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Mechanism of Water Addition to Silatriafulvenes and Silapentafulvenes

Julianna Oláh and Tamás Veszprémi*

Department of Inorganic and Analytical Chemistry, Budapest University of Technology and Economics, H-1521, Budapest, Gellért tér 4, Hungary

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The mechanisms of water (monomeric and dimeric) and methanol addition to 4-silatriafulvene and water addition to 3-silatriafulvene, 5-silapentafulvene, 6-silapentafulvene, and related ring-containing silenes were investigated at the B3LYP/6-31G(d), MP2/6-311++G(d,p), and CBS-QB3 levels of theory. van der Waals complexes and transitions states have been located for all reaction pathways. It is shown that the aromaticity of 4-silatriafulvene and 6-silapentafulvene influences to a great extent both the normal and abnormal addition channels. The nature of the van der Waals complex and the barrier heights are seriously affected by the conservation or loss of aromatic stabilization energy during the reaction.

Introduction

Silenes[1] exhibit high reactivity toward nucleophilic reagents, such as alcohols, water, and hydrogen halides.[2] Early theoretical calculations suggested that the large Si═C bond polarity is the main factor responsible for their high reactivity.[3] In general alcohol reacts regiospecifically with silenes to form alkoxysilanes in a facile bimolecular addition way (*normal* addition), while the *abnormal* addition results in the formation of carbon-substituted silanes. Wiberg proposed a two-step mechanism, involving the formation of an initial silene−alcohol complex followed by proton migration from the alcohol to the carbon of the silene,[4] which was confirmed by theoretical studies.[5,6] The normal addition reaction of silenes starts by the formation of a nucleophilic complex C_N (Figure 1), in which the principal interaction is between the oxygen lone pair and the positively charged silicon atom. The complex is converted to the final product through a low-energy, four-membered-ring transition state. The abnormal way is as an electrophilic pathway, starting by the formation of an electrophilic van der Waals complex C_E (see Figure 1), in which the partially positive hydrogen atom of the water molecule attacks the negatively charged carbon atom or the Si═C double bond. This pathway is highly similar to the water and hydrogen halide addition of C═C double bonds in the gas phase, which are essentially electrophilic additions.[5]

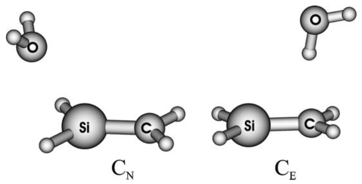

Figure 1. Structure of nucleophilic (C_N) and electrophilic (C_E) complexes of silene with water.

Bendikov et al.[7] studied the normal addition of water and alcohols to substituted silenes. In the case of apolar and strongly polar silenes no van der Waals complexes were found. The activation energy of normal water addition was shown to decrease linearly with the increasing polarity of the Si═C bond. The activation energy of alcohol addition to $H_2Si{=}CH_2$ slightly decreases with the gas phase acidity of the nucleophile, but increases with the increasing polarity of the solvent.

Recently Leigh et al. studied silenes with reduced Si═C bond polarity by experimental and computational means and found weak hydrogen-bonded complexes with monomeric and dimeric water and methanol on the PES instead of Lewis acid−base complexes.[8] The reaction of silenes with the dimeric form of the nucleophile is much more favorable than with the monomer.

However, silenes with reversed Si═C bond polarity frequently exhibit a markedly different reactivity pattern. Reverse polarity of the Si═C bond may be achieved by using π-donor substituents at the carbon end of the bond, by incorporating the Si═C bond in an aromatic ring, as in silabenzenes,[9] or by using electron-donating groups on the silicon end of the bond, as in persilyl-substituted 1-silaallene.[10] The latter compound adds water via the abnormal channel due to the reverse polarity of the Si═C bond.

A fourth way of reducing the polarity of the Si═C bond can be observed in silatriafulvenes. The first 4-silatriafulvene

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* Corresponding author. E-mail: Tveszpremi@mail.bme.hu. Tel: (361) 463-1793. Fax: (361) 463-3642.

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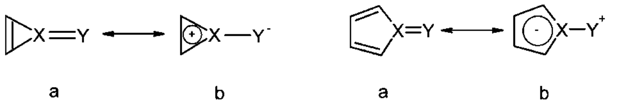
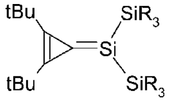
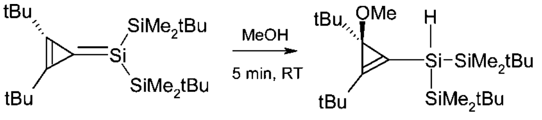
Chart 1. Aromatic Resonance Structures of Triafulvenes and Pentafulvenes



