

A new mechanism for the addition of alcohols to disilenes revealed by DFT and ONIOM calculations

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Abstract

Density functional and ONIOM calculations of alcohol and phenol additions to two (tetramethyl and tetramesityl) disilenes were carried out. The dimer of MeOH adds to $\text{Me}_2\text{Si}=\text{SiMe}_2$ more readily than the monomer. The trimer does not afford the adduct, but a zwitter-ionic intermediate. In the $(\text{CF}_3\text{OH})_2$ addition to $\text{Me}_2\text{Si}=\text{SiMe}_2$, $\text{H}\cdots\text{Si}$ bond formation is more advanced than $\text{O}\cdots\text{Si}$ bond formation in the transition state (TS). Addition of seven phenol derivatives to $\text{Me}_2\text{Si}=\text{SiMe}_2$ was examined, and the dimer reactions were found to be superior to the monomer reaction regardless of the substituents on the benzene rings. $(\text{MeOH})_2$ reacts also with $\text{Mes}_2\text{Si}=\text{SiMes}_2$ favorably, and an isomer of the reactant-like complex (precursor) may afford an adduct of different stereochemistry via internal rotations. Generally, the dimer of the alcohol or phenol is the reactant toward the disilenes. Exceptionally, a monomer of *p*-(dimethylamino)phenol reacts with $\text{Mes}_2\text{Si}=\text{SiMes}_2$ owing to steric congestion by the four mesityl groups.

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Keywords: Disilene; Alcohol addition; Reaction mechanism; Density functional and ONIOM calculations

1. Introduction

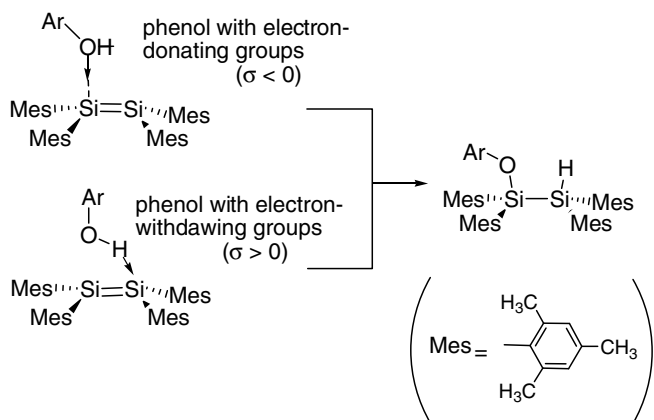
Disilene is a compound with a Si=Si double bond. The first attempt at disilene preparation was made in 1911 [1]. However, the apparent product, 1,2-diethyl-1,2-diphenyldisilene (called “diphenyl diethyl silicoethylene” at that time), was actually a polymer of $(\text{EtPhSi})_n$. Various reactions were conducted to attempt to make disilenes, but the products were only silicon cyclic compounds such as four- [2a], six- [2b] and five- [2c] membered rings. In 1969, a pioneering study was reported to prove the existence of tetramethyldisilene ($\text{Me}_2\text{Si}=\text{SiMe}_2$, **1**) during a thermal decomposition and cycloaddition process [3]. By a similar decomposition and addition reaction, the Si=Si bond was characterized as a double bond due to prevention of free rotation [4]. In 1981, the first stable and isolable disilene, tetramesityldisilene ($\text{Mes}_2\text{Si}=\text{SiMes}_2$, **2**), was suc-

cessfully obtained [5a]. Recently, a novel synthesis of **2** has been reported [5b]. The addition of ethanol to **2** was also examined. Since the first isolation, many synthetic studies on disilene derivatives have been performed [6], and disilenes bearing various substituents have been prepared [7]. In particular, the properties and reactivities of stable and fundamental disilenes have been comprehensively surveyed [7i], and alcohol addition reactions have been extensively studied [8]. While Sakurai et al. postulated [8b] that two alcohol molecules involved in a *trans* addition, Apeloig and Nakash proposed a 1:1 addition path [8c]. For the reactions between the disilene **2** and phenol derivatives, a concave-shaped Hammett plot was reported and mechanistic differences were suggested (Scheme 1) [9a], and kinetic parameters were obtained for two reactions, (*p*- $\text{CF}_3\text{-C}_6\text{H}_4\text{OH} + \mathbf{2}$) and (*p*-methoxyphenol + **2**) [9b].

Much attention has been paid to the mechanism of alcohol addition to disilenes. The diastereoselectivity of the addition of *p*-MeO- $\text{C}_6\text{H}_4\text{OH}$ to *trans*-1,2-di-*tert*-butyl-1,2-dimesityldisilene, $\text{Mes}(t\text{-Bu})\text{Si}=\text{SiMes}(t\text{-Bu})$, in benzene and tetrahydrofuran was examined [8c]. A solvent-dependent

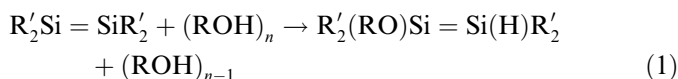
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Scheme 1. Two patterns of the addition reactions of substituted phenols to the tetramesityldisilene **2**, which was suggested in Ref. [9a]. σ is the Hammett constant.

syn:anti product ratio was obtained, and rotation around the Si–Si bond in the zwitterionic intermediate was suggested. Using MO calculations, a four-centered transition-state (TS) geometry was reported by Nagase et al. [10], and similar TS geometries in model reactions, **1** + CH₃OH and **1** + CF₃OH, were obtained [9b]. The reaction of H₂Si=SiH₂ + H₂O was also investigated computationally [11]. In particular, highly accurate calculations, MP2/6-311++G(d,p), B3LYP/6-311++G(d,p) and CBS-Q, were performed for H₂Si=SiH₂ + H₂O, H₂Si=SiH₂ + CH₃OH and H₂Si=SiH₂ + CF₃OH systems [11c]. Four-centered addition TS structures were determined precisely. The initially formed weakly bonded complexes were suggested to determine the regioselectivity and diastereoselectivity. Whereas unimolecular additions of H₂O, CH₃OH and CF₃OH to model disilenes have been examined theoretically, phenol is known spectroscopically to be in the dimer [12a,12b] or trimer form [12c]. Thus, the phenol (and alcohol) dimer or trimer might be the actual reactant with the disilenes. It is necessary computationally to investigate the optimal number *n* in Eq. (1) so as to elucidate the reaction mechanism.



In this work, the addition reactions in Eq. (1) were studied systematically by the use of density functional theory and ONIOM calculations. For the disilene substrate, the substituent R' is methyl or a mesityl group. In the alcohol ROH, the substituent R is methyl, trifluoromethyl or an aryl group. The calculations revealed that the ROH dimer is the reactant (except in one case) toward the disilene substrate.

2. Calculation method

The geometries of the reacting systems were determined by density functional theory calculations, and the B3LYP

method [13] was used. B3LYP was considered to be a suitable method, because it includes the electron correlation effect to some extent. The basis set employed was 6-31G*, and the solvent effect was taken into account by the SCRF = dipole method [14]. For the MeOH addition reactions, the dielectric constant of methanol (=32.63) was used. For additions of phenol derivatives, that of benzene (=2.257) was used according to the experimental solvent [9a]. Then, geometry optimizations were carried out with the RB3LYP/6-31G* SCRF = dipole. For the Me₂Si=Si-Me₂(CH₃OH)_{*n*} system, RB3LYP/6-311 + G(d,p) SCRF = dipole calculations (*n* = 1, 2 and 3) and MP2/6-31G(d,p) calculations (*n* = 1 and 2) were also carried out. We first determined the transition state (TS) structures. TSs were characterized by vibrational analysis, which checked whether the obtained geometries have single imaginary frequencies (*v*[‡]s). Second, intrinsic reaction coordinate (IRC) [15] calculations were carried out. Third, geometry optimizations were made by the use of the geometries and the Hessian force constants at the end of IRC calculations. By consecutive calculations via the force constants, energy-minimum states connected correctly to the TS may be determined.

