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A Combined Experimental and Theoretical Study of the Kinetics and Mechanism of the Addition of Alcohols to Electronically Stabilized Silenes: A New Mechanism for the Addition of Alcohols to the Si=C Bond

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Abstract: The stabilized silene 1,1-bis(trimethylsilyl)-2-adamantylidenesilane (**4**) has been generated by photolysis of a novel trisilacyclobutane derivative in various solvents and studied directly by kinetic UV spectrophotometry. Silene **4** decays with second-order kinetics in degassed hexane solution at 23 °C ($k/\epsilon = 8.6 \times 10^{-6}$ cm s^{-1}) due to head-to-head dimerization. It reacts rapidly with oxygen [$k(25\ °C) \approx 3 \times 10^5$ M^{-1} s^{-1}] but ~10 orders of magnitude more slowly with methanol (MeOH) than other silenes that have been studied previously. The data are consistent with a mechanism involving reaction with the hydrogen-bonded *dimer* of the alcohol, $(MeOH)_2$ ($k = 40 \pm 3$ M^{-1} s^{-1}; $k_H/k_D = 1.7 \pm 0.2$). The stable analogue of silene **4**, 1-*tert*-butyldimethylsilyl-1-trimethylsilyl-2-adamantylidenesilane (**5**), reacts ~50 times more slowly, but via the same mechanism. The mechanism for addition of water and methanol (ROH; R = H, Me) to **4**, **5**, and the model compound 1,1-bis(silyl)-2,2-dimethylsilene (**3a**) has been studied computationally at the B3LYP/6-31G(d) and MP2/6-31G(d) levels of theory. Hydrogen-bonded complexes with monomeric and dimeric methanol, in which the Si=C bond plays the role of nucleophile, have been located computationally for all three silenes. Reaction pathways have been characterized for reaction of the three silenes with monomeric and dimeric ROH and reveal significantly lower barriers for reaction with the dimeric form of the alcohol in each case. The calculations indicate that **5** should be ~40-fold less reactive toward dimeric MeOH than **4**, in excellent agreement with the ~50-fold difference in the experimental rate constants for reaction in hexane solution.

Introduction

Silenes are highly electrophilic, transient molecules that react exothermically with nucleophiles such as water and alcohols, or undergo rapid [2 + 2]-dimerization to yield the corresponding disilacyclobutane derivative in the absence of such reagents.[1−4] The results of early theoretical calculations, probing the effects of substituents on the geometries and electronic structures of the Si=C bond in silene ($H_2Si{=}CH_2$, **1a**), led to the suggestion that Si=C bond polarity is the main factor responsible for the extraordinarily high reactivities of these molecules with nucleophilic reagents.[5] This work showed that σ-donor or π-acceptor substituents at silicon, and/or σ-acceptor or π-donor substituents at carbon, which lead to increased kinetic stability, have the effect of reducing the natural ($^{\delta+}Si{=}C^{\delta-}$) polarity of the bond relative to that in the parent molecule.[5] More recent experimental studies of the kinetics of 1,2-addition of methanol to simple 1- and 2-substituted silene derivatives in solution are fully consistent with the suggested link between Si=C bond polarity and reactivity.[6,7] Further theoretical work has verified that calculated energy barriers for the analogous reaction with water are strongly substituent-dependent, and correlate well with both calculated Si=C bond polarities and the rate constants for reaction of methanol with several of the silenes that have actually been studied experimentally.[8]

[†] McMaster University.

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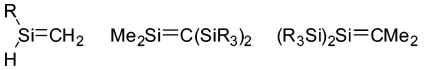
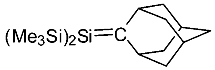
An illustrative example is provided by the model silenes **2a** and **3a**, which bear identical substituents but in opposing locations on the Si═C bond. Ab initio (MP4/6-31+G(d,p)//B3LYP/6-31G(d)) calculations indicate that the Si═C bond in **2a** is substantially more polarized (in the sense $^{\delta+}$Si═C$^{\delta-}$) than that in the parent molecule (**1a**) and exhibits a ~5 kcal/mol lower free energy barrier for 1,2-addition of water, while silene **3a** is substantially less polarized than the parent silene and exhibits a ~11 kcal/mol higher activation barrier for the same reaction.[8] Silenes **1a** and **2a** are predicted to react (with water) via the initial formation of a weak (Lewis acid−base) complex between the silene and the nucleophile which then collapses to product by proton transfer from oxygen to the silenic carbon, while for **3a** and other silenes of polarity lower than that of **1a**, the water−silene complex could not be located, and the reaction is hence predicted to occur *concertedly*. Experimental studies confirm that the trimethylsilyl analogue of **2a** (**2b**[9,10]) is an exceedingly powerful electrophile, reacting with methanol at the diffusion-controlled rate in hexane solution at room temperature.[11] This is ~5 times faster than the analogous reaction of 1-methylsilene (**1b**), the closest model of the parent molecule for which experimental data are currently available, under the same conditions.[6] The evidence indicates that both **1b** and **2b** react with alcohols and other nucleophiles via the stepwise addition mechanism that is predicted by theory; in fact, this appears to be true of *all* of the (30 or so) transient silenes that have been studied to date, but they span a relatively small range in electrophilic reactivity and Si═C bond polarity.[4] These trends suggest that the corresponding trimethylsilyl analogue of **3a** (**3b**) should be at least several orders of magnitude less reactive than **1b** and undergo concerted reaction with alcohols, but this is difficult to test experimentally because the compound is (as yet) unknown. Ultimately, it might be anticipated that, with appropriate substitution, the electronic character of the Si═C bond might be perturbed to such an extent that reaction with nucleophiles proceeds via initial protonation, analogous to the Markovnikov addition mechanism of alkene chemistry, and with the opposite regiochemistry to that normally observed. Indeed, one example of such extreme behavior has been reported.[12]



1 **2** **3**

a. R = H; **b**. R = Me

Two reasonable (and readily accessible) facsimiles of **3** are provided by silenes **4** and **5**, which bear trialkylsilyl substituents at silicon and two alkyl substituents at carbon, analogous to the substitution pattern in **3**.[13] Silene **4**, a transient, can be generated thermally from its 1,2-disilacyclobutane dimer (**6**)[14,15] or photochemically by UV-photolysis of the pyrolysis product of **6**, trisilacyclobutane **7**.[16] Silene **5** is known to be sensitive to oxygen and moisture, but the increased steric hindrance afforded by the −SiMe$_2{}^t$Bu substituent renders it stable toward dimerization, and it is thus isolable.[17]



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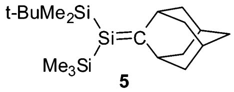

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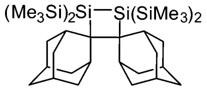

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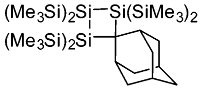

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In this paper, we present the results of a combined experimental and theoretical study of the kinetics and mechanism of 1,2-addition of alcohols and water to silenes **4** and **5**. Our results indicate that the electrophilic reactivities of these two compounds are at least *9* orders of magnitude lower than silenes with trialkylsilyl and alkyl substituents in the opposing positions on the Si═C bond (e.g., **2b**), which in the case of **4** can be linked almost entirely to the electronic effects of the substituents on the polarities of the Si═C bonds in the two molecules. They are also consistent with an intriguing change in the mechanism for the reaction compared to that for **2b** and other relatively polar silene derivatives, which appears to be general (albeit not always easy to detect). Absolute rate constants for the head-to-head dimerization of **4** and for its reaction with oxygen in hexane solution at 23 °C are also reported.

Results

Although **4** is now known to be sufficiently long-lived to be detected by low-temperature NMR spectroscopy,[15] our initial attempts to detect it directly for kinetic measurements were carried out using laser flash photolysis techniques. Indeed, 248 nm laser photolysis of **7** in deoxygenated hexane afforded two long-lived products, one exhibiting $\lambda_{\max} = 320$ nm that is stable over the full 1 s that can be monitored with our system, and the other exhibiting $\lambda_{\max} = 410$ nm and lifetime $\tau = 670 \pm 70$ ms (Figure 1). The two species are readily identified as silene **4** and tetrakis(trimethylsilyl)disilene (**8**; see eq 1), respectively, on the basis of comparisons to the UV spectrum of **5**[18] and to the previously reported spectra of **8**[14] and the related stable derivative **9** ($\lambda_{\max} = 412$ nm).[19] The substantially different lifetimes observed for **4** and **8** indicate that [2 + 2] cycloaddition of the two molecules (to regenerate **7**)[16,20] does not occur to any significant extent under the conditions of this experiment, in which the two species are produced in typical initial concentrations of ~10 μM. In O_2-saturated hexane, the lifetimes of the two species are reduced to $\tau = 240$ μs and $\tau = 43$ μs, respectively, from which can be estimated absolute rate constants for reaction of oxygen with **4** ($k_{O2} \approx 3 \times 10^5$ M^{-1} s^{-1}) and **8** ($k_{O2} \approx 1.6 \times 10^6$ M^{-1} s^{-1}). The latter is in good agreement with our previous determination,[14] while the former is similar