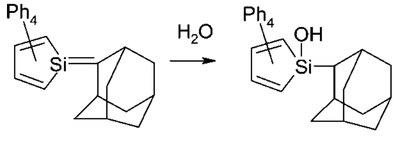
derivative, **1a**, was a reactive intermediate, but it exhibited a very low reactivity toward *tert*-butyl alcohol. The expected facile addition of alcohol to the Si═C bond did not occur even at high temperatures under reflux; instead it isomerized to silacyclobutadiene.[11] Calculations showed that the activation energy of *normal* water addition to the parent 4-silatriafulvene is much larger than in the case of $H_2C{=}SiH_2$ and larger than that of the isomerization reaction toward silacyclobutadiene.[12] The substitution of the $SiMe_3$ groups on **1a** by the bulkier $SiMe_2tBu$ groups led to **1b**, a crystallizable material.[13] It was unreactive toward *tert*-butyl alcohol, but reacted instantaneously with methanol (eq 1). The product showed an inverted regioselectivity, which was attributed to the aromatic resonance structures.



1a $SiR_3 = SiMe_3$
1b $SiR_3 = SiMe_2tBu$



1b **1c** (1)

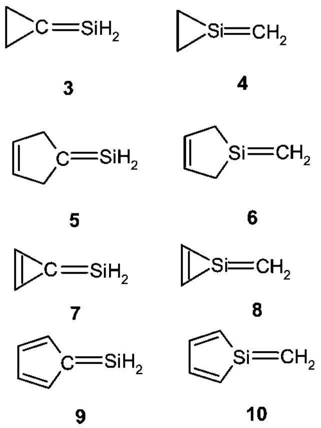


2a **2b** (2)

The first silapentafulvene (**2a**) was also recently reported.[14] The trapped product of its reaction with water was a silanol (**2b**, eq 2), indicating a similar reactivity to most silenes. The apparently different behavior of silatriafulvenes and silapentafulvenes toward nucleophiles poses the question whether the aromaticity of silafulvenes influences their reactivity and, if yes, in what way.

Fulvenes can shift their π-electrons in their ground state (but also in their lowest lying triplet state[15]) due to the influence of dipolar aromatic resonance structures (Chart 1). In triafulvenes the electrons shift toward the exo atom, while in pentafulvenes a shift in the opposite direction is expected. However, the degree of the electron shift depends on the ability of the exo and ring atoms to accommodate or to donate electrons. The aromaticity of triafulvenes increases with the decreasing electronegativity of the exo group.[16] 4-Silatriafulvene and its Ge and Sn analogues are generally regarded as partially aromatic compounds.[17] Höltzl et al. studied triafulvenes with one, two, three, and four phosphorus atoms and pointed out that not only the electronegativity of the exo substituent but also the lengths of the bonds determine the aromaticity.[18]

Chart 2. Studied Molecules



The parent pentafulvene has been known for a century. Microwave spectroscopic measurements[19] and theoretical studies indicate that the molecule is nonaromatic.[20] Saebo et al. found a slight increase in aromaticity when the exo carbon atom was substituted by heavier group 14 elements.[17,21]

In this paper we present a thorough study on the mechanism of water addition to silatriafulvenes and silapentafulvenes and related saturated compounds (Chart 2), in which we replace one of the carbon atoms of the exo double bond by silicon. We investigate whether the aromaticity of these only moderately or hardly aromatic compounds can affect the reactivity of the Si═C double bond, and we try to rationalize the experimentally observed reactivity of silatriafulvenes toward methyl alcohol. Our paper is organized as follows: first we describe the computational methods. The Results and Discussion section starts with a summary on the structure and aromaticity of compounds, followed by the mechanism of water addition to silenes bearing three- or five-membered-ring substituents in opposing locations on the Si═C bond (compounds **3**, **4**, **5**, and **6**). By studying these molecules we can analyze the effect of the ring on the reactivity of the Si═C bond compared to the parent silene. Finally we describe the mechanism of water addition to each silafulvene derivative (compounds **7**, **8**, **9**, and **10**) and the mechanism of methanol addition to **7**.

Theoretical Calculations. Geometry optimizations were performed at the B3LYP/6-31G(d) and MP2/6-311++G(d,p)

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levels of theory using the Gaussian 03 program package.[22] CBS-QB3 calculations were used to obtain reliable energies. Second derivative calculations were carried out to characterize the located stationary points. IRC calculations were performed for all path at the B3LYP/6-31G(d) to confirm the reaction coordinates from transition states in both directions. The stability of the KS wave functions of transition states was analyzed and was found to be stable in all cases. NBO charges were obtained at the MP2/6-311++G(d,p) geometry with the NBO program as implemented in Gaussian 03.[23] In order to estimate the aromaticity of the compounds, Bird and DBCI (double-bond character index) indices calculated at the MP2/6-311++G(d,p) level of theory were used together with the analysis of geometrical parameters. Bird indices[24] have been calculated from Gordy bond orders.[25] DBCI is the average double-bond character of the ring, where the double-bond character of a bond (DBC) between atoms X and Y is defined as $\mathrm{DBC} = (B_1 - R)/(B_1 - B_2)$, where B_1 and B_2 are the bond lengths of reference single and double bonds between X and Y.[26,27] For the starting materials NICS values were calculated at the MP2/6-311++G(d,p) level.[28] It is important to note that we used these indices only to follow the changes in aromaticity along different reaction paths (i.e., reactant, van der Waals complex, TS of the same path) and not to compare the aromaticity of differently substituted species.