Since the size of the tetramesityldisilene **2** is very large, three methyl groups on the phenyl ring were approximated by the semiempirical method, PM3, and ONIOM (RB3LYP/6-31G*: PM3) [16] calculations were carried out. Thus, 12 methyl groups were treated by PM3 and other parts by RB3LYP/6-31G* for the reacting systems including **2**. Single-point RB3LYP/6-31G* SCRF = dipole energy calculations were made, and Gibbs free energies were estimated by the sum of the ONIOM free energy correction and the single-point energy. The relative energies (ΔE and $\underline{\Delta E}$) were obtained by the RB3LYP/6-311 + G(d,p) electronic energy and the RB3LYP/6-31G* (or ONIOM) zero-point vibrational energy. All calculations were carried out using the GAUSSIAN 03 [17] program package.

3. Calculation results and discussion

3.1. Reaction between tetramethyldisilene (Me₂Si=SiMe₂, **1**) and aliphatic alcohols

Fig. 1 shows the stepwise addition path of MeOH to **1**, which was also obtained by Apeloig and Nakash [9b] with RHF/6-31G(d).

The geometries of TS1 and TS2 obtained here are similar to those in Ref. [9b]. TS1 is the rate-determining step and has a well known four-center geometry. The present free activation energy $\Delta G^\ddagger = +5.69$ kcal/mol of TS1 is small. The energy change of **Int** ($\Delta E = -2.00$ kcal/mol) is almost the same as that of TS2 ($\Delta E = -1.97$ kcal/mol). Since **Int** is an extremely transient species, MP2/6-31G(d,p) calculations did not give a stepwise but rather concerted pathway of *n* = 1. TS1 is definitely the rate-determining step, and the method dependence, i.e. presence or

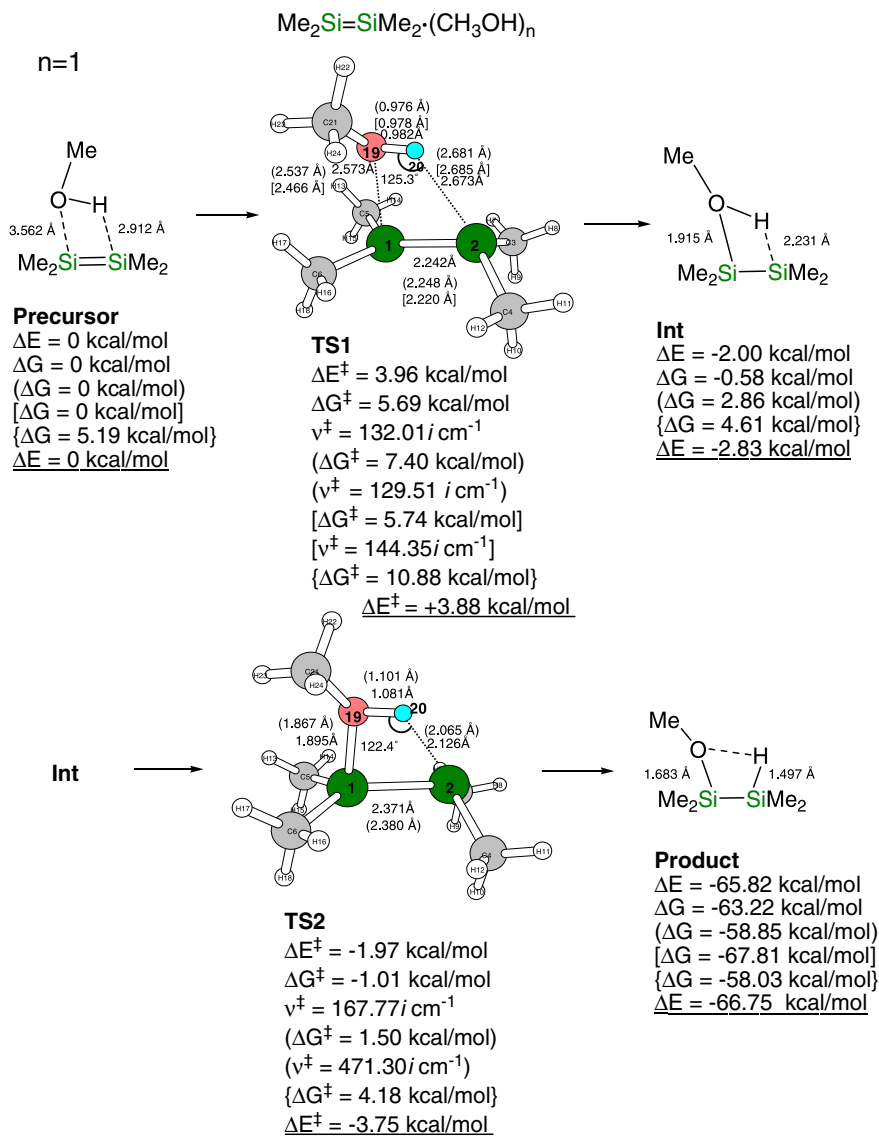


Fig. 1. The stepwise addition pathway of one methanol (MeOH) molecule to the tetramethyldisilene (**I**). “**Int**” is the intermediate. v^\ddagger of TS means for the sole imaginary frequency. The pathway was also reported in Ref. [9b]. The values in parentheses are those calculated by RB3LYP/6-311 + G(d,p) SCRF = dipole, and those in square brackets are by MP2/6-31G(d,p). In braces {}, ΔG and ΔG^\ddagger values of RB3LYP/6-31G* SCRF = dipole relative to the Gibbs free energies of the isolated reactants are shown. ΔE and ΔE^\ddagger are RB3LYP/6-31G* electronic energy differences, and $\underline{\Delta E}$ and $\underline{\Delta E}^\ddagger$ are those with zero-point energy differences.

absence of **Int**, is not a serious problem to compare the $n = 1$ and $n = 2$ reactivities. Except for this dependence, the geometries and ΔG^\ddagger values of TS1 are similar by RB3LYP/6-31G* SCRF = dipole, RB3LYP/6-311 + G(d,p) SCRF = dipole and MP2/6-31G(d,p). Fig. 2 exhibits an MeOH dimer ($n = 2$) addition path. The dimer participation model has not been investigated so far. The reaction occurs concertedly with the hydrogen-bond angle $\text{O}(19)\text{--H}(21)\cdots\text{O}(22) = 163.6^\circ$ at the TS.

The strainless TS geometry gives a smaller $\Delta G^\ddagger = 4.48$ kcal/mol than $\Delta G^\ddagger = 5.69$ kcal/mol in $n = 1$ TS1 (Fig. 1). The good hydrogen-bond directionality leads to the concerted pathway. Fig. 3 shows the $n = 3$ addition path. After the TS, not the adduct but a zwitterionic inter-

mediate (**Int**) was obtained by IRC calculations. After the **Int**, the second TS geometry could not be obtained despite many attempts. **Int** seems not to have a route to the product, because the silicon lone-pair orbital is expanded, deviating from the line of the bond interchange, $\text{O}(25)\text{--H}(26)\cdots\text{Si}(2) \rightarrow \text{O}(25)\cdots\text{H}(26)\text{--Si}(2)$. Thus, the MeOH dimer ($n = 2$) is the best reactant toward the $\text{Si}=\text{Si}$ bond.

