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Arrhenius Parameters for the Addition of Phenols to the Silicon−Silicon Double Bond of Tetramesityldisilene[†]

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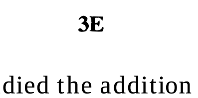
We have measured, *for the first time for a disilene*, the Arrhenius activation energies (E_a) and preexponential factors (ln A) for an addition reaction. The addition reactions of both p-$CH_3OC_6H_4OH$ and p-$F_3CC_6H_4OH$ to tetramesityldisilene (**1**) have positive Arrhenius activation energies of 13.7 and 9.7 kcal/mol, respectively, and highly negative entropies of activation of −34.9 and −45.3 eu, respectively (ln A = 13.0 and 7.8 M^{-1} s^{-1}, respectively). The more negative $\Delta S^{\ddagger}$ value for p-$F_3CC_6H_4OH$ is consistent with a more ordered type of addition in this case. The rates of addition of phenols to **1** ($k \approx 10^{-4}-10^{-2}$ M^{-1} s^{-1}) are dramatically slower, i.e., by a factor of ca. $10^{9}-10^{12}$, compared with the rates of addition of alkyl alcohols to the less hindered (*E*)- and (*Z*)-1,2-dimethyl-1,2-diphenyldisilenes (**3***E* and **3***Z*) and 1,2,2-trimethyl-1-phenyldisilene (**4**) ($k \approx 10^{7}-10^{8}$ M^{-1} s^{-1}).[5] Steric protection of the Si═Si bond in **1** by the bulky mesityl substituents is probably responsible for this large reactivity difference. Competition experiments support this conclusion; EtOH reacts with **3***E* only 1.5 times faster than *i*-PrOH and 19 times faster than *t*-BuOH (similar competition ratios were measured for **3***Z* and **4**),[5] while with **1** EtOH reacts 11 times faster than *i*-PrOH and at least 4000 times faster than *t*-BuOH. Ab initio quantum mechanical calculations (at MP3/6-31G*//HF6-31G*) for the addition of CH_3OH and of CF_3OH to $Me_2Si{=}SiMe_2$ reveal the following: for CH_3OH, the rate-determining step is the nucleophilic attack of the alcohol on the disilene and the reaction proceeds via a zwitterionic alcohol-disilene intermediate; for CF_3OH, the rate-determining step is concerted and the alcohol is involved both as a nucleophile and as an electrohile, with proton transfer being well advanced in the transition state.

Introduction

Following the synthesis of the first stable disilene, tetramesityldisilene (**1**), in 1981,[1] many reactions of disilenes have been reported.[2] The wide variety of reactions known for disilenes makes them an important building block in organosilicon chemistry.[2] However, information about the mechanisms of these reactions is still rather limited.[2a] For example, *activation parameters have not yet been reported even for a single addition process to a disilene.*

Among the reactions of disilenes the 1,2-addition of alcohols to the Si═Si bond is the most studied, but even the mechanism of this reaction is not fully understood.[2] Most of the available data on this reaction mechanism come from studies on the stereochemistry of the addition reaction. West et al. studied the addition of alcohols to the long-lived (*E*)-1,2-di-*tert*-butyl-1,2-dimesityldisilene (**2**),[3,4] and Sekiguchi, Maruki, and Sakurai (SMS) studied the addition of alcohols to the transient disilenes (*E*)- and (*Z*)-1,2-dimethyl-1,2-diphenyldisilene (**3***E* and **3***Z*) and 1,2,2-trimethyl-1-phenyldisilene (**4**).[5] More recently we studied the stereochemistry of the addition of p-$CH_3OC_6H_4OH$ to **2**.[6] All these studies supported a



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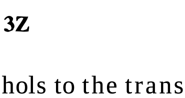

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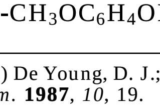
Mes = mesityl = 2,4,6-trimethylphenyl



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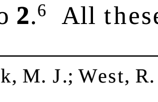

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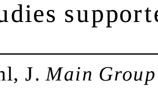

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[†] This paper is dedicated to Prof. Paul von Ragué Schleyer.

(1) West, R.; Fink, M. J.; Michl, J. *Science* **1981**, *214*, 1343.

(2) For recent reviews on disilenes see: (a) Sakurai, H. In *The Chemistry of Organic Silicon Compounds, Part 2*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: New York, in press. (b) Okazaki, R.; West, R. *Adv. Organomet. Chem.* **1996**, *39*, 231. (c) Weidenbruch, M. *Coord. Chem. Rev.* **1994**, *130*, 275. (d) Tsumuraya, T.; Batcheller, S. A.; Masamune, S. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 902. (e) Raabe, G.; Michl, J. in *The Chemistry of Organic Silicon Compound*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; p 1015. (f) West, R. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1201. (g) Raabe, G.; Michl, *Chem. Rev.* **1985**, *85*, 419. (h) West, R. *Pure Appl. Chem.* **1984**, *56*, 163.

(3) De Young, D. J.; Fink, M. J.; West, R. Michl, J. *Main Group Met. Chem.* **1987**, *10*, 19.

(4) Budaraju, J.; Powell, D. R.; West, R. *Main Group Met. Chem.* **1996**, *19*, 531.

