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The Mechanism of 1,2-Addition of Disilene and Silene. 1. Water and Alcohol Addition

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Abstract: The mechanism of 1,2-addition reactions of water, methanol, and trifluoromethanol to Si═Si, Si═C, and C═C bonds has been investigated by ab initio quantum chemical methods. Geometries and relative energies of the stationary points and all the transition states were determined using the MP2/6-311++G(d,p), B3LYP/6-311++G(d,p), and CBS-Q levels of theory. The investigated reactions can be characterized by two main thermodynamical profiles. The type in which the reagent molecule attacks a carbon atom is moderately exothermic, with a high activation barrier. The second type, in which water or alcohol attacks a silicon, is strongly exothermic, with a small activation energy. At the early stage of all the reactions, a weakly bonded initial complex is found which determines the further mechanism of the reaction. On the basis of the HOMO, LUMO, and Laplacian of electron distribution of disilene and silene, several mechanisms have been assumed, depending on the substrate (disilene, substituted disilene, silene, or ethene) and the reagent (water, methanol, or trifluoromethanol). The reaction diagrams and proposed mechanisms explain the experimentally found regioselectivity and diastereoselectivity well.

Introduction

Since the first successful synthesis of stable doubly bonded silicon compounds[1,2] in 1981, a great deal of progress has been made in this area of chemistry. Today, several dozen stable disilenes and silenes are known. Physical, spectroscopic, and structural information is available, and many of their fundamental reactions have been well described.[3] On the other hand, only a very limited amount of information is available about the mechanism of their reactions. The aim of our work was to study the mechanism of water and alcohol addition, the most well-known 1,2-addition reactions of disilenes and silaethenes. In a subsequent work[4] we will present our results on the hydrogen halide addition reactions.

Unsaturated silicon species react efficiently with alcohol and water[3] without an acid catalyst to give addition products. The reaction of stereoisomeric disilene (*E*)-1,2-di-*tert*-butyl-1,2-dimesityldisilene with alcohols has been reported to give a mixture of two diastereomers.[5] From this result, it was suggested that the reactions proceeded in a stepwise manner. On the other hand, Nagase and Kudo,[6] in their early theoretical calculations for the gas-phase water addition to disilene and silene, found that the reaction involved a four-membered transition state and proceeded in a concerted manner. According to Hartree−Fock calculations, the barrier of the reactions was much smaller than in the similar reaction of ethene. Sekiguchi, Maruki, and Sakurai[7,8] have found, however, that transient disilene (*E*)- and (*Z*)-PhMeSi═SiMePh reacted with alcohol in a syn fashion with high diastereoselectivity, the extent of which depended on the concentration and steric bulk of alcohol used. On the basis of photolysis experiments, it was thought that syn and anti adducts, which were preferred at the low and high concentrations of the alcohols, respectively, were formed via intra- and intermolecular transfer of an alcoholic hydrogen atom, respectively, at a four-membered cyclic intermediate. The mechanism of addition of alcohols to silenes was studied somewhat earlier. Nonstereospecific addition was first reported by Brook et al.[9] Wieberg et al. have proposed a two-step mechanism involving an initial silene−alcohol complex followed by an intracomplex migration.[10] Kira, Maruyama, and Sakurai have proposed an inter-/intramolecular proton transfer diversity in the mechanism. It was thought that the addition proceeds by an initial nucleophilic

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attack at silicon to yield a zwitterionic complex which collapses in the second step to alkoxysilane by an intermolecular or intramolecular proton transfer to the silenic carbon.[11] The mechanistic diversity has been supported recently by laser flash photolysis experiments.[12]

Experimental and calculated results suggest that the mechanism of the addition reactions is sensitive to the quality and quantity of the reacting alcohol and the substituents of the unsaturated silicon compounds. Apeloig and Nakash studied the kinetics of para- and meta-substituted phenol addition to tetramesityldisilene.[13,14] From the resulting Hammett plot, the Arrhenius parameters of the reactions of tetramesityl-disilene with p-$CH_3OC_6H_4OH$ and p-$CF_3C_6H_4OH$, and ab initio quantum chemical calculations, they concluded that for electron-rich phenols the rate-determining step is a nucleophilic attack of the alcoholic oxygen and the reaction proceeds via a zwitterionic intermediate. For electron-withdrawing phenols the rate-determining step is, however, concerted and the alcohol is involved both as a nucleophilic and as an electrophilic agent. Studying the phenol concentration, the same authors suggested[15] a different channel of anti product formation with a silyl group rotation around the Si=Si bond. The bimolecular pathway of the anti addition reaction channel was explained in recent theoretical work.[16] Depending on the structure of the double-bonded silicon species, the addition mechanism may change even more drastically. The alcohol addition of 4-silatriafulvene results in a four-membered ring product,[17,18] the first step of this reaction being an isomerization to silylene, and then to silacyclobutadiene, which is followed by the addition.

In this paper we report the results of high-level ab initio calculations for the mechanism of the following reactions:

$$\begin{array}{llllcl}
\textbf{I} & \begin{array}{c}\textbf{A}\\ \textbf{B}\\ \textbf{C}\end{array} & \mathrm{H_2Si{=}SiH_2} + & \begin{array}{l}\mathrm{H_2O}\\ \mathrm{CH_3OH}\\ \mathrm{CF_3OH}\end{array} & = & \begin{array}{l}\mathrm{H_3Si{-}SiH_2OH}\\ \mathrm{H_3Si{-}SiH_2OCH_3}\\ \mathrm{H_3Si{-}SiH_2OCF_3}\end{array}\\
\textbf{II} & \begin{array}{c}\textbf{A}\\ \textbf{B}\end{array} & \mathrm{H_2C{=}SiH_2} + & \begin{array}{l}\mathrm{H_2O}\\ \mathrm{CH_3OH}\end{array} & = & \begin{array}{l}\mathrm{H_3C{-}SiH_2OH}\\ \mathrm{H_3C{-}SiH_2OCH_3}\end{array}\\
\textbf{III} & \begin{array}{c}\textbf{A}\\ \textbf{B}\end{array} & \mathrm{H_2Si{=}CH_2} + & \begin{array}{l}\mathrm{H_2O}\\ \mathrm{CH_3OH}\end{array} & = & \begin{array}{l}\mathrm{H_3Si{-}CH_2OH}\\ \mathrm{H_3Si{-}CH_2OCH_3}\end{array}
\end{array}$$

For comparison, we also studied the H_2O and CH_3OH additions to ethene:

$$\begin{array}{llllcl}
\textbf{IV} & \begin{array}{c}\textbf{A}\\ \textbf{B}\end{array} & \mathrm{H_2C{=}CH_2} + & \begin{array}{l}\mathrm{H_2O}\\ \mathrm{CH_3OH}\end{array} & = & \begin{array}{l}\mathrm{H_3C{-}CH_2OH}\\ \mathrm{H_3C{-}CH_2OCH_3}\end{array}
\end{array}$$

It is generally accepted that the water addition to olefins in solution phase proceeds ionically with acid catalyst, through a protonation as a first step, yielding a carbocation intermediate. The direct bimolecular addition, which is the reverse of the H_2O elimination from alcohols, occurs in the gas phase by pyrolysis.

