STEREOSELECTIVE ADDITION OF ALCOHOLS TO STABLE DISILENES

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ABSTRACT

1,2-Addition of methanol, ethanol and 2-propanol in C_6D_6 to E-1,2-di-*tert*-butyl-1,2-dimesityldisilene (**E-1**), or 1,2-di-*tert*-butyl-1,2-bis(2,4,6-tri*iso*-propylphenyl)disilene (**E-2**), and of methanol and ethanol to Z-1,2-di-*tert*-butyl-1,2-bis(2,4,6-tri*iso*propylphenyl)disilene (**Z-2**), take place across the Si=Si double bond with high *syn* stereoselectivity. Lower stereoselectivity was found for ethanol addition to **E-1** in THF. The results are explained in terms of a pathway involving a zwitterionic intermediate.

INTRODUCTION

Following the isolation of stable disilenes one of the first reactions to be studied was the 1,2-addition of water and alcohols to the Si=Si bond.[1] In an early paper from these laboratories the addition of water, methanol and ethanol to E-1,2-di-tert-butyl-1,2-dimesityldisilene (**E-1**) was reported to give a 1:1 mixture of the two diastereomers of the disilane products, in each case.[2] In contrast, a recent paper by Sekiguchi et al. showed that the addition of 2-propanol and 2-methyl-2-propanol to the transient disilenes, E- and Z-1,2-dimethyl-1,2-diphenyldisilene, takes place with high stereoselectivity to give the *syn* addition product.[3] With ethanol the stereoselectivity was lower, however, and at high concentrations of ethanol a 1:1 mixture of stereoisomers was observed.

Other addition reactions of stable disilenes have shown variable stereoselectivity. The 1,2 addition of Cl_2 and HCl to **E-1** are stereoselective,[2] and the reaction of **E-1** with singlet dioxygen takes place with retention of configuration to give the *trans*-1,2-dioxetane (>99%).[4] Cycloadditions of phenylacetylene and ethoxyacetylene to **E-1** were however reported to give ~ 1:1 mixtures of stereoisomers.[2]

In view of the results reported for transient disilenes, it seemed worthwhile to carry out some alcohol addition reactions of stable stereoisomeric disilenes under carefully controlled conditions, to see if stereoselective reactions might be obtained. In fact, we find that reactions of stable disilenes with alcohols may be highly stereoselective under the proper reaction conditions.

EXPERIMENTAL SECTION

E-1,2-di-*tert*-butyl-1,2-dimesityldisilene (**E-1**),[5] and E and Z-1,2-di-*tert*-butyl-1,2-bis(2,4,6-tri*iso*propylphenyl) disilene (**E-2**, **Z-2**)[6] were prepared as described in the literature, and showed properties identical to those reported earlier. All reactions were performed in oven-dried glassware under an atmosphere of argon or dry nitrogen, using Schlenk techniques. Solvents were thoroughly dried and freshly distilled before use. Methanol, ethanol and 2-propanol were distilled from magnesium and degassed by five freeze-pump-thaw cycles immediately before use. Proton and ^{13}C NMR spectra were determined on a Bruker WP-300 spectrometer and were referenced to residual solvent resources that were calibrated against tetramethylsilane. ^{29}Si NMR spectra were determined on a Bruker WP-270 spectrometer using the INEPT pulse sequence, referenced to external tetramethylsilane. Mass spectra were determined on a Kratos MS-80 spectrometer, EI at 70 ev.

Reactions of **E-1**. a. With methanol. To 3.8 mL of C_6D_6 was added 28 μL of methanol. To an NMR tube containing 15 mg (2.6×10^{-5} mol) of **E-1**, 0.76 mL of the methanol solution (4 equiv) was added. The reaction was followed by ^{1}H NMR, and was complete after 24 h at 25°C, producing only one stereoisomer (>99%) in quantitative conversion. The reaction was repeated using 1 equiv of methanol; it was complete after 48 h, and produced the same single stereoisomer.
^{1}H NMR (C_6D_6): δ1.21 (s, 9H, $C(CH_3)_3$), 1.24 (s, 9H, $C(CH_3)_3$), 1.91 (s, 3H, p-CH_3), 1.97 (s, 3H, p-CH_3), 2.01 (s, 3H, o-CH_3), 2.24 (s, 3H, o-CH_3), 2.59 (s, 3H, o-CH_3), 2.6 (s, 3H, o-CH_3), 3.63 (s, 3H, CH_3O), 4.81 (s, 1H, SiH), 6.36 (s, 1H, ArH), 6.49 (s, 1H, ArH), 6.78 (s, 1H, ArH), 6.83 (s, 1H, ArH)
^{13}C NMR (C_6D_6): δ 20.85, 21.08, 22.31, 24.51, 24.89, 25.56, 26.07, 26.24, 28.98, 30.56, 52.55, 128.64, 129.04, 129.10, 130.06, 131.41, 132.44, 138.19, 138.30, 143.43, 144.42, 144.65, 144.81.
^{29}Si NMR: δ -33.9, 11.9
MS m/e (% inten.) 440 (M+, 2.6), 383 (M+-(t-Bu), 74). HRMS: calcd for $C_{27}H_{44}Si_2O$, m/e 440.28, found m/e 440.29.