(5) Sekiguchi, A.; Maruki, I.; Sakurai, H. *J. Am. Chem. Soc.* **1993,** *115*, 11460.

(6) Apeloig, Y.; Nakash, M. *Organometallics* **1998**, *17*, 1260.

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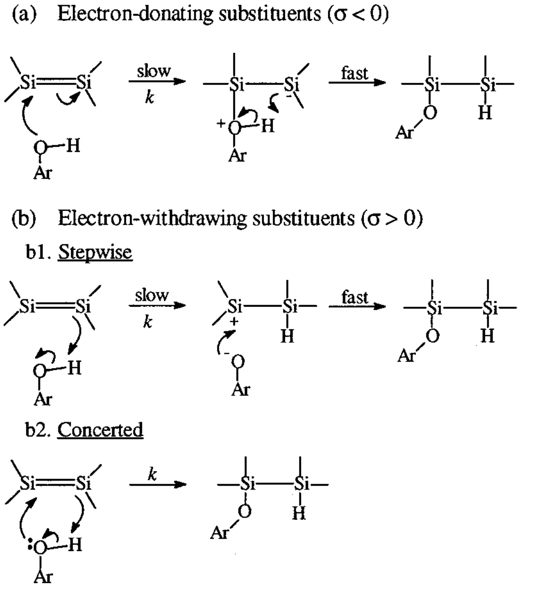
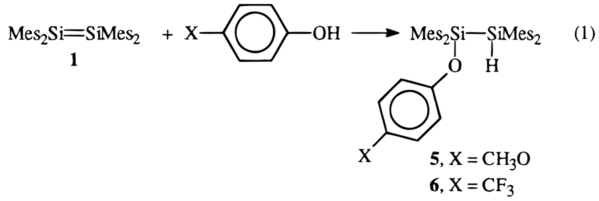
Scheme 1. Schematic Mechanisms for the Addition Reactions of Substituted Phenols to Disilene 1



stepwise mechanism involving a rate-determining nucleophilic attack of the alcoholic oxygen on the coordinatively unsaturated silicon center forming a zwitterionic intermediate, which reacts further either by intramolecular proton migration or in some cases by intermolecular proton abstraction from a second molecule of alcohol,[4,5] to yield the final product. This mechanism is shown schematically (for a phenol and intramolecular proton migration) in Scheme 1a.

Recently, we studied the kinetics of the addition of *para*- and *meta*-substituted phenols to **1**.[7] The resulting Hammett plot had a concave shape with a minimum for the parent phenol (i.e., all the substituted phenols, either with electron-donating or with electron-withdrawing substituents, react faster than PhOH), indicating a change in mechanism, i.e., from a rate-determining nucleophilic step (followed by H transfer), in the case of electron-donating substituents (Scheme 1a), to a rate-determining electophilic step in the case of electron-withdrawing substituents (Scheme 1b).[7] Kinetic isotope effect measurements supported this interpretation.[7] Thus, the small k_H/k_D isotope effect of 0.71, measured in the addition of p-$CH_3OC_6H_4OD$ to **1**, is fully consistent with a rate-determining nucleophilic attack, while the large k_H/k_D isotope effect of 5.27, measured in the addition of p-$F_3CC_6H_4OD$ to **1**, strongly supports a mechanism in which a phenolic H (or D) is transferred to **1** in the rate-determining step. This study provided the first evidence that an alcohol can add electrophilically to a disilene.

To gain further information on the mechanism of addition of phenols to tetramesityldisilene (**1**) we have measured, *for the first time for any disilene either stable or transient,* the Arrhenius parameters for such a reaction. We choose to study the addition reactions of two phenols (eq 1): p-$CH_3OC_6H_4OH$, which represents the group of phenols having electron-donating substituents (relative to H) and which follows the mechanism shown in Scheme 1a,[7] and p-$F_3CC_6H_4OH$, which represents the group of phenols having electron-withdrawing substituents (relative to H) and which follows the mechanisms shown in Scheme 1b.[7] We have also carried out for **1** competition experiments between EtOH, *i*-PrOH, *t*-BuOH, and p-$CH_3OC_6H_4OH$. Additional information was gained through ab initio quantum mechanical calculations for the addition reactions of CH_3OH and CF_3OH to $Me_2Si{=}SiMe_2$.



Results

Measurement of Activation Parameters. The kinetics of the addition of p-$CH_3OC_6H_4OH$ and of p-$CF_3C_6H_4OH$ to **1** in dry benzene was followed spectroscopically by measuring the decay rate of the absorption (A) at 420 nm (corresponding to the Si=Si bond in **1**[1]), following the procedures described previously.[7] A large excess of the phenol was used to enforce pseudo-first-order kinetics. The addition reactions were found to be first-order in both the disilene and the phenol.[7] At all temperatures used, an excellent linear correlation (r = 0.999) was obtained between the experimental measurements and the first-order kinetic law (plot of $\ln(A_t - A_\infty)$ vs time, where A_t and A_∞ denote the absorbance at time t and at the end of the reaction, respectively). The second-order rate constants, k, for the addition of p-$CH_3OC_6H_4OH$ and of p-$F_3CC_6H_4OH$ to **1** at the various temperatures used are summarized in Table 1. The corresponding Arrhenius plots are linear (r = 0.9999 and 0.9997 for p-$CH_3OC_6H_4OH$ and p-$F_3CC_6H_4OH$, respectively). Table 2 lists the corresponding Arrhenius activation energies (E_a) and pre-exponential factors (ln A), along with the corresponding enthalpies ($\Delta H^{\ddagger}$), entropies ($\Delta S^{\ddagger}$), and free energies ($\Delta G^{\ddagger}$) of activation. The addition products obtained in reaction 1, **5** and **6**, were isolated and characterized (see Experimental Section).