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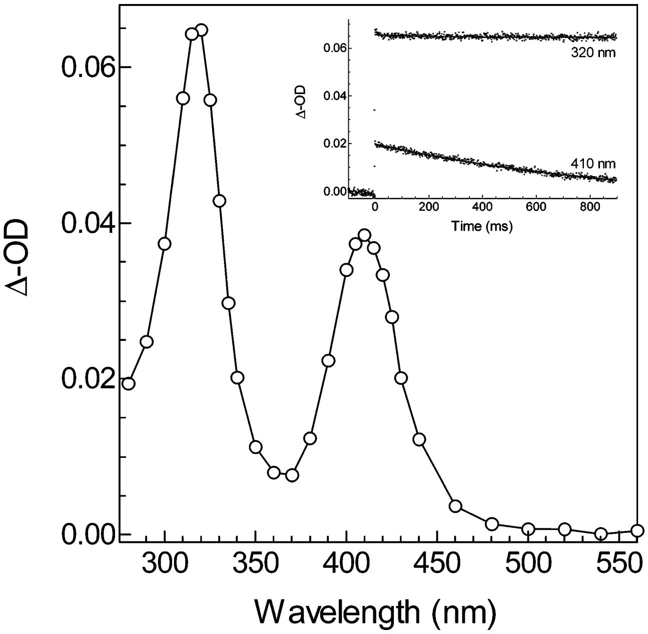
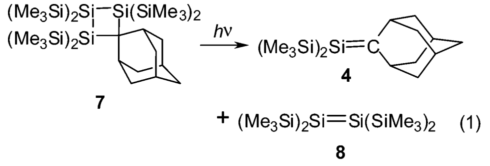


Figure 1. Transient absorption spectrum recorded 1−10 μs after 248-nm pulsed laser excitation of a deoxygenated 0.002 M solution of **7** in hexane. (Inserts) Transient decay profiles recorded at the absorption maxima of 320 nm ($\tau > 60$ s) and 410 nm ($\tau = 670$ ms).

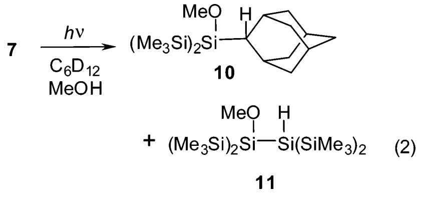
to values reported for other silene derivatives bearing alkyl substituents at the 2-position of the Si=C bond.[4]



$(Me(i\text{-}Pr)_2Si)_2Si{=}Si(SiMe(i\text{-}Pr)_2)_2$

9

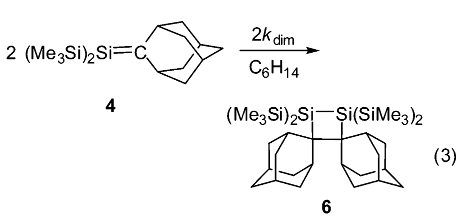
Steady-state photolysis of **7** in cyclohexane-d_{12} containing 0.05 M MeOH affords the methoxysilanes **10** and **11** as the only detectable products (equation 2), consistent with the results of earlier diene-trapping experiments for the molecule.[16] A quantum yield of $\Phi = 0.14 \pm 0.05$ for the formation of the two compounds was determined by chemical actinometry. The quantum yield can be equated to that for formation of **4** and **8**, assuming that trapping of the two species by the alcohol is quantitative. Photolysis of a deoxygenated cyclohexane-d_{12} solution of **7** in the absence of methanol proceeds with similar efficiency to that carried out in the presence of the silene/disilene trap, but affords disilacyclobutane **6** and a complex mixture of other products due (presumably) to oligomerization reactions of disilene **8**.



The same absorption maxima are observed for **4** ($\lambda_{max} = 320$ nm) and **8** ($\lambda_{max} = 410$ nm) in dry, nitrogen-outgassed acetonitrile/THF(5%) solution as those in hexane, although their lifetimes ($\tau_4 = 2.3 \pm 0.1$ ms; $\tau_8 = 0.48 \pm 0.01$ ms) are decreased quite significantly compared to the values in hexane solution. This may be the result of reactions of the two species with the (nitrile) solvent,[21,22] although the possibility has not been investigated further. Addition of up to 1.5 M *n*-butylamine or up to 11 M methanol (MeOH) resulted in efficient quenching of the lifetime of the disilene, as expected,[14] but had no discernible effect on the lifetime of **4**. This establishes an upper limit of $k_{MeOH} < 50$ M^{-1} s^{-1} for the absolute rate constant for reaction of **4** with the alcohol under these conditions, based on the fact that a 10% or higher reduction in lifetime relative to the value in the pure solvent mixture could be reproducibly measured under our experimental conditions.

The silene can also be detected upon laser photolysis of **7** in MeOH/THF (9:1 v/v) solution, where it again exhibits the same absorption maximum as that in hexane and decays with predominant pseudo-first-order kinetics and a lifetime $\tau_{MeOH} = 14 \pm 3$ ms in argon-outgassed solution at 25 °C. A lifetime of $\tau_{MeOD} = 37 \pm 7$ ms was observed in 9:1 MeOD/THF solution under the same conditions, leading to an isotope effect of $k_H/k_D = 2.6 \pm 0.8$ on the decay rate constant for **4** in this solvent mixture. The lifetime of the silene in MeOH/THF is independent of temperature over the 25−50 °C temperature range (e,g., $\tau_{MeOH} = 14.2 \pm 0.7$ ms at 50 °C). Disilene **8** could not be detected under these conditions because of its much greater reactivity toward the alcohol compared to that of **4**.

Silene **4** could also be detected in hexane solution by conventional UV−vis spectrophotometry after brief (254 nm) photolysis of an argon-outgassed 0.03 M solution of **7** to 5−10% conversion; its lifetime was on the order of 20 min under these conditions. This was extended to ~4 h when the silene was generated in freeze−pump−thaw degassed solution in a sealed cell at 24 °C. Under these conditions, the decay of **4** fit to pure second-order kinetics ($r^2 = 0.9998$; see Supporting Information) over the 0−85% conversion range, consistent with [2 + 2]-dimerization (to yield **6**; eq 3) being the dominant mode of decay of the silene; the data afford a second-order rate coefficient of $k_{dim}/\epsilon = 8.6 \times 10^{-6}$ cm s^{-1}, from which can be estimated an absolute rate constant of $k_{dim} \approx 0.13$ M^{-1} s^{-1}, assuming the extinction coefficient of **4** at its absorption maximum is the same as that reported for **5** ($\lambda_{max} = 322$ nm; $\epsilon_{max} = 15000$ dm^3 mol^{-1} cm^{-1} in pentane[17]).



The decay of **4** in deoxygenated hexane is accelerated and follows clean pseudo-first-order kinetics in the presence of 3−30 mM MeOH or MeOD; Figure 2a shows plots of the pseudo-first-order rate constants for decay of **4** (k_{decay}) as a function of MeOL (L = H or D) concentration. The dotted lines in the figure correspond to the least-squares fit of the data to a second-order

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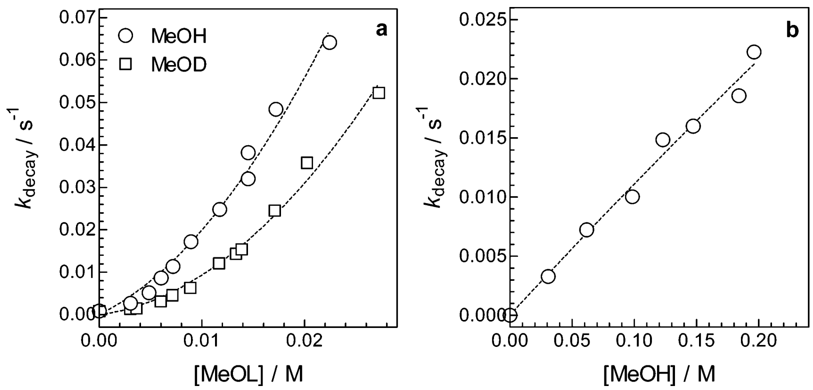

Figure 2. Plots of the pseudo-first-order decay rate constant (k_{decay}) vs bulk MeOL concentration (L = H or D) for silenes **4** (a) and **5** (b) in hexane solution at 23−25 °C. The dotted lines in (a) are the least-squares fits of the data to a second-order polynomial in [MeOL], while that in (b) is the linear least-squares fit.