Discussion

In Table 1 selected bond lengths, NBO charges, aromaticity indices, relative Gibbs free energies at 298 K at the CBS-QB3 level, and relative energies at the CBS-QB3 and MP2/6-311++G(d,p) levels are presented for the optimized stationary points. The numbering of molecules is shown in Chart 3. Since the MP2 and B3LYP calculations give similar geometrical parameters, only the MP2 values are summarized. In some cases negative Bird indices have been obtained. It is only possible if the standard deviation of the bond orders in the ring exceeds that with alternating single and double bonds. Thus negative Bird indices refer to the presence of strongly localized bonds. The geometry of **5**, **7**, and **8** is nonplanar, while the other molecules possess a planar skeleton. In the case of triafulvenes it is expected that the contribution of the aromatic resonance structures is larger in the nonplanar form.[29] Geometrical data reveal a significant bond alternation in the case of all molecules, which is reflected by the Bird and DBCI indices, too. According to the NICS indices none of the compounds are aromatic; the lowest value (−5.6) is calculated for **9**, suggesting a slightly aromatic system. This is in accordance with the results of previous studies.[21]

Since the reactivity of Si=C bonds strongly depends on their polarity, we investigated the NBO charges on these atoms, as well as in the rings (see Table 1). When silicon is in the ring, the charge difference between the double-bonded carbon and silicon is much larger (~1.5) than in the isomers with silicon in exo position (~2.7) (Table S1) due to the electronegativity difference between carbon and silicon. If silicon is in exo position, it is bonded to hydrogens, while when it is in the ring, it is bonded to two additional carbon atoms. Since carbon atoms more efficiently withdraw the electrons than hydrogens, the silicon bears a larger positive charge when bonded to carbons. The charge differences between the carbon and silicon atoms in the reactants clearly show the effect of aromatic resonance structures. The polarity of the Si=C bond in nonfulvenic structures falls between the two fulvenic structures. In triafulvenes the charge is smaller, while in pentafulvenes, the charge is larger on the exo atom than in the nonfulvenic structures. When silicon is in exo position, the changes in polarity are more pronounced, indicating a larger contribution of the aromatic resonance structures. Analysis of the total charge on the rings supports the above conclusions. The charge on the rings in triafulvenes **7** and **8** is larger and in pentafulvenes **9** and **10** is much smaller than in the nonfulvenic analogues.

Water Addition Reactions. In all cases both the normal and abnormal addition channels were investigated. Similarly to the reactivity of the parent silene, the initial step of all studied reactions is the formation of a weakly bonded complex bearing several characteristic features. The geometry of the reactant molecules in the complexes is almost unchanged, although the OH bond in water is slightly elongated. The distance between the reactants depends on the orientation of the two molecules, the attacked atom, and the ring type. Although the energy gain relative to the initial state is between 0.2 and 9 kcal/mol (at the CBS-QB3 level), the Gibbs free energy is always positive due to the negative entropy factors, with the exception of the nucleophilic complex of **9**. The orientation of the reacting agents indicates the electrophilic or nucleophilic nature of the attack. A small but systematic change on the charge at the water molecule supports this character. In electrophilic complexes (C_E) the charge on the water molecule is negative, while in the nucleophilic complexes it is a small positive value.

Nonfulvenic Structures (3−6). The results strongly resemble the previous findings in the case of the water addition to the parent silene, regarding the structure, nature, and energy of van der Waals complexes, transition states, and products.[5] The normal addition starts by the formation of a nucleophilic (C_N) and the abnormal channel by the formation of an electrophilic (C_E) van der Waals complex. The energies of the two complexes are very similar. In the case of **6** only a C_N was found by the MP2 method, and we could not locate the TS for the abnormal addition of water to **5** (T_E) by the MP2 method.