On the basis of some previous theoretical study of the addition of HF, HCl, and other molecules,[19] it might be supposed that reagents in dimeric or oligomeric forms may react with a lower activation barrier than in those monomeric form. In this study, we assumed that the doubly bonded substrate interacts with a monomeric water or alcohol. The reactions with a dimer will be considered in a following work.

Calculations

Quantum chemical calculations were carried out with the Gaussian 94 program package.[20] In our previous works on the addition mechanism of 4-silatriafulvene and some substituted disilene and silene derivatives,[18,21] we studied the effect of basis sets and electron correlation using the standard 6-31G(d) and 6-311++G(d,p) basis and several correlation methods, such as MP2, MP3, MP4SDQ, and QCISD. It was found that the geometry was not sensitive to the basis; however, a considerable difference between the HF and correlated methods was observed. In this work the 6-311++G(d,p) basis set was used. Geometry was optimized using the MP2 level of theory and the density functional theory (DFT). In the DFT calculations the Becke three-parameter hybrid functional[22] was employed combined with the Lee−Yang−Parr correlation functional.[23] Transition states for the reactions were fully optimized using the eigenvector following method. Each reaction path was confirmed by intrinsic reaction coordinate (IRC) calculations using the MP2/6-311++G(d,p) level. Second derivatives and harmonic vibrational frequencies were calculated for all the stable molecules and transition states investigated. The existence of only one imaginary frequency for the transition states was checked. All the calculated energy data were corrected by the zero-point energy (ZPE). For all the adduct molecules, a BSSE correction was carried out according to the counterpoise procedure.[24]

To obtain accurate thermodynamical data for the reaction energies, enthalpies, and free energies, CBS-Q calculations[25] were carried out for all the stable structures and transition states. For electron densities, a natural bond orbital analysis was applied.[26]

Results and Discussion

The calculated thermodynamical data and selected geometrical parameters are given in Tables 1 and 2. As the MP2 and B3LYP methods give very similar molecular geometry, only the MP2 results are presented in Table 2. Compared to the data from the MP2, DFT, and CBS-Q methods, the MP2-computed thermodynamical data are generally closer to the highly accurate CBS-Q results than the DFT results.

All the reactions can be characterized by two main thermodynamic profiles (Table 1). When the reagent molecule attacks a carbon atom (reactions **III** and **IV**), the reaction is moderately exothermic ($\Delta E > -30$ kcal/mol), with a high (>40 kcal/mol) activation energy. On the other hand, when the reagent attacks a silicon atom (reactions **I** and **II**), the barrier is small (<10 kcal/mol), and the reaction is strongly exothermic ($\Delta E < -60$ kcal/mol). These findings are consistent with the experimental

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Table 1. Thermodynamical Data of Stationary Points in Reactions **I**−**IVA**, **-B,** and **-C** in kcal/mol

		CBS-Q		MP2[a]		B3LYP[a]	
reaction	stat. point	Δ*E*	Δ*G*^{298K}	Δ*E*	Δ*G*^{298K}	Δ*E*	Δ*G*^{298K}
$H_2Si{=}SiH_2 + H_2O$ (**IA**)	reagent	0.0	0.0	0.0	0.0	0.0	0.0
	C_E	−2.2	3.2	0.1	4.6	−1.5	4.9
	T_E	0.8	8.6	0.7	9.1	1.4	9.6
	C_N	−0.6	7.3	0.4	5.0	−0.7	5.7
	T_N	3.9	12.8	5.0	14.4	6.4	15.6
	C_L	−2.2	6.8	−1.4	7.1	−1.1	7.3
	T_L	−1.7	7.1	−2.0	7.1	−1.5	7.5
	P_f	−63.3	−54.6	−62.0	−53.5	−57.6	−49.3
$H_2Si{=}SiH_2 + CH_3OH$ (**IB**)	reagent	0.0	0.0	0.0	0.0	0.0	0.0
	C_E	−2.3	2.9	−0.8	5.7	−0.7	4.9
	T_E	−1.3	6.8	−1.9	6.2	0.4	8.9
	C_N	−5.6	3.8	−6.6	2.8	−9.0	0.0
	T_N	−2.8	7.2	−2.0	8.5	1.9	12.1
	C_L	−7.8	2.0	−8.0	2.1	−5.2	4.8
	T_L	−7.4	2.6	−8.8	1.6	−5.6	4.5
	P_f	−66.2	−56.2	−65.2	−55.4	−59.1	−49.3
$H_2Si{=}SiH_2 + CF_3OH$ (**IC**)	reagent	0.0	0.0	0.0	0.0	0.0	0.0
	C_E	−4.5	1.7	−2.3	5.9	−2.6	4.7
	T	3.2	14.0	3.9	14.5	6.0	16.7
	P_f	−66.5	−56.2	−65.8	−56.1	−59.6	−49.5
$H_2C{=}SiH_2 + H_2O$ (**IIA**)	reagent	0.0	0.0	0.0	0.0	0.0	0.0
	C_N	−1.0	6.0	−0.3	6.8	−0.6	6.3
	C_L	−1.1[b]	6.2[b]	−2.1	5.1	−1.0	6.1
	T_L	1.7	11.0	3.0	12.5	4.1	13.3
	P_f	−71.0	−62.2	−66.8	−57.9	−64.3	−55.5
$H_2C{=}SiH_2 + CH_3OH$ (**IIB**)	reagent	0.0	0.0	0.0	0.0	0.0	0.0
	C_N	−4.0	4.1	−1.4	8.1	−1.6	7.1
	C_L	−4.1[b]	4.5[b]	−3.9	5.3	−1.9	6.9
	T_L	−2.9	7.6	−2.2	8.7	0.9	11.5
	P_f	−73.4	−63.3	−69.3	−59.0	−65.3	−55.2
$H_2Si{=}CH_2 + H_2O$ (**IIIA**)	reagent	0.0	0.0	0.0	0.0	0.0	0.0
	C_E	−1.9	3.8	−0.8	5.6	−1.3	4.4
	T	42.8	52.1	47.9	57.2	40.8	49.9
	P_f	−21.8	−12.9	−21.3	−12.2	−20.8	−11.9
$H_2Si{=}CH_2 + CH_3OH$ (**IIIB**)	reagent	0.0	0.0	0.0	0.0	0.0	0.0
	C_E	−3.0	3.2	−1.7	5.4	−1.7	5.1
	T	37.6	47.6	40.9	51.7	36.4	47.0
	P_f	−28.7	−18.1	−28.5	−17.7	−25.8	−15.0
$H_2C{=}CH_2 + H_2O$ (**IVA**)	reagent	0.0	0.0	0.0	0.0	0.0	0.0
	C_E	−1.5	2.7	−0.4	4.6	−0.5	4.1
	T	56.4	64.5	56.1	64.5	53.4	61.4
	P_f	−10.1	−1.8	−10.1	−2.0	−8.4	−0.4
$H_2C{=}CH_2 + CH_3OH$ (**IVB**)	reagent	0.0	0.0	0.0	0.0	0.0	0.0
	C_E	−2.3	2.6	−1.0	4.7	−0.8	4.1
	T	49.8	59.2	49.6	59.5	49.2	58.7
	P_f	−16.5	−6.7	−16.6	−6.7	−13.0	−3.1

[a] Using 6-311++G(d,p) basis. C_E and C_N energies and free energies were corrected with the CP method. [b] CBS-Q energies were calculated with using HF/6-31+G(d) geometries for frequencies and MP2/6-31+G(d) geometries for energy extrapolations.

results. The addition to silicon always occurs in a facile bimolecular way. Water and alcohol additions to silenes result normally in silyl ethers or silanols, and the "abnormal" way to give carbon-substituted silanes has never been observed. For the addition reactions of olefins, high activation energy is necessary in the gas phase, and in solution phase they proceed ionically with acid catalyst.