Competition Experiments. Competition experiments (see Experimental Section) in benzene show that the rates of addition of alcohols to **1** decrease in the following order (relative rates are given in parentheses): EtOH (77) > *i*-PrOH (7) > p-$CH_3OC_6H_4OH$ (1) ≫ *t*-BuOH (0.02).[8]

Discussion

The addition reactions to **1** of both p-$CH_3OC_6H_4OH$ and p-$F_3CC_6H_4OH$ have positive Arrhenius activation

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(7) Apeloig, Y.; Nakash, M. *J. Am. Chem. Soc.* **1996,** *118,* 9798.

(8) The relative rate for *t*-BuOH is based on the following considerations: The addition product of *t*-BuOH to **1** could not be detected even in the presence of a 1000 molar excess of *t*-BuOH (5 M *t*-BuOH compared with 0.005 M of **1**). Under these conditions only the water addition (>95%) product is observed (resulting from the traces of water present in the reaction mixture[9]). In the reaction of **1** with *i*-PrOH (under the same experimental conditions) traces of water addition product (estimated to be less than 5% of the product mixture) were detected. On the basis of these observations, we estimate that *t*-BuOH reacts with **1** *at least* 361 times ((95:5):(5:95) = 361)) slower (this is a lower limit) than *i*-PrOH (as stated above, we do not have proof that *t*-BuOH reacts at all with **1** under these conditions).

Table 1. Rate Constants at Various Temperatures for the Reaction of p-$CH_3OC_6H_4OH$ and of p-$F_3CC_6H_4OH$ with 1

phenol	$10^4k \pm SD^a$ (M^{-1} s^{-1})	T (K)	phenol	$10^4k \pm SD^a$ (M^{-1} s^{-1})	T (K)
p-$CH_3OC_6H_4OH$	10.7 ± 0.7	348	p-$F_3CC_6H_4OH$	19.2 ± 0.4	348
	6.4 ± 0.5	339		13.4 ± 0.2	339
	3.6 ± 0.2	330		9.1 ± 0.1	330
				5.9 ± 0.1	321

[a] SD = standard deviation.

Table 2. Energies and Entropies of Activation in the Addition of p-$CH_3OC_6H_4OH$ and of p-$F_3CC_6H_4OH$ to 1

phenol	$E_a{}^a \pm SD^b$ (kcal/mol)	ln $A \pm SD^b$ (M^{-1} s^{-1})	$\Delta S^{\ddagger\,c} \pm SD^b$ (eu)	$\Delta G^{\ddagger\,d}$ (kcal/mol)
p-$F_3CC_6H_4OH$	9.7 ± 0.2	7.8 ± 0.2	−45.3 ± 0.7	24.8
p-$CH_3OC_6H_4OH$	13.7 ± 0.2	13.0 ± 0.2	−34.9 ± 0.6	25.1

[a] $\Delta H^\ddagger = E_a - RT$, where $RT = 0.6$ kcal/mol at 298 K. [b] SD = standard deviation. [c] At 348 K. [d] $\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$; calculated for $T = 348$ K.

energies and highly negative entropies of activation (Table 2). The energies of activation, E_a, are relatively high, 13.7 and 9.7 kcal/mol, respectively; the corresponding free energies of activation, $\Delta G^\ddagger$, of 25.1 and 24.8 kcal/mol, respectively (Table 2), are substantially higher due to the contribution of entropy. These values are substantially higher than the $\Delta G^\ddagger$ value of only 6.6 kcal/mol, which can be estimated for the addition of EtOH to $Me_2Si{=}SiMePh$ by using the Eyring equation and the experimental rate constant of 1.9×10^8 M^{-1} s^{-1} at 293 K.[5]