b. With ethanol. 1. A solution of 42 μL of ethanol in 3.8 mL of C_6D_6 was prepared. To an NMR tube containing 15 mg (2.6×10^{-5} mol) of disilene, 0.76 mL of the solution was added(4 equiv). The NMR tube was sealed and mixed and the reaction was followed by ^{1}H NMR; it was complete in 24 h at room temperature. Similar reactions were carried out using 1 equiv and 10 equiv of ethanol; these required 48 h and about 5 h for completion. All three reactions produced only a single stereoisomer of **3**.
^{1}H NMR (C_6D_6): δ 0.92 (t, 3H, O-CH_2-CH_3 J=6.9 Hz), 1.23 (s, 9H, $C(CH_3)_3$), 1.25 (s, 9H, $C(CH_3)_3$), 1.96 (s, 6H, p-CH_3), 2.01 (s, 3H, o-CH_3); 2.28 (s, 3H, o-CH_3), 2.62 (s, 3H, o-CH_3), 2.64 (s, 3H, o-CH_3), 4.04 (q, 2H, OCH_2CH_3, J=6.9 Hz), 4.82 (s, 1H, SiH), 6.36 (s, 1H, ArH), 6.50 (s, 1H, ArH), 6.78 (s, 1H, ArH) 6.83 (s, 1H, Ar-H).
^{13}C NMR: δ 18.3, 20.6, 20.9, 22.2, 24.4, 25.1, 25.7, 26.1, 26.4, 29.1, 30.6, 60.7, 128.3, 129.0, 129.1, 130.1, 131.2, 132.2, 138.2, 138.3, 143.5, 144.2, 144.5, 144.7.
^{29}Si NMR: δ -33.5, 11.8
M.S. m/e (% intensity) 454 (M+, 1.4), 397 (M+-(t-Bu), 67.34). HRMS: for $C_{28}H_{46}Si_2O$, m/e 454.31; found, m/e 454.31.

2. The addition was repeated as in b.1. above, using THF as a solvent instead of C_6D_6 and 4 equiv of ethanol. In this case a 96:4 ratio of two stereoisomers was obtained, the major isomer being identical to the one obtained in the C_6D_6 reactions.

3. In 1.44 mL of THF was dissolved 20 mg of **E-1**. In a dry box, this solution was added dropwise over 10 min to 2.16 mL of THF containing 7.7 μL of ethanol. The mixture was heated to reflux temperature, 65°C, and refluxed overnight; the solvent was then removed under vacuum, and the residue was examined by NMR in C_6D_6 solution. The ^{1}H NMR was consistent with a 1:3 mixture of the stereoisomers of **3**. Some of the proton resonances for the minor stereoisomer could not be observed because of overlap. The assignments and comparison with the resonances for the major isomer are given in Table 1.

4. Attempted rearrangement. 15 mg of the major stereoisomer of **3** in 0.76 mL of C_6D_6 containing 4 equiv of ethanol was refluxed overnight. Examination of the ^{1}H NMR spectrum of the recovered product showed that no change had taken place. In another experiment, solid **3**, 15 mg, was dissolved in 4 mL of a 1:1 THF-ethanol mixture and refluxed overnight. No change was detectable by ^{1}H NMR.

c. With 2-propanol. In the same manner as described above for methanol addition, 15 mg of **E-1** was treated with 1 and 4 equiv of 2-propanol in C_6D_6. Negligible reaction took place at 25°C. The NMR tube with 4 equiv of 2-propanol was heated to 40°C for 48 h, whereupon reaction was complete to produce a single stereoisomer in quantitative yield by NMR. Reaction with 1 equiv of 2-

propanol required 7 d at 50°C for completion. Only a single stereoisomer of the alcohol adduct was obtained, along with about 5% of an unidentified decomposition product.

