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A Mechanistic Study of the Addition of Alcohol to a Five-Membered Ring Silene via a Photochemical Reaction

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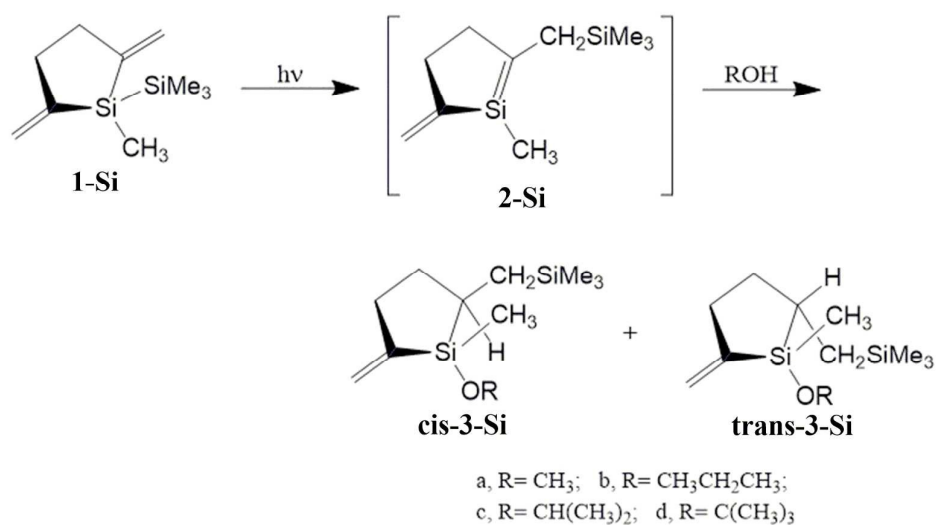
Abstract

The mechanism for the photochemical rearrangement of a cyclic divinylsilane (**1-Si**) in its first excited state ($^1\pi \rightarrow ^1\pi^*$) is determined using the CAS/6-311G(d) and MP2-CAS/6-311++G(3df,3pd) levels of theory. The photoproduct, a cyclic silene, reacts with various alcohols to yield a mixture of cis- and trans- adducts. The two reaction pathways are denoted as the cis- addition path (path A) and the trans- addition path (path B). These model studies demonstrate that conical intersections play a crucial role in the photo-rearrangements of cyclic divinylsilanes. The theoretical evidence also demonstrates that the addition of alcohol to a cyclic divinylsilane follows the reaction path: cyclic divinylsilane \rightarrow Franck-Condon region \rightarrow conical intersection \rightarrow photoproduct (cyclic silene) \rightarrow local intermediate (with alcohol) \rightarrow transition state \rightarrow cis- or trans- adduct. The theoretical studies demonstrate that the steric effects as well as the concentrations of CH₃OH must have a dominant role in determining the yields of the final adducts with stereochemistry. The same mechanism for the carbon derivative (**1-C**) is also considered in this work.

However, the theoretical results indicate that **1-C** does not undergo a methanol addition reaction via the photochemical reaction pathway, since its energy of conical intersection (**S₁/S₀-CI-C**) is above that of its FC (**FC-C**). The reason for these phenomena could be due to the fact that the atomic radius of carbon is much smaller than that of silicon (77 and 117 pm, respectively). As a result, it would cause the conformation for **1-C** is more sterically congested than that for **1-Si**, along the 1,3-silyl-migration pathway.