Fig. 4 shows the concerted CF_3OH addition path, which was also obtained in Ref. [9b]. Our ΔG^\ddagger value ($=12.28$ kcal/mol) is small. Fig. 5 shows the concerted $(\text{CF}_3\text{OH})_2$ addition path. The strainless TS geometry gave a remarkably small ΔG^\ddagger ($=3.17$ kcal/mol). At the TS, $\text{H}(23)\cdots\text{Si}(2)$ bond formation is advanced much more than that in Fig. 2. That is, the contrast suggested in Scheme 1 is described by that

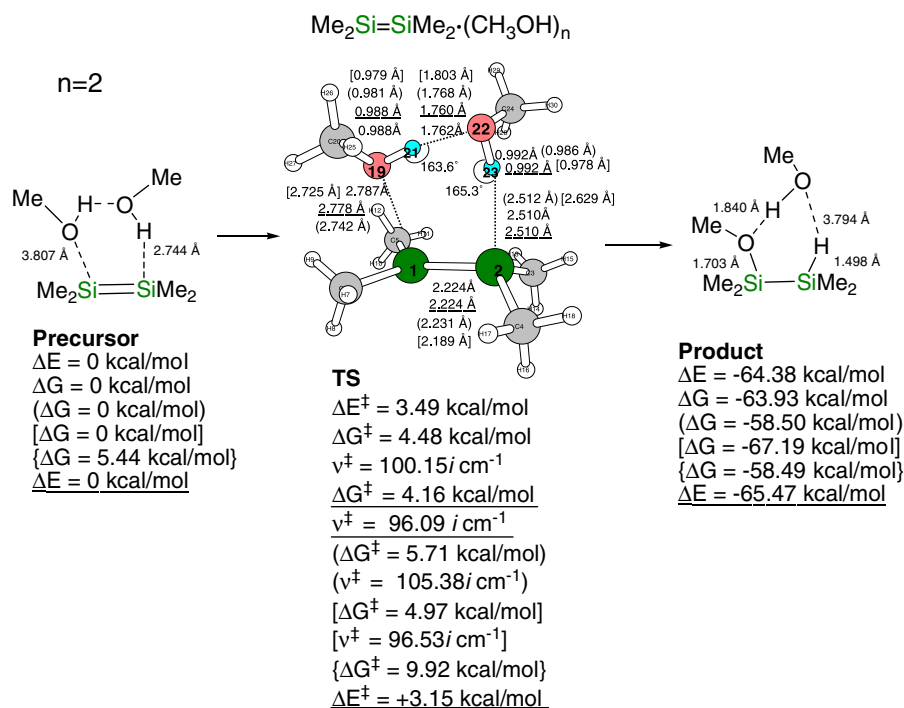


Fig. 2. The concerted addition path of two MeOH molecules to **1**. The underlined numbers were obtained by gas-phase RB3LYP/6-31G* calculations.

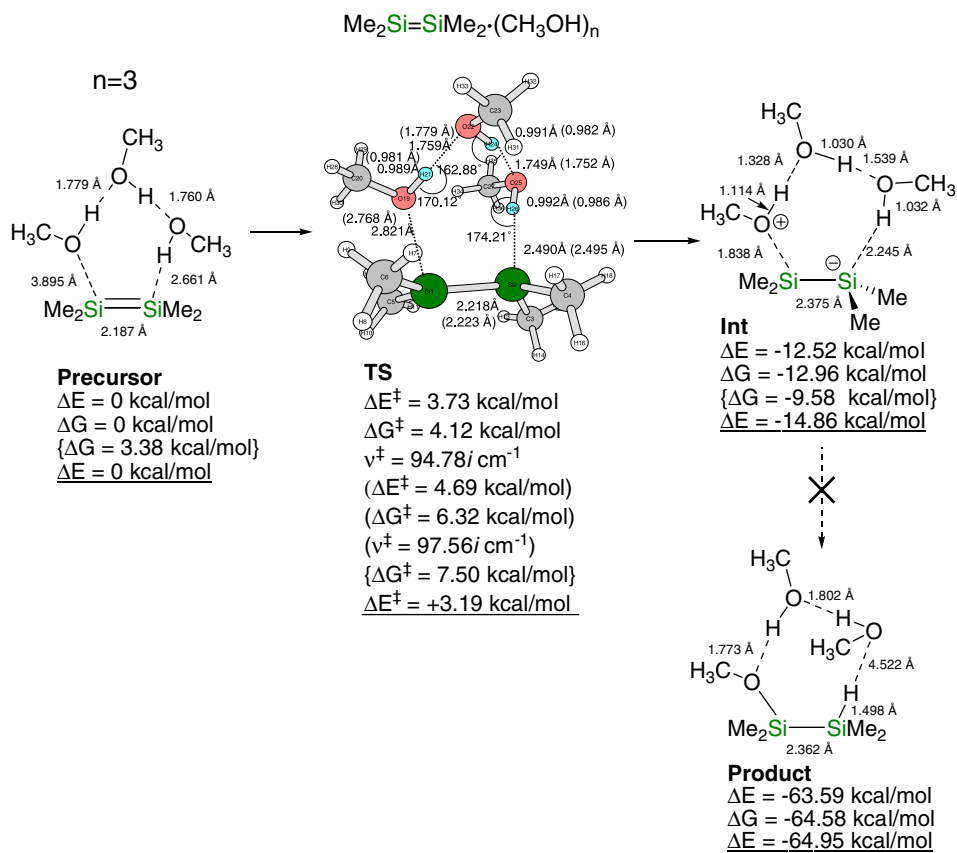


Fig. 3. The concerted addition path of three MeOH molecules to **1** up to a zwitterionic intermediate (not up to the product). The path, **Int** → product, was not obtained. Values in braces are relative to the Gibbs free energies of $\text{Me}_2\text{Si}=\text{SiMe}_2$ and $(\text{MeOH})_3$.

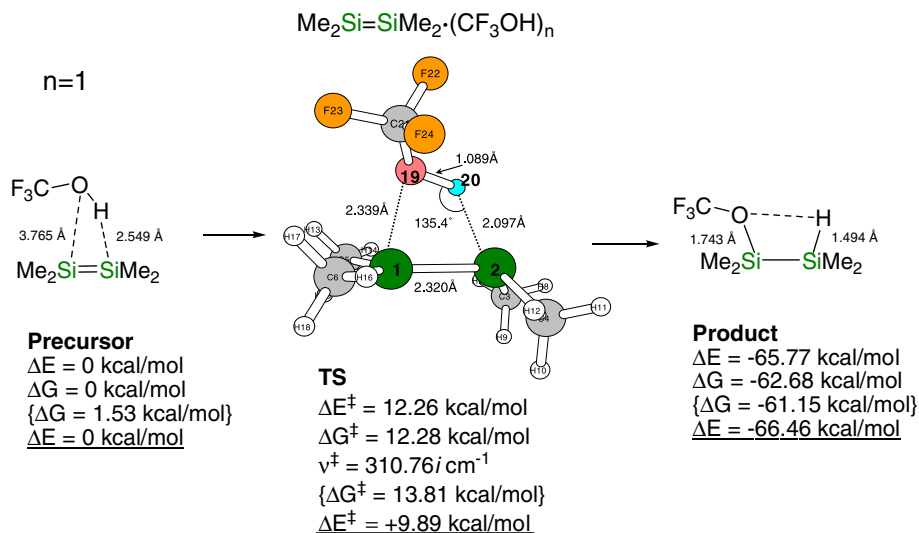


Fig. 4. The concerted addition path of one trifluoromethanol (CF_3OH) to **1**. The path was also reported in Ref. [9b]. In braces, ΔG and ΔG^\ddagger values are relative to the energies of the isolated states of the disilene and CF_3OH .