Table 1. ^{1}H NMR for Stereoisomers of **3**.

δ,major isomer	δ, minor isomer	type	assign.
1.23	1.25	s, 18 H	$C(CH_3)_3$
1.25	1.26	s, 18 H	$C(CH_3)_3$
1.95	1.95	s, 6 H	p-CH_3
2.01	1.99	s, 3 H	o-CH_3
2.28	2.24	s, 3 H	o-CH_3
2.61	2.55	s, 3 H	o-CH_3
2.64	2.59	s, 3 H	o-CH_3
4.82	4.79	s, 1 H	Si-H
6.35	6.35	s, 1 H	Ar-H
6.49	6.47	s, 1 H	Ar-H
6.76	6.71	s, 1 H	Ar-H
6.83	6.81	s, 1 H	Ar-H

^{1}H NMR (C_6D_6): δ1.23 (s, 9H, $C(CH_3)_3$), 1.25 (s, 9H, $C(CH_3)_3$), 1.32 (d, 3H, $OCH(\underline{CH}_3)_2$.J=6.9 Hz) 1.34 (d, 3H, $OCH(\underline{CH}_3)_2$.J=6.9 Hz), 1.94 (s, 3H, p-CH_3), 2.01 (s, 3H, p-CH_3), 2.08 (s, 3H, o-CH_3), 2.29 (s, 3H, o-CH_3), 2.61 (s, 3H, o-CH_3), 2.72 (s, 3H, o-CH_3), 4.56 (sept, 1H, $O\underline{CH}(CH_3)_2$,J=6.9 Hz), 4.83 (s, 1H, SiH), 6.48 (s, 1H, ArH), 6.76 (s, 1H, ArH), 6.83 (s, 1H, ArH), 7.15 (s, 1H, ArH).
^{13}C NMR (C_6D_6): δ 20.8, 21.1, 22.9, 25.3, 25.7, 25.8, 26.1, 26.2, 26.6, 28.8, 30.7, 68.5, 128.8, 129.2, 129.3, 130.1, 131.9, 132.4, 137.9, 138.2, 143.4, 144.5, 144.6, 144.7.
^{29}Si NMR: δ -32.5, 11.4
MS: m/e (% inten.): 468 (M+, 0.2), 411 (M+-(t-Bu), 25.5). HRMS calc. for $C_{29}H_{48}Si_2O$, m/e 468.33, found, m/e 468.33.

Reactions of **E-2**. a. With methanol. To 3.8 mL of C_6D_6 was added 55 μL of methanol. 0.76 mL of this solution (10 equiv) was added to an NMR tube containing 15 mg (2.6 x 10-5 mol) of **E-2**. No reaction was observed by NMR after 2 d at 25°C. The tube was heated to 40° C for an additional 2 d, when the ^{1}H NMR indicated partial(~50%) addition. The tube was then heated to 50°C for 24 h, whereupon the NMR showed the reaction to be complete. The product was a single stereoisomer, accompanied by a few % of an unidentified decomposition product.
^{1}H NMR (C_6D_6): δ 0.32 (d, 3H, J=6.5 Hz), 0.63 (d, 3H, J=6.5 Hz), 0.75 (d, 3H, J=6.5 Hz), 1.14 (d, 6H, J=6.5 Hz), 1.15 (d, 6H, J=6.5 Hz), 1.24 (d, 3H, J=6.5 Hz), 1.28 (s, 9H, $C(CH_3)_3$), 1.30 (s, 9H, $C(CH_3)_3$), 1.38 (m, 6H), 1.46 (d, 3H, J=6.5 HZ), 1.59 (d, 3H, J=6.4 Hz), 2.62 (m, 3H, 3 $C\underline{H}(CH_3)_2$), 3.46 (sept, 1H, J=6.4 Hz), 3.59 (sept, 1H, J=6.5 Hz), 3.60 (s, 3H, OCH_3), 3.92 (sept, 1H, J=6.4 Hz), 5.06 (s, 1H, SiH), 6.96 (s, 2H, ArH), 7.18 (s, 1H, ArH), 7.22 (s, 1H, ArH).
^{13}C NMR (C_6D_6): δ 22.02, 23.85, 23.93, 24.03, 24.17, 24.22, 24.39, 24.50, 24.82, 25.24, 25.29, 26.64, 27.16, 27.44, 30.31, 32.02, 32.27, 34.30, (2C), 34.61, 36.04, 37.18, 52.45, 121.86, 122.21, 122.46, 122.62, 130.45, 132.53, 149.79, 150.13, 155.42, 155.80, 156.07, 156.75.
MS m/e (% inten.): 608 (M+, 0.487), 551 (M+-(t-Bu), 11.6). HRMS: Calc for $C_{39}H_{68}Si_2O$, m/e 608.49, found, m/e 608.48.