I. Introduction

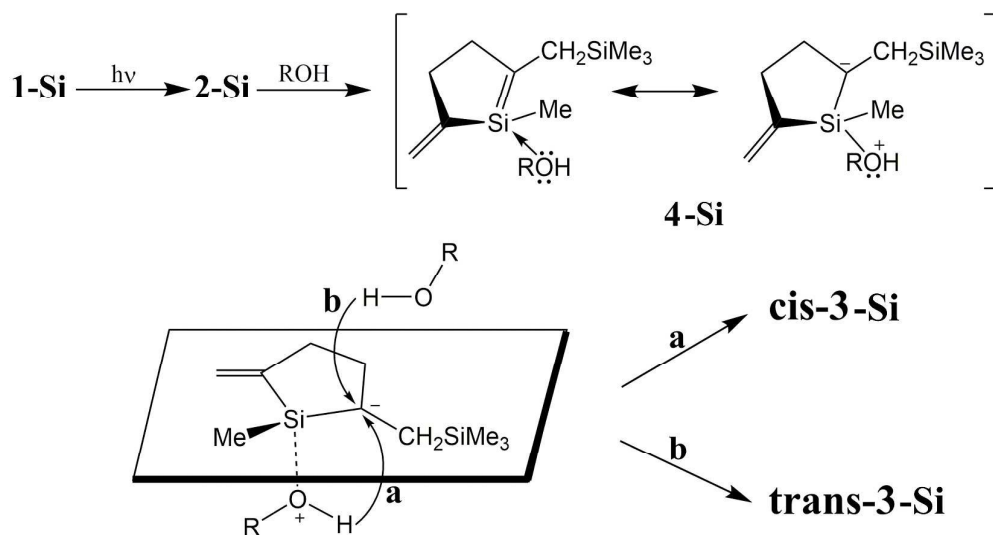
Silenes that feature a C=Si bond are important intermediates in a wide variety of thermal and photochemical reactions in organosilicon compounds.¹ In fact, because of the large difference in the electronegativity values for carbon and silicon, the C=Si bond is quite polar and strongly electrophilic, so silenes exhibit high reactivity toward nucleophiles, wherein the silicon atom is the site that is attacked by water, alcohols, amines and other nucleophiles, which are important both fundamentally and practically.^{1,2}



Scheme 1

It has been reported by Kira and co-workers that the irradiation of a cyclic divinylsilane (**1-Si**) in various alcohols (see a, b, c, and d in Scheme 1) gives a mixture of *cis*- (**cis-3-Si**) and *trans*- adducts (**trans-3-Si**),³ as shown in Scheme 1. Namely, the stereochemistry for the addition of a series of alcohols to a cyclic conjugated silene (**2-Si**) that is produced by the photolysis of **1-Si**, was determined.³ One intriguing hypothesis was derived to describe the mechanism for these alcohol addition reactions of **1-Si**, as schematically illustrated in Scheme

2.^{3,4} Kira and co-workers proposed that this reaction involves two competing routes (path a and path b): one of which involves intramolecular H-transfer and the other of which involves protonation of the complex by a second molecule of alcohol. It was suggested that *syn*- addition (**cis-3-Si**) results from intramolecular proton transfer and the intermolecular proton transfer pathway results in the *anti*- addition (**trans-3-Si**).³ Schemes 1 and 2, also show that the 1,3-silyl migration from silicon to carbon plays a prominent role in this type of photo-isomerization reaction. In fact, many reactions that involve photochemical 1,3-silyl migrations from carbon to carbon,⁵ or between heteroatoms,⁶ have been reported. However, there have been few theoretical studies of the mechanistic and stereochemical details.⁷



These previous experimental results inspire this study. To the author's best knowledge, no theoretical studies have reported the photochemical mechanisms for cyclic divinylsilane **1-Si**. In order to determine the mechanisms for the chemical processes shown in Scheme 1, a theoretical study of the photo- and

thermal reactions of **1-Si** is undertaken. For comparison, the photochemical reaction mechanism for a similar molecule, cyclic divinylethane **1-C**, is also studied. In particular, it is shown that the conical intersections⁸ play a crucial role in the photochemical rearrangements of **1-Si** and **1-C**. The reaction process is explained in terms of this information. It is envisioned that this combination of observed experimental work and theoretical study allows a comprehensive understanding of the excited state behavior of cyclic divinylidisilanes.

