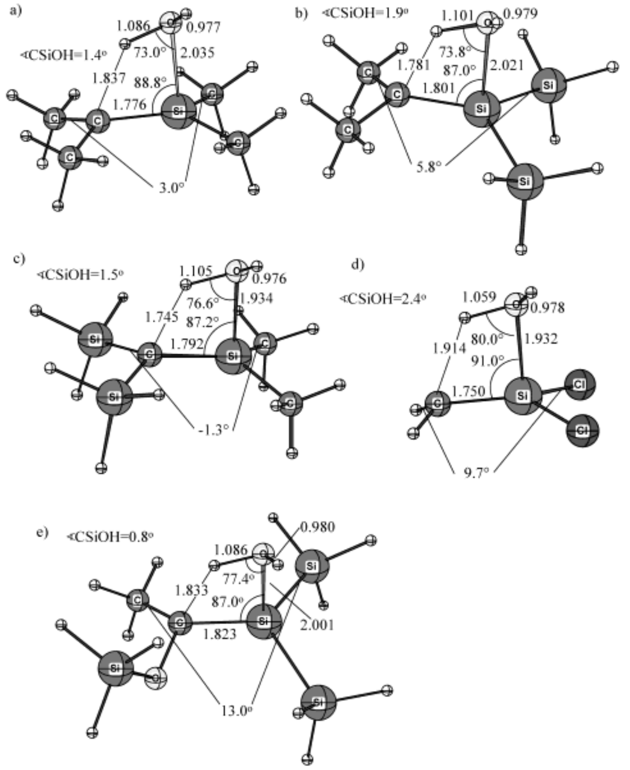

Figure 4. Optimized transition state structures (at B3LYP/6-31G(d)) for the addition of water to (a) silene **4**, (b) silene **5**, (c) silene **2**, (d) silene **3**, and (e) silene **6**. Bond lengths are in Å and bond angles in deg.

Table 8. Bond Lengths (Å, at B3LYP/6-31G(d)) and Natural Bond Orders (MP2/6-31G(d)//B3LYP/6-31G(d)) for Silenes 1−6

silene	r(Si=C)[a]	t(Si=C)[b]	c(Si=C)[c]	i(Si=C)[d]
$H_2Si{=}CH_2$ (**1**)	1.710	2.009	1.371	0.638
$Me_2Si{=}C(SiH_3)_2$ (**2**)	1.721	1.838	0.972	0.866
$Cl_2Si{=}CH_2$ (**3**)	1.690	1.851	1.227	0.624
$Me_2Si{=}CMe_2$ (**4**)	1.727	1.826	1.162	0.665
$(H_3Si)_2Si{=}CMe_2$ (**5**)	1.750	1.827	1.304	0.523
$(H_3Si)_2Si{=}C(Me)OSiH_3$ (**6**)	1.769	1.786	1.305	0.481

[a] Bond length. [b] Total bond order. [c] Covalent part of the bond order. [d] Ionic part of the bond order.

The Si=C bond lengths, as well as the NRT Si=C bond order for silenes **1**−**6**, are presented in Table 8. Some general trends are obvious from Tables 7 and 8. There is a reasonably good linear correlation between the Si=C bond length (Table 8) and the bond polarity (Table 7). A more polar Si=C bond is shorter. The NRT

Table 9. Calculated Energies (kcal/mol) for the Reaction of Silenes 1−6 with Water[a,b]