The initial step of water or alcohol addition is always the formation of a weakly bonded van der Waals complex. Such "precursor" complexes were found and studied in the recent literature for several chemical reactions.[10,27] The final product is reached via a transition state, except in reactions **IA**, **IB**, **IIA** and **IIB**. In these cases, two stable complexes separated by a second transition state were found, a weakly bonded initial complex and a second zwitterionic complex.

The geometry of the reactant molecules in the complexes is almost unchanged compared to that of the initial reactants (Table 2). The characteristic distance between the two reactants depends on the orientation of the two molecules and the type of double-bonded substrate. While the energy gain relative to the initial state is between 0.6 and 5.6 kcal/mol (at the CBS-Q level), the Gibbs free energy is always positive due to the negative entropy factor (Table 1). The stabilization of alcohol complexes is always slightly larger than that of the water complexes. The orientation of the reacting agents in the initial complex clearly indicates the electrophilic or nucleophilic character of the attack. A small but systematic charge transfer between the two agents (Table 2) also supports this model. The shape of the orbitals in the complexes is usually very similar to that of the separated

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Table 2. Selected Geometrical Data[a−c] and Charges[d] in Reactions **I**−**IVA**, **-B**, and **-C**

		geometrical data						charge		
reaction: $H_2X^1{=}X^2H_2 + ZOH$	stat. point	$r(X^1X^2)$	$r(OH)$	$r(X^2O)$	$r(XH)$	α_2	α_1	X^2	X^1	ZOH
$H_2Si{=}SiH_2 + H_2O$ (**IA**)	reagent	2.163	0.959			145.1	−145.1	0.304	0.304	0.000
	C_E	2.162	0.962		2.979	−150.8	152.0	0.385	0.294	−0.009
	T_E	2.194	0.965	2.513	3.135	−169.2	128.2	0.730	−0.010	0.034
	C_N	2.187	0.962	2.506		144.8	−134.3	0.573	0.155	0.048
	T_N	2.363	0.983	1.934	2.801	164.9	91.9	0.933	−0.013	0.148
	C_L	2.296	0.989	1.974	2.523	171.7	105.7	0.890	−0.148	0.099
	T_L	2.328	1.131	1.857	1.971	165.5	115.1	0.928	0.027	−0.138
	P_f	2.339		1.637		120.3	119.9	1.145	0.544	−
$H_2Si{=}SiH_2 + CH_3OH$ (**IB**)	reagent	2.162	0.959			145.1	−145.1	0.304	0.304	0.000
	C_E	2.161	0.963		2.898	−148.2	148.1	0.312	0.278	−0.013
	T_E	2.167	0.975	3.276	3.088	−151.2	144.9	0.409	0.175	0.012
	C_N	2.238	0.970	2.061	3.775	136.6	−109.1	0.638	−0.018	0.140
	T_N	2.359	0.985	1.905	2.705	161.3	−92.1	0.836	−0.080	0.169
	C_L	2.306	0.989	1.919	2.517	169.4	103.1	0.776	−0.147	0.109
	T_L	2.332	1.144	1.831	1.954	165.2	114.1	0.832	0.018	−0.143
	P_f	2.338		1.668		122.8	120.1	1.046	0.465	−
$H_2Si{=}SiH_2 + CF_3OH$ (**IC**)	reagent	2.162	0.963			145.1	−145.1	0.304	0.304	0.000
	C_E	2.161	0.974		2.768	148.9	−149.1	0.337	0.251	−0.035
	T	2.315	1.056	2.004	2.160	176.7	107.9	0.794	−0.046	−0.070
	P_f	2.328		1.710		127.6	118.6	1.009	0.477	−
$H_2C{=}SiH_2 + H_2O$ (**IIA**)	reagent	1.710	0.959			180.0	180.0	0.980	−1.036	0.000
	C_N	1.710	0.961	2.666	4.147	167.4	−173.0	1.067	−1.132	0.037
	C_L	1.710	0.962	2.650	3.484	170.2	177.0	1.074	−1.146	0.036
	T_L	1.764	1.081	1.929	1.769	161.7	146.5	1.273	−1.324	0.010
	P_f	1.857		1.672		122.1	121.6	1.480	−1.075	−
$H_2C{=}SiH_2 + CH_3OH$ (**IIB**)	reagent	1.710	0.959			180.0	180.0	0.980	−1.036	0.000
	C_N	1.712	0.963	2.334		163.0	−176.3	1.099	−1.200	0.081
	C_L	1.713	0.965	2.286	3.059	163.0	−179.2	1.115	−1.222	0.087
	T_L	1.766	1.078	1.902	1.778	160.7	145.7	1.281	−1.331	−0.015
	P_f	1.859		1.665		122.7	121.5	1.483	−1.075	−
$H_2Si{=}CH_2 + H_2O$ (**IIIA**)	reagent	1.710	0.959			180.0	180.0	−1.036	0.980	0.000
	C_E	1.712	0.964		2.392	174.3	177.0	−1.098	1.022	−0.008
	T	1.869	1.002	1.779	2.314	155.5	109.2	−0.505	0.301	0.182
	P_f	1.891		1.432		119.2	118.5	−0.436	0.964	−
$H_2Si{=}CH_2 + CH_3OH$ (**IIIB**)	reagent	1.710	0.959			180.0	180.0	−1.036	0.980	0.000
	C_E	1.713	0.964		2.337	174.6	177.0	−1.093	1.016	−0.010
	T	1.851	0.997	1.814	2.333	157.2	111.8	−0.532	0.316	0.182
	P_f	1.892		1.420		120.6	118.8	−0.436	0.970	−
$H_2C{=}CH_2 + H_2O$ (**IVA**)	reagent	1.338	0.959			180.0	180.0	−0.345	−0.345	0.000
	C_E	1.340	0.961		2.545	179.5	179.5	−0.360	−0.360	−0.004
	T	1.414	1.243	1.850	1.425	158.6	149.4	−0.076	−0.752	0.053
	P_f	1.514		1.426		120.3	121.0	−0.005	−0.568	−
$H_2C{=}CH_2 + CH_3OH$ (**IVB**)	reagent	1.338	0.959			180.0	180.0	−0.345	−0.345	0.000
	C_E	1.341	0.961		2.525	179.5	179.5	−0.359	−0.359	−0.004
	T	1.426	1.192	1.769	1.493	153.7	148.1	−0.084	−0.764	0.077
	P_f	1.514		1.414		121.0	120.9	−0.002	−0.565	−

[a] Calculated at the MP2/6-311++G(d,p) level. [b] Distances in angstroms, angles in degree. [c] α_1 and α_2 are the dihedral angles between the HX^1H plane and $X^1{-}X^2$ bond and the HX^2H plane and $X^2{-}X^1$ bond, respectively. [d] NBO charges.

component molecules. The shift of the orbital energies, however, indicates a trend, which is also understandable on the basis of the FMO theory. In a nucleophilic interaction (NI) between the HOMO of the reagent and the LUMO of disilene or silene, the LUMO level moves upward and the HOMO moves downward. Therefore, in the next step of the reaction, an electrophilic attack (EA, between the HOMO of disilene or silene and the LUMO of the reagent) is expected. On the other hand, an electrophilic interaction (EI) between the LUMO of the reagent and the HOMO of the target molecule results in the shifts of the HOMO down and the LUMO up. Therefore, in the second step, an opposite nucleophilic attack (NA) of the reagent to disilene (silene) is expected via the interaction of reagent HOMO (n_O) with disilene (silene) LUMO (π^*).