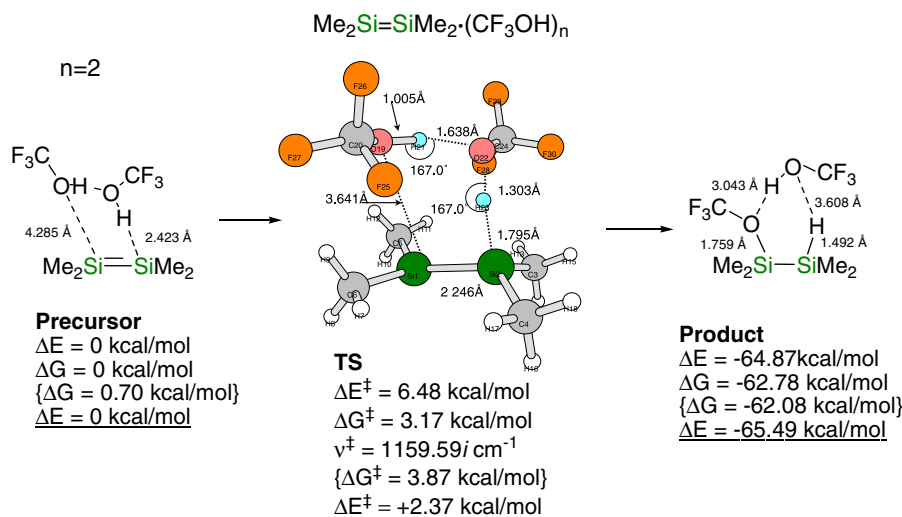


Fig. 5. The concerted addition path of two CF_3OH molecules to **1**. Values in braces are relative to Gibbs free energies of $\text{Me}_2\text{Si}=\text{SiMe}_2 + (\text{CF}_3\text{OH})_2$. $\Delta S^\ddagger = -3.60$ e.u. and $\{\Delta S^\ddagger = -39.70$ e.u.} were obtained.

between $(\text{CF}_3\text{OH})_2$ addition and $(\text{MeOH})_2$ addition, and the high reactivity of the CF_3OH dimer has been demonstrated.

The high reactivities of dimeric reagents toward double bonds were reported in reactions of [ethylene + $(\text{HF})_2$] [18] and [formaldehyde + $(\text{MeLi})_2 + \text{H}_2\text{O}$] [19]. In their transition states, bond interchanges occur readily along the strainless circuits composed of covalent and intermolecular bonds.

Indeed, the result of $\Delta E^\ddagger = 6.48$ kcal/mol $>$ $\Delta G^\ddagger = 3.17$ kcal/mol appears to be curious, but the difference comes from that of the zero-point vibrational energies (ZPEs), ZPE (precursor) = 131.45 kcal/mol and ZPE (TS) = 127.34 kcal/mol. Thus, the ZPE-containing energy

difference, $\underline{\Delta E}^\ddagger = 2.37$ kcal/mol is similar to $\Delta G^\ddagger = 3.17$ kcal/mol.

The dimerization energies for $\text{MeOH} + \text{MeOH} \rightarrow \text{MeOH} \cdots \text{MeOH}$ and $\text{CF}_3\text{OH} + \text{CF}_3\text{OH} \rightarrow \text{CF}_3\text{OH} \cdots \text{CF}_3\text{OH}$ were computed to be ΔU^0 ($T = 0$ K) = -5.52 kcal/mol and ΔU^0 ($T = 0$ K) = -5.86 kcal/mol, respectively. The dimerization enhances the acidities of terminal protons, $\text{MeOH} \cdots \text{MeO}-\text{H}$ (+0.411) compared with $\text{MeO}-\text{H}$ (+0.395) and $\text{CF}_3\text{OH} \cdots \text{CF}_3\text{O}-\text{H}$ (+0.456) compared with $\text{CF}_3\text{O}-\text{H}$ (+0.439). Acidities are represented by Mulliken electronic charges. The dimerization enhances the basicities of the reaction-center oxygens, $\text{MeO}(-0.660)-\text{H} \cdots \text{MeOH}$ compared with $\text{MeO}(-0.619)-\text{H}$ and $\text{CF}_3\text{O}(-0.607)-\text{H} \cdots \text{CF}_3\text{OH}$ compared with $\text{CF}_3(-0.575)-$

H. Thus, the alcohol dimer is more reactive than the dimer, in addition to the hydrogen-bond directionality.

3.2. Reactions between tetramethyldisilene ($\text{Me}_2\text{Si}=\text{SiMe}_2$, **1**) and phenol derivatives

Addition reactions between **1** and the seven phenols shown in Scheme 2 were investigated.

For each phenol derivative, $n = 1$ and $n = 2$ addition paths were determined. Two activation free energies were calculated. One is that relative to the Gibbs free energies of the two isolated reactants, **1** and the phenol derivative. The other is that relative to the precursor (i.e., the weakly bound complex prior to the addition TS). Table 1 shows the two free energy changes.

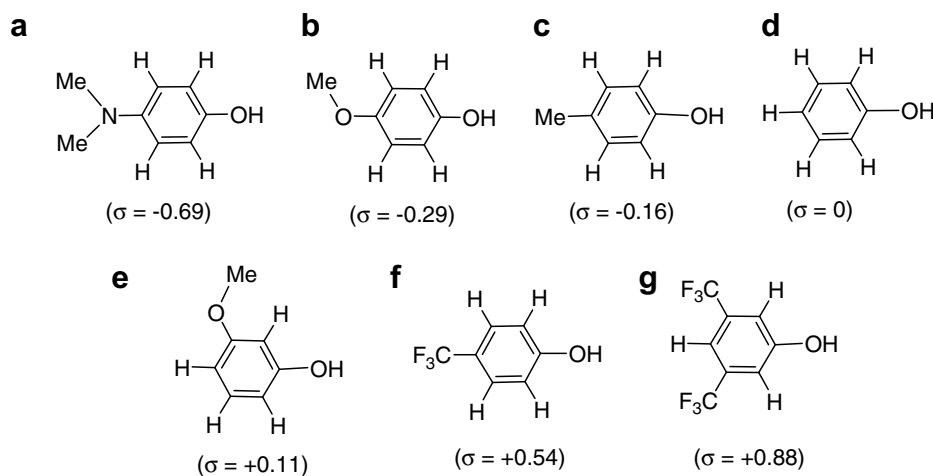
In both changes, the ΔG^\ddagger values of $n = 2$ paths are smaller than those of the $n = 1$ paths regardless of the substituent on the phenyl ring. The difference in the $n = 1$ and $n = 2$ energies for the electron-withdrawing substituents is larger than that for the electron-donating substituents. For instance, while $\Delta G^\ddagger(n = 1, \text{g}) = 14.9 \text{ kcal/mol} \gg \Delta G^\ddagger(n = 2, \text{g}) = 9.41 \text{ kcal/mol}$ (relative to reactants), $\Delta G^\ddagger(n = 1, \text{a}) = 12.39 \text{ kcal/mol} \geq \Delta G^\ddagger(n = 2, \text{a}) = 10.83 \text{ kcal/mol}$. The ΔG^\ddagger values relative to the reactants were found to be similar, irrespective of the substituents. The trend for the concave

Hammett plots in Ref. [9a] was not obtained for the tetramethyldisilene substrate. Aside from the trend, it is confirmed that $n = 2$ is the reactant toward the tetramethyldisilene **1**.