Comparison of our kinetic results with those of Sekiguchi, Maruki, and Sakurai shows that the rates of addition of phenols to **1** ($k \approx 10^{-4}-10^{-2}$ M^{-1} s^{-1})[7] are dramatically slower, i.e., by a factor of ca. 10^9-10^{12} (equivalent to a difference of ca. 12−17 kcal/mol at 25 °C in the corresponding activation free energies), compared with the rates of addition of alkyl alcohols to the less hindered (*E*)- and (*Z*)-1,2-dimethyl-1,2-diphenyldisilene (**3***E* and **3***Z*) and 1,2,2-trimethyl-1-phenyldisilene (**4**) ($k \approx 10^7-10^8$ M^{-1} s^{-1}).[5] This huge reactivity difference between the addition of phenols to **1** and the addition of alkyl alcohols to **3***E*, **3***Z*, and **4** is not due to the different nucleophiles used in the two studies. Thus, *i*-PrOH and EtOH react with **1** only 7 and 77 times faster than p-$CH_3OC_6H_4OH$, respectively. It is also unlikely that the electronic effects of the disilene substituents, e.g., phenyl or methyl in **3** or **4** vs mesityl in **1** are responsible for the dramatic $10^9 - 10^{12}$ reactivity difference. We therefore attribute the large reactivity difference between **1** and **3** (or **4**) to the larger steric bulk of the mesityl substituents in **1**, which shield the Si═Si bond from attack. This steric shielding was always believed to be the major factor which allowed the isolation of **1**,[1] but the huge rate deceleration which results from the shielding of the Si═Si bond by the mesityl groups was determined quantitatively only in this study. This conclusion is further supported by the different relative reactivities of alkyl alcohols in their addition to **1** and to the transient disilenes **3***E*, **3***Z*, and **4**.[5] Thus, EtOH reacts with **3***E* only 1.5 times faster than *i*-PrOH and only 19 times faster than *t*-BuOH (similar relative rates were obtained for **3***Z* and **4**[5]), while in the reaction with **1**, which is substantially more sensitive than **3***E* to steric effects, EtOH reacts 11 times faster than *i*-PrOH and at least 4000 times faster than *t*-BuOH. Thus, **1** is much more selective than **3** (or **4**), especially toward bulky nucleophiles such as *t*-BuOH.

The very large difference in the reactivity of **1** compared with that of **3** and **4** makes it of interest to study the rates of addition to disilenes having substituents with sizes intermediate between those present in **3** or **4** and in **1**, e.g., $MeMesSi{=}SiMesMe$, $(Me_3Si)MesSi{=}SiMes(SiMe_3)$, $PhMesSi{=}SiMesPh$, etc. Such studies, in addition to their mechanistic interest, will be of practical importance as they will allow one to predict the stability of disilenes toward nucleophilic attack and to identify which are the smallest protecting groups which will still allow the isolation of a stable disilene.

The only other available activation parameters for an addition reaction to multiple bonds to silicon are those reported recently by Bradaric, Leigh and co-workers[10] for the addition of MeOH, *t*-BuOH, and acetic acid to a silene, $Ph_2Si{=}CH_2$, for which $E_a = -2.5$, −0.4 and 1.9 kcal/mol, respectively, and $\Delta S^\ddagger$ (at 296 K) = −27, −24, and −13 eu, respectively.[10] The activation energies measured for $Ph_2Si{=}CH_2$ are again much lower than for disilene **1**, and in the reaction with MeOH and *t*-BuOH they are actually negative, indicating that the proton transfer step is slower than the reversible formation of the alcohol−silene complex and that both steps are enthalpically lower in energy than the starting materials.[10]

The entropies of activation that we measured for the addition of p-$CH_3OC_6H_4OH$ and p-$F_3CC_6H_4OH$ to **1** are −34.9 and −45.3 eu, respectively (see Table 2). These high negative $\Delta S^\ddagger$ values are expected for a bimolecular transition state[11] and indicate that these reactions proceed via relatively ordered transition states. The fact that $\Delta S^\ddagger$ for the addition of p-$F_3CC_6H_4OH$ to **1** is by 10.4 eu more negative than for the addition of p-$CH_3OC_6H_4OH$ to **1** points to a more ordered and compact transition state structure in the addition of p-$F_3CC_6H_4OH$ to **1**. Note, however, that as we compare $\Delta S^\ddagger$ values for reactions which follow different mechanisms (i.e., nucleophilic vs electrophilic),[7] the above conclusion is not unequivocal. Yet we believe that the above conclusion is valid since the ab initio calculations described below show that the transition state structure in the addition of the electron-poor alcohol CF_3OH to $Me_2Si{=}SiMe_2$ is more compact than that in the addition of CH_3OH to $Me_2Si{=}SiMe_2$.

Molecular Orbital Calculations. To gain a better understanding of the mechanism for the addition reactions of alcohols and phenols to disilenes, we have also carried out ab initio quantum mechanical calculations for the addition of CH_3OH and of CF_3OH to Me_2-

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(9) Although the solvent and alcohols were carefully dried and Schlenk techniques were used in all manipulations, some traces of water apparently remain in the solvent, the alcohol, or remains absorbed on the glassware. The fact that even under these carefully controlled conditions some water addition product was still detected indicates that water is substantially more reactive toward **1** than alcohols.

(10) Bradaric, C. J.; Leigh, W. J. *J. Am. Chem. Soc.* **1996** *118*, 8971.

(11) For example, a $\Delta S^\ddagger$ value of −34 eu was measured in the somewhat related nucleophilic vinylic substitution reaction of piperidine with $(PhCO)MeC{=}CHCl$. For other $\Delta S^\ddagger$ values in nucleophilic vinylic substitution reactions see: Rappoport, Z. *Advances in Physical Organic Chemistry*; Gold, V., Ed; Academic Press: London, 1969; Vol. 7, p 1.