II. Computational Methods

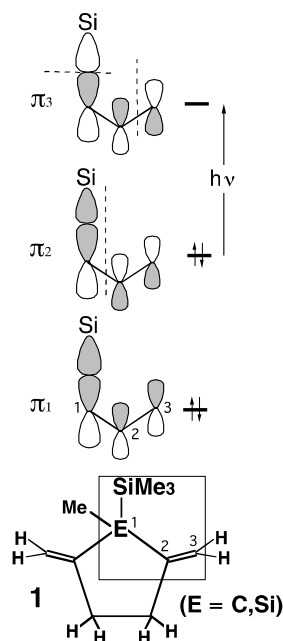
The CASSCF calculations were performed using the multi-configurational self-consistent field (MCSCF) program in GAUSSIAN 09.⁹ The active spaces that are used to describe the photoreactions of **1-C** and **1-Si** and methanol respectively comprise six electrons in six orbitals and six electrons in four orbitals. The CASSCF method was used with the 6-311G(d) basis sets for geometry optimization. That is to say, the present computations should be written as CAS(6,6 + 6,4)/6-311G(d). The state averaging was used 50% for singlet ground state (S_0) and singlet first excited state (S_1), respectively. The energy convergence of the conical intersection points was set up to 10^{-6} Hartrees. The optimization of the conical intersections was achieved in the $(f - 2)$ -dimensional intersection space, using the method of Bearpark et al.,¹⁰ which is implemented in the Gaussian 09 program.

The multi-reference Møller-Plesset (MP2-CAS) algorithm¹¹, as implemented in the GAUSSIAN 09 program package, was used to correct the energetics for dynamic electron correlation. Unless otherwise stated, the relative energies that are given in the text are those determined at the MP2-CAS(6,6 +

6,4)/6-311++G(3df,3pd) level, using the CAS(6,6 + 6,4)/6-311G(d) geometry (hereafter respectively designed MP2-CAS and CASSCF).

III. General Consideration

Reactant **1** has three p- π atomic orbitals that contain four electrons, which is analogous to an allyl anion,¹² and these form the basis for this study and are shown in Scheme 3. Scheme 3 shows that in the highest occupied molecular orbital (π_2), the HOMO is occupied by two electrons and there is a nodal plane between the silicon and carbon atoms. However, in the lowest unoccupied molecular orbital (LUMO, π_3), there are anti-bonding interactions between the center and the terminal carbon, and the silicon atoms. It is apparent that the lowest singlet $\pi \rightarrow \pi^*$ excitation is the singlet π_2 (HOMO) \rightarrow π_3 (LUMO) transition. The reason for using four orbitals ($2 \sigma + 2 \pi$) rather than six orbitals ($2 \sigma + 4 \pi$) in Scheme 3 is simply because of simplifying the orbital interactions. From Scheme 3, one may concentrate on the simple MO picture to easily understand the origin of the conical intersection. It is noted that if the π and π^* levels in the allyl-like system are mixed the electron density is redistributed.



Scheme 3

The significant feature of the photochemical mechanism of **1** is the location of the conical intersection in the excited- and ground-electronic states. In this study, the p - π orbital model, as outlined in Scheme 3, is used to determine the conical intersection of the photo-isomerization of the five-membered-ring silane (**1-Si**) and ethane (**1-C**). Since a cyclic silene, **2-Si**, is observed as a singlet photoproduct of a cyclic divinylsilane, **1-Si** (Scheme 1),³ there must also be a photochemical 1,3-silyl migration of **1-Si**. Therefore, a [1,3] sigmatropic shift mechanism that is based on the Woodward-Hoffmann rules (four-electron, photochemically allowed)^{12,13} is suggested for the conversion of the five-membered-ring divinylsilane (**1-Si**) to a cyclic silene (**2-Si**).