Table 1. Calculated Energies (B3LYP/6-31G(d)//B3LYP/6-31G(d); kcal mol^{-1}) for the Reaction of Silenes **3a**, **4**, **5** with Water and MeOH[a−d]

	3a		**4**		**5**	
	Δ*E*	Δ*G*°	Δ*E*	Δ*G*°	Δ*E*	Δ*G*°
H_2O complex	not found		−4.6 (0.3)	3.7	−5.0 (−0.3)	2.7
H_2O TS	10.1 [12.0]	19.7 [22.4]	9.9	21.0	10.1	20.3
MeOH complex	−3.0 (−0.2) *−1.7 (−1.2)*	5.4	−4.0 (−0.2)	6.8	−5.0 (−0.8)	4.5
MeOH TS	9.2 [8.0] *14.4*	20.6 [20.4]	10.4	22.9	10.8	23.2
$(H_2O)_2$ complex[e]	−6.7 (−0.7)	4.7	−9.0 (−0.9)	4.2	−9.0 (−1.8)	2.9
$(H_2O)_2$ TS[e]	−2.6 [−0.7]	11.0 [13.4]	−0.9	14.7	0.9	15.8
$(MeOH)_2$ complex[e]	−6.3 (−0.9) *−4.7 (−3.9)*	5.0	−8.1 (−1.3)	4.5	−8.3 (−1.7)	3.9
$(MeOH)_2$ TS[e]	−2.3 [−5.6] *3.4*	12.1 [9.9]	2.6	19.3	5.1	21.5
MeOH product	−59.4	−49.1	−54.8	−44.9	−52.9	−40.6

[a] Relative energies (free energies) of water and methanol H-bonded dimers vs the two monomers (in kcal mol^{-1}) are as follows: B3LYP/6-31G(d)//B3LYP/6-31G(d), −5.2 (+0.2) and −5.8 (+2.2); MP2/6-31G(d)//MP2/6-31G(d), −5.0 (+0.5) and −6.4 (+1.6). The methanol dimer is 4.8 kcal mol^{-1} more stable than two methanol monomers at B3LYP/6-311+G(d,p)//B3LYP/6-31G(d). A second minimal conformation was found for the MeOH dimer at the B3LYP/6-31G(d)//B3LYP/6-31G(d) level, with energy (free energy) of −5.7 kcal mol^{-1} (1.4 kcal mol^{-1}). [b] Values in parentheses are after correction for basis set superposition error. [c] Values in square parentheses are at MP2/6-31G(d)//MP2/6-31G(d). [d] Values in italics are at B3LYP/6-311+G(d,p)//B3LYP/6-31G(d). [e] Energies are vs ROH dimer and silene.

polynomial in [MeOL] although, as can be seen quite clearly in the case of MeOH, the low concentration points (which are the most accurate of the set) fit rather poorly to this simple model.

Addition of MeOH (0.03−0.2 M) to solutions of **5** in argon-outgassed hexane caused the silene to decay with clean pseudo-first-order kinetics and exhibit lifetimes in the range of 45−350 s. In this case, a plot of k_{decay} vs [MeOH] was linear, affording a slope of 0.11 ± 0.01 M^{-1} s^{-1} (see Figure 2b).

Computational Studies. DFT calculations were carried out at the B3LYP/6-31G(d) level of theory, to investigate the addition of water and MeOH to silenes **3a**, **4**, and **5**. Calculations were carried out on the reactions of the three silenes with H_2O and MeOH in both their monomeric and hydrogen-bonded dimeric forms. Dimerization energies (Δ*E*) for H_2O and MeOH were found to be $\Delta E = -5.2$ and −5.8 kcal mol^{-1}, in good agreement with the ab initio MP2/6-31G(d)//MP2/6-31G(d) values of −5.0 and −6.4 kcal mol^{-1}, respectively, and with the results of previous calculations at higher levels of theory.[23] The computed standard free energies for ROH dimerization were slightly positive in both cases: $\Delta G° = +0.2$ and +2.2 kcal mol^{-1} for H_2O and MeOH at the B3LYP/6-31G(d) level and +0.5 and +1.6 kcal mol^{-1} at MP2/6-31G(d), respectively. The B3LYP/6-31G(d) results for addition of monomeric H_2O to **3a** agree quite closely with those reported in our earlier study.[8]

Weak association complexes were located for **3a** and $(H_2O)_2$, MeOH, and $(MeOH)_2$, and for **4** and **5** with all four ROH species studied, as were transition states for reactions of each of the three silenes with each of the four ROH species. Energies were also calculated at the ab initio (MP2/6-31G(d)//MP2/6-31G(d)) level of theory for the reactants and transition states for reactions of each of the four species with silene **3a**, and are in reasonable agreement with the B3LYP/6-31G(d)//B3LYP/6-31G(d) values. Single-point calculations at the B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) level were performed for the reaction of silene **3a** with methanol to probe the influence of a larger basis set on the calculated energies. IRC calculations were carried out for the reaction of dimeric water with silene **3a**, which confirmed the reaction pathway for the model compound.

Table 1 lists the calculated energies and Gibbs free energies for each of the complexes and transition states. Basis set superposition errors (BSSE) were evaluated for each of the complexes by the counterpoise corrections method,[24] and the resulting corrected Δ*E* values are also included in the table. Table 2 lists total Mulliken charges at the silenic silicon and

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Table 2. Total Mulliken Charges (B3LYP/6-31G(d)) on the Multiply Bonded Silicon and Carbon Atoms along the Reaction Paths of Reaction of Silenes **3a**, **4**, **5** with Water and Methanol[a]

	3a		**4**		**5**	
	Si=	C=	Si=	C=	Si=	C=
silene	0.03 (0.46)	−0.01 (−0.52)	−0.14	−0.01	−0.16	−0.01
H_2O complex	not found		−0.17	−0.04	−0.19	0.04
H_2O TS	0.37	−0.23	0.26	−0.25	0.24	−0.26
MeOH complex	0.00 (0.44)	−0.04 (−0.54)	−0.16	−0.04	−0.19	−0.04
MeOH TS	0.39 (0.86)	−0.23 (−0.82)	0.29	−0.25	0.26	−0.26
$(H_2O)_2$ complex	0.03	−0.06	−0.17	−0.07	−0.18	−0.07
$(H_2O)_2$ TS	0.39	−0.27	0.28	−0.29	0.26	−0.28
$(MeOH)_2$ complex	0.03 (0.50)	−0.07 (−0.60)	−0.17	−0.06	−0.18	−0.06
$(MeOH)_2$ TS	0.41 (0.95)	−0.27 (−0.92)	0.29	−0.28	0.29	−0.29
MeOH product	0.65	−0.27	0.62	−0.31	0.63	−0.31

[a] NPA charges for the reaction of **3a** with methanol are given in parentheses.

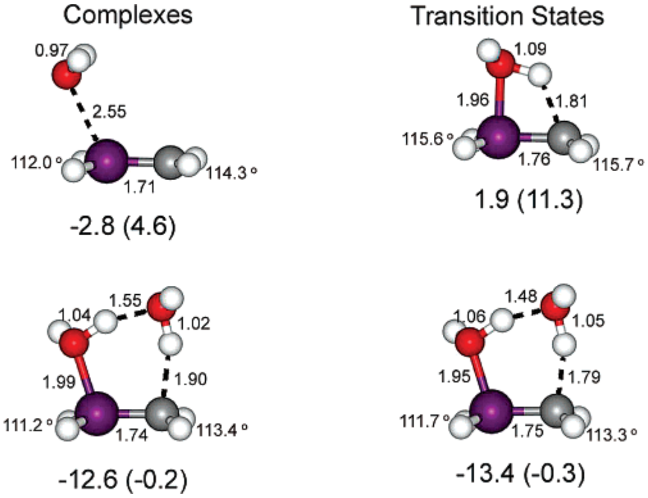


Figure 3. Calculated (MP2/6-31G(d)//MP2/6-31G(d)) structures and energies (free energies) of complexes and transition states for reaction of silene (**1a**) with monomeric and dimeric water, showing relevant bond distances and angles.

carbon atoms in the various species listed in Table 1. Atomic charges were also calculated by natural population analysis (NPA) for the reaction of silene **3a** with methanol (see Table 2) and parallel the Mulliken charges quite closely. Relevant bond distances and angles, which are presented in some detail in the Discussion section, are included in the Supporting Information.

Finally, calculations were carried out for the reactions of monomeric and dimeric water with the parent silene (**1a**) at the MP2/6-31G(d)//MP2/6-31G(d) level of theory. As in earlier studies of the addition of monomeric water to **1a**,[8] both a prereaction complex and transition state for its collapse to product were located at energies of −12.6 and −13.4 kcal mol^{-1}, respectively, relative to the isolated silene and water dimer. Energies and geometries of the complexes and transition states are shown in Figure 3. All attempts to locate a transition state for reaction of **1a** with either water or methanol dimers at the B3LYP/6-31G(d) level of theory were unsuccessful.

Discussion

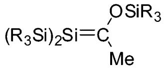
The experimental results indicate that **4** and **5** are both extremely weak electrophiles, reacting with methanol some 8−10 orders of magnitude more slowly than other, simpler silenes that have been studied to date.[4,25−27] The calculations confirm the expectation that the polarities of the Si═C bonds in **4** and **5** are similar to that reported previously for the model compound **3a** ($\Delta(t) = 0.05$ e at MP2/6-31G(d)//B3LYP/6-31G(d), where $\Delta(t)$ is the calculated total Mulliken charge on Si minus that on C); this can in turn be compared to the corresponding $\Delta(t)$ values of 0.88 e and 1.32 e for **1a** and **2a**, respectively.[8] The calculated (B3LYP/6-31G(d)) free energies of activation for addition of water to the three model compounds increase in the order **2a** (3.7 kcal mol^{-1}) < **1a** (8.7 kcal mol^{-1}) < **3a** (19.7 kcal mol^{-1}),[8] in good qualitative agreement with the trend in the second-order rate constants for reactions of MeOH with **2b** ($k_{MeOH} = 1.3 \times 10^{10}$ M^{-1} s^{-1}),[11] **1b** ($k_{MeOH} = 4.4 \times 10^{9}$ M^{-1} s^{-1}),[6] and **4** ($k_{MeOH} < 50$ M^{-1} s^{-1}) in hexane at ambient temperatures. As will be discussed in more detail below, the computational results indicate a difference of only 1.2 kcal mol^{-1} between the calculated enthalpic barriers for the addition of a single molecule of MeOH to **3a** and **4**, despite the fact that the latter carries much bulkier substituents. This suggests that the low reactivity of **4** toward this alcohol is due primarily to the electronic effects of the substituents, and confirms the link between electrophilic reactivity and Si═C bond polarity.

