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Articles

Solvent-Dependent Stereoselectivity in the Addition of *p*-$CH_3OC_6H_4OH$ to (*E*)-1,2-Di-*tert*-butyl-1,2-dimesityldisilene. Evidence for Rotation around the Si−Si Bond in the Zwitterionic Intermediate

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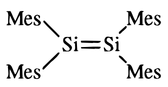
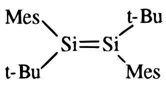
The diastereoselectivity of the addition of *p*-$CH_3OC_6H_4OH$ to (*E*)-1,2-di-*tert*-butyl-1,2-dimesityldisilene (**2**) in benzene and in THF is reported, and the mechanistic implications of the results are discussed. In both benzene and in THF the stereochemistry of the products is independent of the phenol concentration (in the range of phenol excess of 2−300 equiv). The *syn:anti* product ratio is 90:10 in benzene and of 20:80 in THF, i.e., with stereochemical preference opposite to that in benzene. The finding that the stereochemistry of the products is independent of the phenol concentration indicates that in the second step of the addition reaction intermolecular proton transfer (from a second molecule of phenol) does not occur. Thus, the *anti*-addition product results from rotation around the Si−Si bond in the zwitterionic intermediate followed by intramolecular proton transfer. The very different product ratios in benzene and in THF support the formation of zwitterionic intermediates and suggest a longer lifetime of the zwitterionic intermediates in THF than in benzene.

Introduction

Following the synthesis of the first stable disilene, tetramesityldisilene (**1**), in 1981,[1] many reactions of disilenes have been reported.[2] However, information about the mechanisms of these reactions is still rather scarce.[2a] Among the reactions of disilenes the mechanism of the 1,2-addition reaction of alcohols is the most studied, but even this mechanism is not fully understood.[2a] Addition of alcohols to (*E*)-1,2-di-*tert*-butyl-1,2-dimesityldisilene (**2**) in THF gave a 1:1 mixture of the two diastereoisomeric alkoxysilanes, suggesting a stepwise mechanism involving a zwitterionic intermediate.[3] In contrast, theoretical calculations predicted that the gas-phase addition of water to disilene proceeds via a four-center concerted transition state, leading to *syn*-addition.[4] Sekiguchi, Maruki, and Sakurai (SMS) found recently that in hexane the addition of 2-propanol and of *tert*-butanol to the transient disilenes, (*E*)- and (*Z*)-1,2-dimethyl-1,2-diphenyldisilene, occurs with high *syn*-diastereoselectivity,[5] in agreement with the calculations.[4] However, the addition of ethanol occurred with high *syn*-diastereoselectivity only at low ethanol concentrations (up to 0.85 M), but the amount of the *anti*-addition product increases as a function of ethanol concentration reaching a 1:1 mixture at ethanol concentration of 5.7 M.[5] No significant kinetic deuterium isotope effect was found when ethanol-d_1 was used. SMS concluded that the rate-determining step of the addition reaction involves a nucleophilic attack of the alcoholic oxygen on the coordinatively unsaturated silicon center, forming a four-membered zwitterionic intermediate which reacts either intramolecularly to give a *syn*-addition product



1



2

Mes = mesityl = 2,4,6-trimethylphenyl

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[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*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: New York, in press; Vol. 2. (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 Compounds*; 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, J. *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] Nagase, S.; Kudo, T.; Ito, K. In *Applied Quantum Chemistry*; Smith, V. H., Jr., Schaefer, H. F., III, Morokuma, K., Eds.; Reidel: Dordrecht, The Netherlands, 1986.

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

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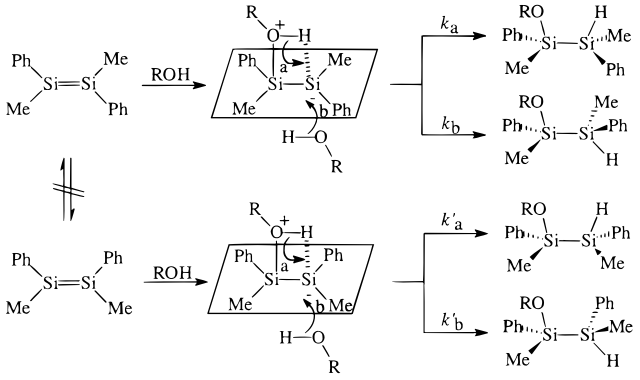
Scheme 1. Schematic Mechanism for the Addition of Alkyl Alcohols to PhMeSi=SiMePh[5]



or intermolecularly (at high alcohol concentrations) to give an *anti*-addition product (see Scheme 1).[5] This mechanism was supported recently by West et. al., who found that in benzene the addition of alcohols to **2** occurs with high *syn*-stereoselectivity, while in THF addition of EtOH leads to mixtures of diastereoisomers (in which the composition depended on the reaction conditions).[6]