In the right of Table 1, figure numbers are shown, where Fig. Ss are in the Supporting Information. Typically, three TS geometries (Figs. 6–8) are examined. Fig. 6 shows the reaction path of $n = 2$ (a), where the shape of the reaction center of the strainless TS geometry is close to that in Fig. 2 ($\text{Me}_2\text{Si}=\text{SiMe}_2 + (\text{MeOH})_2$). The $\text{O}(19)\cdots\text{Si}(1)$ bond formation is more advanced than $\text{H}(23)\cdots\text{Si}(2)$ formation according to Scheme 1. Two aryl groups do not sterically hinder approach to the tetramethyldisilene. The phenol substituents influence appreciably the TS geometries, and TS for 3,5-(CF_3) $_2\text{C}_6\text{H}_3\text{OH}$ is later than those for p -(H_3C) $_2\text{N}-\text{C}_6\text{H}_4\text{OH}$ and phenol.

3.3. Reactions between tetramesityldisilene ($\text{Mes}_2\text{Si}=\text{SiMes}_2$, **2**) and methanol and rotation around the Si–Si bond

The addition of a MeOH molecule ($n = 1$) to the tetramesityldisilene ($\text{Mes}_2\text{Si}=\text{SiMes}_2$, **2**) was traced, and the result is shown in Fig. S12 (Supporting Information). A stepwise path similar to that in Fig. 1 was obtained with $\Delta G^\ddagger(\text{TS1}) = 14.05 \text{ kcal/mol}$ and $\Delta G^\ddagger(\text{TS2}) = 9.50 \text{ kcal/}$

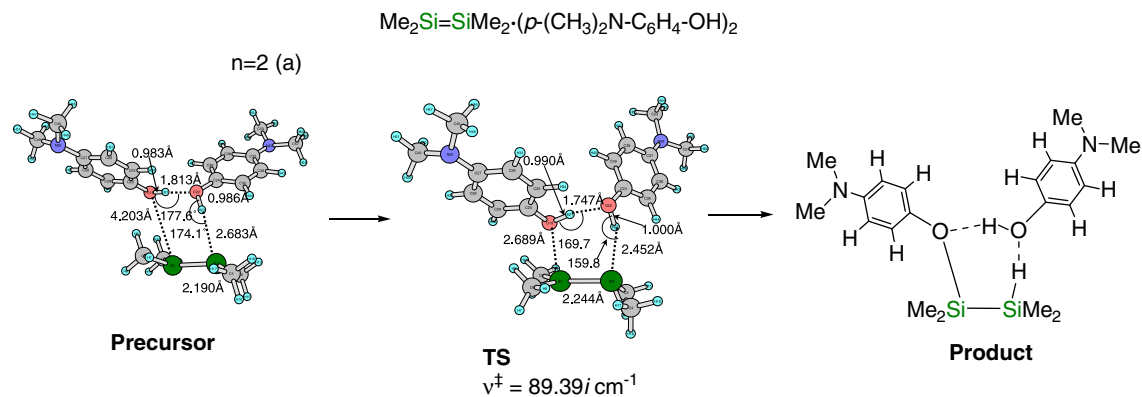
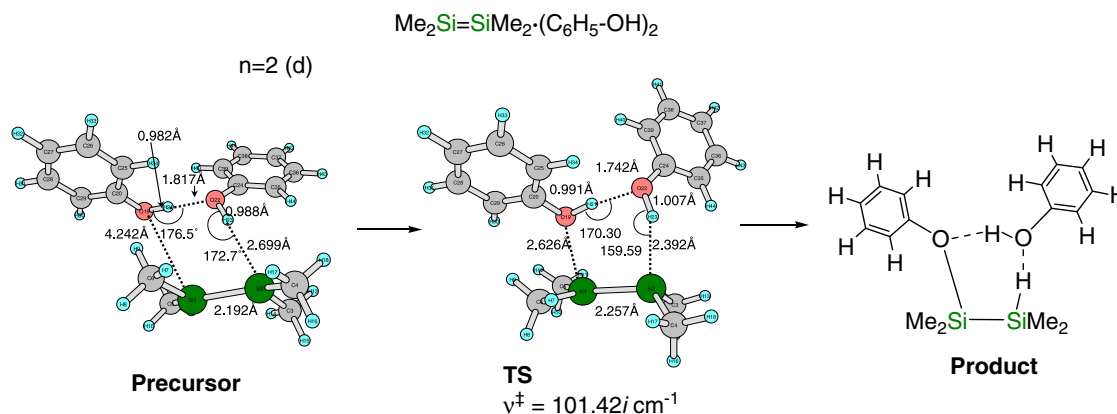
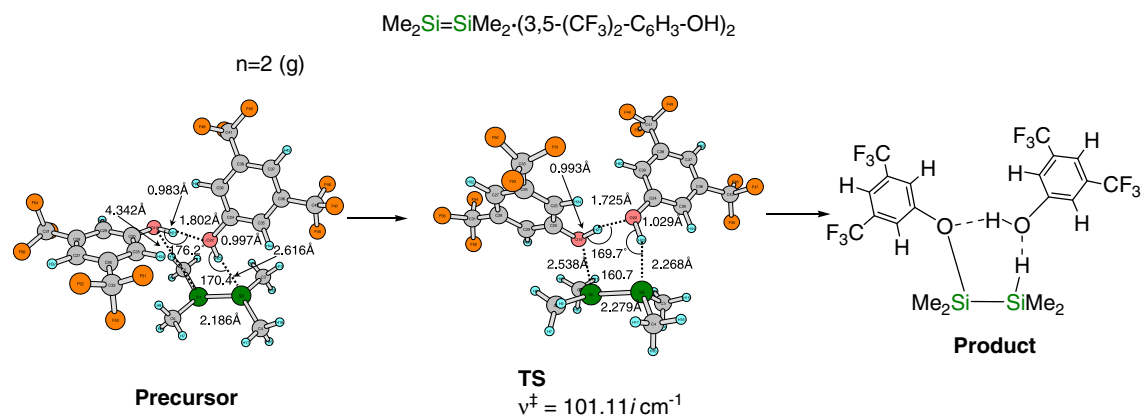


Scheme 2. Structural formulae of the substituted phenols used in the kinetic study [9a] and the present study.

Table 1
The calculated activation free energies (RB3LYP/6-31G* SCRF = dipole in kcal/mol, $T = 298.15 \text{ K}$, $p = 1 \text{ atm}$) for the addition reactions in Eq. (1)

	Substituent(s) on ArOH	ΔG^\ddagger (relative to reactants) ^a		ΔG^\ddagger (relative to precursor)		TS geometries	
		$n = 1$	$n = 2$	$n = 1$	$n = 2$	$n = 1$	$n = 2$
(a)	p -(H_3C) $_2\text{N}$ -	12.39 (12.68)	10.83 (9.99)	7.53	5.98	Fig. S1	Fig. 6
(b)	p - CH_3O -	13.42	10.32	8.68	6.62	Fig. S2	Fig. S8
(c)	p - CH_3 -	12.39	10.72	8.57	6.34	Fig. S3	Fig. S9
(d)	H-(parent)	13.48 (13.56)	10.53 (10.08)	8.89	6.54	Fig. S4	Fig. 7
(e)	m - CH_3O -	13.15	10.61	8.89	6.99	Fig. S5	Fig. S10
(f)	p - CF_3 -	14.49	10.92	10.60	8.37	Fig. S6	Fig. S11
(g)	3,5-(CF_3) $_2$ -	14.90 (14.52)	9.41 (9.59)	13.04	7.22	Fig. S7	Fig. 8

^a Relative to disilene and $(\text{ArOH})_n$. Values in parentheses for (a), (d) and (g) are by gas-phase calculations.