Reaction IA. Three different initial van der Waals complexes (C_E, C_N, C_C, Figure 1) were found in the disilene + water (**IA**) reaction. The water molecule in C_C approaches disilene in the hypothetical plane of the disilene molecule, keeping the C_2 symmetry. From the orientation of the attack and the Laplacian distribution of electron density, it is clear that C_C is formed at the initial stage of a nucleophilic process controlled by the electrostatic attraction between the reagent molecules. This

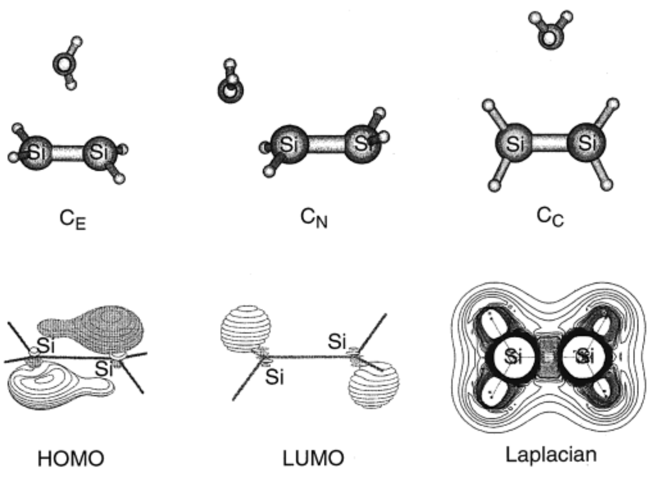

Figure 1. Weakly bonded van der Waals complexes with water.[32]

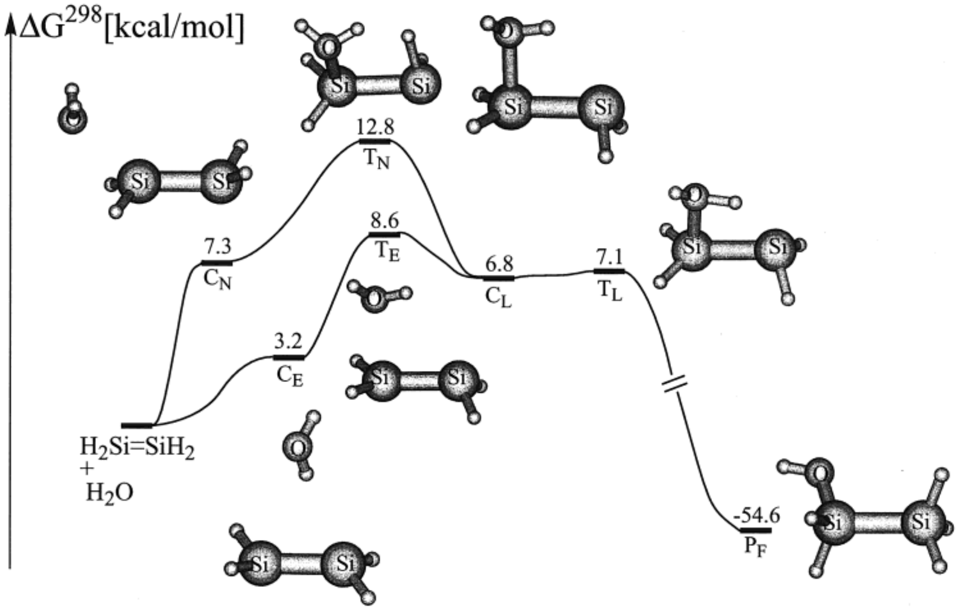

Figure 2. Free energy diagram at the CBS-Q level of theory for the reaction channels of disilene + water reaction.

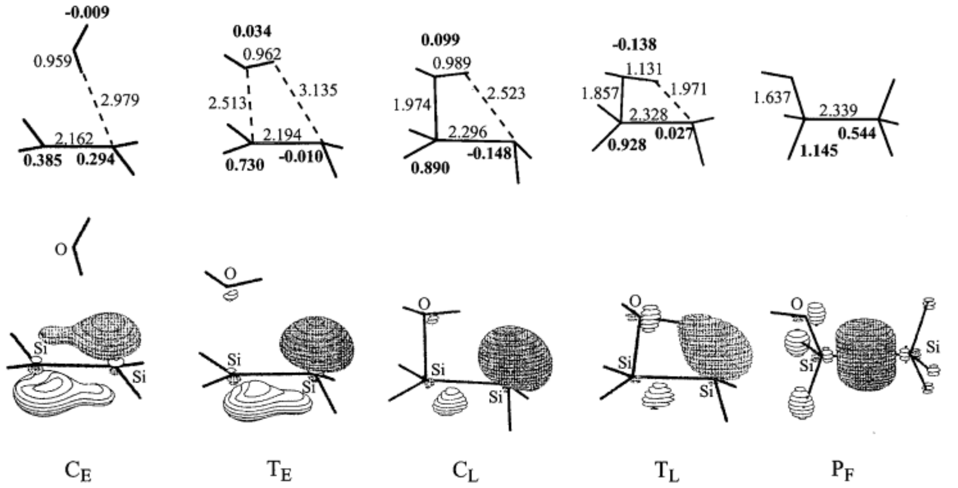

Figure 3. Geometry, partial charges, and the shape of the HOMO in the stationary points of the electrophilic channel of the reaction **IA** at the MP2/6-311++G(d,p) level.

reaction, however, does not lead to the expected 1,2-addition product, since siloxane is formed by an insertion to the Si═Si bond after a high-energy transition state. This channel has never been observed in experiments and, because of the high activation energy, it cannot compete with the addition reaction.

The other two complexes (C$_N$, C$_E$) belong to two possible addition reaction channels (Figure 2). The complex C$_E$ clearly suggests an electrophilic interaction between the water hydrogen and the HOMO of disilene (Figure 1). Despite the long H···Si distance (2.98 Å), the group charge on water is slightly negative ($\delta = -0.009$), indicative of some charge transfer between the reactant molecules. The complex is only slightly stabilized ($\Delta E = 2.2$ kcal/mol) in comparison to the energy of the initial molecules.

The symmetrical orientation of the water molecule (C_s symmetry) in the complex C$_N$ suggests a nucleophilic interaction. In the language of FMO theory, the lone pair of water oxygen approaches the LUMO of disilene. The stabilization energy of the complex is only 0.6 kcal/mol (at the CBS-Q level), and the Si−O distance is 2.51 Å. The clearly nucleophilic interaction is also proved by the positive charge ($\delta = 0.048$) on the water molecule.