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 phenol, indicating a change in mechanism from a rate-determining nucleophilic step for electron-rich phenols (relative to phenol) to a rate-determining electophilic step for electron-poor phenols (relative to phenol).[7] Kinetic isotope effects strongly supported this interpretation.[7] Since **1** is symmetric, only one product results either from *syn* or from *anti*-addition, and therefore, the interesting mechanistic question of intra- vs intermolecular proton transfer, as suggested by Scheme 1, could not be answered by our study.[7]

In this paper we report the diastereoselectivity of the addition of p-$CH_3OC_6H_4OH$ to (E)-1,2-di-*tert*-butyl-1,2-dimesityldisilene (**2**) in benzene and in THF and discuss the mechanistic implications of the results. We find that the addition of alcohols to disilenes is more complex than previously believed,[3-6] and we present, for the first time, evidence that rotation around the Si−Si bond in the zwitterioic intermediate (which is formed in the first step of the addition reaction) plays a major role in determining the stereochemistry of the products.

Results

(a) Product Study and Analysis. The addition reactions of p-$CH_3OC_6H_4OH$ to **2** were carried out under argon at 65 °C in dry benzene and in dry THF, using Schlenk techniques. In all experiments, 2 mL of the phenol solution (in either benzene or THF) was added to solid disilene **2** (0.00587 mmol, 0.003 M), the phenol being in molar excess of 2, 10, 100, and 300. The disappearance of the yellow color (which indicates the presence of disilene **2**) determined the completion of the reaction. The ratio between the two diastereoisomeric addition products (i.e., the phenoxysilanes) was determined at the end of the reaction by the ratio in the ^{1}H NMR spectrum of the Si−H hydrogens belonging to the *syn*- and *anti*-phenoxysilanes. Further heating of the reaction mixture did not change the *syn:anti* product ratio, implying that it is kinetically controlled. The stereochemistry of the *syn*-addition product (**5**) was established by X-ray crystallography and its molecular structure is shown in Figure 1. Additional crystallographic data for **5** are presented in Table 1, selected bond lengths and bond angles are summarized in Table 2, and other details are given in the Supporting Information.

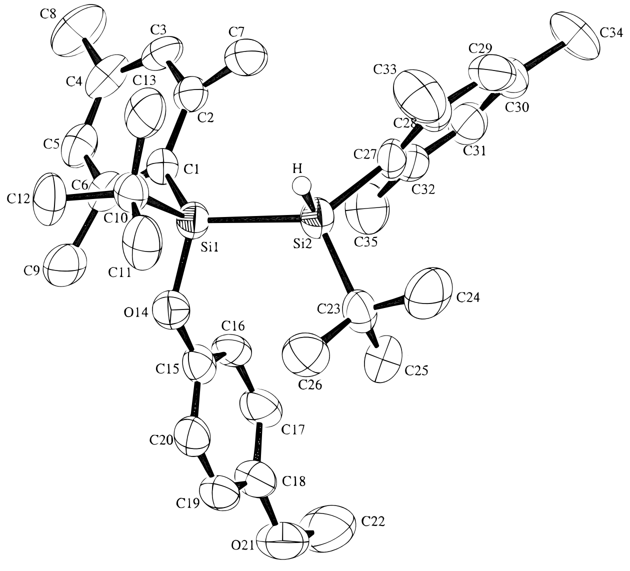


Figure 1. ORTEP diagram of **5**.

Table 1. Crystallographic Data and Structure Refinement for 5

empirical formula	$C_{33}H_{48}O_2Si_2$
fw	532.89
T, K	293
cryst system	monoclinic
space group	$P2_1/n$
a, Å	19.236(10)
b, Å	8.328(4)
c, Å	21.230(10)
β, deg	110.12(5)
V, Å^3	3193
Z	4
d(calc), g/cm?	1.108
cryst size, mm	0.20 × 0.25 × 0.35
μ(Mo Kα), mm^{-1}	0.137
F(000)	1160
2θ range, deg	2.04−24.02
scan mode	$\omega/2\theta$
scan speed, deg/min	2
scan width (ω), deg	1.1
index ranges	$-22 \le h \le 20, 0 \le k \le 9, 0 \le l \le 24$
reflcns collcd	5153
indepdt reflcns	5013
final R indices ($I > 2\sigma(I)$)	$R = 0.0939$, w$R2 = 0.1633$
goodness-of-fit on F^2	1.104
largest diff peak, e/Å^3	0.233