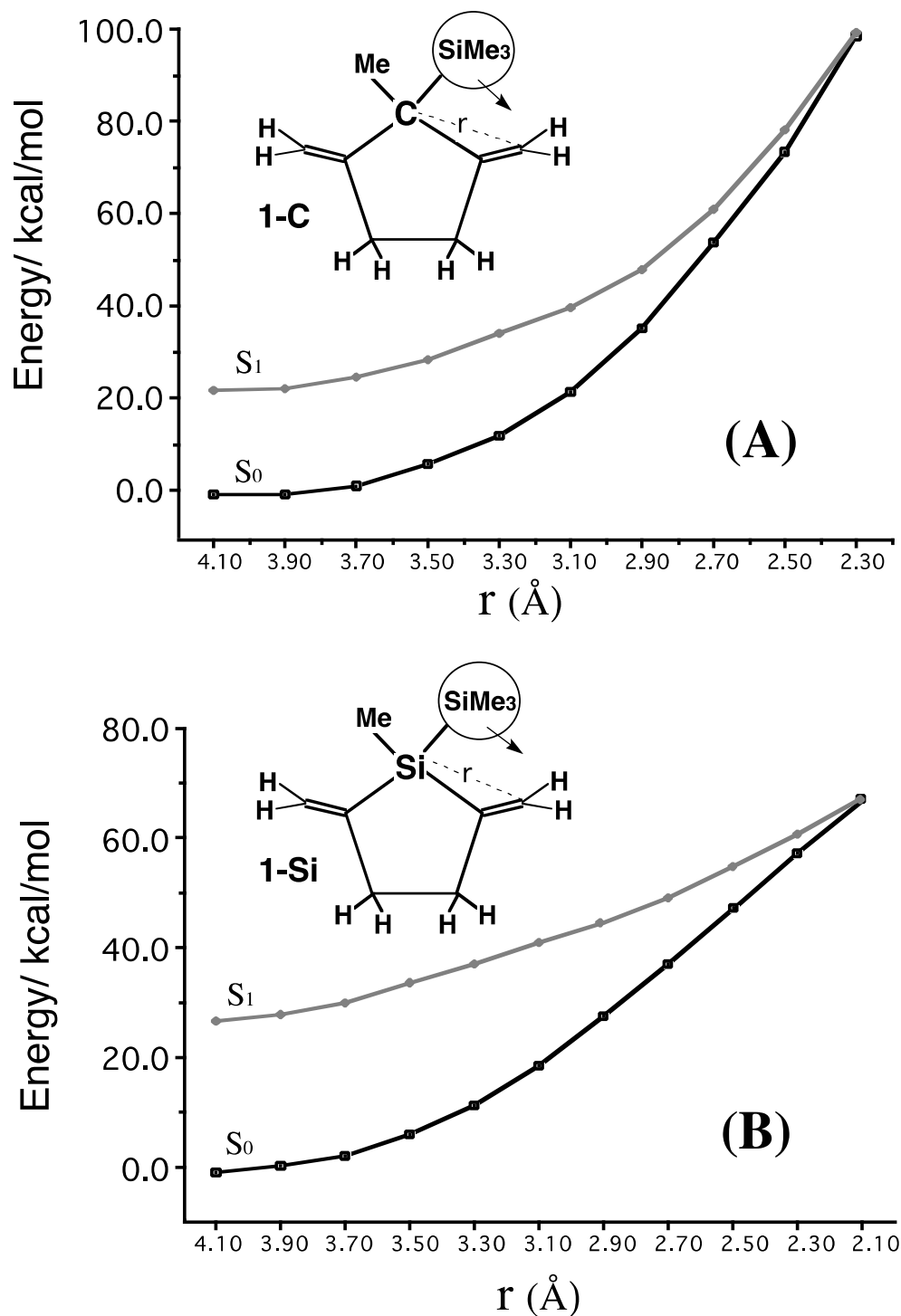


Figure 1: The estimated energy pathway for the migration of 1,3-SiMe₃ migration in reactants (**1-C** and **1-Si** for (A) and (B), respectively) along the distance, r , coordinate optimized for the S_0 and S_1 states at the CAS(6,6)/6-311G(d) level of theory. The relative energy difference with respect to S_0 structures was used. Also see ref. (14) and Supporting Information.