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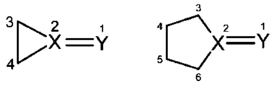
Table 1. Selected Geometrical Parameters (bond distances in Å), NBO Charges, Aromaticity Indices, Relative Gibbs Free Energies at 298 K at the CBS-QB3 Level, and Relative Energies at the CBS-QB3 and MP2/6-311++G(d,p) Levels (in parentheses) in kcal/mol for the Optimized Stationary Points of the Studied 1,2-Addition Channels (numbering of the atoms is shown in Chart 3)

		geometrical parameters						NBO charges						aromaticity	
		Si−C	C−O	Si−O	O−H	C−H	Si−H	Si	C	H_2O	ring[a]	Δ*G*	Δ*E*	Bird	DBCI
3	R	1.696						1.073	−0.729	0	−0.683	0	0(0)	84	0.16
	C_E	1.700	3.174	3.937	0.966	2.433	2.976	1.084	−0.768	−0.008	−0.691	5.0	−2.5(−4.4)	86	0.15
	T_E	1.862	1.841	2.870	0.989	2.128	2.439	0.264	−0.066	0.191	−0.023	48.4	38.5(40.8)	83	0.14
	P_A	1.876	1.424					1.088	−0.173			−23.1	−33.0(−35.0)	95	0.09
	C_N	1.697	4.039	2.839	0.961	4.427	3.397	1.184	−0.807	0.017	−0.784	7.8	−0.2(−2.9)	83	0.16
	T_N	1.755	2.561	1.944	1.503	1.832	2.045	1.464	−1.050	0.041	−1.038	14.1	4.5(3.4)	98	0.10
	P_N	1.844		1.671				1.624	−0.735			−65.2	−74.5(−74.4)	86	0.06
4	R	1.703						1.541	−1.201	0	0.751	0	0(0)	32	0.07
	C_E	1.711	3.397	3.128	0.964	2.635	2.816	1.593	−1.258	−0.001	0.812	5.8	−2.6(−4.7)	31	0.06
	T_E	1.868	1.969		0.981		2.473	0.576	−0.268	0.135	−0.202	45.7	36.6(37.3)	99	−0.11
	P_A	1.884	1.435					1.353	−0.396			−20.4	−29.8(−32.7)	69	0.03
	C_N	1.708		2.407	0.965			1.661	−1.334	0.062	0.831	5.8	−2.6(−5.2)	36	0.08
	T_N	1.764		1.926	1.068	1.806		1.760	−1.420	0.039	0.935	7.7	−2.2(−2.4)	41	0.06
	P_N	1.853		1.665				1.906	−1.047			−69.6	−79.1(−78.4)	40	0.04
5	R	1.726						1.033	−0.627	0	−0.642	0	0(0)	9	0.23
	C_E	1.729	3.412	3.908	0.965	2.542	2.947	1.057	−0.663	−0.006	−0.670	4.7	−1.5(−5.8)	8	0.23
	T_E[c]														
	P_A	1.902	1.451					1.092	−0.124			−17.1	−26.4(−28.6)	2	0.20
	C_N	1.726	4.151	2.927	0.961	4.501	3.459	1.144	−0.708	0.014	−0.742	5.9	0.7(−2.7)	9	0.23
	T_N	1.777	2.588	1.931	1.087	1.785	1.987	1.463	−0.962	0.005	−1.006	16.5	7.6(7.2)	4	0.20
	P_N	1.873		1.673					1.629			−58.4	−66.9(−66.8)	−2	0.18
6	R	1.709						1.618	−1.209	0	0.775	0	0(0)	5	0.19
	T_E	1.866	1.820	2.814	1.001	2.124	2.339	0.762	−0.356	0.120	−0.120	55.7	46.5(47.1)	−15	0.10
	P_A	1.896	1.442					1.480	−0.409			−13.2	−22(−25.3)	2	0.17
	C_N	1.710	3.597	2.680	0.962	3.542	3.075	1.740	−1.306	0.027	0.848	5.2	−2.1(−5.6)	7	0.20
	T_N	1.767	2.567	1.954	1.076	1.772	2.003	1.893	−1.450	0.011	0.999	8.7	−0.6(−0.4)	7	0.19
	P_N	1.862		1.677				1.982	−1.058			−65.7	−74.6(−77.4)	8	0.24
7	R	1.743						0.619	−0.474	0	−0.241	0	0(0)	34	0.61
	C_E	1.760	3.232	3.673	0.968	2.578	2.734	0.512	−0.410	−0.019	−0.117	4.5	−3(−5.6)	41	0.64
	T_{E1}	1.943	1.747	2.638	1.175	2.015	1.851	0.451	−0.131	−0.074	0.072	42.7	33.1(32.2)	36	0.62
	P_A	1.884	1.428					1.093	−0.163			−21.2	−30.6(−33.9)	7	0.47
	T_N	1.798	2.551	1.961	1.043	1.855	2.111	1.307	−0.967	0.009	−0.846	24.2	11.5(13.6)	−3	0.46
	P_N	1.855		1.673				1.609	−0.729			−56.0	−64.8(−65.8)	−23	0.37
	C_E[b]	1.761	3.195	3.627	0.967	2.516	2.692	0.514	−0.410	−0.021	−0.120	3.2	−5.3(−7.4)	41	0.64
	T_N[b]	1.792	2.570	1.964	1.029	1.907	2.127	1.306	−0.977	0.033	−0.865	20.8	10.3(8.8)	−4	0.45
	P_N[b]	1.856		1.669				1.611	−0.733			−57.8	−67.8(−68.6)	−23	0.37
8	R	1.701						1.574	−1.293	0	0.831	0	0(0)	75	0.62
	C_E	1.711	3.195	3.717	0.969	2.229	2.930	1.614	−1.347	−0.012	0.889	4.6	−3.7(−5.3)	78	0.64
	T_E	1.887	2.006	2.857	0.986	2.295	2.393	0.632	−0.280	0.090	−0.148	51.7	41.5(45.1)	23	0.43
	P_A	1.893	1.440					1.362	−0.415			−17.4	−27.6(−28.8)	50	0.55
	T_N	1.766	2.535	1.945	1.055	1.808	2.034	1.753	−1.447	0.047	0.953	8.3	−2.4(−1.9)	68	0.60
	P_N	1.865		1.666				1.876	−1.060			−68.8	−79.1(−77.4)	69	0.61
9	R	1.736						1.251	−0.717	0	−0.849	0	0(0)	58	0.54
	T_E	1.918	1.682	2.752	1.011	2.060	2.303	0.371	−0.120	0.227	−0.162	56.5	46.6(50.6)	51	0.52
	P_A	1.935	1.426					1.114	−0.124			−7.4	−17.2(−17.1)	40	0.49
	C_N	1.749	2.914	2.054	0.973	2.670	2.449	1.492	−0.840	0.134	−1.175	−0.6	−9(−11.9)	75	0.56
	T_N	1.802	2.493	1.847	1.157	1.606	1.937	1.546	−0.913	0.012	−1.120	6.0	−3.5(−2.9)	66	0.55
	P_N	1.896		1.670				1.622	−0.711			−53.1	−62.4(−61.1)	49	0.51
10	R	1.717						1.553	−1.133	0	0.699	0	0(0)	35	0.47
	C_E	1.719	3.320	3.819	0.960	2.380	2.972	1.588	−1.193	−0.007	0.751	4.4	−1.5(−3.9)	28	0.48
	T_E	1.868	1.734	2.798	1.000	2.099	2.384	0.794	−0.372	0.175	−0.179	60.1	50(42.3)	40	0.45
	P_A	1.898	1.440					1.440	−0.400			−10.7	−20(−22.2)	21	0.41
	T_N	1.772	2.551	1.928	1.082	1.760	2.000	1.839	−1.416	0.016	0.959	11.9	2.1(3.0)	26	0.43
	P_N	1.861		1.671				1.938	1.938			−62.0	−71.6(−70.9)	15	0.39