The effects of Si═C bond polarity are also known to affect the regiochemistry and kinetics of the [2 + 2]-dimerization of silenes, although the effects on the rate constant for the process are already known to be substantially smaller than those on nucleophilic addition reactions.[4] For example, the relatively polar silenes **12a**, **1b**, and 1,1-dimethylsilene (**13**) undergo head-to-tail dimerization with rate constants close to the encounter-controlled limit in solution or the gas phase,[28−30] whereas the nonpolar analogue **14b** dimerizes with head-to-head regiochemistry and a rate constant of $k_{dim} = 2.6 \times 10^{7}$ M^{-1} s^{-1} in cyclohexane at 27 °C.[31] The calculated Mulliken $\Delta(t)$ value for the model compound **14a** is even negative, −0.26 e.[8] The value of $k_{dim} \approx 0.13$ M^{-1} s^{-1} measured in the present work for the head-to-head [2 + 2]-dimerization of **4** indicates that, not surprisingly, steric effects play a much greater role than bond polarity effects on the kinetics of this reaction compared to those of nucleophilic addition.

$Ar_2Si{=}CH_2$ $Me_2Si{=}CH_2$

12 **13**

a. Ar = C_6H_5
b. Ar = 4-$F_3CC_6H_4$



$(R_3Si)_2Si{=}C(OSiR_3)Me$

14

a. R = H
b. R = Me

On the other hand, Si═C bond polarity has little or no effect on the reaction of silenes with oxygen.[4] In this case, the kinetics are controlled mainly by the radical-stabilizing effects of the substituents on the silenic carbon, because the reaction is with the triplet ground state of oxygen and hence must proceed via the initial formation of a triplet 1,4-biradical, in which one of the unpaired spins is localized on the silenic carbon (eq 4). Accordingly, C-substituted silenes show consistently higher reactivity toward oxygen than those without substituents at the

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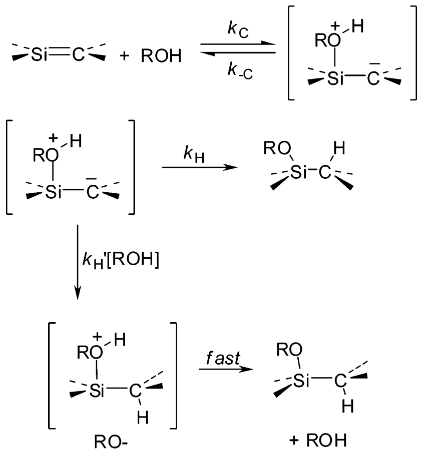
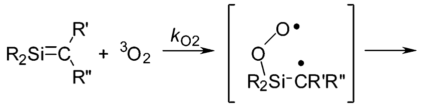
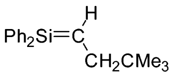
Scheme 1



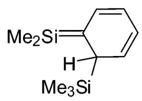
silenic carbon.[4] As might thus be expected, the value estimated here for **4** ($k_{O2} \approx 3 \times 10^5$ M^{-1} s^{-1}) is quite close to those reported by Conlin and co-workers for **14b** ($k_{O2} \approx 7 \times 10^5$ M^{-1} s^{-1})[31] and by us for **15** ($k_{O2} = 6.5 \times 10^5$ M^{-1} s^{-1})[27] under similar conditions, but is significantly lower than that reported for the transient 1-silahexatriene derivative **16** ($k_{O2} = 8.5 \times 10^8$ M^{-1} s^{-1}).[32]



(4)



15



16

With the general trends in the reactivities of **4** and **5** placed in perspective against previous results, we now turn to a more detailed analysis of the experimental results for the reaction with methanol. The mechanism of the addition of alcohols and other nucleophiles to silenes in solution has been extensively studied,[3,4,8,33] but most of the experimental results reported to date have focused on relatively short-lived derivatives with Si═C bonds of polarities similar to that in the parent molecule.[5] It is well established that for silenes of this type, the mechanism involves initial, reversible nucleophilic attack at silicon to form a zwitterionic complex that proceeds to product via rate-controlling proton transfer from the nucleophilic center to the silenic carbon (Scheme 1). The proton-transfer step occurs via competing uni- and bimolecular pathways, the latter involving catalysis by a second molecule of alcohol; the unimolecular pathway results in overall *syn*-addition and second-order kinetics (first-order in both silene and alcohol), while the catalytic pathway occurs via a protonation−deprotonation sequence and results in net *trans*-addition of RO−H and overall third-order kinetics.[26,34] As a result, this mechanism leads to a quadratic dependence of the silene decay rate constant (k_{decay}) on alcohol concentration *in polar solvents* under conditions where the two proton-transfer pathways are competitive. As well, the overall second-order pathway exhibits (small) primary kinetic isotope effects and negative activation energies. Theoretical studies of the reactions of **1a** and other polar silenes with water and alcohols are also in agreement with this mechanism.[8,33,35] It should be noted that the quadratic dependence of k_{decay} on alcohol concentration cannot always be observed; whether it can be with a given silene depends on the magnitude of the overall *second*-order rate constant and the maximum time resolution of the kinetic method employed. The relatively polar silenes that have been studied to date exhibit second-order rate constants that vary over the 10^6−10^{10} M^{-1} s^{-1} range and have all been studied using nanosecond techniques; as a result, the third-order component has generally been detected by direct kinetic measurements only for those derivatives at the lower end (10^6−10^8 M^{-1} s^{-1}) of this reactivity range.

Further evidence for the mechanism has been provided by the spectroscopic detection of ether−silene complexes with polar silenes such as **1a**,[36] **1b**,[36] 1,1-dimethylsilene (**13**),[36] the 1,1-diarylsilenes **12a** and **12b**,[37,38] and the 1-silahexatriene derivative **16**,[39] as well as by the isolation and crystallographic characterization of a stable silene−ether complex.[40] The equilibrium constant for complexation of silenes with ethers is exquisitely sensitive to substituents and follows the same trend as the rate constants for addition of MeOH and other nucleophiles.[38] For example, **12b** forms a stronger complex with THF than **12a**[38] and also reacts more rapidly with MeOH.[37,38] On the other hand, 2-neopentyl-1,1-diphenylsilene (**15**) reacts with MeOH via the same mechanism as **12a** but ~2 orders of magnitude more slowly; it does not form a detectable complex with THF.[27] Theory predicts a similar sensitivity toward complexation of silenes with water. A weak Lewis acid−base complex is an energy minimum on the calculated potential energy surface for the reaction with **1a**,[8,33,41] and the complex with the more polar derivative **2a** enjoys even greater stabilization.[8] On the other hand, no complexes can be located for the less polar silene derivatives **3a**, **17**, and **18**, which as a consequence are predicted to react *concertedly*.[8,42] As would be expected, these differences are also reflected in the transition states for the reaction, which increase in energy with decreasing Si═C bond polarity. The trends suggest that as Si═C bond polarity is reduced even moderately from the highly polar end of the scale, the mechanism for alcohol addition should change from the stepwise addition mechanism of Scheme 1 to a concerted one. Not surprisingly, no evidence for the formation of THF complexes can be observed experimentally for silenes **4** (vide supra) and **5**.[8] Clearly, these silenes are not expected to react with alcohols via the same stepwise mechanism that has been established for (substantially more) polar silenes.