	complex			TS			product		
silene	ΔE	ΔS	ΔG	$\Delta E^{\#}$	$\Delta S^{\#}$	$\Delta G^{\#}$	ΔE	ΔS	ΔG
$H_2Si{=}CH_2$ (**1**)	−2.17 (−5.76)	−25.7	3.63	4.76 (−1.73)	−37.1	8.66	−70.75 (−77.30)	−34.4	−64.34
$Me_2Si{=}C(SiH_3)_2$ (**2**)	−7.43 (−10.30)	−34.8	1.74	−3.29 (−7.58)	−41.8	3.67	−65.32 (−67.44)	−40.8	−54.01
$Cl_2Si{=}CH_2$ (**3**)	−7.50 (−10.59)	−33.1	2.83	−4.15 (−9.35)	−38.2	2.20	−86.81 (−93.43)	−38.8	−75.42
$Me_2Si{=}CMe_2$ (**4**)		*c*		7.90 (3.07)	−38.7	13.24	−71.92 (−74.90)	−36.7	−62.06
$(H_3Si)_2Si{=}CMe_2$ (**5**)		*c*		15.77 (10.55)	−36.4	19.68	−57.71 (−62.43)	−38.2	−49.93
$(H_3Si)_2Si{=}C(Me)OSiH_3$ (**6**)		*c*		16.15 (12.32)	−40.17	22.54	−55.63 (−59.82)	−36.94	−47.20

[a] The energies given are relative to the corresponding infinitively separated silene and water. [b] ΔE values are at MP4/6-31+G(d,p)//B3LYP/6-31G(d) (values in parentheses are at B3LYP/6-31G(d)); ΔG and ΔS values are at B3LYP/6-31G(d). [c] Not found.

Table 10. Calculated Activation Energies (kcal/mol) for the Addition of Water and Methanol to Silenes 7−9[a,b] **and Experimental Rate Constants for the Addition of Methanol**[c]

	water			methanol			
silene	$\Delta E^{\#}$	$\Delta S^{\#}$	$\Delta G^{\#}$	$\Delta E^{\#}$	$\Delta S^{\#}$	$\Delta G^{\#}$	exp $k/10^8\ M^{-1}\ s^{-1}$
$Me_2Si{=}C(SiMe_3)H$ (**7**)	−0.33 (−5.10)	−44.3	7.07	−5.24 (−5.02)	−46.2	7.52	85[9d]
$Me(HCC)Si{=}CH_2$ (**8**)[d]	1.34 (−3.77)	−38.1	6.74	−3.64 (−3.68)	−40.1	7.26	100[9c]
$Me(Me_3Si)Si{=}CH_2$ (**9**)	5.36 (0.26)	−39.4	10.81	0.80 (0.64)	−41.4	11.59	1.8[9c]

[a] The energies given are relative to the corresponding infinitively separated silene and water. [b] ΔE values are at MP4/6-31+G(d,p)//B3LYP/6-31G(d) (values in parentheses are at B3LYP/6-31G(d)); ΔG and ΔS values are at B3LYP/6-31G(d). [c] Experimental data of Leigh et al.[9c,d] [d] A complex between **8** and water was located. $\Delta E = -6.90$ and -4.38 kcal/mol at B3LYP/6-31G(d) and MP4/6-31+G(d,p)//B3LYP/6-31G(d), respectively.

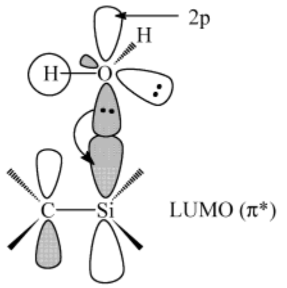

Figure 5. Schematic drawing of the orbital interactions in the transition state for the addition of water to silenes.

analysis clearly shows that with an increase in polarity, the covalent character of the Si=C bond decreases and the ionic character increases (Table 8). In general, all Si=C bonds have a relatively high ionic character. According to the NRT analysis the most ionic silene is **2**, while the least ionic silene is **6**. The total bond order varies over a relatively narrow range from 1.79 for **6** to 2.01 for **1**.

(2) Activation Energies for Addition of Water. The transition structures for the addition of water to silenes **2**−**6** are shown in Figure 4. All structures are quite similar and they all have a four-centered structure involving the Si=C double bond, the oxygen, and one of the hydrogen atoms of the water molecule. These four atoms are nearly in the same plane (the largest H−O−Si−C dihedral angle of 2.4° is calculated for **3**). This geometry is consistent with the orbital picture depicted in Figure 5, according to which in the transition state electrons flow from the 2p(O) orbital into the π^*(Si=C) orbital.