Figure 2 shows the scheme of the two different reaction channels of disilene + H$_2$O reactions, starting from the two initial complexes, C$_E$ and C$_N$, respectively. It can be seen that the different initial complexes C$_N$ and C$_E$ lead to the same “second” complex, C$_L$. Although the activation energies on the two paths to C$_L$ differ by only 3.1 kcal/mol (CBS-Q level), the structures of the two transition states (T$_N$ and T$_E$) are essentially different and suggest two essentially different processes.

In the “electrophilic” channel, C$_E$−T$_E$−C$_L$, the first electrophilic interaction is followed by a nucleophilic attack (EI−NA). For this, the oxygen lone pair approaches silicon with a rotation of a water molecule around the Si−H axis (Figure 3). The transition state, T$_E$, can be characterized by small geometric changes and only by a moderate activation energy (0.7−1.4 kcal/mol). The Si−O distance is 2.51 Å, and the Si−Si bond length elongates slightly to 2.19 Å, which indicates a considerable double bond character. The shape of the HOMO also supports this fact. The process C$_E$−T$_E$−C$_L$ is accompanied by a charge shift from the negative disilene to the positive water and inside the disilene moiety from Si^1 to Si^2. This reaction channel ends in a syn product.[28]

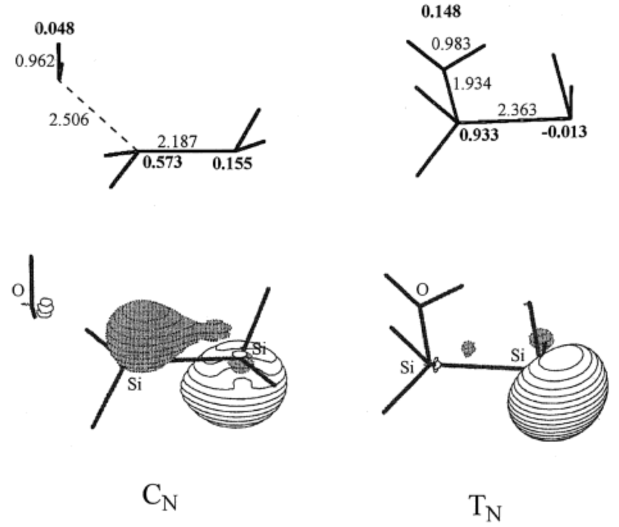

Figure 4. Geometry, partial charges, and the shape of the HOMO in the stationary points of the nucleophilic channel in **IA** at the MP2/6-311++G(d,p) level.

The "nucleophilic" channel, $C_N-T_N-C_L$, suggests a NI–EA process. From the initial complex, C_N, one of the water hydrogens turns toward the HOMO lobe of disilene (antarafacial approach, similarly to a [2 + 2] cycloaddition). This step is, however, accompanied by drastic geometric changes. During this process, one of the SiH_2 groups becomes pyramidal and rotates by 180° through the Si–Si bond, giving a clear theoretical proof for the experimental suggestion[15] of anti product formation: the reaction channel which starts from C_N finishes in an anti-oriented silanole.[28] At the transition state, T_N, the rotation is 90°degrees (Figure 4). Obviously, at this stage the π-bond has already disappeared, the Si–Si bond is extremely long (2.36 Å, longer than the Si–Si single bond in the product silanol), and the pyramidal Si^1 carries both electrons of the earlier π-bond in a lone electron pair.[29] The Si–O distance is also much shorter (1.93 Å) than in the case of T_E, indicating the enhanced interaction. Although the activation energy is somewhat higher than that of the $C_E-T_E-C_L$ channel, the 3.9 kcal/mol value (Table 1) indicates that this reaction channel is also feasible.

From both T_E and T_N, the same stable complex, C_L can be reached. In this stage, the structure at Si^2 becomes almost planar, while that of the neighboring Si^1 is strongly pyramidal (Figures 2 and 3). The Si–Si π-bond has already disappeared in C_L, and the respective MO shifted toward Si^1 and formed a regular lone electron pair on the strongly pyramidal silicon. This is the HOMO of the molecule. Although the complex formed is far in structure and energy ($\Delta E = -1.1$ to -2.2 kcal/mol, depending on the level of theory) from the final product, P_f, even in this period of the reaction the Si–Si bond is close to the final Si–Si single bond. One of the water hydrogens turns toward Si^1, but the O–H distance is only slightly longer than that at the beginning of the reaction and the Si–H distance (2.52 Å) seems to be too long for any reasonable interaction. Considering the charge distribution of the molecule, this stage of the reaction is in accord with the zwitterionic structure suggested on the basis of earlier experimental results.[5–8,11]

The most important process of the next transition state, T_L, is the beginning of O–H bond breaking and a parallel Si–H bond formation. The Si–O and Si–H distances are shortened to 1.86 and 1.97 Å, respectively, and the O–H distance is elongated to 1.13 Å, while the Si–Si bond length practically reaches its final value. It forms a four-membered ring shape, which was found in previous studies.[6,14,15] The lone pair on Si^1 shifts toward the approaching hydrogen, indicating an increasing interaction and an incipient chemical bond between the H and Si^1 atoms (Figure 3).

Reactions IB, IC. The calculations with methanol instead of water (**IB**) provide similar C_N and C_E type complexes. The character of the two parallel reaction channels is also similar to that of **IA** (Figure 5). The free energy difference between C_N and C_E and between T_N and T_E is very small (about 0.5 kcal/mol); therefore, in this reaction the expected ratio of syn and anti products is around 50%. Obviously, the ratio may change with the substituents on disilene and with the character of the reagent alcohol.

The clearest example for the latter factor is the addition reaction with trifluoromethanol (Figure 6). Since the OH group in CF_3OH is poorer in electrons than that in H_2O or CH_3OH, it is reasonable that the reaction of disilene with trifluoromethanol (**IC**) gives only one C_E type complex and the nucleophilic channel is missing. As a consequence, only syn product is expected in this reaction. This finding is also supported by the experiments.[15] Although the geometry of C_E is very similar to that in reaction **IB**, there are some striking differences in the subsequent steps of the reaction. The most conspicuous difference is the lack of a second stable complex. The geometry of the transition state is close to that of the second transition state (T_L) in reaction **IB**, with short Si–O and Si–H distances (Si–O, 2.00 Å; Si–H, 2.16 Å). The charge separation between the two silicon atoms is smaller than that in **IA** or **IB**, while the activation barrier is much larger ($\Delta G = 14.0$ kcal/mol) than that in any transition states of **IA** or **IB**.

The addition of methanol to disilene can be characterized by negative activation energies and strongly negative entropies of activation. These phenomena have been reported for a number of bimolecular reactions of reactive intermediates.[12a,30] The mechanistic explanation is clear from the data of Table 1 and Figures 2 and 5. The complex formation for both electrophilic and nucleophilic direction is exothermic. The transition states, T_E and T_N, for the second complex formation (and T_L for the final product) are of lower energy than the thermodynamically unstable initial states. Nevertheless, the free energy barrier is higher than those for either complex formation or the starting molecules. For the more acidic reagent CF_3OH, the barrier is high and the activation energy is positive.