b. With ethanol. In a manner similar to that described above, 20 μL of ethanol (4 equiv) in 0.76 mL of C_6D_6 was added to 15 mg of **E-2**. The mixture was kept at 40° for 2 d, but only slight reaction was observed after this time. The tube was then heated to 50°C for 2 d, leading to complete reaction as shown by NMR, to give a single stereoisomer. A small amount of decomposition byproduct was also produced.

^{1}H NMR (C_6D_6): δ 0.30 (d, 3H, J=6.9 Hz), 0.73 (d, 3H, J=6.3 Hz), 0.85 (d, 3H, J=6.9 Hz), 1.11 (d, 12H, J=6.9 Hz), 1.12 (t, 3H, O-$CH_2\underline{CH_3}$,J=6.9 Hz), 1.25 (d, 3H, J=6.5 Hz), 1.28 (s, 9H, $C(CH_3)_3$), 1.30 (s, 9H, $C(CH_3)_3$), 1.39 (d, 3H), 1.41 (d, 3H), 1.47 (d, 3H, J=6.5 Hz), 1.57 (d, 3H), 2.74 (m, 3H, 3 $\underline{CH}(CH_3)_2$), 3.43 (m, 1H), 3.75 (sept,1H, J=6.9 Hz), 3.9 (sept, 1H, J=6.4 Hz), 4.06 (q, 2H, $O\underline{CH_2}CH_3$, J=6.9 Hz), 5.11 (s, 1H, SiH), 6.97 (s, 2H, ArH), 7.19 (s, 1H, ArH), 7.22 (s, 1H, ArH).
^{13}C NMR (C_6D_6): δ 18.46, 21.95, 23.85, 23.93, 23.96, 24.18, 24.44, 24.50, 24.60, 25.23, 25.26, 25.71, 16.74, 27.05, 27.16, 30.39, 31.37, 32.32, 34.21, 34.32, 34.60,36.16, 37.23, 60.13, 121.76, 122.21, 122.53, 122.74, 130.74, 132.23, 149.63, 150.12, 155.49, 155.70, 155.83, 156.98.
^{29}Si NMR: δ -31.35, 11.90
MS m/e (% inten.): 622 (M+, 0.20), 565 (M+-(t-Bu), 4.38), 362 (M+-(t-Bu +Ar), 26.76). HRMS: Calc for $C_{40}H_{70}Si_2O$, m/e 622.52, found, m/e 622.50.