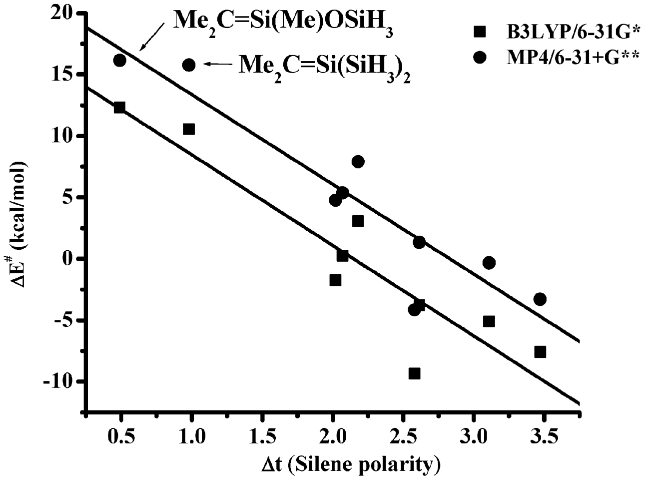

Figure 6. Correlation between the calculated activation barriers ($\Delta E^{\#}$) for water addition to silenes **1**−**9** and the silene polarity Δt (the difference between the total NBO charges on silicon and carbon, at MP4/6-31+G(d,p)//B3LYP/6-31G(d) (●) or at B3LYP/6-31G(d) (■).

The calculated relative energies at MP4/6-31+G(d,p)//B3LYP/6-31G(d) for the addition of water to silenes **1**−**9** are given in Table 9 and Table 10. The effect of the substituents on the activation energies is large, spanning a range of 20 kcal/mol. Thus, the activation energy for the addition of water to silenes **2** and **3** is negative, about −4 kcal/mol, while for silenes **5** and **6** the barriers for water addition are significant, ca. 16 kcal/mol.

One of the most interesting findings of our study is the fact that the activation barriers for the addition of water to silenes correlate linearly with the silene polarity, Δt, as measured by the difference in the total charge at the Si and at the C atoms of the Si=C bond. Thus, correlation of the calculated NBO polarity, Δt, with the activation energies for water addition to silenes **1**−**9**, shown in Figure 6, reveals a linear dependence (r = 0.92−0.93). An even better correlation (r = 0.97−0.98) was found when using Mülliken charges. In other words, **the less polar the silene, the higher is the activation energy for water addition**. This correlation can be very helpful in designing models for the synthesis of kinetically stable silenes.[39]

The computational results, particularly those for **7**−**9**, correlate nicely with the recent kinetic measurements of Leigh et al.[9] (Table 10). Since the experimental activation energies are temperature dependent the best possible comparison of the calculated activation energies is with measured absolute rate constants.[9] Experimentally $Me_2Si{=}C(SiMe_3)H$ (**7**) and $Me(HCC)Si{=}CH_2$ (**8**) react with methanol at a diffusion limit rate while $Me(Me_3Si)Si{=}CH_2$ (**9**) reacts with methanol at least 55 times slower. In agreement, the calculated activation barrier for the addition of methanol to **9** is by 4.3 kcal/mol higher than to **8**.[40] Comparison of the calculated activation energies of silenes **7** and **9** points to the fact that silyl substituents can either enhance or reduce the rate of addition, depending if substitution is at the carbon end or at the silicon end of the Si=C bond, respectively.