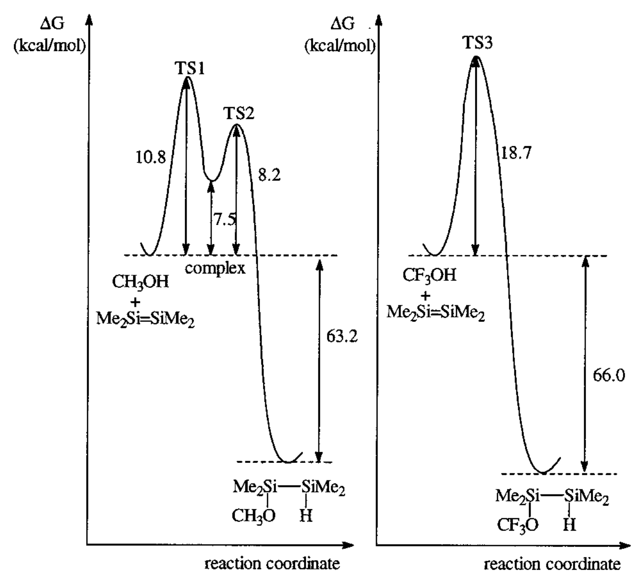

Figure 1. Calculated free energy reaction profiles at MP3/6-31G*//HF-6-31G* for the addition of CH_3OH and of CF_3OH to $Me_2Si{=}SiMe_2$.[12]

$Si{=}SiMe_2$. In the calculations CH_3OH serves as a model for an electron-rich alcohol such as p-$CH_3OC_6H_4OH$, CF_3OH serves as a model for an electron-poor alcohol such as p-$F_3CC_6H_4OH$, and $Me_2Si{=}SiMe_2$ serves as a model for $Mes_2Si{=}SiMes_2$. The computational methods that were used are described in the Experimental Section.

The rate-determining step in the addition of alcohols and of phenols to disilenes is bimolecular, and therefore, entropy plays an important role. We have consequently chosen to discuss and analyze the calculated reaction paths in terms of the calculated free energy differences, ΔG and $\Delta G^{\ddagger}$ (at 298 K), of these reactions as shown in Figure 1.[12] The calculated structures (at HF/6-31G*) of the rate-determining transition states for the addition of CH_3OH to $Me_2Si{=}SiMe_2$, TS1 (and for the product determining transition state, TS2), and for the addition of CF_3OH to $Me_2Si{=}SiMe_2$, TS3, are shown in Figure 2.

The calculated (HF/6-31G*) $\Delta S^{\ddagger}$ for the rate-determining step in the addition of CH_3OH to $Me_2Si{=}SiMe_2$ (TS1) is −37.6 eu, and for the addition of CF_3OH to $Me_2Si{=}SiMe_2$ (TS3) $\Delta S^{\ddagger}$ is −43.5 eu. These values are in nice agreement with the experimental entropies of activation that were measured for the addition of p-$CH_3OC_6H_4OH$ and p-$F_3CC_6H_4OH$ to **1**, of −34.9 and −45.3 eu, respectively (see Table 2). This good agreement adds credibility to the calculations.

The results of the calculations support in general the mechanisms proposed in Scheme 1. Thus, we find a change in the mechanism of alcohol addition to $Me_2Si{=}SiMe_2$ on going from CH_3OH to CF_3OH, i.e., from a rate-determining nucleophilic attack for CH_3OH to a rate-determining electrophilic attack for CF_3OH. These theoretical findings are in agreement with the change in mechanism found experimentally for the addition to **1** of p-$CH_3OC_6H_4OH$ (nucleophilic mechanism) and p-$F_3CC_6H_4OH$ (electrophilic mechanism).[7] In addition, the calculations show that the addition of both CH_3OH and CF_3OH to $Me_2Si{=}SiMe_2$ are highly exothermic, in agreement with the experimental observation that addition reactions of alcohols to disilene **2** are not reversible.[4,6] The calculations reveal another important mechanistic difference between the addition to $Me_2Si{=}SiMe_2$ of CH_3OH and of CF_3OH. The calculations predict a stepwise mechanism for the addition of CH_3OH to $Me_2Si{=}SiMe_2$ (as shown in Scheme 1a), but the addition of CF_3OH to $Me_2Si{=}SiMe_2$ is calculated to proceed via a concerted-asynchronous mechanism (as shown in mechanism b2 in Scheme 1). Thus, for CF_3OH the concerted electrophilic mechanism is favored over a stepwise electrophilic addition (mechanism b1 in Scheme 1).

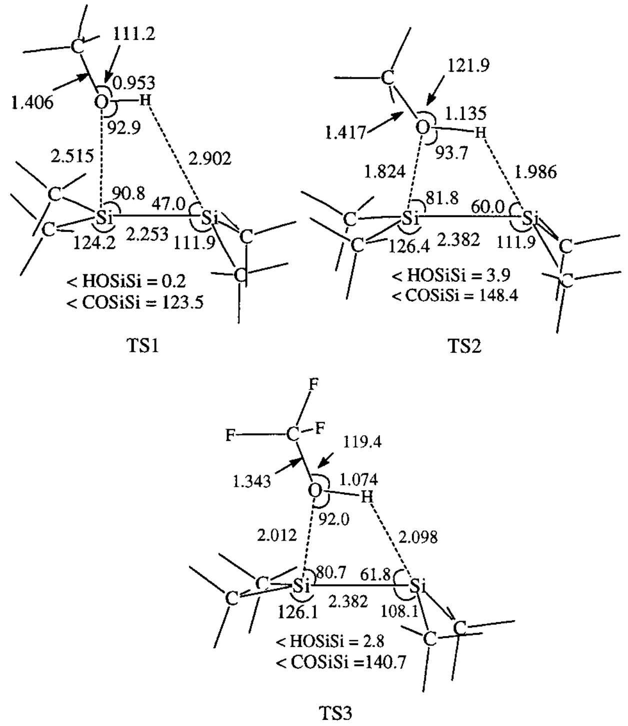

Figure 2. Calculated structures (HF/6-31G*) of the rate-determining transition states for the addition of CH_3OH and of CF_3OH to $Me_2Si{=}SiMe_2$.