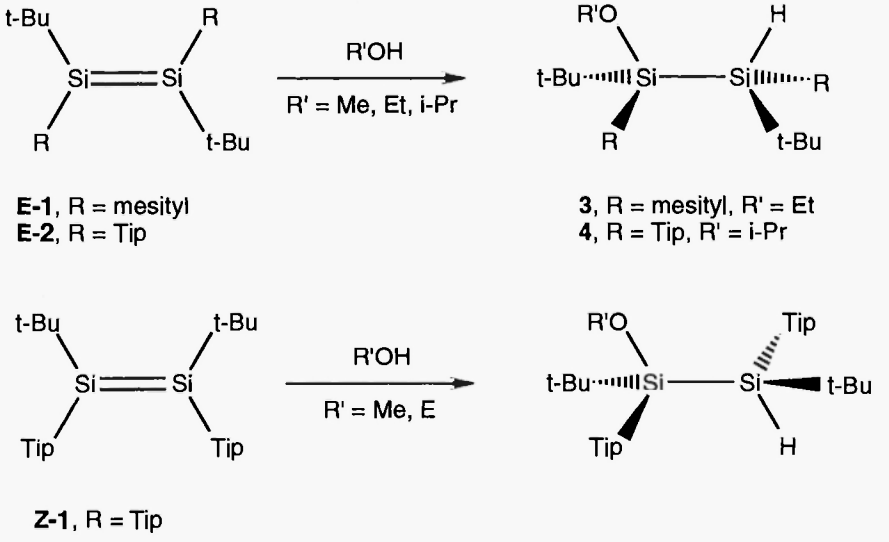
c. With 2-propanol. Using the same procedure, 9.5 μL of 2-propanol (4 equiv) was added to 15 mg (2.6×10^{-5} mol) **E-2**. Reaction was complete after 3 d at 50°C, as shown by ^{1}H NMR. A single stereoisomer, **4**, was produced along with a small amount of decomposition product. Crystals of **4** suitable for X-ray diffraction were grown from diethyl ether-hexane solution.
^{1}H NMR (C_6D_6): δ 0.77 (d, 3H), 0.88 (d, 3H), 0.96 (s, 9H, $C(CH_3)_3$), 0.98 (s, 9H, $C(CH_3)_3$), 1.04 (d, 3H), 1.19, (d, 3H), 1.15 (m, 15H), 1.38 (m, 15H), 2.72 (m, 3H, 3 $\underline{CH}(CH_3)_2$), 3.27 (m, 1H), 3.93 (m, 2H), 4.63 (m, 1H), 5.08 (s, 1H, SiH), 6.96 (s, 2H, ArH), 7.21 (s, 2H, ArH).
^{13}C NMR (C_6D_6): δ 18.47, 21.95, 23.85, 23.93, 23.97, 24.19, 24.44, 24.49, 24.59, 25.23, 25.26, 25.70, 26.74, 27.04, 27.09, 27.17, 30.39, 31.38, 32.32, 34.21, 34.33, 34.59, 36.17, 37.23, 60.12, 121.77, 122.22, 122.52, 122.74, 130.73, 132.22, 149.63, 150.11, 155.47, 155.70, 155.83, 156.97.
^{29}Si NMR: δ -36.89, 11.09
MS m/e (% inten.) 636 (M+, 0.2), 579 (M+-(t-Bu), 3.36). HRMS: Calcd for $C_{41}H_{71}Si_2O$, m/e 635.54, found, m/e 635.52.

Reactions of **Z-2**. a. With methanol. In the reaction described above, 70 μL of methanol (10 equiv) in 0.76 mL of C_6D_6 was added to 15 mg (2.6×10^{-5} mol) of **Z-2**. After 6 d at 25°, the reaction was complete as judged by ^{1}H NMR, to produce quantitatively only one stereoisomer, different from the isomer formed from **E-2**.
^{1}H NMR (C_6D_6): δ 0.74 (d, 6H, J=6.4 Hz), 0.85 (d, 6H, J=6.2 Hz), 1.16 (m, 12H), 1.19 (d, 12H, J=6.4 Hz), 1.27 (s, 9H, $C(CH_3)_3$), 1.3 (s, 9H, $C(CH_3)_3$), 2.74 (m, 2H), 3.05 (m, 1H), 3.3 (s, 3H, OCH_3), 3.38 (m, 1H), 3.51 (m, 1H), 3.84 (m, 1H), 4.89 (s, 1H, SiH), 6.96 (s, 2H, ArH), 7.2 (s, 2H, ArH).
^{13}C NMR (C_6D_6): δ 22.39, 24.0, (3C), 24.33, 24.84, 25.77, 25.94, 25.99, 27.48, 28.57, 29.58, 31.37, 32.43, 33.91, 34.42, 34.48, 34.67, 35.09, 37.34, 52.53, 1120.97, 121.25, 122.37, 122.78, 130.6, 132.6, 150.0, 150.04, 155.39, 156.02, 156.26, 157.79.
HRMS: Calcd for $C_{39}H_{68}Si_2O$, 608.49, found 608.47