Reactions IVA, IVB (Figure 7). Only one initial complex has been found in the reaction between ethene and water/methanol. Since carbon is more electronegative than silicon, the lack of a nucleophilic complex is understandable. In the complex, the hydrogen of the OH group points toward the π-system of ethene (C–H distance = 2.53–2.55 Å), keeping

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[28] Although the calculations were carried out for disilene, the results may predict the diastereoselectivity of substituted disilenes. We use syn and anti symbols in this sense.

[29] We have studied the biradical character of the process during the Si–Si bond rotation. It was found that the occupation number of all the occupied natural orbitals of T_N is 2.000, and that of all the unoccupied NO is zero. This result proves that the process of SiH_2 rotation has no significant multiconfigurational character.

[30] (a) Moss, R. A. *Acc. Chem. Res.* **1989**, *22*, 15. (b) Mayr, H.; Schneider, R.; Grabis, U. *J. Am. Chem. Soc.* **1990**, *112*, 4460. (c) Baggott, J. E.; Blitz, M. A.; Frey, H. M.; Walsh, R. *J. Am. Chem. Soc.* **1990**, *112*, 8337. (d) Blitz, M. A.; Frey, H. M.; Tabbutt, F. D.; Walsh, R. *J. Phys. Chem.* **1990**, *94*, 3294. (e) Becerra, R.; Walsh, R. *Int. J. Chem. Kinet.* **1994**, *26*, 45. (f) Zhang, S.; Conlin, R. T.; McGarry, P. F.; Scaiano, J. C. *Organometallics* **1992**, *11*, 2317.

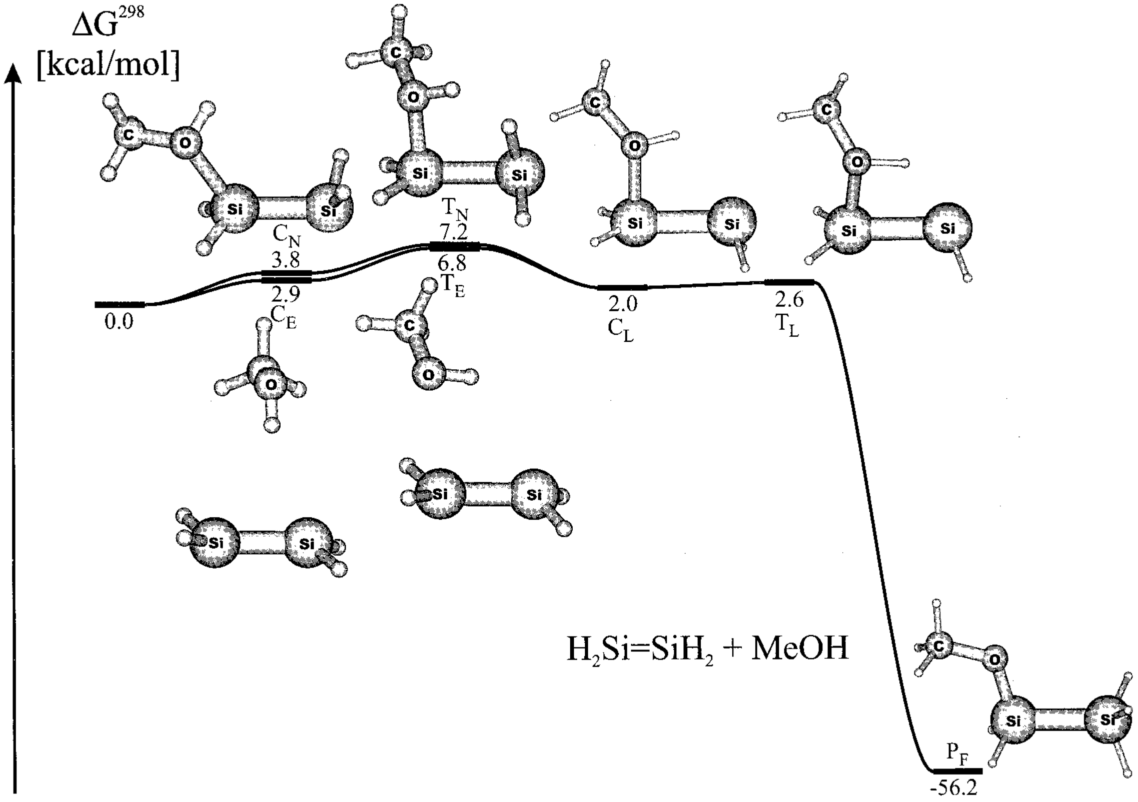

Figure 5. Free energy diagram for the reaction channels of disilene + methanol at the CBS-Q level of theory.

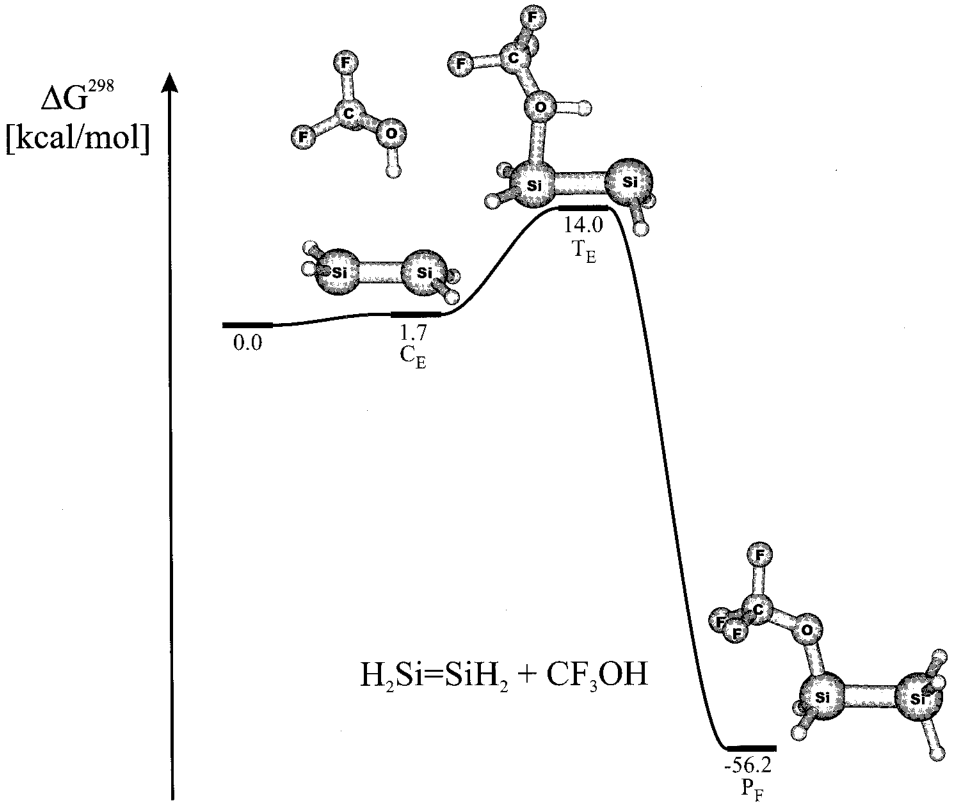

Figure 6. Free energy diagram for the reaction channels of disilene + trifluoromethanol reaction at the CBS-Q level of theory.

the C_s symmetry. The original geometry and the shape of the HOMO are almost unchanged, but a slight charge transfer from ethene to water proves the electrophilic process.