For the addition of CH_3OH to $Me_2Si{=}SiMe_2$ we find computationally a stepwise mechanism (see Figure 1). In the rate-determining nucleophilic step the alcoholic oxygen attacks the silicon atom of the disilene (TS1 in Figure 2) to form an alcohol−disilene zwitterionic complex. The second step, which has a lower barrier (i.e., TS2), involves a proton transfer step to form the final addition product. The calculated free energy of activation ($\Delta G^{\ddagger}$) of the rate-determining step in the addition of CH_3OH to $Me_2Si{=}SiMe_2$ is 10.8 kcal/mol. This value is somewhat higher than the value of 6.6 kcal/mol measured for the addition of EtOH to $Me_2Si{=}SiMePh$ (see above).[5] The small difference between the experimental and the calculated $\Delta G^{\ddagger}$ values may result from several reasons: (a) a better stabilization by the phenyl group of the zwitterionic intermediate formed in the addition of the alcohol to $Me_2Si{=}SiMePh$, compared with $Me_2Si{=}SiMe_2$; (b) the fact that the

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[12] Calculated according to eq 2, where ΔE is the energy difference (between the different steps in Figure 1) calculated at the MP3/6-31G*//6-31G* level and ΔS is the entropy differences (between the different steps shown in Figure 1) calculated at the HF/6-31G* level. The temperature used in eq 2 is T = 298 K.

$$\Delta G = \Delta E - T\Delta S \qquad (2)$$

calculations describe the reaction in the gas phase, which is expected to have higher $\Delta G^{\ddagger}$ values than the same reaction in solution where polar transition states can be stabilized by the solvent; (c) an inadequate level of the calculations. In any case, the calculated $\Delta G^{\ddagger}$ values for methanol addition to $Me_2Si{=}SiMe_2$ are by 14−15 kcal/mol lower than the experimental $\Delta G^{\ddagger}$ for the addition of phenols to **1**, demonstrating again the huge protecting steric effect of the mesityl groups.

In contrast to the addition of CH_3OH to $Me_2Si{=}SiMe_2$, we could not locate a stationary point for a complex between $Me_2Si{=}SiMe_2$ and CF_3OH and the calculations predict that this reaction proceeds via a one-step concerted (but asynchronous) mechanism. In the transition state of this reaction the alcohol is involved both as a nucleophile and as an electrophile, with proton transfer being well advanced (see TS3 in Figure 2).

Examination of the rate-determining transition state structures for the addition of CH_3OH to $Me_2Si{=}SiMe_2$, TS1, and for the addition of CF_3OH to $Me_2Si{=}SiMe_2$, TS3 (see Figure 2), shows that TS1 can be characterized as occurring "earlier" along the reaction coordinate than TS3. For example, in TS1 the forming Si···O bond is relatively long; $r(Si-O) = 2.515$ Å, and O−H bond cleavage is not involved ($r(O-H) = 0.953$ Å relative to 0.946 Å in CH_3OH). In TS3 the Si···O distance is significantly shorter, 2.012 Å and the O−H bond elongates considerably to 1.074 Å (the calculated O−H bond length in CF_3OH is 0.950 Å). In addition, the Si−Si bond length is shorter and the forming Si···H bond is longer in TS1 than in TS3; i.e., $r(Si-Si) = 2.253$ Å vs 2.382 Å, respectively (the calculated $r(Si-Si)$ in $Me_2Si{=}SiMe_2$ is 2.138 Å), and $r(Si\cdots H) = 2.902$ Å vs 2.098 Å, respectively. For comparison, in $(CH_3O)Me_2Si-SiMe_2H$, the addition product of CH_3OH to $Me_2Si{=}SiMe_2$, the calculated Si−O, Si−Si, and Si−H bond lengths are (HF/6-31G*): 1.662, 2.355, and 1.488 Å, respectively.

Furthermore, the transition state for the reaction of CF_3OH with $Me_2Si{=}SiMe_2$ shows a substantially advanced electrophilic character, which is practically nonexistent in the reaction of CH_3OH with $Me_2Si{=}SiMe_2$. The electrophilic character of TS3 is evident from the following evidence: (1) the relatively short Si- - -H distance of 2.098 Å indicating considerable Si−H bonding in the transition state. (2) the fact that the imaginary frequency in TS3 describes hydrogen transfer from the OH group to the disilene (in contrast to TS1 where the imaginary frequency is associated mainly with the attack of oxygen on the silicon); (3) the high calculated isotope effect k_H/k_D of 4.30 (see below).