The Si−Si bond length in **5** is 2.426 Å. This value is only slightly shorter than in (Tip)(t-Bu)(i-PrO)Si−SiH(Tip)(t-Bu) (2.441 Å, Tip = 2,4,6-triisopropylphenyl)[6] and is intermediate between that in $Me_3Si-SiMe_3$ (2.340 Å) and t-$Bu_3Si-Si(t$-$Bu)_3$ (2.697 Å),[8] reflecting the substantial steric repulsions between the groups around the adjacent silicon groups. An unusual feature of the

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

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

(8) Sheldrick, W. S. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; p 227.

Table 2. Selected Bond Lengths (Å) and Angles (deg) in 5

Si(1)–O(14)	1.674(8)	Si(1)–Si(2)	2.426(5)
Si(1)–C(1)	1.898(7)	Si(2)–C(27)	1.903(10)
Si(1)–C(10)	1.908(8)	Si(2)–C(23)	1.924(8)
O(14)–Si(1)–Si(2)	105.8(3)	C(27)–Si(2)–Si(1)	123.0(3)
C(1)–Si(1)–Si(2)	122.7(3)	C(23)–Si(2)–S(1)	116.7(4)
C(10)–Si(1)–Si(2)	106.6(2)		
O(14)–Si(1)–Si(2)-C(23)	−6.9	C(1)–Si(1)–Si(2)–C(27)	2.5
O(14)–Si(1)–Si(2)-C(27)	130.9	C(10)–Si(1)–Si(2)–C(23)	100.4
C(1)–Si(1)–Si(2)-C(23)	−135.3	C(10)–Si(1)–Si(2)–C(27)	−121.8

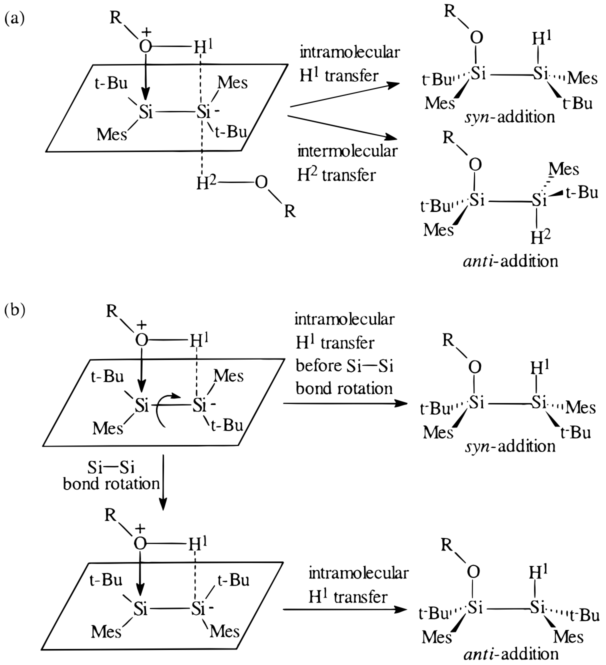
structure is the remarkable eclipsing of all the bonds around the central Si–Si bond. Thus, the C(27)Si(2)-Si(1)C(1) and the C(23)Si(2)Si(1)O(14) dihedral angles are 2.5° (indicating Mes–Mes eclipsing) and −6.9° (indicating *t*-Bu-OC_6H_4OMe eclipsing), respectively. It is likely that this unusual eclipsing of the bonds around the Si–Si bond reflects the attempt of the molecule to minimize steric interactions by placing the large *t*-Bu groups in an eclipsing position to the smallest available groups; i.e., in **5** one of the *t*-Bu groups (bonded to Si(1)) eclipses the small hydrogen atom (bonded to Si(2)) (this is probably the dominant effect) and the second *t*-Bu group eclipses the $OC_6H_4OCH_3$ group, which is smaller than mesityl (the other group present on Si(1)). This eclipsed conformation is probably sterically more favorable than one of the possible staggered conformations. A small torsion angle of 20° (but larger than in **5**) was found in the analogous (Tip)(*t*-Bu)(*i*-PrO)Si–SiH(Tip)(*t*-Bu),[6] where the Mes groups of **5** are substituted with the larger Tip groups.

Analysis of the product composition shows that the stereochemistry of the products in the addition of p-$CH_3OC_6H_4OH$ to **2**, in either benzene or THF, *is independent of the phenol concentration* (in the range of phenol excess of 2–300 equiv). *In benzene a syn:anti product ratio of 90:10 is obtained while in THF the product ratio is syn:anti 20:80*, i.e., with stereochemical preference opposite to that in benzene.