b. With ethanol. In the usual way, 15 mg (2.6×10^{-5} mol) of **Z-2** was treated with 77 μL of ethanol (10 equiv). The reaction required 24 d at 25°C for completion, and the product consisted of a single isomer, different from the isomer obtained from **E-2** with ethanol.
^{1}H NMR (C_6D_6): δ 0.73 (d, 3H, J=6.2 Hz), 0.86 (d, 3H, J=6.2 Hz), 0.93 (t, 3H, J=6.5 Hz, $OCH_2\underline{CH_3}$), 1.16 (d, 6H, J=6.4 Hz),1.21 (d,6H, J=6.9 Hz), 1.27 (s, 9H, $C(CH_3)_3$), 1.30 (s, 9H, $C(CH_3)_3$), 1.44 (d, 12H, J=6.4 Hz), 1.51 (d, 6H, J=6.4 Hz), 2.65 (sept, 1H, J=6.2 Hz), 2.78 (sept, 1H, J=6.5 Hz), 3.43 (sept, 1H, J=6.2 Hz), 3.72 (sept, 1H, J=6.2 Hz), 3.93 (sept, 1H, J=6.3 Hz), 4.09 (m, 1H), 4.25, (q, 2H, J=6.5 Hz, OCH_2CH_3), 5.14 (s, 1H, SiH), 7.0 (s, 1H, ArH), 7.2 (s, 3H, ArH).
HRMS: Calcd for $C_{40}H_{70}Si_2O$, m/e 622.52, found m/e 622.53

RESULTS AND DISCUSSION

The experimental results for the alcohol addition reactions in C_6D_6 are summarized in Scheme 1.



Scheme 1. Reactions of stable disilenes with alcohols in C_6D_6 solution. Tip = 2,4,6-tri*iso*propylphenyl.

Addition reactions with all three disilenes were stereospecific. In the reactions with stereoisomers **E-2** and **Z-2**, a single stereoisomer was observed for each alcohol with **E-2**, and a different isomer was formed for the same alcohol with **Z-2**. The formation of a single stereoisomer suggests *syn* addition, which was confirmed by an X-ray diffraction study of **4**, the 2-propanol adduct of **Z-2**. A thermal ellipsoid diagram for **4** is shown in Figure 1.[7] The one unusual feature of the structure is the remarkably tight (20°) torsion angle between the two hindered aromatic rings.

Among the three disilenes, **E-1** was more reactive than **E-2** which was more reactive than **Z-2**. As expected, the reactivity of the alcohols decreased, MeOH>EtOH>iPrOH. With 2-propanol, heating of the reaction mixtures was necessary to bring about reaction in a reasonable time. This led to formation of small amounts of an unidentified decomposition product of the disilene, along with the *syn*-addition compound.

Using our typical protocol, addition of an alcohol solution in C_6D_6 to solid disilene, the amount of alcohol did not affect the stereochemistry. Only a single stereoisomer was obtained (>99%) even with 10 equiv of alcohol. Changing the solvent to THF, however, influenced the result, so that with **E-1** and ethanol 4% of the other stereoisomer was produced. And, where disilene **E-1** was slowly added to ethanol in THF (similar to the reaction protocol of de Young et al.[2]) the reaction product was a 1:3 mixture of the *anti* and *syn* adducts.

These results can be rationalized in terms of the mechanism proposed by Sekiguchi and coworkers, shown in Scheme 2, proceeding through an intermediate zwitterion **5**. The more polar solvent THF may stabilize **5**, giving time for intermolecular transfer of a proton to take place to produce some of the *anti*-addition isomer. In C_6D_6 no such stabilization takes place, so only intramolecular transfer occurs to give exclusively the *syn* addition product.

In conclusion, we find that addition of alcohols to stable disilenes can take place stereospecifically via *syn* addition. Mixtures of diastereoisomers may also be formed, depending on the reaction conditions. These results are consistent with those for transient disilenes, and with the recently proposed mechanism for the addition reaction.[3]