[a] Charge on the ring refers to the sum of the charges on all atoms of the ring including the charge of hydrogens attached to the ring. [b] Reaction with MetOH. [c] **6**C_E, **7**C_N, **8**C_N, and **9**C_E were not found on the PES; 10C_N was found only with the B3LYP method.

Chart 3. Numbering of the Studied Molecules



The Gibbs free energies of activation of the normal and abnormal addition channels are 6−10 and 40−50 kcal/mol, respectively. The TS of the normal addition, T_N, shows moderate changes compared to the free reactants. The carbon atom is slightly pyramidalized, while the silicon is almost planar. The Si···O distance is relatively long, the O−H bond is slightly elongated, and the Si−C distance is closer to a double bond (~1.7 Å) than to a single bond (~1.85 Å). The high exothermicity of the reaction channel is due to the replacement of a weak Si−C *π*-bond by a strong Si−O bond. In these reactions only the *syn* product is expected, and *anti* product formation is possible only with the reaction of a second nucleophile, as proposed earlier.[30] The *abnormal* addition follows an electrophilic channel via C_E and an energy-rich transition state (T_E).

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(30) Although the calculations were carried out for symmetrically substituted silenes, the results may predict the diastereoselectivity of substituted silenes. We use *syn* and *anti* symbols in this sense.

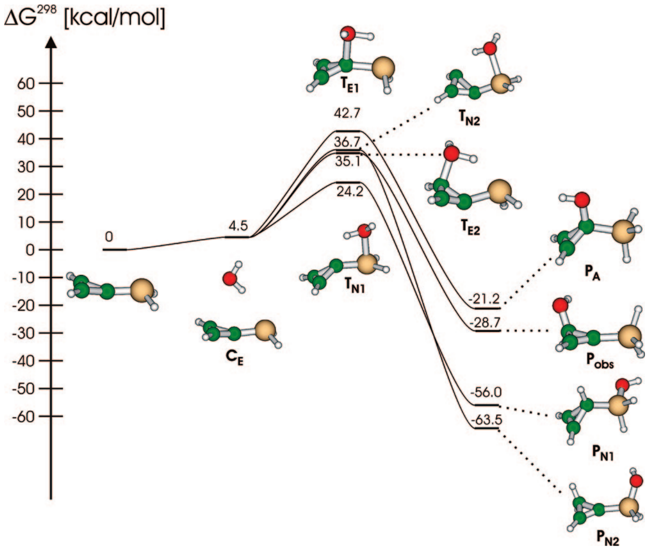

Figure 2. Gibbs free energy diagram at the CBS-QB3 level for the reaction channels of 4-silatriafulvene (**7**) + water reactions.