(b) Kinetic Measurements. The kinetics of the addition of p-$CH_3OC_6H_4OH$ to **2** in dry benzene was followed spectroscopically, as described previously,[7] by measuring the decay rate of the absorption (A) at 400 nm (corresponding to the Si=Si bond in **2**[9]). A large excess of the phenol (i.e., 50–6000-fold larger than that of **2**) was used to enforce pseudo-first-order kinetics. The excellent linear correlations ($r = 0.999$) obtained between the experimental measurements and the first-order kinetic law (plot of $\ln(A - A_\infty)$ vs time) and for the plot of the pseudo-first-order rate constants (k_{obs}) vs phenol concentration imply that the studied addition reactions are indeed first-order in both the disilene and the phenol.

The second-order rate constants, k, for the addition of p-$CH_3OC_6H_4OH$ to **2** is 2.33×10^{-3} M^{-1} s^{-1}, only 1.7 times larger (under the same conditions) than for the addition of p-$CH_3OC_6H_4OH$ to **1**.[7] Assuming that this rate difference results mainly from steric factors, we conclude that disilenes **1** and **2** have very similar steric demands toward the addition of p-$CH_3OC_6H_4OH$. This result and the finding that no complex is formed between **1** and THF,[10] leads us to conclude that **2** also does not form a complex with THF.

Scheme 2. Possible Modes for the Addition of Alcohols to Disilene 2



Discussion

The mechanism proposed in the literature for the addition of alcohols to disilenes involves a stepwise addition in which a zwitterionic intermediate is formed in the nucleophilic rate-determining step[2,3,5,6] and this is followed by a fast proton transfer (either inter- or intramolecular) that terminates the reaction (Scheme 1). We have shown recently that p-$CH_3OC_6H_4OH$ also follows this general nucleophilic addition mechanism.[7] According to this mechanism three competitive processes in the zwitterionic intermediates determine the diastereochemistry of the products (see Scheme 2): (1) intramolecular proton transfer; (2) intermolecular proton transfer from a second molecule of alcohol; (3) rotation around the Si–Si bond in the zwiterionic intermediate. If intramolecular proton transfer (i.e., H^1, Scheme 2) is faster than both intermolecular proton transfer (i.e., H^2) and than Si–Si bond rotation, this would lead to a *syn*-addition product (Scheme 2). An *anti*-addition product can be formed in two ways: (a) if intermolecular proton transfer (H^2) from a second molecule of alcohol (assumed to occur *anti* due to steric reasons) is faster than intramolecular proton transfer (H^1) (this is the mechanism (i.e., part a in Scheme 2) observed by previous workers);[5,6] (b) if rotation around the Si–Si bond in the zwitterioic intermediate followed by an intramolecular proton transfer is faster than intermolecular proton transfer (see part b in Scheme 2[11]).

(a) Addition in Benzene. The cis ⇌ trans equilibrium of disilene **2** in benzene at 25 °C lies mainly (98%)

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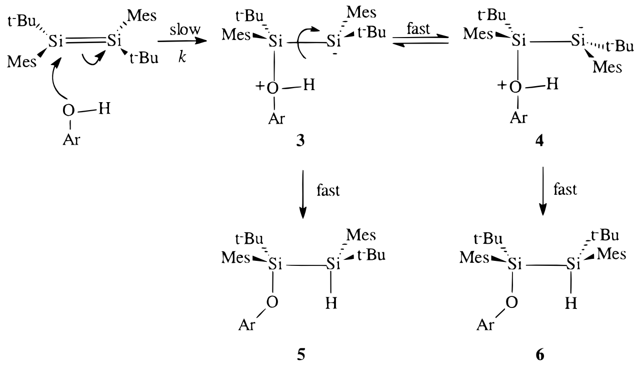
[9] Michalczyk, M. J.; West, R.; Michl, J. *J. Am. Chem. Soc.* **1984**, *106*, 821.

[10] Wind, M.; Powell, D. R.; West, R. *Organometallics* **1996** *15*, 5772.