The mechanism of the reactions is similar to **IC** as the second stable complex is missing and the product is obtained via one transition state. The geometry of this transition state contains, however, new features. While in the case of disilene oxygen is closer to silicon than hydrogen, the C^1−H(O) distance in reactions **IV** is much shorter (1.43 Å) than the C^2−O distance (1.85 Å). While the Si−Si bond of T_L in the respective disilene reactions **IA**−**IC** almost reaches the single bond distance, in **IVA**−**IVB** it is less than halfway between the single and double

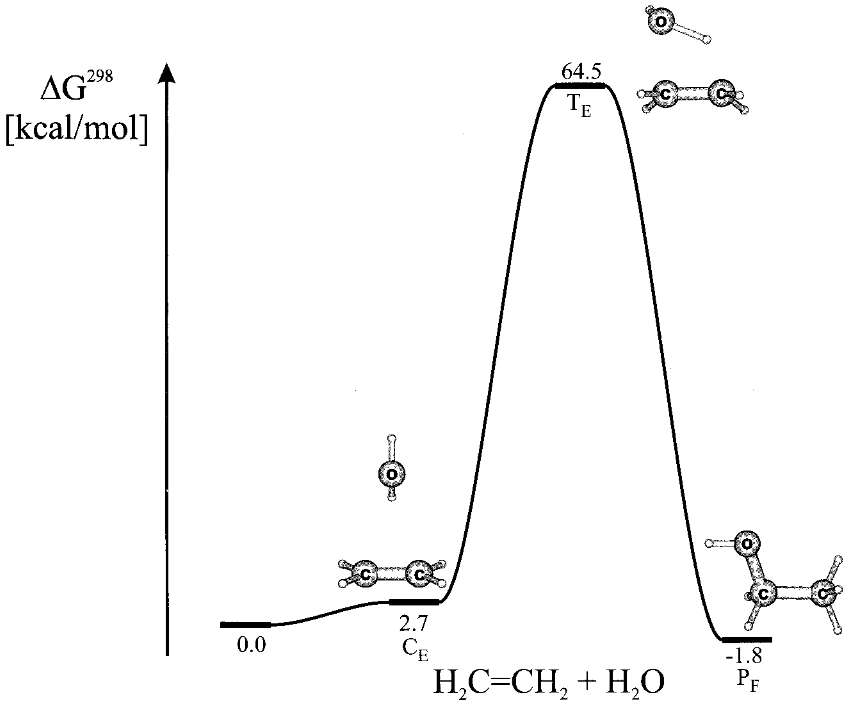

Figure 7. Free energy diagram at the CBS-Q level of theory for the reaction channels of ethene + water reaction.

bonds. Accordingly, in the shape of the HOMO, the residue of the fading π-bond is well recognizable. The O−H bond (1.24 and 1.19 Å, respectively) is definitely longer than the same bond in the transition states of **IA**, **IB**, or **IC** (1.13, 1.14, and 1.06 Å, respectively). All these facts indicate that, whereas in disilene reactions the Si−O bond formation precedes the O−H bond breaking and the final Si−H bond formation, in the addition with C═C bonds the C−H bond formation and the simultaneous O−H bond breaking are followed by the final C−O bond formation. Comparing the charge distributions of **IA** and **IVA**, the relative charge separation along the C−C and Si−Si bonds is similar, since the Si^2 and C^2 are much more positive than Si^1 and C^1, respectively, throughout the reaction path. Obviously, both carbon atoms are more negative than silicons because of the electronegativity difference. The calculated activation free energy is extremely high (64.5 and 59.2 kcal/mol for **IVA** and **IVB**, respectively), suggesting that the direct bimolecular reaction between olefins and alcohol or water does not proceed easily. Since olefins are thermodynamically much more stable than disilenes, the exothermicity of **IVA** and **IVB** is much less than that of **IA** and **IB**.

Reactions IIA, IIB, IIIA, and IIIB. As one can see from the energetics (Figure 8), the two concurrent directions of the addition reaction (**II** vs **III**) are extremely different. Whereas the reaction channel **II** seems to be a facile process with a low activation energy, the barrier of **III** is high, although somewhat lower than those in **IVA** and **IVB**. This result immediately explains the experimental facts: the product of addition of alcohol to silene is always an alkoxysilane.

The thermodynamic profile of **IIB** supports the negative Arrhenius plots for alcohol addition found in the reaction of 1,1-diphenylsilene with methanol.[12a] In that experiment, the authors suggested from the kinetic results that the transition state of the reaction is about 2.5 kcal/mol lower in energy than the starting materials, which is in excellent agreement with our result ($\Delta E = -2.9$ kcal/mol).

The initial complexes of silene + water and silene + methanol reactions reflect well the chemist's expectation for the further processes. Electrophilic (C_E) type complexes can be found in the **IIIA** and **IIIB** reactions, while nucleophilic C_N complexes start the **IIA** and **IIB** reactions (Figure 8). Because of the substantial electronegativity difference between carbon and silicon, the Si═C bond is strongly polar, and silicon is more positive than in disilene. Therefore, it is reasonable to expect only a C_E complex for the **IIIA** and **IIIB** reactions and a C_N complex for **IIA** and **IIB**. Although the C···H distance (2.39 Å) is shorter in C_E than in the respective complex in **IVA**, the complexes show obvious structual similarities. Similarly, the Si−O bond in the C_N complex is elongated (2.67 Å in **IIA** and 2.33 Å in **IIB**), but the symmetry and orientation of the reagent molecules are close in comparison to those in **IA** and **IB**. Although we could not localize the T_N transition state between C_N and C_L, by studying the reaction path two important factors have been gained. First, the energy barrier between the two complexes is very small. Second, in contrast to the nucleophilic addition of disilene (**IA−IC)**, the $C_N-T_N-C_L-T_L-$ P_f channel of **IIA** and **IIB** does not exhibit rotation of the CH_2 group. A possible reason for this is the enhanced π-bond energy in comparison to that of disilenes. The 12 kcal/mol difference in the π-bond strengths of disilene and silene is enough to prevent rotation during the reaction.[31] Consequently, only the syn product is expected in an intramolecular addition of alcohol to silenes, and anti product formation is possible only with the reaction of a second alcohol (intermolecular). As a result, the anti−syn ratio should increase in these reactions with increasing alcohol concentration.

Important differences can be observed, however, between the C_L complexes of **IA** and **IIA**. The Si−O distance (2.65 Å) is very long, and, as a consequence, the Si−C bond is almost unchanged, although the bond polarity has increased and the

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(31) The double bond strength can be obtained by calculating the rotation barrier around the E═E double bond. Using the MCSCF/6-31G(d) level of theory (see: Schmidt, M. W.; Truong, P. N.; Gordon, M. S. *J. Am. Chem. Soc.* **1987**, *109*, 5217), the rotation barrier of Si═Si, Si═C, and C═C is 23.3, 35.6, and 65.0 kcal/mol, respectively.

(32) All figures were made using the MOLDEN program (Schaftenaar, G. *MOLDEN 3.6*; CMBI, University Nijmegen, The Netherlands).