Fig. 6. The concerted addition path of two *p*-(dimethylamino)phenol molecules to **1**. The ΔG^\ddagger value is in Table 1.Fig. 7. The concerted addition path of two phenol molecules to **1**.Fig. 8. The concerted addition path of two 3,5-bis(trifluoromethyl)phenol molecules to **1**.

mol by ONIOM free energies. Fig. 9 shows the $n = 2$ path, which is also a stepwise path and is in contrast with the concerted path of $n = 2$ (Fig. 2). $\Delta G^\ddagger(\text{TS1}) = 10.04$ kcal/mol and $\Delta G^\ddagger(\text{TS2}) = 3.67$ kcal/mol of $n = 2$ are smaller than the respective ΔG^\ddagger 's of $n = 1$. Thus, the MeOH dimer is the reactant toward the substrate **2**. The result of $\Delta G^\ddagger(\text{TS1}, \text{ Fig. 9}) = +7.65$ (10.04) kcal/mol $>$ $\Delta G^\ddagger(\text{TS}, \text{ Fig. 2}) = +4.48$ kcal/mol was obtained. The result demonstrates that steric crowding by the four mesityl groups works to enlarge the activation free energy.

3.4. Reactions between tetramesityldisilene ($\text{Me}_2\text{Si}=\text{SiMe}_2$, **2**) and phenol derivatives

In this subsection, three typical phenols, (a), (d) and (g) in Scheme 2, were employed as reactants toward the disilene substrate **2**. So far, the alcohol and phenol dimers were shown to be the reactants toward the disilenes (**1** and **2**). However, for *p*-(dimethylamino)phenol (a), exceptionally, $n = 1$ ($\Delta G^\ddagger = 35.75$ kcal/mol, TS, Fig. 10) is more favorable than $n = 2$ ($\Delta G^\ddagger = 38.45$ kcal/mol, TS1, Fig. S13 in

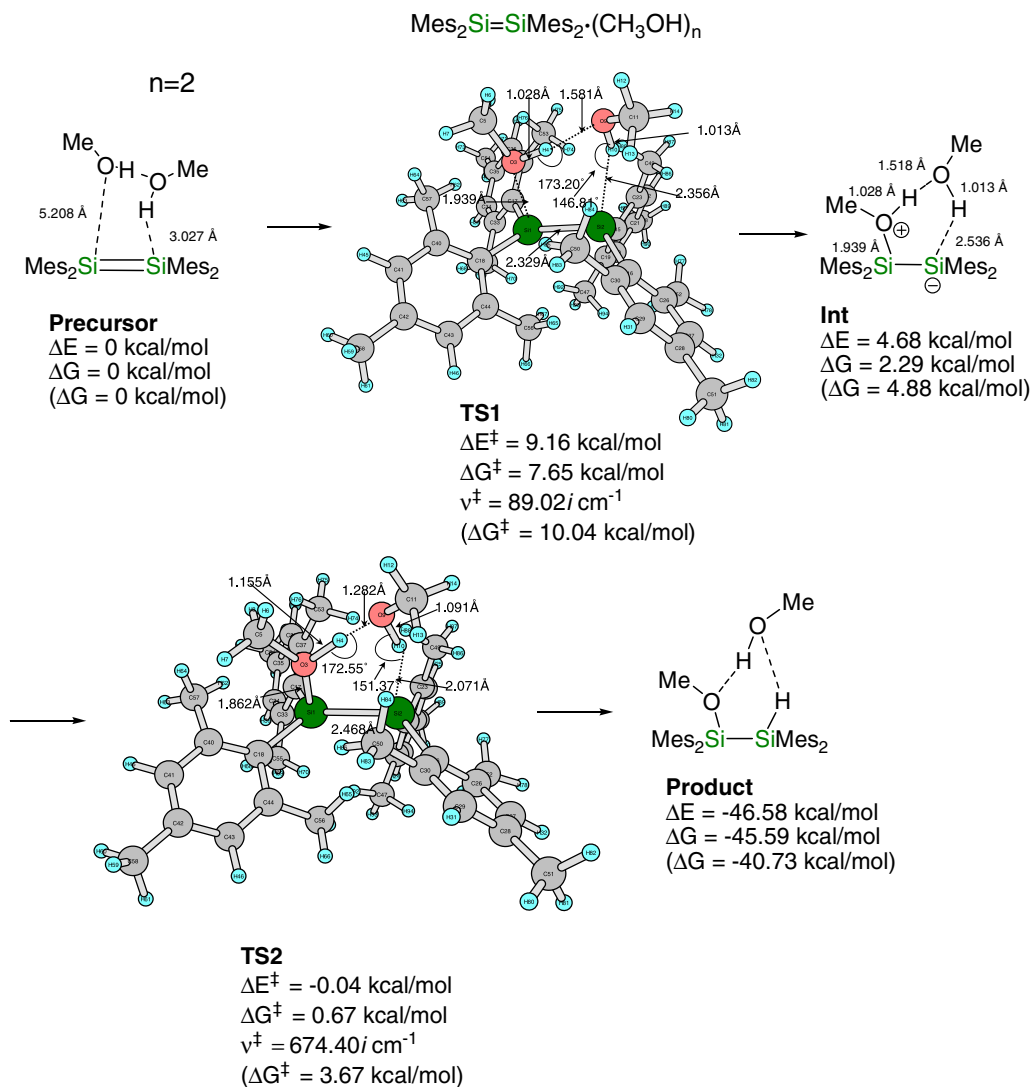


Fig. 9. The stepwise addition path of two MeOH molecules to tetramesityldisilene **2**. Values without parentheses are by RB3LYP/6-31G* SCRF = dipole single-point calculations. Those with parentheses are changes in the ONIOM free energies. The mesityl group (Mes) is defined in Scheme 1.

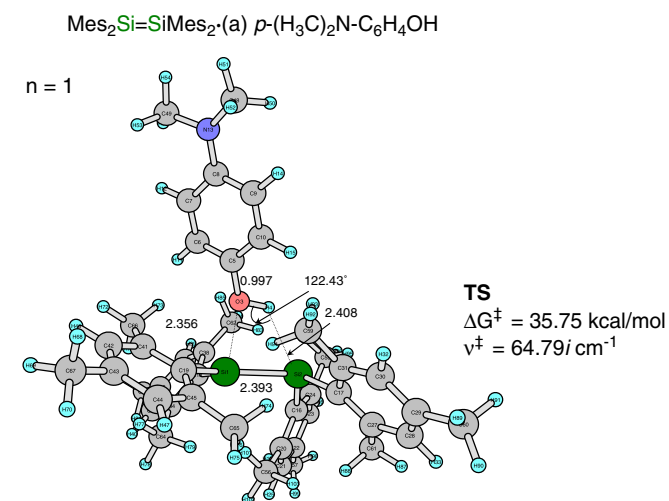


Fig. 10. The concerted addition path of one *p*-(dimethylamino)phenol molecule to **2**.