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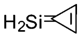
$Me_2Si{=}CMe_2$

17



18

It is clear from the kinetic results for reaction of **4** with MeOH in hexane solution (Figure 2) that the actual reaction mechanism is more complicated than one in which a single molecule of methanol adds in concerted fashion across the Si=C bond, since such a mechanism would be expected to result in an approximately linear dependence of k_{decay} on alcohol concentration over the range of concentrations studied in this experiment. In fact, such a mechanism would be expected to reveal itself in a plot of k_{decay} vs [ROH] that exhibits *downward* curvature because methanol and other alcohols self-associate in hydrocarbon solvents, existing as mixtures of monomer, hydrogen-bonded dimers, and higher (hydrogen-bonded) oligomers.[43,44] This association equilibrium is normally expressed in terms of two equilibrium constants, one for formation of dimers from the monomer and one for the formation of trimers, which are grouped together with higher oligomers. This is detailed in eq 5, where K_2 and K_3 are the equilibrium constants for formation of the dimer $(MeOH)_2$ and trimer $(MeOH)_3$, respectively, from the monomeric form. Plots of the concentrations of monomeric, dimeric, and trimeric MeOH as a function of bulk alcohol concentration in hexane solution at 23 °C, calculated from equilibrium constants ($K_2 = 38.8\ M^{-1}$; $K_3 = 97.9\ M^{-1}$) extrapolated from the data of Landeck and co-workers,[43] illustrate the point particularly concisely and are shown in the Supporting Information. They strongly suggest the kinetic data of Figure 2 to be inconsistent with a mechanism involving concerted reaction of the monomeric form of the alcohol with **4** and **5**.

$$\mathrm{MeOH} \xrightleftharpoons{K_2\,[\mathrm{MeOH}]} (\mathrm{MeOH})_2 \xrightleftharpoons{K_3\,[\mathrm{MeOH}]} (\mathrm{MeOH})_3 \qquad (5)$$

On the other hand, plots of k_{decay} versus the calculated concentrations of MeOL dimers (L = H or D) are linear for both silenes, as shown in Figure 4. The slopes of the plots are the absolute second-order rate constants for reactions of the silenes with the dimeric form(s) of the alcohol (eq 6): $k_{(MeOH)_2} = 40 \pm 3\ M^{-1}\ s^{-1}$ and $k_{(MeOD)_2} = 23.6 \pm 1.2\ M^{-1}\ s^{-1}$ for **4** and $k_{(MeOH)_2} = 0.79 \pm 0.08\ M^{-1}\ s^{-1}$ for **5**. The ratio of the rate constants for reaction of $(MeOH)_2$ and $(MeOD)_2$ with **4** affords an isotope effect $k_H/k_D = 1.7 \pm 0.2$. It is interesting to note that the plots of k_{decay} versus either the bulk or methanol dimer concentrations are both linear for silene **5**; this is expected because the concentration of methanol dimers is approximately linearly related to the bulk concentration over the 0.06−0.3 M concentration range (see Supporting Information). It should also be noted that a deviation of ±10% in the extrapolated values of the equilibrium constants results in a change of 10−20% in the rate constants, which better defines the uncertainties in the values. Nevertheless, we consider the error in the isotope effect to be smaller than this, since the equilibrium constants for oligomerization of the protiated and deuterated alcohol in hexane are quite similar.[43] The isotope effect on the rate constant for reaction of **4** with $(MeOH)_2$ is small but clearly a primary one, indicating that proton transfer from oxygen to the silenic carbon occurs in the rate-controlling step of the reaction. The data are consistent with either a concerted mechanism or a stepwise one involving the initial (reversible) formation of a silene−$(MeOH)_2$ complex, with product formation occurring in a second (rate-controlling) step. The transition state for the product-forming step in either mechanism is envisaged as structure **19**.

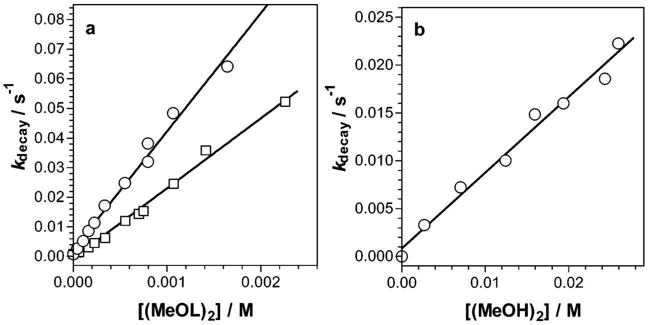
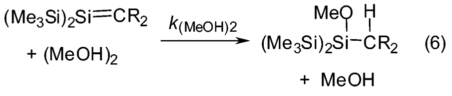
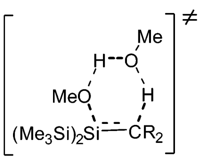


Figure 4. Plots of k_{decay} vs the concentration of dimeric MeOL (L = H, ○; L = D, □) for silenes **4** (a) and **5** (b) in hexane solution at 23−25 °C. The solid lines represent the linear least-squares fits of the data.



$$(Me_3Si)_2Si{=}CR_2 + (MeOH)_2 \xrightarrow{k_{(MeOH)2}} (Me_3Si)_2Si(OMe){-}CR_2H + MeOH \qquad (6)$$



19

While the data for **4** and **5** in hexane are thus consistent with reaction of the dimeric form of the alcohol with the Si=C bonds in these molecules, it should be noted that this mechanism is kinetically indistinguishable from that of Scheme 1 (with $k_H \ll k_H'[MeOH]$), in which reaction is initiated by the formation of a complex between the monomeric form of the alcohol, and the complex proceeds to product via protonation−deprotonation by a second molecule of (monomeric) alcohol. As mentioned above, this mechanism is thought to be responsible for the formation of anti-addition products in the reaction of cyclic silenes with alcohols.[26,34] To the extent that such a mechanism involves the formation of an ion pair in the rate-controlling (anti-protonation) step, it can most likely be ruled out in nonpolar solvents. The involvement of dimers and/or higher oligomers has been proposed previously to explain similar kinetic effects on the reactions of alcohols with carbenium ions[45] and carbenes[46−52] in nonpolar solvents, and on the 1,2-additions of water, alcohols, and/or amines with isocyanates[53] and ketenes,[54]

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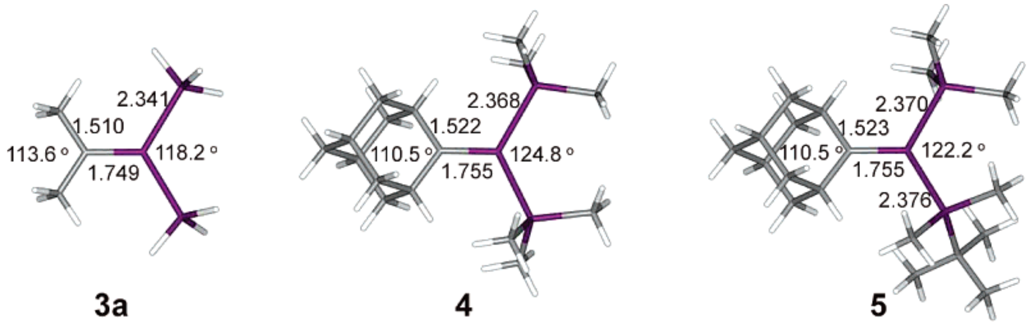

Figure 5. Calculated (B3LYP/6-31G(d)) structures of silenes **3a**, **4**, and **5**, showing relevant bond distances and angles.

and is supported by theoretical calculations in a number of cases.[53,55−57] Similar behavior has been observed for siloxycarbenes and related carbocations in polar solvents (in which alcohol oligomerization does not occur at submolar concentrations) and was interpreted in terms of a two-step, nucleophilic attack/proton-transfer mechanism analogous to that of Scheme 1 for electrophilic silenes.[58]

We have investigated the dimer addition mechanism in detail using computational methods, comparing the energetics associated with the addition of water and methanol monomers and the corresponding H-bonded dimers to the Si═C bonds in **3a**, **4**, and **5** at the B3LYP/6-31G(d) level of theory. To check the reliability of the DFT method for distinguishing between the two possible reaction pathways, we have also performed ab initio MP2/6-31G(d) calculations on the reactants and transition states for reactions of **3a** with water and methanol in their monomeric and dimeric forms. As can be seen from the data listed in Table 1, the DFT and ab initio calculations for **3a** agree quite closely. The effect of a larger basis set on the calculated results for **3a** was also tested. Activation barriers calculated at the B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) level are ∼5−6 kcal/mol higher than the corresponding B3LYP/6-31G(d) values, but the differences are roughly the same for both the monomer- and dimer-addition pathways. Use of the larger basis set has relatively small effects on the H_2O and MeOH complexation energies (see Table 1) and leads to significantly smaller BSSEs, as expected. Finally, IRC calculations were carried out for reaction of the water dimer with silene **3a**, confirming the reaction pathway. We conclude from the results of the higher level calculations for **3a** that the B3LYP/6-31G(d) level of theory is appropriate for studying the reaction mechanisms under consideration in this work.

Comparison of the calculated structures of **3a**, **4**, and **5** (see Figure 5) shows a very slight elongation of the Si═C, C−C, and Si−Si bond distances, modest contraction of the C−C−C bond angles, and a widening of the Si−Si−Si single bond angles in the adamantylidenesilanes compared to the corresponding structural features in the model compound (**3a**). The differences in the bond angles are most significant but seem quite reasonable, considering the differences in the sizes of the trialkylsilyl substituents in **4** and **5** compared to that of the SiH_3 groups in **3a**, and the structural characteristics of the adamantyl groups that comprise the C-termini of the Si═C bonds in **4** and **5**. The calculated Mulliken charges at the silenic Si (+0.03) and C (−0.01) atoms in **3a** agree quite closely with those reported earlier[8] and are indicative of a very nonpolar Si═C bond compared to that in the parent molecule, in which the charges at Si and C are +0.32 and −0.56, respectively, at the same level of theory.[8] Interestingly, the corresponding charges in **4** (Si, −0.14; C, −0.01) and **5** (Si, −0.16; C, −0.01) indicate a reversal in Si═C bond polarity in these compounds, compared to that in **3a**, and a change in the nucleophilic site from carbon to silicon. While a similar result was obtained previously with the Brook silene **14a**, a natural bond order (NBO) analysis afforded different results, indicating the bond polarization to be in the same sense as in the parent silene (although considerably weaker);[8] comparison of the Mulliken and NPA charges for **3a** (Table 2) suggests that the same is likely to be true of **4** and **5.** This is consistent with the regiochemistry of alcohol additions to **4**, **5**, and silenes of the type modeled by **14a**.[2,3] The main inferences to be taken from the Mulliken charge analysis are that the Si═C bonds in **4** and **5** are of similar or even lower polarity than that in **3a**, and they are also more electron rich. This should result in a lower electrophilicity of the Si═C bonds in these compounds, consistent with experimental observation, and might also be indicative of a certain amount of *nucleophilic* character.