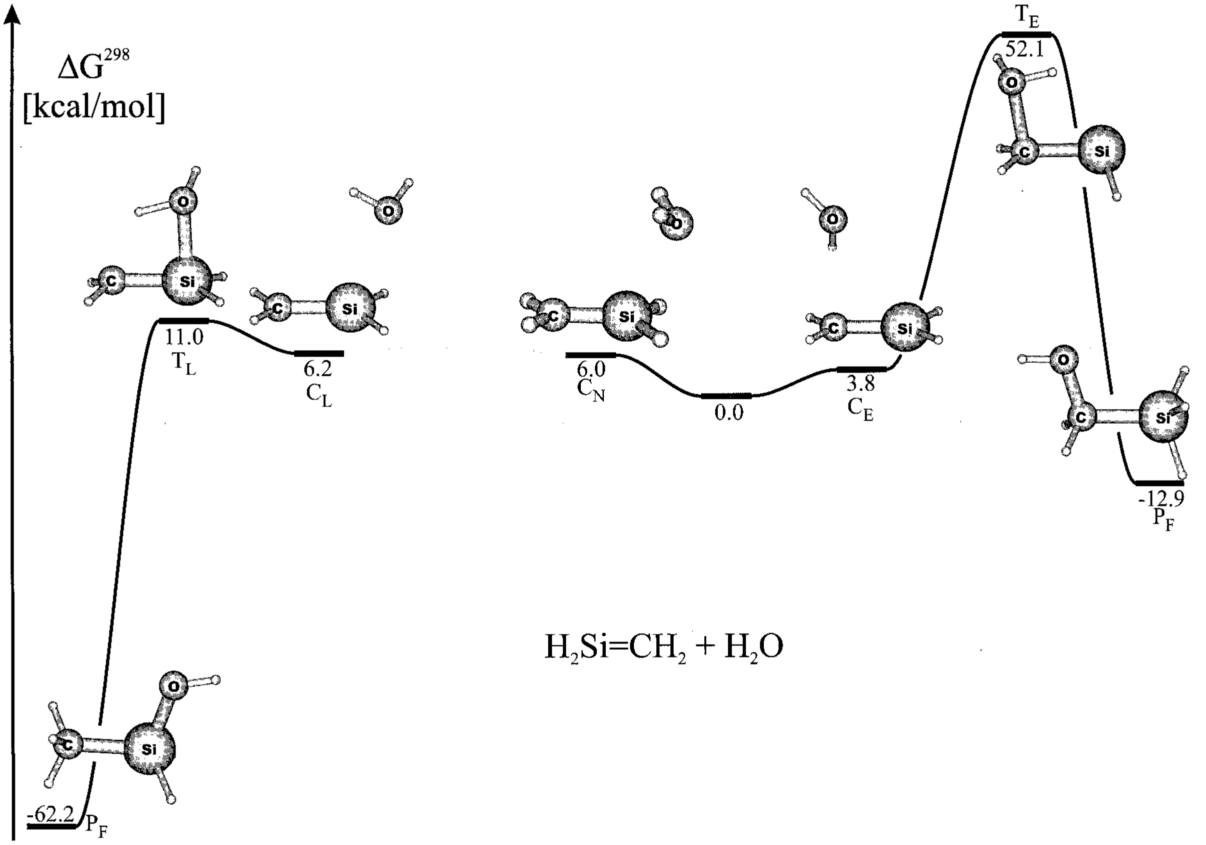

Figure 8. Free energy diagram at the CBS-Q level of theory for the reaction channels of **IIA** and **IIIA**.

π-bond has been distorted compared to those in the initial phase of the reaction. The positive charge on H_2O ($\delta = +0.036$) suggests a similarity to the zwitterionic structure proposed in earlier studies.[6,14,15]

The final transition states of silene + water/methanol reactions (T_L, Figure 8) bear the marks of both ethene and disilene additions. In the case of **IIIA** and **IIIB**, the transition structure can be characterized by a short (1.78−1.81 Å) C−O bond and by a much longer Si−H(O) (2.31−2.33 Å) distance. Although silicon is the positive center at C_E, the nucleophilic oxygen attacks carbon instead of silicon to lead to the transition state, giving the final products with C−O bonding. The Si−C bond (1.85−1.87 Å) is almost as long as that in the final product. The π-charge, which was originally concentrated on carbon, shifts toward silicon, and, as a consequence, silicon becomes strongly pyramidal and the HOMO has a lone pair character. Although silicon remains the positive center of the molecule, it is much less positive than before or later during the reaction. The charge distribution after the first electrophilic interaction indicates the EI−NA case, in accord with the FMO model.

The Si−O bond in T_L of **IIA** and **IIB** is about 1.9 Å, somewhat longer than the C−H(O) distance (about 1.77 Å). Considering the final Si−O and C−H bond and the slightly elongated O−H distance, this fact does not indicate the H−C bond formation as a first step of the reaction. The Si−C bond is only moderately elongated, and the π-bond is only partially broken. In accord with the NI−EA model, the high positive charge on the water moiety in C_N is reduced in T.

Conclusions

The investigated bimolecular addition reactions can be characterized by two different thermodynamical profiles. If the reagent attacks a doubly bonded silicon atom (reactions **I** and **II**), the activation barrier is small and the reaction is strongly exothermic. If, however, the reagent attacks a doubly bonded carbon (reactions **III**, **IV**), the barrier is high and the reaction is moderately exothermic. The initial step of all the reactions is the formation of a weakly bonded complex between the reagent and target molecule. The character of the complex determines the mechanism of the reaction, which explains the experimentally observed regioselectivity and diastereoselectivity. In the case of **IA** and **IB**, two possible concurrent reaction channels have been found. The one which starts from an “electrophilic” initial complex, explains the formation of syn addition product during the reaction. The other reaction path, which suggests a nucleophilic initial step followed by a silyl group rotation around the Si−Si bond, supports the anti addition product formation. The syn−anti ratio is almost 1:1 in the reaction of disilene and methyl alcohol. This ratio can be, however, strongly modified by the substituents on the disilene and the type of alcohol. On the other hand, the nucleophilic channel in **IIA**−**B** suggests the appearance of the syn product, and the only source of anti product is the reaction of the zwitterionic intermediate with a second alcohol molecule. Finally, reactions **III** and **IV** are always electrophilic. Whereas in the electrophilic channel of disilene reactions (**IA**−**B**) the Si−O bond formation precedes the O−H bond breaking and the final Si−H bond formation, in the reactions **III** and **IV** the C−H bond formation and the simultaneous O−H bond breaking are followed by the final C−O bond formation.

Although all the conclusions drawn on the basis of our calculations support and explain the results of the experiments well, we should emphasize that our calculations reflect rigorously only the mechanism of the gas-phase addition reactions. In nonpolar solvents, the calculations may reflect the real situation well. In polar solutions, however, solvents may assist the formation of more polar complexes and stabilize transition states with large dipole moments. In the case of only one reaction channel, it may change the energetics of the reaction. If the reaction has several parallel channels, this may change the original product ratio.

Acknowledgment. This work was supported in part by OTKA 029976. This work is dedicated to Professor Rolf Gleiter on the occasion of his 65th birthday.

Supporting Information Available: Tables of geometry and energy values (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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