Supporting Information). This is in contrast with the result in Table 1(a), $\Delta G^\ddagger(n=1) > \Delta G^\ddagger(n=2)$. Toward the sterically congested Si(1)=Si(2) bond of **2**, the nucleophilic and concerted approach of one molecule is likely. By congestion, the dimer ($n=2$) is obligated to undergo a stepwise path via TS1 (Fig. S13) and TS2 (Fig. S14).

The phenol reactant (d) toward **2** was examined. The phenol dimer ($n=2$) reacts with **2** in a stepwise path via TS1 (Fig. 11, $\Delta G^\ddagger = 33.44$ kcal/mol) and TS2 (Fig. S16, $\Delta G^\ddagger = 28.31$ kcal/mol). On the other hand, the monomer ($n=1$) reacts concertedly by $\Delta G^\ddagger = 37.25$ kcal/mol (Fig. S15, Supporting Information). The $n=2$ reaction is more favorable than the $n=1$ reaction. For the reactant (g), the superiority of $n=2$ ($\Delta G^\ddagger = 27.65$ kcal/mol, Fig. 12) over $n=1$ ($\Delta G^\ddagger = 37.00$ kcal/mol, Fig. S17) is more distinct. The addition of the 3,5-(CF₃)₂ substituted phenol (g) proceeds concertedly for both $n=1$ and $n=2$.

The additions of the phenol derivatives to **2** are reviewed. Owing to the steric congestion of the tetra-mesi-

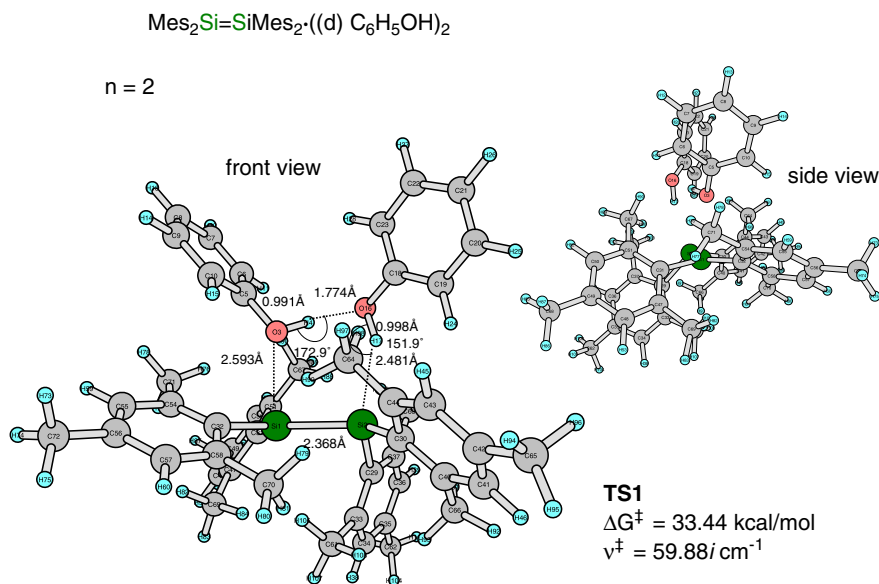


Fig. 11. The first transition state of the stepwise addition path of two phenol molecules to **2**. The second TS is shown in Fig. S16 (Supporting Information).

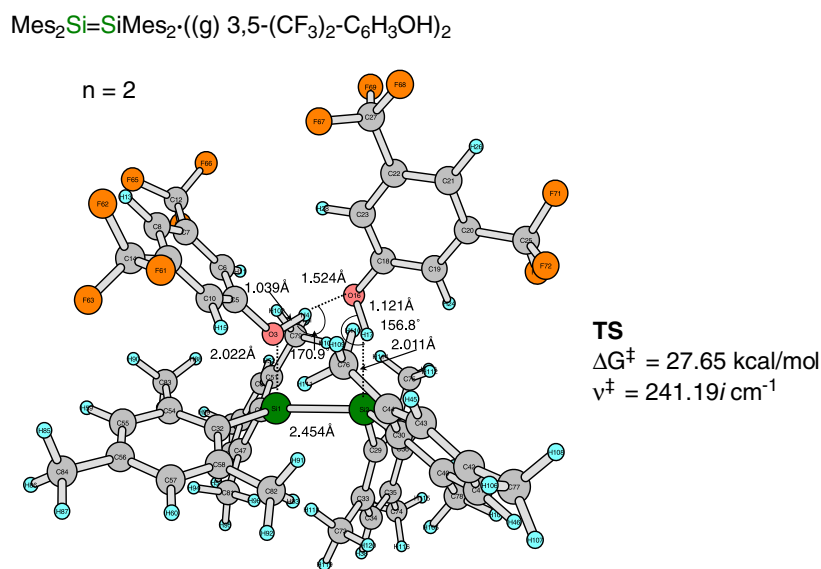


Fig. 12. The concerted addition path of two 3,5-bis(trifluoromethyl)phenol molecules to **2**.

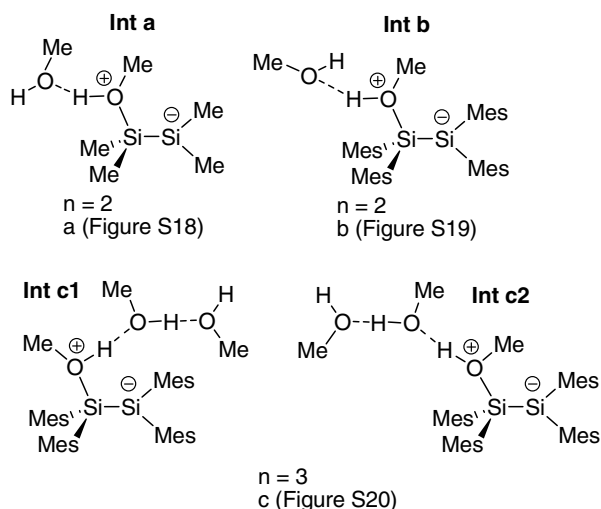
tyl groups of **2**, the calculated ΔG^\ddagger values are larger than those for the tetramethyldisilene **1**. The dimers ($n = 2$) of the nucleophilic phenols are obligated to add to **2** in the stepwise paths.

The present ΔG^\ddagger values, ΔG^\ddagger ($n = 1$, *p*-(dimethylamino)-) = 35.75 kcal/mol > ΔG^\ddagger ($n = 2$, H-) = 33.44 kcal/mol > ΔG^\ddagger ($n = 2$, 3,5-(CF₃)₂-) = 27.65 kcal/mol, are inconsistent with the experimental ΔG^\ddagger values of the concave Hammett plots [9a]. In this case, there is no agreement in the values between calculations and experiment.

So far, reaction paths of additions of alcohols and phenols to disilenes have been investigated. Other precursor and/or intermediate geometries might lead to other reaction channels. First, geometric isomers of the $n = 2$ precur-

sor of Fig. 2 ((MeOH)₂ + Me₂Si=SiMe₂) have been sought but have not been found. Second, isomers of **Int** in Fig. 3 ($n = 3$, (MeOH)₃ + Me₂Si=SiMe₂) have been sought, and an optimized geometry (**Int a**) has been obtained (Scheme 3a, Fig. S18 in Supporting Information).