In the TS the O−H bond is elongated only to ~0.98 Å, and the Si−C bond is almost as long as in the product. The *π*-charge, which was originally concentrated on carbon, shifts toward silicon, and as a consequence, the silicon becomes strongly pyramidal. The reaction ends in a moderately stabilized product.

4-Silatriafulvene, 7. The structure of 4-silatriafulvenes may be described as having a conjugated double-bond system; therefore the addition to the exo Si═C bond will be called 1,2-addition, while we will use 1,4-addition to describe the experimentally observed reaction between **1b** and methanol[13] (eq 1) in an analogous way to the 1,4-additions of butadiene. Here, we consider four different reaction channels for water addition: the normal 1,2- and 1,4-additions leading to a silanol and the abnormal 1,2- and 1,4-additions leading to silanes. The thermodynamic profiles of the reactions are presented in Figure 2, and the data for the 1,2- and 1,4-additions are collected in Tables 1 and 2, respectively. The reaction profiles were calculated considering monomeric and dimeric water as a nucleophile (see Table 3). We could locate only one electrophilic complex C_E on the PES. The missing C_N can be explained by the very low charge on Si. The favorable interaction between the LUMO of water and the HOMO of **7** is supported by the relatively high HOMO energy of **7** (see Table S2). In the complex the water moiety has a positive charge (0.019*e*). The charge on the ring decreases by 0.13*e*, compared to the average decrease of 0.03*e* in other electrophilic complexes. The polarity of the Si═C bond is further reduced, indicating an increased contribution of the aromatic resonance structure in the complex, which is supported by the DBCI and Bird indices.

Starting from the complex the reaction may follow various reaction paths. The normal 1,2-channel via T_{N1} shows a drastic charge transfer between the complex and the TS. The charge on silicon increases almost three times compared to the complex, and the carbon, as well as the whole ring, becomes highly negative. This follows the same pattern as the charge shifts in other normal additions, but its effect on the energy and aromaticity of the molecule is severe. Since the negative charge shifts back to the ring, the aromaticity of the molecule disappears, and in the TS the aromatic stabilization of the complex must be surmounted as extra energy, resulting in a high barrier and a relatively small reaction heat.

The 1,2 abnormal addition of water is an electrophilic channel and followed by essentially different events. The charge shifts are in accordance with those observed for the other molecules; that is, the carbon atom becomes less negative and the silicon less positive, but these changes work in the direction of maintaining (or even increasing) the aromaticity of **7**. In the T_{E1}transition state the charge on the ring and the whole triafulvene moiety is positive (!), and this is the only TS found in this study where the charge on the water moiety is negative. The Si−C and O−H bonds are extremely long, and the Si−H distance is very short. The larger aromaticity of the ring is supported by an earlier study, which has found a correlation between the aromaticity of the three-membered ring in substituted 4-silatriafulvenes and the Si−C bond length.[29] The O−H distance is close to that in the TS of the ethylene + water reaction (1.243 Å), which proceeds via an electrophilic ionic mechanism.[5] These results somewhat resemble the findings of Burk et al. that the protonated forms of substituted triafulvenes are much more aromatic than the neutral molecule.[16] The aromaticity indices support the larger aromaticity of T_{E1} than that of the reactant. The aromaticity of the van der Waals complex is more or less preserved in the TS, resulting in a relatively low barrier.

There are two possible 1,4-addition channels (Table 2). The normal 1,4-addition leads to a silanol product (P_{N2}), while the experimentally observed abnormal channel leads to a silane (P_{obs}). Both channels start from C_E, as above and proceed via five-membered-ring transition states (see Figure 2) with similar energies. The barriers are very similar and fall between the barriers of the two 1,2-channels. It is expected that the strain in these five-membered-ring TSs is smaller than in the usual four-membered-ring TS. The C−C bond lengths in the ring resemble more the product than the reactant.

As an earlier study showed that the water addition reaction proceeds more easily with the dimeric form of the nucleophile, we studied all four reaction channels with a water dimer. The calculated activation energies and reaction heats are collected in Table 3. In all cases lowering of the barriers is observed, which is largest in the case of the 1,4-additions. As a consequence, the difference between the activation energies of the normal 1,2-addition and the 1,4-addition channels is reduced to 4 kcal/mol.

As experimentally alcohol addition to **1a** and **1b** was reported, we compare two competing reaction channels for methanol addition to **7**: the normal 1,2-addition pathway (Table 1) and the 1,4-pathway leading to the experimentally observed product (Table 2). We found only one electrophilic van der Waals complex on the PES. The charge transfer between the fragments is slightly larger than in the case of the water addition. The structures of C_E and of the transition states are similar to those observed in the case of the water addition, but the activation energies are smaller.