Figure 1 shows the semi-quantitative potential energy surfaces for the S_0 and S_1 states of **1**, when the Si—C distance, r , increases.¹⁴ Although the distance, r , is obtained without full optimization of **1**, it at least demonstrates that there can be a degeneracy between the HOMO and the LUMO, because of the distance in the Si—C direction. The formation of this type of degenerate point also provides further evidence of an improved intramolecular migration in the five-membered ring geometry and of the possible existence of a conical intersection, from where decay to the ground state is fully efficient. Accordingly, these results are used to interpret the mechanism for the photochemical isomerization reactions of **1-C** and **1-Si**, in the next section.

IV. Results and Discussion

The qualitative potential energy surfaces are schematically illustrated in Figure 2. For the **1-Si** and **1-C** systems, Table 1 shows all of the relative energies of the stationary points in relation to their corresponding reactants, at the MP2-CAS/6-311++G(3df,3pd)//CAS/6-311G(d) levels of theory. The calculated geometrical parameters for the stationary points for **1-Si** are also given in Figures 3 (photochemical reaction) and 4 (thermal reaction). The Cartesian coordinates and the energies that are calculated for the various points, at the CASSCF and MP2-CAS levels of theory, are available as supporting information. The **1-Si** molecule is considered firstly, since experimentally reported information for this model is available.³

The vertical excitation energy (**FC-Si**) for **1-Si** was calculated to lie 114 kcal/mol above the ground-state surface at the MP2-CAS level of theory. This

theoretically predicted value is in good agreement with the experimentally reported data (254 nm = 113 kcal/mol).³ Therefore, the computed energies that are given in this work should be reliable for the further discussion of the reaction mechanisms, for which there is no experimental information. Five interesting conclusions can be drawn from Table 1 and Figure 3 (**1-Si**), as follows.