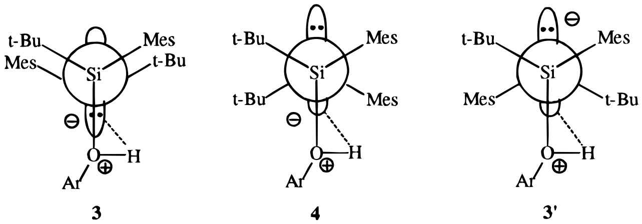
Scheme 3. Schematic Mechanism for the Addition of p-$CH_3OC_6H_4OH$ to 2



toward the trans isomer.[9] According to the Gibbs equation the cis isomer does not exceed 4% at 65 °C (our reaction temperature). Therefore, the formation of 10% of the *anti*-addition product (**6**) supports the presence of a zwitterionic intermediate (Scheme 3). The finding that the stereochemistry of the products is independent of the phenol concentration indicates that intermolecular proton transfer (from a second molecule of phenol) does not compete effectively with intramolecular proton transfer. These findings lead us to conclude that the *anti*-addition product **6** results from rotation around the Si−Si bond in the zwitterionic intermediate **3**,[11] followed by fast intramolecular proton transfer (Scheme 3). The observed *syn*:*anti* product ratio of 9:1 implies, to a first approximation, that the intramolecular trapping of **3** is 9 times faster than the rotation around the Si−Si bond. This is, to our best knowledge, *the first clear evidence that in such addition reactions rotation around the Si−Si bond in the zwitterionic intermediate affects the stereochemical outcome of the reaction.*

(b) Addition in THF. The formation of the *anti* product **6** as the major product (80%) in THF provides additional support for the existence of a zwitterionic intermediate. As the stereochemistry of the products does not depend on the phenol concentration, we conclude that also in THF *anti*-**6** results from rotation around the Si−Si bond in **3** followed by intramolecular proton transfer, both processes being faster than intermolecular proton transfer (Scheme 3). The fact that the **5**:**6** product ratio in benzene and in THF is so dramatically different, i.e., **5** is preferred in benzene while **6** is preferred in THF, suggests that the more polar THF solvent ($\epsilon = 7.4$, $E_T = 37.4$,[12] compared with $\epsilon = 2.3$ and $E_T = 34.5$[12] for benzene) stabilizes the zwitterionic intermediates **3** and **4** making them sufficiently long-lived to allow rotation around the Si−Si bond before the terminating intramolecular proton transfer occurs. The dominance of **6** in THF probably reflects the equilibrium constant of the zwitterions (**3** $\rightleftharpoons$ **4**), which is likely to be determined by steric factors, as shown clearly in the Newman projections of **3** and **4** in Chart 1. In **4** the two *tert*-butyl substituents and the two mesityl groups are more remote from each other (i.e., *gauche*-orientation) than in **3** where the mesityl and the *tert*-butyl groups are *eclipsed*. Consequently, **4** dominates the **3** $\rightleftharpoons$ **4** equilibrium. Note that release of the steric congestion in **3** by inversion about the Si^- center to give **3′** (which sterically is preferred over **4** because in **3′** there are no *t*-Bu···*t*-Bu *gauche* interactions) probably involves a much higher barrier than that for the rotation around the Si−Si bond to give **4**.[11] Furthermore, intramolecular hydrogen transfer in **3’** and **3** leads to the same (*syn*) product.[13]

Chart 1. Newman Projections of the Zwitterions 3, 4, and 3′



(c) Comparison with Previous Studies. Our conclusion that in the addition of p-$CH_3OC_6H_4OH$ to **2** (both in benzene and in THF) the *anti*-addition product results from fast rotation around the Si−Si bond in the zwitterionic intermediates is different from the conclusions reached previously for the addition of alkyl alcohols to transient disilenes in hexane[5] and to **2** in THF,[6] where the *anti*-products were attributed to an intermolecular proton transfer. A priori, the opposite could have been expected because phenol is significantly more acidic than alkyl alcohols and therefore intermolecular proton transfer could have been expected to occur faster with p-$CH_3OC_6H_4OH$ than with alkyl alcohols.

Why does intermolecular proton transfer compete effectively in the addition of EtOH to MePhSi=SiPhMe

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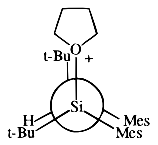
[11] Note that inversion around the Si^- center will not affect the stereochemistry of the products. In any case, inversion probably cannot compete with the other processes, as the barrier to inversion about the Si atom in R_3Si^- was estimated to be higher than 24 kcal/mol; see: Lambert, J. B.; Schultz, W. J., Jr. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; p 1007.

[12] Abraham, M. H. *Prog. Phys. Org. Chem.* **1974**, *11*, 1.