6-Silapentafulvene, 9. Only 1,2-additions were studied, and the energy profiles are depicted in Figure 3. Due to the aromatic resonance structures in **9**, the silicon atom is more positive than in other molecules, and the LUMO energy of the compound is very low. We found only one nucleophilic complex, C_N, which is clearly stabilized by the interaction between the oxygen lone pair and the LUMO of the pentafulvene. The charge transfer (0.13*e*) between the fragments is larger than in any other complex found in this study. However, the Si−O distance is only 2.05 Å, more than 0.5 Å shorter than in the other nucleophilic complexes, and its Gibbs free energy of formation is negative. These two factors together could imply that this is not a weakly bound van der Waals but a zwitterionic complex, similar to the one found on the pathways of water addition to

Table 2. Selected Geometrical Parameters (bond distances in Å), NBO Charges, Relative Gibbs Free Energies at 298 K at the CBS-QB3 Level, and Relative Energies at the CBS-QB3 and MP2/6-311++G(d,p) (in parentheses) Levels in kcal/mol for the Optimized Stationary Points of Studied 1,4-Addition Channels of H_2O and Methanol to 7 (numbering of the atoms is shown in Chart 3)

		geometrical parameters							NBO charges							
		Si−C_2	C_2−C_3	C_3−C_4	C_2−C_4	C_3−O	O−H	Si−H	Si	C_2	C_3	C_4	H_2O	ring[b]	Δ*G*	Δ*E*
7	R	1.743	1.460	1.322	1.460				0.619	−0.474	−0.110	−0.110	0	−0.241	0	0(0)
	C_E	1.760	1.449	1.325	1.449	3.225	0.968	2.734	0.512	−0.410	−0.085	−0.085	−0.019	−0.117	4.5	−3(−5.6)
	T_{E2}	1.884	1.469	1.412	1.354	1.676	1.110	2.055	0.411	−0.293	0.083	−0.232	0.054	−0.036	35.1	25.0(22.7)
	P_{obs}	1.849	1.519	1.464	1.357	1.415			1.076	−0.495	0.140	−0.124			−28.7	−37.6(−42.1)
	C_E[a]	1.761	1.449	1.325	1.449	3.030	0.967	2.692	0.514	−0.410	−0.072	−0.102	−0.021	−0.120	3.2	−5.3(−7.4)
	T_{E2}[a]	1.882	1.474	1.415	1.354	1.644	1.069	2.144	0.377	−0.298	0.079	−0.244	0.118	−0.059	27.3	15.9(13.2)
	P_{obs}[a]	1.849	1.523	1.465	1.327	1.405			1.078	−0.498	0.149	−0.119			−33.7	−44.3(−48.7)
	T_{N2}	1.713	1.681[c]	1.358	1.390	1.681	0.997	2.184[d]	1.473	−0.956	−0.512	0.018	0.063	−1.082	36.7	27.4(24.1)
	P_{N2}	1.842	1.548	1.493	1.316			1.665	1.602	−0.535	−0.359	−0.118			−63.5	−72.3(−74.1)

[a] Reaction with MetOH. [b] Charge on the ring refers to the sum of the charges on all atoms of the ring including the charge of hydrogens attached to the ring. [c] C_3−H bond distance. [d] Si−O bond distance.

Table 3. Relative Gibbs Free Energies at 298 K at the CBS-QB3 Level and Relative Energies at the CBS-QB3 and MP2/6-311++G(d,p) (in parentheses) Levels in kcal/mol for the Transition States ($\Delta E^{\#}$, $\Delta G^{\#}$) and Products ($\Delta E^{product}$, $\Delta G^{product}$) of the Studied 1,2 and 1,4 Water Dimer Addition Channels to 7 (energies are compared to the energy of the free silatriafulvene molecule and a water dimer)

	$\Delta E^{\#}$	$\Delta G^{\#}$	$\Delta E^{product}$	$\Delta G^{product}$
1,2 normal addition	7.8(4.6)	20.1	−65.1(−66.5)	−54.1
1,2 abnormal addition	23.4(21.8)	35.8		
1,4 normal addition	11.7 (7.9)	23.9	−72.4 (−74.6)	−61.6
1,4 abnormal addition	11.8 (8.5)	24.9		

$H_2Si{=}SiH_2$.[5] The complexation with water induces an extra electron transfer from the silicon to the ring besides the electron flow from the water molecule. The increase in the negative charge of the ring is considerably larger than the positive charge on the water. The aromaticity of C_N is larger than that of **9**, which is enough to compensate the effect of the negative entropy change. Starting from C_N two pathways exist. The normal addition proceeds via T_N, in which the charge on silicon further increases and on carbon further decreases. The very short Si−O and very long O••H bonds indicate a later TS than in the case of other molecules. The aromaticity of **9** is preserved in the TS, which is in accordance with the calculated very low barrier.