The electrophilic character of the transition state may become even more pronounced in a significantly more bulky system where the small proton has a bigger steric advantage over the OR group, as is the case in the experimentally studied reaction of p-$CF_3C_6H_4OH$ with **1**, where we have shown that the rate-determining step is electrophilic in nature.[7]

TS2, the transition state which connects the complex and the product in the addition of CH_3OH to $Me_2Si{=}SiMe_2$, is more compact than TS1 and its structure resembles that of TS3, the main difference being that the Si···O separation is shorter in TS2 (1.824 Å) than in TS3 (2.012 Å).

We note that in all the three transition structures the COSiSi dihedral angle is in the range of 123−148°, consistent with the silicon being attacked by one of the oxygen's sp^3 lone pairs (a COSiSi dihedral angle of ca. 0 or 90° is expected if the oxygen utilizes an sp^2 or a 2p lone-pair orbital, respectively). We also note that in the three transition states the silicon atom which is attacked by the hydrogen pyramidalizes more than the silicon atom which is attacked by the oxygen.

The agreement between the calculated and experimental $\Delta S^{\ddagger}$ values and the calculated structures of the rate-determining transition states TS1 and TS3 reinforces our conclusion that, in the addition of electron-poor alcohols (and phenols) to disilenes, the transition state is more compact and ordered than in the addition of electron-rich alcohols and phenols.

The calculated k_H/k_D isotope effects for the addition of CH_3OH and of CF_3OH to $Me_2Si{=}SiMe_2$ are 0.94 and 4.30, respectively. These calculated values are in good agreement with the experimental kinetic isotope effects that we measured for the addition of p-$CH_3OC_6H_4OH$ and p-$F_3CC_6H_4OH$ to **1**, of $k_H/k_D = 0.71$ and $k_H/k_D = 5.27$, respectively.[7] This good agreement further supports the relevance of the model calculations to the experimental results.

Conclusions

The addition of substituted phenols to $Mes_2Si{=}SiMes_2$ involves relatively high activation energies and high negative entropies of activation. The entire evidence which has accumulated on these reactions shows that phenols carrying electron-donating substituents, e.g., p-$CH_3OC_6H_4OH$, add to $Mes_2Si{=}SiMes_2$ via a two-step process with a rate-determining nucleophilic attack, forming a zwitterionic intermediate. This conclusion is supported by ab inition calculations which find a similar mechanism for the addition of CH_3OH to $Mes_2Si{=}SiMes_2$. On the other hand, phenols carrying electron-withdrawing substituents, e.g., p-$F_3CC_6H_4OH$, add to $Mes_2Si{=}SiMes_2$ via a rate-determining electrophilic step in which the phenolic hydrogen is transferred to the unsaturated silicon atom. Ab initio molecular orbital calculations for the addition of CF_3OH to $Me_2Si{=}SiMe_2$ support this conclusion and predict that the reaction is concerted. It is not clear at this point if this conclusion is valid also for the addition of p-$F_3CC_6H_4OH$ to $Mes_2Si{=}SiMes_2$. Further studies, e.g., of the stereochemistry of this reaction need to be carried out in order to establish the mechanistic details of this reaction and, in particular, whether it is a two-step reaction or concerted.

Experimental Section

General Procedures. All experiments and manipulations were performed in oven-dried glassware under argon using Schlenk techniques. ^1H NMR and ^{13}C NMR spectra were collected on a Bruker EM-200 or EM-400 spectrometer. Chemical shifts are reported in parts per million; ^1H NMR and ^{13}C NMR spectra were measured in benzene-d_6 using the solvent peak as reference. High-resolution mass spectra were recorded on a Varian-Mat 711 mass spectrometer. Benzene was distilled from sodium benzophenone ketyl under argon into a dried Schlenk vessel containing Na/K alloy. The benzene was degassed and distilled prior to use. The preparation of **1** is described in the literature.[13] p-$CH_3OC_6H_4OH$ and p-$F_3CC_6H_4OH$ are commercially available. p-$CH_3OC_6H_4OH$ and p-$F_3CC_6H_4OH$ were dried in the following way: A solution of the phenol in anhydrous diethyl ether was stirred with $MgSO_4$, the solution was filtered under argon to a dried Schlenk vessel, the solvent was removed by vacuum, and the phenol was dissolved in dry benzene. Potassium (~10% molar) was added to the phenol solution to form ~10% of the corresponding phenoxide (which would trap traces of water), the solvent was removed by vacuum, and the phenol was distilled to a dried Schlenk vessel.

In the kinetic studies the progress of the reaction was monitored by use of an HP 8452A diode-array spectrophotometer. The kinetic studies were carried out in deoxygenated dry benzene, in a cuvette sealed under vacuum. ^1H NMR spectra were collected at the end of the kinetic measurements, to verify that the addition products were obtained (e.g., production of the corresponding silanol would indicate the presence of water).

Preparative Reaction of Tetramesityldisilene (1) with *p*-$CH_3OC_6H_4OH$. A 2 mL volume of a dried benzene solution of disilene **1** (0.055 mmol) and 2 mL of a dried benzene solution of p-$CH_3OC_6H_4OH$ (0.55 mmol) were mixed in a dried Schlenk vessel which was closed under vacuum. After overnight reflux the solvent and the excess of phenol were removed in a vacuum leaving a white solid, **5**. **5** was purified by chromatography on a precoated TLC plate (0.5 mm silica gel F-254), using a 15:85 CH_2Cl_2/hexane mixture as the eluent, and was characterized by ^1H NMR, ^{13}C NMR, and HRMS.