As in the earlier theoretical study,[8] no indication of a stabilized complex between monomeric H_2O and **3a** could be found. In contrast, complexes between **3a** and monomeric MeOH and the H-bonded dimers of both water and methanol were located, with energies (ΔE) of −3.0, −6.7, and −6.3 kcal mol^{-1}, respectively, relative to the silene and corresponding ROH species; complexes were also located for **4** and **5** in all four cases. It should be noted that the relatively large stabilization energies of the complexes appear to be mostly due to basis set superposition errors (BSSEs) present in the calculations. Indeed, if corrections for BSSE are included, the energy of the **4**−H_2O complex becomes slightly positive (0.3 kcal mol^{-1}), which might suggest that the complex is an artifact of basis set superposition error and does not correspond to a true energy minimum. However, previous experience has shown that use of the counterpoise method[24] for calculating basis set superposition errors usually overestimates them, and sometimes does not improve the calculated relative energies systematically.[59,60] The

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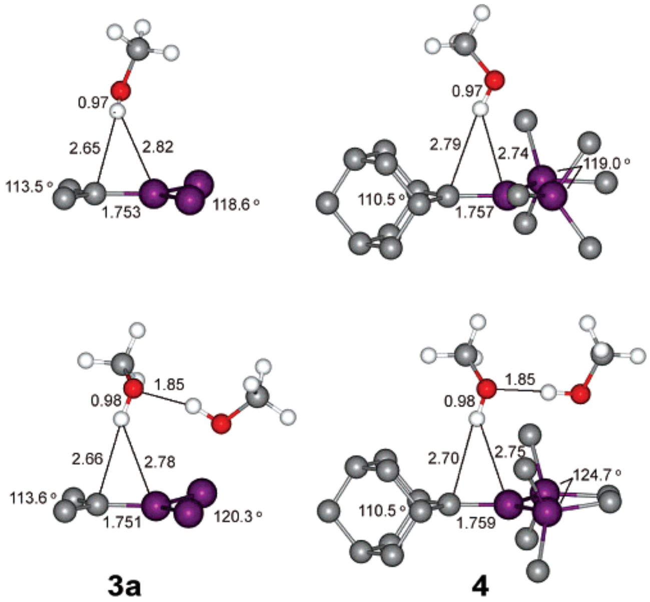

Figure 6. Calculated (B3LYP/6-31G(d)) structures of the complexes of **3a** and **4** with MeOH and $(MeOH)_2$, showing relevant bond distances and angles.

stabilization energies of the **5**−H_2O complex and the silene−MeOH complexes for all three silenes remain slightly negative even after correction for basis set superposition errors (Table 1).

Figure 6 illustrates the B3LYP/6-31G(d) geometries of the complexes of monomeric and dimeric MeOH with **3a** and **4**, with the relevant bond angles and distances indicated. The most striking aspect of the structures of these species is the orientation of the ROH component with respect to the silene, consistent with a weak hydrogen-bonding interaction between the ROH component and the Si═C bond *and no interaction between oxygen and silicon*. This contrasts with the Lewis acid−base interaction between silicon and the ROH oxygen that characterizes the complexes of alcohols and water with the parent silene[8,33,35] (see Figure 3) and other relatively polar derivatives.[8] Interestingly, the structures are strikingly similar to that reported by Veszpremi et al. for the complex of ethylene with water.[33] The calculations indicate somewhat greater stabilization of the complexes with **4** and **5** than those with **3a**, which is consistent with the indication from the Mulliken charges that the Si═C bonds in these compounds are somewhat more electron-rich than that in **3a** (vide supra). In all three cases, the ROH dimer−silene complexes are significantly stabilized relative to the corresponding ROH monomer−silene complexes, which is consistent with the higher acidity of the dimeric form of ROH compared to that of the monomer. The Si═C centered bond distances and angles in the complexes are nearly identical to those in the free species in all cases. Slight elongation of the O−H bonds is evident in the complexes compared to those in the free species, with the differences being slightly larger in the $(ROH)_2$ complexes. The main change that occurs upon complexation is a slight increase in negative charge density in the Si═C bond, and it is generally more pronounced in the $(ROH)_2$ complexes (see Table 2); the changes are small, with the main increase in negative charge occurring at the silenic carbon atom in most cases.

Inspection of the calculated transition-state energies for addition of monomeric and dimeric ROH to the three silenes (Table 1) indicates substantially lower activation energies for reaction with the dimeric forms of H_2O and MeOH in all three cases, predicting even negative values for addition of water and methanol dimers to the model compound **3a**. The differences for all three silenes are quite pronounced, with the activation energies for dimer-addition ranging from 12.7 to 9.2 kcal mol^{-1} lower than those for monomer addition in the case of water and 11.5 to 5.7 kcal mol^{-1} lower in the case of methanol, throughout the series of silenes **3a**, **4**, and **5**. The activation energy for addition of monomeric water to **3a** ($\Delta E = 10.1$ kcal mol^{-1}) is almost identical to those found for the corresponding reactions of H_2O with **4** ($\Delta E = 9.9$ kcal mol^{-1}) and **5** ($\Delta E = 10.1$ kcal mol^{-1}), indicating there to be no steric effect on the reaction with monomeric H_2O. The activation energies for addition of monomeric MeOH are quite similar to those for addition of H_2O, but show a small regular variation between **3a** ($\Delta E = 9.2$ kcal mol^{-1}) and **5** ($\Delta E = 10.8$ kcal mol^{-1}). The spread continues to increase with increasing steric bulk in the substrate, to differences of 3.5 and 7.4 kcal mol^{-1} between the activation energies for addition of $(H_2O)_2$ and $(MeOH)_2$, respectively, to **3a** and **5**. In each case, the activation energy for reaction of **4** is intermediate between the two extremes, and slightly closer to the value obtained for **5**. A regular trend is also evident in the differences between the activation energies for addition of monomeric and dimeric MeOH to the three silenes, diminishing in size as one proceeds from the least hindered derivative (**3a**; $\Delta(\Delta E) \approx 11.5$ kcal mol^{-1}) to the most hindered (**5**; $\Delta(\Delta E) \approx 5.7$ kcal mol^{-1}), with that for **4** ($\Delta(\Delta E) \approx 7.8$ kcal mol^{-1}) falling in between.

Figure 7 shows the calculated structures of the transition states for addition of MeOH and $(MeOH)_2$ to **3a** and **4**, along with those of the final products of the reactions in their minimum energy (anti) conformations. As would be expected considering the calculated 55−60 kcal mol^{-1} overall reaction exothermicities, they are all decidedly reactantlike; the Si═C and O−H bond distances are elongated by only ∼0.05 and ∼0.1 Å compared to their values in the reactants, while the developing C−H and Si−O bonds are still considerably longer than those in the final products. Interestingly, the Si−O bond lengths in all four species are considerably closer to their final equilibrium values than are the C−H bond lengths, which is consistent with the notion from the Mulliken charge analysis that these silenes are somewhat more nucleophilic than electrophilic. In the transition states for reaction with the dimeric substrates, the two rupturing O−H bonds are of roughly the same length, while the hydrogen bonds linking the two moieties have contracted by ∼0.4 Å from their values in the silene−$(ROH)_2$ complexes. The Mulliken charges indicate the changes in polarization at the transition state to be similar to those found with ROH additions to more polar silenes, with silicon bearing substantial positive charge and carbon bearing significant negative charge. While the relevant bond lengths and angles are still a considerable distance from their final values in the products, the redistribution of charge is nearly complete at the transition state. The reduced strain in the cyclic six-membered transition state for ROH-dimer addition compared to that in the four-membered transition state for monomer addition allows for greater C−H/Si−O bond development at a lower cost in terms of O−H bond

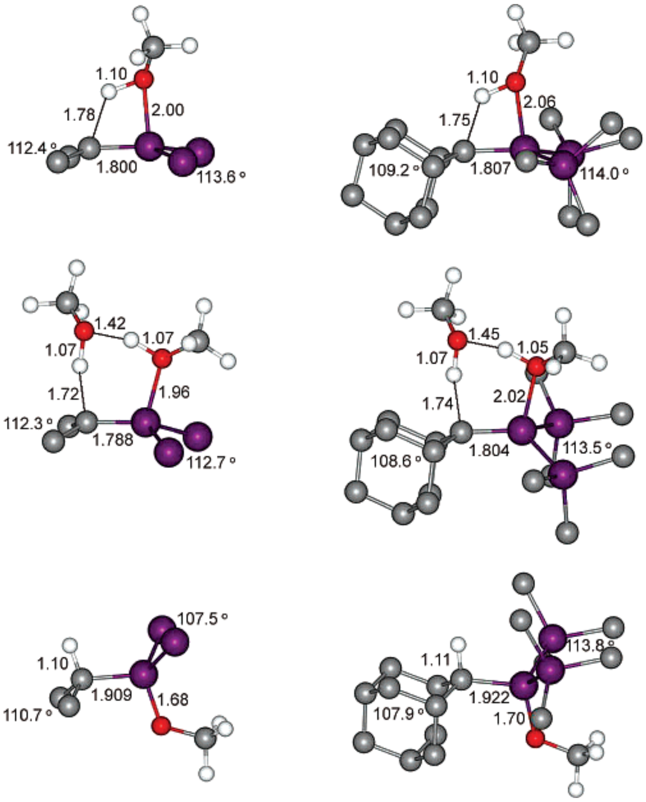

Figure 7. Calculated (B3LYP/6-31G(d)) structures of the transition states and products of reaction of **3a** and **4** with MeOH and $(MeOH)_2$, showing relevant bond distances and angles.