[13] A reviewer has suggested that as the THF solvent is more basic than p-$CH_3OC_6H_4OH$ (used as the nucleophile) and especially as THF is present in a very large excess, we should consider the possibility that a complex between **2** and THF (despite the fact that such a complex was not observed for **1** in the solid state[6]) plays a role in determining the stereochemistry of the phenol addition reaction. According to this reasoning the **1**·THF complex will be protonated to give the relatively long-lived intermediate Mes(*t*-Bu)HSi−SiMes(*t*-Bu)·THF^+ (**7**) which would reach equilibrium by rotation around the Si-Si bond (as well as by fast THF exchange), before being captured by the phenol. Assuming that **7** adapts the same conformation as **5**, i.e., with the large *tert*-butyl groups eclipsing the hydrogen and the relatively small phenoxyl group on the adjacent silicon, than the most stable conformation of **7** is expected to be **7a**.



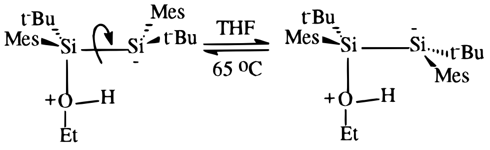
7a

Backside attack of the phenol on **7a** leads to the *anti*-product **6**. So, in principle this mechanism can account for the predominant *anti*-addition in THF. However, preliminary ab initio molecular orbital calculations indicate that this is probably not the most likely mechanism for the addition of phenols to **2** (and probably the same applies also to **1**) in THF. Thus, at MP3/6-31G*//6−31G* the calculated complexation energy of C_6H_5OH to $H_2Si=SiH_2$ is only 2.9 kcal mol^{-1}. The complexation energy of C_6H_5OH to **2** (or to **1**) is expected to be even lower due to steric crowding, as is also reflected in the relatively slow reaction rates of **1** and **2** relative to other transient disilenes (see above). In view of these computational results we therefore conclude that it is unlikely that a **2**·THF complex is formed and that it plays a major role in the phenol addition reaction.

but not in the addition of p-$CH_3OC_6H_4OH$ to **2**?[14] We believe that this mechanistic difference is due mainly to the steric differences between these systems. The *t*-Bu and mesityl substituents present in **2** are much larger than the Me and Ph substituents present in the transient MePhSi═SiPhMe.[5] Thus, EtOH can approach the zwitterionic intermediate in the case of MePhSi═SiPhMe (leading to *anti*-addition via intermolecular proton transfer), while a similar intermolecular proton transfer is sterically hindered and thus much slower in the addition of p-$CH_3OC_6H_4OH$ to the highly congested **2**. This conclusion is supported by the much slower (by a factor of ca. 10^9-10^{12}) rates of addition of phenols to **1**[7] (and to **2**; see above) compared with the rates of addition of alkyl alcohols to MePhSi═SiPhMe[5] and Me_2Si═SiPhMe[5].

The different mechanism suggested for the addition to **2** of p-$CH_3OC_6H_4OH$ (Scheme 3) and of EtOH[6] (Scheme 2a) is more difficult to explain. One possible explanation is that as p-$CH_3OC_6H_4OH$ has a larger molecular volume than EtOH,[15] steric effects will slow down the rate of intermolecular proton transfer from the phenol relative to proton transfer from the smaller ethanol. The size difference between EtOH and p-$CH_3OC_6H_4OH$ may be especially important in highly congested intermediates such as **3** and **4**. However, as West et al.[6] did not report the dependence of the product diastereoselectivity on the concentration of EtOH, it is possible that also with EtOH the *anti*-product is produced via rotation around the Si−Si bond in the zwitterionic intermediate.[16] This point deserves additional study.

Why in THF is the *syn* product preferred in the addition of EtOH (0.137 M) to **2**,[6] while the *anti*-product dominates in the addition of p-$CH_3OC_6H_4OH$ to **2** (under the same concentration range)? At this point we cannot offer a clear-cut explanation for this intriguing difference, but we will discuss below several possible explanations. One possibility is that the different product ratios reflects a different rotation equilibrium constant for the relevant zwitterionic intermediates, i.e., **3** $\rightleftharpoons$ **4** (where **4** dominates) vs **8** $\rightleftharpoons$ **9** (where **8** dominates), but we see no reason why this should be the case. It is also possible that the different product ratios result from different rates of intramolecular proton transfer in **8** vs **3**. The rate of intramolecular proton transfer in the intermediate zwitterions is expected to depend on the acidity of the protonated silyl ether. However, as the acidity of the protonated (aryloxy)silane, p-$CH_3OC_6H_4OH^+$(Si), is probably much higher than that of EtO^+H(Si),[17] more *syn*-addition for (p-$CH_3OC_6H_4OH$ + **2**) than for (EtOH + **2**) is expected, contrary to the observation. The most likely explanation is that the different sterechemistry results from the longer lifetime (due to a higher stability) of the zwitterionic intermediate **3** compared with that of **8**, due to the presence in **3** of the p-$CH_3OC_6H_4$ group which is expected to better stabilize the positive charge than the Et substituent present in **8**.[17] If this argument is correct, than **3** can reach rotational equilibrium (in which **4** dominates) before intramolecular proton transfer occurs (leading to an *anti*-product), while the less stable **8** is protonated intramolecularly before reaching equilibrium with **9**, thus leading mainly to *syn*-addition.