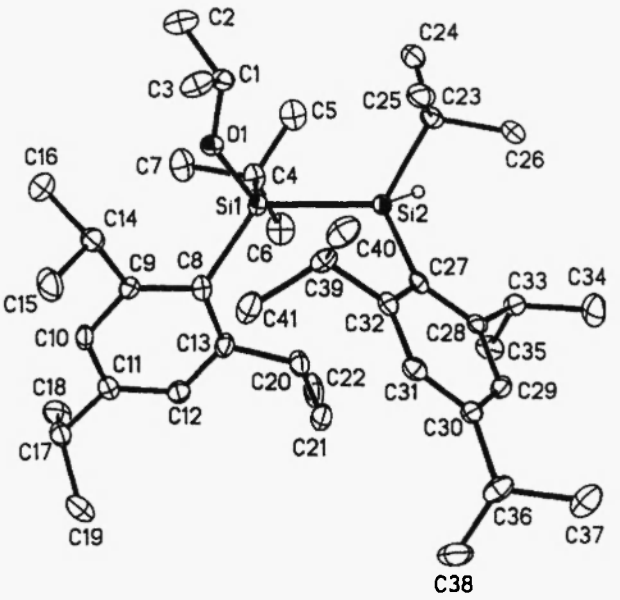
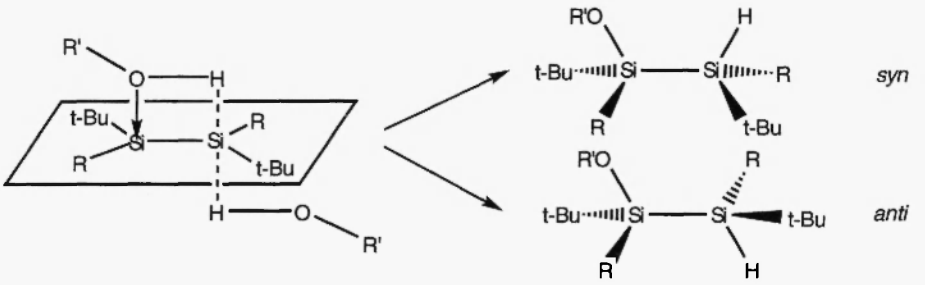


Figure 1. Diagram of x-ray structure of **4** (50% thermal ellipsoids), showing *syn* stereochemistry. Selected bond lengths (pm) and angles (deg): Si(1)-Si(2), 244.1; Si(1)-O(1) 163.9; Si(1)-C(4) 193.6; Si(1)-C(8), 194.1; Si(2)-C(23) 195.5; Si(2)-C(27) 191.6; O(1)-Si(1)-Si(2), 112.2; O(1)-Si(1)-Si(2)-C(27), 106.2; C(4)-Si(1)-Si(2)-C(27), -138.9; C(8)-Si(1)-Si(2)-C(27), -20.3; O(1)-Si(1)-Si(2)-C(23), -28.8; C(4)-Si(1)-Si(2)-C(23), 86.0; C(8)-Si(1)-Si(2)-C(23), -155.4.



R = mesityl, Tip; R' = Me, Et, i-Pr

Scheme 2. The mechanism for alchohol addition to disilenes according to Sekiguchi et al.,[3] applied to stable disilenes **E-1** and **E-2**. Intramolecular proton transfer from the alcohol molecule attached to the silicon atom in the zwitterionic intermediate **5** leads to *syn*-addition. Protonation from a second alcohol molecule could lead to *anti*-addition.

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Supporting Material Available. Tables of data collection information, atomic coordinates and isotropic displacement parameters, bond lengths and angles and structure factors for **4** (23 pages), may be obtained from the authors on request.

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7. Crystal structure analysis: colorless crystals of **4** were grown by slow evaporation from diethyl ether-hexane solution. $C_{41}H_{72}OSi_2$. M =637.17. monoclinic, space group $P2_1/c$. a =15.070(2), b =14.490(2), c =18.758(3) Å, β=100.144(12)°, V =4032.0(10) Å^3. Z=4. ρ_{calc}=1.050 g cm^{-3}. T=113(2)K. Data were collected on a crystal of dimensions 0.5 x 0.4 x 0.1 with a Siemens P4 diffractometer equipped with graphite-monochromated Mo Kα radiation, λ=0.71073 Å using ω scans. $2\theta_{max}$ =45°. 5311 data were collected; 5074 independent (R_{int}=0.0395); 5068 data were used in refinement. No absorption correction was applied, μ=0.116 mm^{-1}. The structure was solved by direct methods and refined by full-matrix least-squares on ΔF^2 using the SHELXTL+ software.[8] All non-hydrogen atoms were refined with anisotropic displacement parameters; hydrogens were included in idealized geometry with isotropic displacement parameters equivalent to 1.2 x the isotropic equivalent displacement factor for the bonded carbon. At convergence, the 397 variables refined to R(F)=0.0486 for the observed (I>2 σ(I)) data, wR(F^2)=0.1394 for the refined data, S=1.013. Maximum and minimum values of the final difference map were 0.503 and -0.400 e Å^{-3}, respectively. Further details of the crystal structure investigation may be obtained from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ (UK), on quoting the full journal citation.
8. G.M Sheldrick, *SHELXTL Version 5 Reference Manual.* Siemens Analytical X-ray Instruments, Madison, WI 53719-1173, USA, 1994.

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