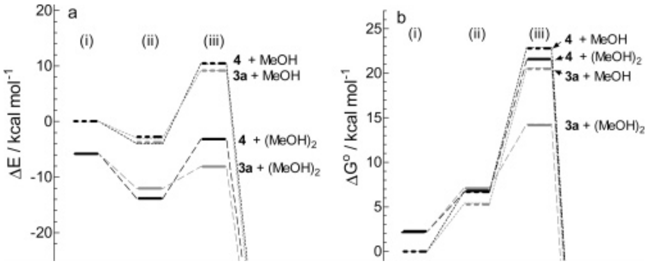

Figure 8. Calculated (B3LYP/6-31G(d)) energies (ΔE; a) and standard Gibbs free energies ($\Delta G°$; b) of (i) reactants, (ii) complexes, and (iii) transition states in the reactions of **3a** with MeOH (gray - - -) and $(MeOH)_2$ (gray — —) and of **4** with MeOH (black - - -) and $(MeOH)_2$ (black — —). Energies are referenced to the free silenes and two isolated MeOH molecules in all cases. Note that the H-bonded dimer addition pathways are offset from the monomer pathways by the energy and free energy of dimerization of MeOH ($\Delta E = -5.8$ kcal mol^{-1} and $\Delta G° = +2.2$ kcal mol^{-1}).

rupture, and hence a lower-energy transition structure. Judging from the fact that similar effects are observed in ROH additions to other multiply bonded systems,[53,56,57] the phenomenon appears to be a general one. Indeed, reaction of the parent silene (**1a**) with dimeric water is predicted to proceed with *no* barrier at the MP2/6-31G(d) level of theory (Figure 3), in contrast to the 1.9 kcal mol^{-1} activation energy for addition of the monomer.[8]

Figure 8 summarizes the B3LYP/6-31G(d) energies for the addition of monomeric and dimeric MeOH to **3a** and **4**; those for reactions of **5** with the two forms of the alcohol are similar to the corresponding values for **4** and have been omitted for clarity. The variations in the free energies of activation for both water and methanol addition, and the differences between the monomer and dimer reaction pathways, are considerably smaller than the corresponding variations in the enthalpies, because the entropies of activation for addition of dimeric ROH are significantly more positive than for addition of the monomers. Nevertheless, the trends are the same as those in the ΔE values in all cases, verifying the higher predicted reactivities of all three silenes toward the dimeric form of ROH compared to that toward the monomeric form. It should be noted that in both cases, the dimer reaction pathway begins at higher free energy than the monomer pathway; this difference persists in the H-bonded complexes but then reverses as the reactions proceed to their respective transition states. The complexes are predicted to possess significantly higher free energies than the reactants, in which case they should not play a kinetically significant role in these reactions; certainly, the experiments carried out in the present work neither support nor rule out their possible intermediacy in the reactions of **4** and **5** with MeOH in hexane solution.

It is interesting to note that the calculated free energies predict **5** to be roughly 40 times less reactive than **4** toward $(MeOH)_2$, but of similar reactivity toward addition of the monomeric alcohol. The former agrees remarkably well with the ~50-fold difference in the experimental rate constants for reaction of the dimeric alcohol with the two silenes in hexane solution.

Summary and Conclusions

1,1-Bis(trimethylsilyl)-2-adamantylidenesilane (**4**) reacts with methanol and methanol-O*d* up to 10 orders of magnitude more slowly than other transient silenes that have been studied previously but exhibits "normal" reactivity toward oxygen ($k \approx 3 \times 10^5$ M^{-1} s^{-1} at 25 °C). Silene **4** decays with pure second-order kinetics in rigorously degassed hexane solution at 23 °C and with an absolute rate constant of $k \approx 0.13$ M^{-1} s^{-1}, which is associated with head-to-head dimerization. Plots of k_{decay} vs [MeOL] (L = H or D) exhibit positive curvature over the 0−0.02 M concentration range, which is shown to be consistent with a mechanism involving reaction of the silene with the hydrogen-bonded *dimer* of the alcohol ($k = 40 \pm 3$ M^{-1} s^{-1}; $k_H/k_D = 1.7 \pm 0.2$). The stable silene analogue **5** appears to react via the same mechanism, and a rate constant of $k = 0.79 \pm 0.08$ M^{-1} s^{-1} for reaction with methanol (dimers) has been determined.

The mechanism for addition of water and methanol to **4**, **5**, and the model compound 1,1-bis(silyl)-2,2-dimethylsilene (**3a**) has been studied in detail at the B3LYP/6-31G(d) level of theory, with corroboration from higher-level calculations on the latter compound. The results of the DFT calculations indicate that (1) the Si═C bonds in these molecules are significantly less polar than that in the parent compound ($H_2Si{=}CH_2$, **1a**) and (2) they do not form Lewis acid−base complexes with water or methanol of the type characteristic of the parent compound or other, more polar, silene derivatives. Rather, the calculations have located weak *hydrogen-bonded* complexes with monomeric and dimeric water and methanol, suggesting that these silenes possess borderline *nucleophilic* character. Calculated activation energies for the addition of monomeric H_2O and MeOH to **3a**, **4**, and **5** are similar and significantly higher than for the parent silene, which suggests that the low reactivity of silene **4** with monomeric methanol in solution is mainly the result of the electronic effects of the substituents and not steric effects. The activation energy for reaction of **3a** with the MeOH dimer is predicted to be ~11.5 kcal mol^{-1} lower than that for reaction with the monomeric form. The differences are less pronounced in the cases of **4** and **5** (7.8 and 5.7 kcal mol^{-1}, respectively), but are nevertheless consistent with the results for the model compound. These differences are also reflected in the calculated free energies of activation for the three silenes, and correlate well with the experimentally determined absolute rate constants for reaction of methanol dimers with **4** and **5**. In particular, the calculations predict **5** to be ~40 times less reactive than **4** toward $(MeOH)_2$ in the gas phase, which can be compared with the ~50-fold difference exhibited by the absolute rate constants for reaction of **4** and **5** in hexane solution.

The lower activation energy and free energy for reaction of hydrogen-bonded ROH dimers relative to those for monomeric ROH addition is also predicted for reaction of the parent compound (**1a**) with water and, hence, appears to be general. There is, however, no experimental kinetic evidence that yet exists in support of the theoretical prediction. This is because for the relatively polar silene derivatives that have been studied experimentally the monomeric addition pathway is itself so fast that it dominates reactivity in the (millimolar) ROH concentration ranges that have been studied, where the lifetime of the silene is on the order of a few hundred nanoseconds or greater. For the dimer-addition pathway to be detected in kinetic experiments with these substantially more reactive compounds, measurements on the nanosecond or subnanosecond time scale will be necessary.

The dimer-addition mechanism is unlikely to be kinetically observable in polar solvents such as acetonitrile, especially at concentrations lower than ~0.5 M where self-association of methanol is unimportant due to the vastly superior H-bond accepting properties of the solvent.[58] Unfortunately, the reaction of **4** with MeOH in MeCN is too slow to be studied in this solvent, where the lifetime is on the order of ~2 ms due (presumably) to quenching by reaction with the solvent. While it is evident that the lifetime in (nearly) neat methanol solution is controlled by reaction with the alcohol solvent (provided it is scrupulously deoxygenated), the full form of the rate law under these conditions cannot be determined; thus, little mechanistic information can be derived, other than to say that the observation of a significant solvent isotope effect demands that proton transfer be involved in the rate-controlling step for reaction. It is possible that the substantially more polar solvent promotes a further change in mechanism, perhaps to one in which reaction is initiated by protonation of the Si═C bond, akin to the Markovnikov addition mechanism in alkene chemistry. Future work from our laboratories will address this intriguing possibility in more detail.

Experimental Section

^1H NMR spectra were recorded on a Bruker AV600 spectrometer in C_6D_6 or cyclohexane-d_{12} solution and were referenced to the peak due to residual protons in the solvent. Ultraviolet absorption spectra and kinetic determination on time scales longer than one second were recorded on a Varian Cary 50 spectrometer. Low-resolution mass spectra and GC/MS analyses were determined using a Hewlett-Packard 5890 series II gas chromatograph equipped with a HP-5971A mass selective detector and a SPB-5 capillary column (30 m × 0.25 m i.d.; 1.0 μm; Supelco, Inc.). Steady-state photolyses were carried out in a Rayonet photochemical reactor (Southern New England Ultraviolet Co.) equipped with three or more RPR-2537 (254 nm) lamps.