(3) Complex Formation. The more polar the silene the stronger is the complex that it forms with H_2O. The **3**−water complex is by 7.5 kcal more stable than the reactants and for **2** such a complex is by 7.4 kcal/mol more stable than the reactants (Table 9).[41] In contrast, silene−water complexes could not be located for the nonpolar **5** and **6** as well as for the highly polar **4**. These theoretical findings are in agreement with experimental facts; a silene−THF complex was found experimentally for $Me_2Si{=}C(SiMe_3)SiMe_2Bu$-*t* (**12**),[42] an analogue of **2**. The experimental Si=C and Si···O bond distances in **12**·THF are 1.747 and 1.878 Å, respectively, while the calculated bonds in **2**·H_2O are 1.741 and 2.165 Å, respectively.[43] So, the reported **12**·THF complex is somewhat more strongly bound than the calculated **2**·H_2O complex, even though the calculations neglect the steric interactions which are expected to weaken the **12**·THF complex. We have tried to isolate a complex between *t*-$BuMe_2Si(Me_3Si)Si{=}(2\text{-Ad})$ (**11**) (an analogue of $(H_3Si)_2Si{=}CMe_2$) and THF, but such a complex could not be isolated. A C_6D_6 solution of **11** with 3 equiv of THF shows the same ^1H, ^{13}C, and ^{29}Si NMR as pure **11**, indicating that a complex is not formed.[44]

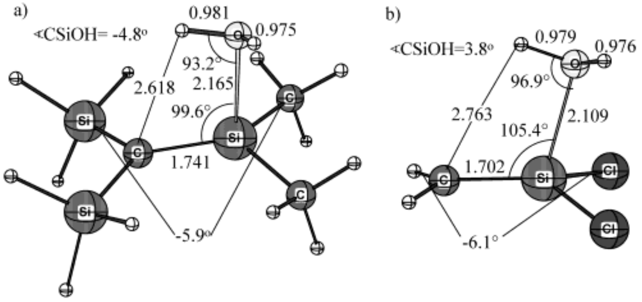

Figure 7. Optimized structures (at B3LYP/6-31G(d)) of complexes between water and (a) silene **2** and (b) silene **3**. Bond lengths are in Å and bond angles in deg.

Table 11. Calculated Isotope Effects (IE) for the Addition of Nucleophiles to Silenes (at B3LYP/6-31G(d))

reaction	IE
$Me_2Si{=}C(SiH_3)_2$ (**2**) + H_2O	0.66[a]
$H_2Si{=}CH_2$ (**1**) + H_2O	1.69[b]
$H_2Si{=}CH_2$ (**1**) + MeOH	2.38[b]
$H_2Si{=}CH_2$ (**1**) + t-BuOH	2.64[b]
$Me_2Si{=}C(SiH_3)_2$ (**2**) + H_2O	2.09[b]
$Me_2Si{=}CMe_2$ (**4**) + H_2O	1.83[b]
$(H_3Si)_2Si{=}CMe_2$ (**5**) + H_2O	2.22[b]

[a] For complex formation. [b] At the transition state.

The calculated geometries for the silene−water complexes are presented in Figure 7. They are similar to the geometries of the corresponding transition states (Figure 6) but they have longer C···H distances (of ca. 2.7 Å) and shorter O−H bonds (of ca. 0.98 Å).

(4) Isotope Effects (IE). The calculated equilibrium isotope effects for complex **2**·H_2O and the kinetic isotope effect (KIEs) for addition of water and alcohols to silenes **1**, **2**, **4**, and **5** are given in Table 11. The IE for the formation of complex **2** is less than 1, which clearly shows the nucleophilic character of the process. The KIE for the TSs vary in the range of 1.69−2.64, which supports the conclusion that in these TSs there is some electrophilic hydrogen participation.[45] The KIE for the addition of *t*-BuOH to **1** is larger (2.64) than for the addition of methanol (2.38) and water (1.69). Apparently, the addition of *t*-BuOH has a more pronounced electrophilic contribution than the addition of methanol or of water. For the addition of phenols to disilenes ($Mes_2Si{=}SiMes_2$) both electrophilic and nucleophilic mechanisms were reported, depending on the substituent on the phenol.[46] For a nucleophilic dominating addition the measured KIE is 0.71 (calculated 0.94) and for an electrophilic dominating addition the measured KIE is 5.27 (calculated 4.30).[46] These data support the conclusion that in addition to silenes the formation of the complex has a strongly predominating nucleophilic character, while in the TS both nucleophilic and electrophilic contributions are important.