8 **9**

Conclusions

The very different product ratio obtained in the addition of p-$CH_3OC_6H_4OH$ to **2** in benzene (*syn:anti* product ratio of 9:1) and in THF (*syn:anti* product ratio of 2:8) supports the formation of a zwitterionic intermediate in the first step of the reaction. We find that the products' diastereoselectivity is not dependent on the phenol concentration. Therefore, we conclude that rotation around the Si−Si bond in the zwitterionic intermediate followed by a fast intramolecular proton transfer is responsible for the *anti*-addition product; intermolecular proton transfer does not compete effectively. This conclusion is different from that proposed for the addition of alkyl alcohols to transient disilenes[5] and for the addition of EtOH to **2**,[6] where (in both cases) *anti*-addition products were explained by an intermolecular proton transfer from a second molecule of alcohol. This study demonstrates that the addition of alcohols to disilenes is more complex than previously believed,[3−6] and this calls for additional studies of this interesting reaction.

Experimental Section

General Procedures. All experiments and manipulations were performed in oven-dried glassware under argon using Schlenk techniques. NMR spectra were collected on a Bruker EM-200 or EM-400 spectrometer. Chemical shifts are reported in parts per million; ^1H 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. All solvents were distilled from sodium or potassium/benzophenone ketyl under argon into a dried Schlenk vessel containing Na/K alloy. The solvents were degassed and distilled prior to use.

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(14) As SMS generated transient disilenes (for which the exact concentration is not known) and used a higher alcohol concentration range (0.85−5.68 M)[5] than we used (0.006−0.88 M), it is also possible that the above mechanistic difference is derived from this difference in the concentrations of the alcohol/phenol. Unfortunately, due to poor solubility we could not increase the phenol concentration above 0.9 M.

(15) We are not aware of steric parameters for p-$CH_3OC_6H_4OH$ or C_6H_5O, and therefore, a quantitative comparison with EtOH could not be made. However, as disilene **2** is substituted with large groups, it is reasonable that this particular steric environment will differentiate between EtOH and p-$CH_3OC_6H_4OH$ which has a much larger van der Waals volume.

(16) The experiments of West et al.[6] were carried out under somewhat different conditions (such as temperature and technique of mixing the disilene and the EtOH solutions) than ours, and these differences may also be responsible for the different results.

(17) Data on the relative stabilities of protonated alcohols in THF are not available. The pK_a values in H_2O are −2.4 (EtO^+H_2) and −6.7 (PhO^+H_2); see: Arnett, E. M. *Prog. Phys. Org. Chem.* **1963**, *1*, 223. Note however that the relative energies of the protonated species are reversed in the gas phase; i.e., PhO^+H_2 is by 8 kcal/mol more stable than EtO^+H_2 (see: Lias, S. G.; Liebman, J. F.; Levin, R. D. *J. Phys. Chem. Ref. Data* **1984** *13*, 695). Whether the situation in THF is similar to that in water or in the gas phase is difficult to judge.

The preparation of **2** is described in the literature.[18] p-CH_3-OC_6H_4OH is commercially available, and it was dried as follows: 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% M) 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 into a dried Schlenk vessel.

The kinetic experiments were followed by a HP 8452A diode-array spectrophotometer and were carried out in deoxygenated dry benzene at 75 °C, 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).

Product Isolation in the Reaction of (*E*)-1,2-Di-*tert*-butyl-1,2-dimesityldisilene (2) with *p*-$CH_3OC_6H_4OH$. A 2 mL solution of disilene **2** (0.055 mmol) in dry benzene was mixed in a dried Schlenk vessel with a 2 mL solution of p-CH_3-OC_6H_4OH (0.55 mmol) in dry benzene which was sealed under vacuum. After overnight reflux the solvent and the excess of phenol were removed in vacuum, leaving a white solid which consists, according to ^1H NMR, of a *syn:anti* product ratio of 90:10, respectively. When the reaction was carried out in the same way but using dry THF as the solvent, a *syn:anti* product ratio of 20:80 was obtained.

The phenol addition products were isolated on a precoated TLC plate (0.5 mm silica gel F-254) using 15% CH_2Cl_2/85% hexane as the eluent and were characterized by ^1H and ^{13}C NMR and HRMS and for the *syn*-addition product (**5**) also by X-ray crystallography. Colorless crystals of **5** were obtained from an *n*-hexane solution at 5 °C.