Cyclohexane-d_{12} (Cambridge Isotope Laboratories, Inc.), benzene-d_6 (Cambridge Isotope Laboratories, Inc.), *n*-butylamine (Aldrich), methanol (Aldrich), and methanol-O*d* (Aldrich) were of the highest purity available and were used as received from the suppliers. Hexane (BDH Omnisolv) was distilled from sodium/potassium amalgam, while tetrahydrofuran (HPLC Grade; Caledon) and acetonitrile (HPLC grade; Caledon) were dried by passage through columns of activated alumina using a SolvTek solvent purification system. 1,1,2,2,3,3-Hexakis(trimethylsilyl)spiro[(4,4′-adamantane)trisilacyclobutane] (**7**), 1,1,2,2-tetrakis(trimethylsilyl)dispiro[3,3′,4,4′-biadamantane-1,2-disilacyclobutane] (**6**), and 1-*tert*-butyldimethylsilyl-1-trimethylsilyl-2-adamantylidenesilane (**5**) were synthesized as described previously.[13,16,17] The sample of **7** used in photolysis experiments was purified by several recrystallizations from hexane, and was of 98% or greater purity as determined by ^1H NMR spectroscopy.

Steady-State Photolysis of 7 in the Presence of Methanol. A 0.02 M solution of **7** in cyclohexane-d_{12} was placed in a quartz NMR tube, and the tube was capped with a rubber septum. The solution was deoxygenated with dry argon for 20 min, and then methanol (0.05 M) was added via syringe. The solution was photolyzed for ~7 min (~10% conversion) with three RPR-2537 lamps, with periodic monitoring by ^1H NMR spectroscopy. The photolysis produced equal amounts of 2-[bis(trimethylsilyl)methoxysilyl]adamantane (**10**), which was identified in the crude reaction mixture by comparison to previously reported data,[14] and a second product that was identified as 2,3-bis(trimethylsilyl)-2-methoxy-1,1,1,4,4,4-hexamethyltetrasilane (**11**) on the basis of the following spectroscopic data: ^1H NMR (C_6D_{12}) $\delta = 0.23$ (18H, s), 0.24 (18H, s), 3.52 (3H, s), 3.55 (1H, s); ^{29}Si NMR (C_6D_{12}) $\delta = -15.5$, -11.1, 11.0, 12.7; GC/MS (EI) *m/z*: 380 (3), 365 (17), 307 (6), 291 (13), 276 (5), 233 (6), 217 (14), 205 (20), 202 (46), 187 (9), 175 (13), 157 (17), 143 (10), 131 (14), 117 (15), 101 (7), 89 (9), 73 (100), 59 (29). The same compound is formed as the major silicon-containing product of photolysis of disilacyclobutane **6** (0.02 M) in C_6D_{12} containing MeOH (0.05 M).

The quantum yield for formation of **10** and **11** was estimated by merry-go-round photolysis of deoxygenated solutions of **7** (0.022 M) and 1,1-diphenylsilacyclobutane (Ph_2SCB; 0.06 M) in cyclohexane-d_{12} containing methanol (0.22 M) and dichloromethane (0.028 M) as internal standard, in a Rayonet photochemical reactor equipped with three RPR-2537 low-pressure Hg lamps. The photolyses were monitored at time intervals between 0 and ~35% conversion of **7** by 600 MHz ^1H NMR spectroscopy. The quantum yields for the formation of **10** and **11** from **7** were calculated from the relative slopes of concentration vs time plots for the formation of the two compounds and methoxymethyldiphenylsilane ($Ph_2MeSiOMe$) from Ph_2SCB (see Supporting Information) and the reported quantum yield of the latter ($\Phi = 0.21 \pm 0.03$).[61] The slopes of the plots were: **10**, 0.000580 ± 0.000044; **11**, 0.000586 ± 0.000032; $Ph_2MeSiOMe$, 0.000895 ± 0.000161.

Steady-State Photolysis of 7 in the Absence of Added Reagents. A 0.01 M solution of **7** in hexane (~3 mL) was placed in a 1 cm × 1 cm Suprasil quartz cell equipped with a Teflon stopcock. The solution was degassed with six freeze/pump/thaw cycles, and the cell was backfilled with argon and sealed. The solution was photolyzed for 3 min with 12 RPR-2537 lamps, resulting in the formation of **4** in a concentration of ~0.0004 M, based on the static absorbance of the solution at 340 nm ($\epsilon \approx 5000$ dm^3 mol^{-1} cm^{-1}).[17] The solution was then allowed to stand for 4 days at 24 °C. The hexane was evaporated under reduced pressure, and the contents of the cell were dissolved in C_6D_6 and placed in a NMR tube. The ^1H NMR spectrum showed singlets at δ 0.512 and 0.446 due to **7**, a prominent singlet at δ 0.382 which is tentatively ascribed to oligomerization products of disilene **8**, and two weak resonances at δ 0.395 and 0.441, which were shown to be due to **6** by spiking the mixture with a small amount of an authentic sample.

Determination of the Rate Constants for Reaction of 4 with Methanol and Methanol-O*d* in Hexane at 23 °C. A 0.002 M solution

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of **7** in hexane (2 mL) was placed in a 7 mm × 7 mm Suprasil quartz cell that was capped with a septum. The solution was deoxygenated with a continuous stream of argon for 20 min, and then photolyzed for 30 s with twelve RPR-2537 lamps. Aliquots of either methanol (0.25 M) or methanol-O*d* (0.25 M) in hexane were added with a microliter syringe. The solution was then shaken vigorously, and the absorbance at 320 nm was monitored as a function of time by UV/vis spectrophotometry. Rate constants for consumption of **4** (see Supporting Information) were then determined by nonlinear least-squares fitting of the data to single exponential decays.

Determination of the Rate Constant for Reaction of 5 with Methanol in Hexane at 23 °C. A solution of **5** (∼0.0002 M) in hexane (2 mL) was made up in a nitrogen-flushed glovebag, placed in a 7 mm × 7 mm Suprasil quartz cuvette that was capped with a rubber septum. The solution was deoxygenated with a continuous stream of argon for 20 min, and the cell was removed to the atmosphere. Methanol was added as the neat liquid with a microliter syringe in appropriate amounts to achieve concentrations in the 0.03−0.2 M range. The solution was then shaken, and the absorbance at 320 nm was monitored as a function of time by UV spectrophotometry.

Laser Flash Photolysis. Laser flash photolysis experiments employed the pulses produced from a Lambda Physik Compex 120 excimer laser filled with F_2/Kr/Ne mixtures (248 nm; 25 ns; 90−110 mJ), and a Luzchem Research mLFP-111 laser flash photolysis system, modified as described previously.[62] Solutions of **7** were prepared at concentrations of $\sim 2.0 \times 10^{-4}$ M [such that the absorbance at the excitation wavelength (248 nm) was ∼0.7] and were flowed through a 7 mm × 7 mm Suprasil flow cell from a calibrated 100-mL reservoir. Solutions were deoxygenated with a stream of dry nitrogen or argon. Solution temperatures were measured with a Teflon-coated copper/constantan thermocouple inserted directly into the flow cell. Transient decay and growth rate constants were calculated by nonlinear least-squares analysis of the absorbance-time profiles using the Prism 3.0 software package (GraphPad Software, Inc.) and the appropriate user-defined fitting equations, after importing the raw data from the Luzchem mLFP software. Reagents were added directly to the reservoir by microliter syringe as aliquots of standard solutions. Rate constants were calculated by linear least-squares analysis of decay rate/concentration data (5−7 points) that spanned as large a range in transient decay rate as possible. Errors are quoted as twice the standard deviation obtained from the least-squares analyses. Transient absorption spectra were recorded in point-by-point fashion over four selected time windows after the laser pulse.

Computational Methods. The GAUSSIAN 03[63] series of programs was used for all calculations. All molecules were fully optimized using the hybrid density functional[64,65] B3LYP[66,67] level of theory with the 6-31G(d) basis set. Transition state structures were located using the TS routine of Gaussian 03. Frequency calculations were performed at the same level for all stationary points, to identify them as minima or saddle points. Detailed IRC analysis for addition of a single water molecule to silene **1a** was performed in ref 8; similar analysis was carried out here for the reaction of water dimer with silene **3a** and confirmed the reaction pathway. Mulliken and NPA charges were calculated at the B3LYP/6-31G(d) level. Energies were also calculated at the B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) and MP2/6-31G(d)//MP2/6-31G(d) levels of theory for reactants and transition states for the reactions of silene **3a**, for comparison to the B3LYP/6-31G(d) values. Basis set superposition errors (BSSEs) were estimated using the counterpoise corrections method.[24] Except for the B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) values, all calculated energies include corrections for unscaled zero-point vibrational energies. Free energies were calculated at 298 K.

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Supporting Information Available: Quantum yield and kinetic data; plots of the calculated concentrations of mono-, di-, and oligomeric MeOH as a function of bulk MeOH concentration in hexane at 23 °C; figures showing the optimized geometry and Cartesian coordinates of all calculated molecules; tables of absolute and relative calculated energies; full citation for ref 63. This material is available free of charge via the Internet at http://pubs.acs.org.

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