Analytical data for the addition product (**5**): ^1H NMR (C_6D_6, 200 MHz) δ 2.09 (s, 6H, p-CH_3), 2.10 (s, 6H, p-CH_3), 2.35 (s, 12H, o-CH_3), 2.38 (s, 12H, o-CH_3), 3.24 (s, 3H, p-CH_3O), 5.71 (s, 1H, SiH), 6.56 (d, 2H, $J = 0.045$ Hz, PhH), 6.67 (s, 4H, ArH), 6.72 (s, 4H, ArH), 6.75 (d, 2H, $J = 0.045$ Hz, PhH); ^{13}C NMR (C_6D_6, 400 MHz) δ 21.11 (CH_3), 24.15 (CH_3), 24.66 (CH_3), 55.05 (CH_3O), 114.72 (Ph), 119.75 (Ph), 128.97 (Ar), 129.85 (Ar), 131.19 (Ph), 133.92 (Ph), 138.74 (Ar), 139.44 (Ar), 144.68 (Ar), 145.47 (Ar), 149.69 (Ph), 154.42 (Ph); exact mass for $C_{43}Si_2H_{52}O_2$, calculated *m/e* 656.3505, found 656.3502 (M^+, 1.68%).

Preparative Reaction of Tetramesityldisilene (1) with *p*-$F_3CC_6H_4OH$. A 2 mL volume of a dried benzene solution of disilene **1** (0.055 mmol) and 2 mL of a dried benzene solution of p-$F_3CC_6H_4OH$ (0.55 mmol) were mixed in a dried Schlenk vessel which was closed under vacuum. After an overnight reflux the solvent and the excess of phenol were removed in a vacuum leaving a white solid, **6**. **6** was purified by chromatography on a precoated TLC plate (0.5 mm silica gel F-254), using 15:85 CH_2Cl_2/hexane mixture as the eluent, and was characterized by ^1H NMR, ^{13}C NMR, and HRMS.

Analytical data for the addition product (**6**): ^1H NMR (C_6D_6, 200 MHz) δ 2.07 (s, 6H, p-CH_3), 2.10 (s, 6H, p-CH_3), 2.25 (s, 12H, o-CH_3), 2.28 (s, 12H, o-CH_3), 5.68 (s, 1H, SiH), 6.64 (s, 4H, ArH), 6.67 (d, 2H, PhH), 6.70 (s, 4H, ArH), 7.16 (d, 2H, PhH); ^{13}C NMR (C_6D_6, 400 MHz) δ 21.06 (CH_3), 24.05 (CH_3), 24.57 (CH_3), 119.51 (Ph), 126.88 (Ph), 129.03 (Ar), 129.97 (Ar), 130.64 (Ph), 133.09 (Ph), 139.01 (Ar), 139.86 (Ar), 144.56 (Ar), 145.29 (Ar), 158.67 (Ph) (one of the aromatic signals and the CF_3 signal were covered under the solvent signal); exact mass for $C_{43}Si_2H_{49}OF_3$, calculated *m/e* 694.3274, found 694.3205 (M^+, 0.21%).

Competition Experiments. The addition reactions were carried out in dry benzene at room temperature under argon, using Schlenk techniques. i-PrOH:EtOH and p-$CH_3OC_6H_4$-OH:i-PrOH molar ratios of 10:1, respectively, were used. The alcohol with the higher concentration (of the two alcohols used) was in a 300 molar excess relative to **1** (to impose completion of the reaction in 8–10 h). In all experiments, 2 mL of the mixture of alcohols in dry benzene was added to a 2 mL solution of **1** (0.01 mmol) in dry benzene. The end of the reaction was determined by the disappearance of the yellow color (indicating the presence of **1**). The ratio between the two addition products was determined by the ratio in the ^1H NMR spectrum of the Si–H peaks of the corresponding alkoxysilanes.[14]

Computational Methods. Molecular orbital calculations were carried out using standard ab initio methods[15] as implemented in the Gaussian 94 series of programs.[16] The geometries of all the reactants, transition structures, intermediates, and products were optimized using restricted Hartree–Fock theory and the 6-31G* basis set. All structures were verified to be either minima or transition states by their Hessian matrixes, which have either zero (minima) or one (transition state) imaginary frequency. The vibrational frequency calculations were also used to calculate the entropies of each of the species. The total energy of each HF/6-31G* stationary point was calculated with the inclusion of electron correlation using third-order Møller–Plesset theory[17] and the 6-31G* basis set (denoted as MP3/6-31G*//HF/6-31G*). Kinetic isotope effects were calculated with the QUIVER program[18] using the HF/6-31G* force constants.

In general we find very small differences between the MP2/6-31G* and MP3/6-31G* results (and with MP3/6-311+G-(2df,p)//MP2/6-31G* results for the smaller $H_2Si{=}SiH_2 + CH_3OH$ system), and in this paper we therefore quote only the higher level MP3/6-31G* energies and believe that the results will not change significantly when higher levels of theory (which are outside our present capabilities) will be applied to these systems.

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