The one-center adduct **Int a** is 8.18 kcal/mol less stable (in Gibbs free energy, $T = 298.15 \text{ K}$ and $p = 1 \text{ atm}$) than **Int** in Fig. 3. From the intermediate **Int a**, only the rotation path to **Int** is present and other reaction channels are absent. In Scheme 3b, a one-center adduct of Me₂Si=SiMe₂ + (MeOH)₂, **Int b**, is shown, and the optimized geometry is shown in Fig. S19. **Int b** is an isomer of **Int** in Fig. 9, and **Int b** is 19.30 kcal/mol less stable than **Int** in Fig. 9. In Scheme 3c, two one-center adducts, **Int c1** and



Scheme 3. Zwitterionic intermediates calculated.

Int c2, are shown, which are composed of $\text{Me}_2\text{Si}=\text{SiMe}_2$ and $(\text{MeOH})_3$. Their optimized geometries are shown in Fig. S20. **Int c1** is 0.71 kcal/mol less stable than **Int c2**. Those zwitterionic intermediates in Scheme 4 are transient species and might be concerned with the stereochemical change of the products [8c]. The mechanism of stereochemical scrambling is beyond the scope of the present study.

3.5. Comparison of precursor and TS geometries between disilene $(\text{MeOH})_2$ and silene $(\text{MeOH})_2$

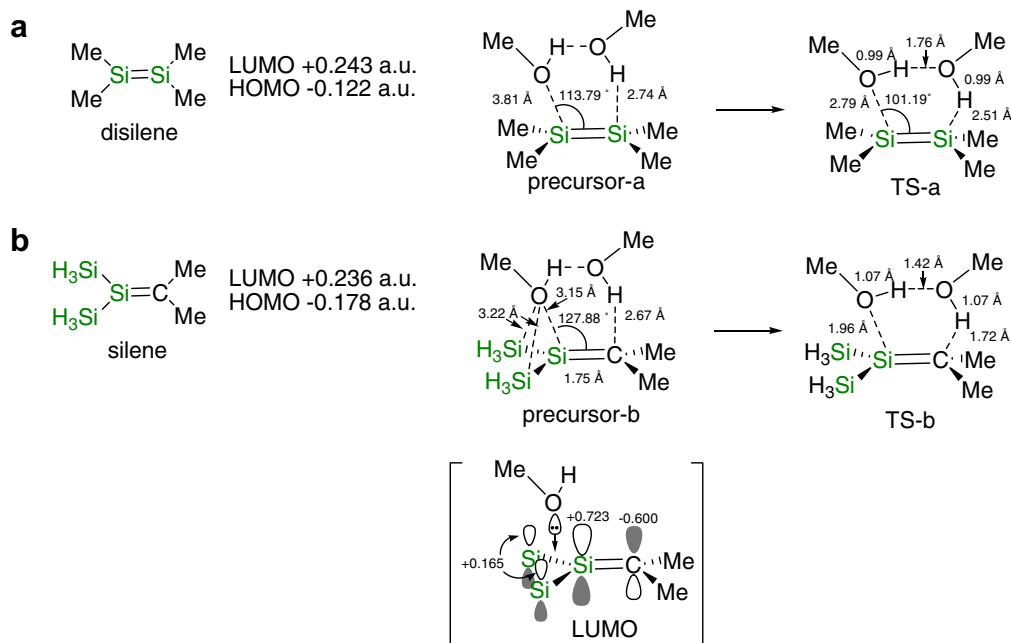
Recently, calculations of MeOH addition to silenes were reported [20]. MeOH monomer and dimers were adopted

in RB3LYP/6-31G* and MP2/6-31G* calculations, while the trimer addition was not examined. The dimer addition, $(\text{H}_3\text{Si})_2\text{Si}=\text{CMe}_2 + (\text{MeOH})_2$, is comparable with that in Fig. 2. The comparison is illustrated in Scheme 4. Geometries of precursor-a and TS-a are those in Fig. 2, and those of precursor-b and TS-b are in Fig. 7 of Ref. [20]. The geometry of precursor-a is substantially different from that of precursor-b. In the latter, the left sided MeOH molecule is located outside the Si–C region. The molecule is bound to three Si sites. The triple coordination is understandable in terms of the LUMO shape of $(\text{H}_3\text{Si})_2\text{Si}=\text{CMe}_2$. The lobes on three Si atoms have the same positive signs, with which the lone-pair orbital of the MeOH oxygen may overlap effectively.

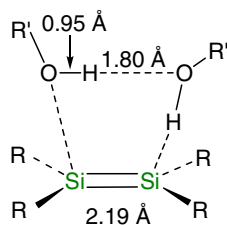
FMO energies are compared. Orbital energies of LUMO (+0.243 a.u. and +0.236 a.u.) are similar, which indicates that the electrophilicity of the disilene is similar to that of the silene. In contrast, HOMO of disilene (−0.122 a.u.) is higher than that of silene (−0.178 a.u.); the nucleophilicity of the former is larger than the latter. The TS geometries reflect the nucleophilicity difference. In TS-a, $\text{Me}_2\text{Si}=\text{SiMe}_2$ is distant from $(\text{MeOH})_2$ as an “early” transition state [21]. But, in TS-b, the MeOH dimer is obligated to be closer to $(\text{H}_3\text{Si})_2\text{Si}=\text{CMe}_2$ to enhance the nucleophilicity through the $\text{O} \rightarrow \text{Si} \rightarrow \text{C}$ electronic charge migration.

4. Concluding remarks

In this work, the addition reactions of alcohols and phenols to the disilenes **1** and **2** have been investigated by DFT and ONIOM calculations. For tetramethyldisilene (**1**), not the monomers ($n = 1$) but the dimers ($n = 2$) of the alcohols



Scheme 4. Comparison of FMO energies (a.u. unit, 1 a.u. = 627.51 kcal/mol), precursor and TS geometries between $\text{Me}_2\text{Si}=\text{SiMe}_2(\text{MeOH})_2$ (a) and $(\text{H}_3\text{Si})_2\text{Si}=\text{CMe}_2(\text{MeOH})_2$ (b). Geometries of precursor-b and TS-b were taken from Ref. [20]. Orbital energies of HOMO and LUMO and LUMO orbital coefficients were calculated with RHF/STO-3G*.



Scheme 5. A molecular model composed of the disilene and the alcohol dimer with standard bond lengths. The Si=Si standard bond length is taken from M. Kaftory, M. Kapon, M. Botoshansky, in: Z. Rappoport, Y. Apeloig (Eds.), *The Chemistry of Organic Silicon Compounds*, vol. 2, Wiley-VCH, Chichester, 1998, p. 181.

and phenols are the reactants for concerted additions. The superiority of $n = 2$ over $n = 1$ is more distinct for alcohols with electron-withdrawing groups than for those with electron-donating groups. The molecular model shown in Scheme 5 demonstrates that the dimer participates in the addition via a proton relay, $\text{O}-\text{H}\cdots\text{O} \rightarrow \text{O}\cdots\text{H}-\text{O}$ [22].

For tetramesityldisilene (**2**), the dimer of the nucleophilic alcohol adds by a stepwise path owing to steric congestion. By the congestion, exceptionally, the monomer ($n = 1$) of the phenol (a) with the most electron-donating group among the seven (Scheme 2) adds to **2**.

Appendix A. Supplementary material

Figs. S1–S20 and the Cartesian coordinates of the optimized geometries of Figs 1–12 and S1–S20. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2008.01.035](https://doi.org/10.1016/j.jorganchem.2008.01.035).

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