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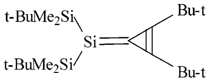
[39] Silene (**13**) was synthesized very recently and its X-ray structure was determined (Sakamoto, K.; Ogasawara, J.; Kon, Y.; Sunagawa, T.; Kabuto, C.; Kira, M. *Angew. Chem., Int. Ed. Engl.* **2002**, *41*. 1402). Both the silafulvene skeleton and the two silyl groups on the silicon atom of the Si=C double bond reduce its polarity and increase its kinetic stability. In line with the correlation in Figure 6 our calculations find that the barrier for water addition to the model system **14** is 21.1 kcal/mol (at MP4/6-311++G(d,p)//MP2/6-31G(d) + ZPVE). For calculations on a smaller model system see ref 13.



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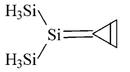

14

[40] A relative rate of 55 corresponds to an energy difference of 2.4 kcal/mol at 298 K. Note that in the gas phase the effect of substituents is expected to be larger than that in solution.

[41] Note that the complexation energy of water to H_2Si is larger, about 12 kcal/mol. Belzner, J.; Ihmels, H. *Adv. Organomet. Chem.* **1998**, *43*, 1.

[42] Wiberg, N.; Wagner, G.; Müller, G.; Riede, J. *J. Organomet. Chem.* **1984**, *271*, 381.

[43] For a detailed discussion of the complex between the parent silene **1** and diethyl ether, see: Auner, N.; Grobe, J.; Müller, T.; Rathmann, H. W. *Organometallics* **2000**, *19*, 3476.

[44] Apeloig, Y.; Bendikov, M. Experimental details will be reported elsewhere.

[45] KIE from the silene−water complex to TS would be even larger, around 3 (calculated KIE from reactants to TS divided by equilibrium IE for silene−water complex formation).

[46] (a) Apeloig, Y.; Nakash, M. *J. Am. Chem. Soc.* **1996**, *118*, 9798. (b) Apeloig, Y.; Nakash, M. *Organometallics* **1998**, *17*, 2307.

Conclusions

A systematic theoretical study of the addition of water and alcohols to silenes was carried out. The energy barriers for the addition reaction, which denote the kinetic stability of the silene, strongly depend on the substituents. In particular, silyl substitution at the sp^2 silicon atom stabilizes the silene considerably toward nucleophilic attack. Polar silenes (**1**−**4**) exhibit low or even negative activation energies (−3 to 8 kcal/mol); on the other hand, substituents which strongly reduce the polarity of the silene, as in **5** and **6**, significantly increase the activation barrier for addition of H_2O, i.e., to ca. 16 kcal/mol. The calculated activation energies show good correlation with the polarity of the silenes, i.e., Δt (Δt = the difference in the total charge between the doubly bonded Si and C atoms), so that the higher the polarity of the silene the lower is the activation barrier for water addition. Thus, the polarity of a silene is a good indicator for predicting its kinetic stability toward the addition of nucleophiles. This finding, together with the well-established kinetic stabilization of silenes by bulky substituents, forms the strategy for designing novel kinetically stable silenes. The ability of silenes to form complexes with Lewis bases is also related to its polarity.

Acknowledgment. This paper is dedicated to Professor Amitai Halevi on the occasion of his 80th birthday. The authors thank Prof. W. J. Leigh for helpful discussions and N. Sigal for help. This research was supported by the United States−Israel Binational Foundation (BSF) and the Minerva Foundation in Munich, and by the Fund for the Promotion of Research at the Technion.

Supporting Information Available: Absolute energies, optimized geometries (in Cartesian coordinates) for all calculated compounds at B3LYP/6-31G(d) and absolute energies, and relative energies and geometries for water addition to silene **1** at different theoretical levels. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0202571