Analytical Data for 5. ^1H NMR (C_6D_6, 200 MHz): δ 6.98 (d, 2H, $J = 0.045$ Hz, PhH), 6.84 (s, 1H, ArH), 6.77 (s, 1H, ArH), 6.69 (d, 2H, $J = 0.045$ Hz, PhH), 6.63 (s, 1H, ArH), 6.45 (s, 1H, ArH), 4.96 (s, 1H, SiH), 3.28 (s, 3H, p-CH_3O), 2.64 (s, 3H, CH_3), 2.58 (s, 3H, CH_3), 2.41 (s, 3H, CH_3), 2.07 (s, 3H, CH_3), 1.99 (s, 3H, CH_3), 1.92 (s, 3H, CH_3), 1.39 (s, 9H, *t*-Bu), 1.01 (s, 9H, *t*-Bu). ^{13}C NMR (C_6D_6, 400 MHz): δ 20.83, 21.08, 22.59, 23.72, 25.08, 26.24, 26.69, 26.93, 28.48 ($(CH_3)_3C$), 30.33 ($(CH_3)_3C$), 55.14 (CH_3O), 114.77, 121.33, 128.82, 129.33, 130.55, 131.61, 132.04, 138.49, 138.92 144.19, 144.32, 144.65, 145.67, 149.50, 154.75; three of the aromatic signals were covered under the solvent signal. Exact mass for $C_{33}Si_2H_{48}O_2$: calcd, *m/e* 532.3193; found, 532.3191 (M^+, 3.97%).

Analytical Data for 6. ^1H NMR (C_6D_6, 200 MHz): δ 6.78 (s, 2H, ArH), 6.63 (d, 2H, $J = 0.045$ Hz, PhH), 6.64 (s, 2H, ArH), 6.36 (d, 2H, $J = 0.045$ Hz, PhH), 5.00 (s, 1H, SiH), 3.27 (s, 3H, p-CH_3O), 2.72 (s, 3H, CH_3), 2.60 (s, 3H, CH_3), 2.42 (s, 3H, CH_3), 2.34 (s, 3H, CH_3), 2.12 (s, 3H, CH_3), 2.06 (s, 3H, CH_3), 1.28 (s, 9H, *t*-Bu), 1.12 (s, 9H, *t*-Bu). ^{13}C NMR (C_6D_6, 400 MHz): δ 20.96, 21.05, 22.29, 23.51, 24.78, 26.72, 26.85, 28.69 ($(CH_3)_3C$), 30.21, 30.61 ($(CH_3)_3C$), 54.99 (CH_3O), 114.20, 120.27, 131.12, 132.216, 138.31, 139.16, 144.38, 145.05, 146.47, 149.17, 154.39, 155.02; six of the aromatic signals were covered under the solvent signal. Exact mass for $C_{33}Si_2H_{48}O_2$: calcd, *m/e* 532.3193; found, 532.3208 (M^+, 7.47%).

X-ray Structure Analysis of 5. Crystals of **5** were obtained by slow cooling from *n*-hexane at 5 °C. Intensities were collected on a Philips PW 1100/20 four-circle diffractometer using Mo Kα radiation ($\lambda = 0.7107$ Å) and a graphite monochromator. Accurate unit cell parameters and orientation matrix were determined from 25 centered reflections within angular range $2.7 < \theta < 8.4°$. Intensities of three standard reflections were monitored every 120 min, but variations no higher than 5% were detected. A total of 5153 reflections were collected of which 5013 were unique. The structure was solved by the SHELXS-86 program[19] and refined by the SHELXL93 program[20] by full-matrix least squares on F^2. Non-hydrogen atoms were refined anisotropically, and hydrogens, isotropically. The applied weighting scheme was $w^{-1} = \sigma^2(F_o^2) + (0.0499P)^2 + 2.58P$, where $P = (F_o^2 + 2F_c^2)/3$. The final refinement cycle included 5010 reflections and 526 parameters. The final indices R1 and wR2 for 2090 reflections with $I > 2\sigma(I)$ were 0.0939 and 0.1633. The mean and maximum Δ/σ were 0.011 and 0.295, respectively, and the largest residual density was 0.232 e/Å^3.

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Supporting Information Available: Tables of crystal data, bond distances and angles, anisotropic displacement coefficients, atomic (hydrogen and non-hydrogen) coordinates, and isotropic displacement coefficients (6 pages). Ordering information is given on any current masthead page.

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