The abnormal channel is similar to those of the nonfulvenic structures. The aromaticity is seriously reduced in the TS, resulting in very high activation energy (56 kcal/mol). The product is only a bit more stable than the separated molecules.

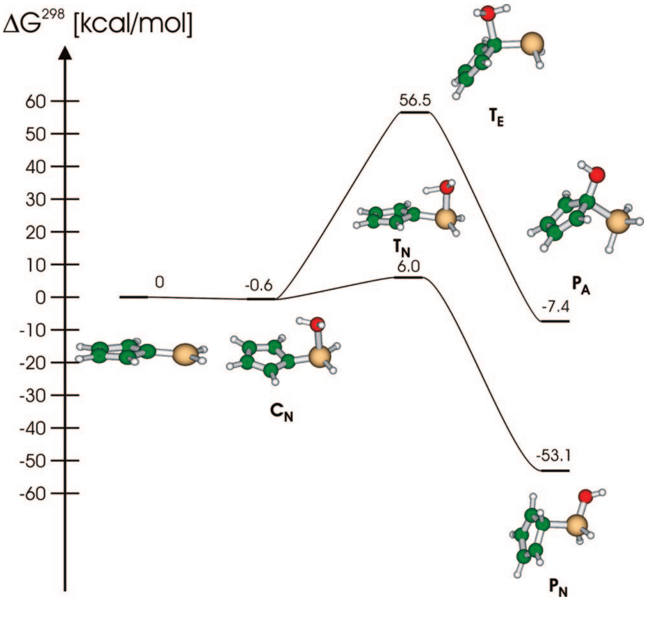

Figure 3. Gibbs free energy diagram at the CBS-QB3 level for the reaction channels of 6-silapentafulvene (**9**) + water reactions.

3-Silatriafulvene (8) and 5-Silapentafulvene (10). 5-Silapentafulvene, **10**, is the simplest model compound of **2a**. On the basis of the aromatic resonance structures of these molecules, one might expect a similar effect of aromaticity on the barrier heights to that shown for **7** and **9**; such phenomenon is not observed. The water addition reaction of these molecules proceeds very similarly to other Si=C bonds, but only an C_E could be found on the PES, due to the strong polarity of the Si=C bond. This resembles the water addition reaction of $H_2Si{=}SiHF$[31] or the hydrogen halide addition of disilene and silene.[6] The Gibbs free energies of activation of the normal and abnormal channels are very similar to the values of the nonfulvenic compounds. This result is in very good accordance with the experimental finding that the water addition of **2a** leads to the expected silanol product (eq 2).[14]

It is important to note the apparent failure of the Bird and DBCI indices in predicting the aromaticity of these compounds. This can be illustrated by the Bird indices of the two products of **8**. The Bird index of **8**P_A is 49.64, while it is 69.41 for **8**P_N. This is not due to a larger aromaticity of any ring, as there is no possibility for conjugation, as the silicon is tetravalent. This effect is an artifact of the Bird index, as it measures the bond equalization in the ring. It is, indeed, true that the bond lengths are more equalized in **8**P_N than in **8**P_A, but it is the effect of the fourth substituent on silicon. In **8**P_A, silicon is bonded to hydrogen, while in **8**P_N to oxygen. Oxygen creates a large positive charge on silicon; thus the Si−C single bonds in the ring become more polarized, thus shorter. It looks like there was delocalization in the ring compared to **8**P_A.

Conclusions

The replacement of the hydrogen atoms on either the Si or the C atom of the parent silene by three- or five-membered rings does not influence the reaction mechanism of water addition to the Si=C bond when there is no conjugation between the ring and the exo bond. However, the aromaticity of fulvenes may influence considerably the structures and energies of the van der Waals complexes and transition states. We showed that in the case of 4-silatriafulvene, **7**, and 6-silapentafulvene, **9**, the aromaticity determines the primary interaction between the water and the fulvene moiety and always works in the direction of maintaining or increasing the aromaticity of complex. The conservation or loss of aromatic stabilization in the TS seriously

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(31) Takahashi, M.; Veszprémi, T.; Kira, M. *Organometallics* **2004**, *23*, 5768–5778.

influences the activation energies of the 1,2-addition channels of **7** and **9**. Methanol and water additions of **7** proceed in a very similar manner, but the barriers are lower for methanol addition. A new 1,4-addition pathway was identified for water addition to **7**.

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Supporting Information Available: Gibbs free energy diagram at the CBS-QB3 level for the reaction channels of 4-silatriafulvene (**7**) + methanol reactions, charge difference ($q_{Si} - q_C$) on the atoms of the Si−C double bond in reactants, and HOMO−LUMO energies of the reactants. This material is available free of charge via the Internet at http://pubs.acs.org.

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