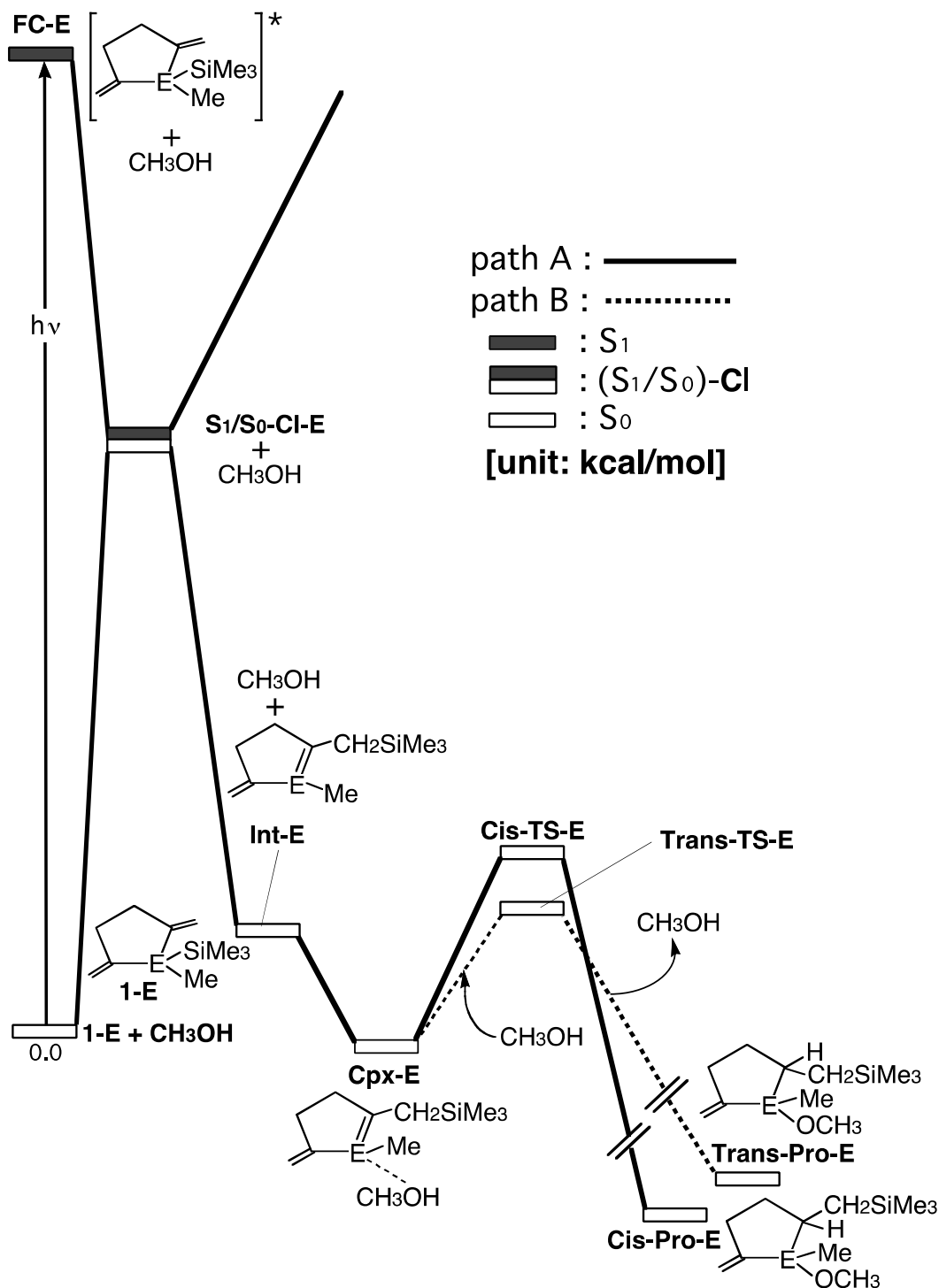


Figure 2: The qualitative energy profiles for the methanol addition reactions of **1-E** ($E = C$ and Si). The abbreviations, FC and CI, respectively represent Frank–Condon and conical intersection. The relative energy differences with respect to the reactants (**1-E** and CH_3OH) at the ground (S_0) state are given in Table 1.

Table 1.

The relative energies (kcal/mol) for the methanol addition reactions of **1-E** (**E** = C and Si) are determined at the MP2-CAS/6-311++G(3df,3pd)//CAS/6-311G(d) level of theory. The solvent effect (SCRF = PCM, solvent = *i*-PrOH) have been considered using the CAS/6-311G(d) + PCM(solvent = *i*-PrOH)//CAS/6-311G(d) method, whose computational results are collected in the parenthesis. The abbreviations, **FC**, **CI**, **Int**, **Cpx**, **TS** and **Pro**, respectively represent Frank–Condon, conical intersection, intermediate, complex, and products. The potential energy surfaces are shown in Figure 2. For more information, see the text.

Molecules	1-Si	1-C
1-E + CH₃OH	0.0 (0.0)	0.0 (0.0)
FC-E + CH₃OH	114.2 (115.1)	90.6 (90.9)
S₁/S₀-CI-E + CH₃OH	86.8 (85.1)	95.8 (95.5)
Int-E + CH₃OH	16.4 (15.6)	13.8 (12.8)
Cpx-E	-0.41 (1.1)	-3.6 (-4.2)
Trans-TS-E	21.9 (22.3)	12.4 (12.7)
Trans-Pro-E	-31.4 (-31.3)	-8.3 (-6.8)
Cis-TS-E	26.9 (27.2)	20.9 (19.3)
Cis-Pro-E	-34.6 (-34.8)	-9.6 (-8.8)

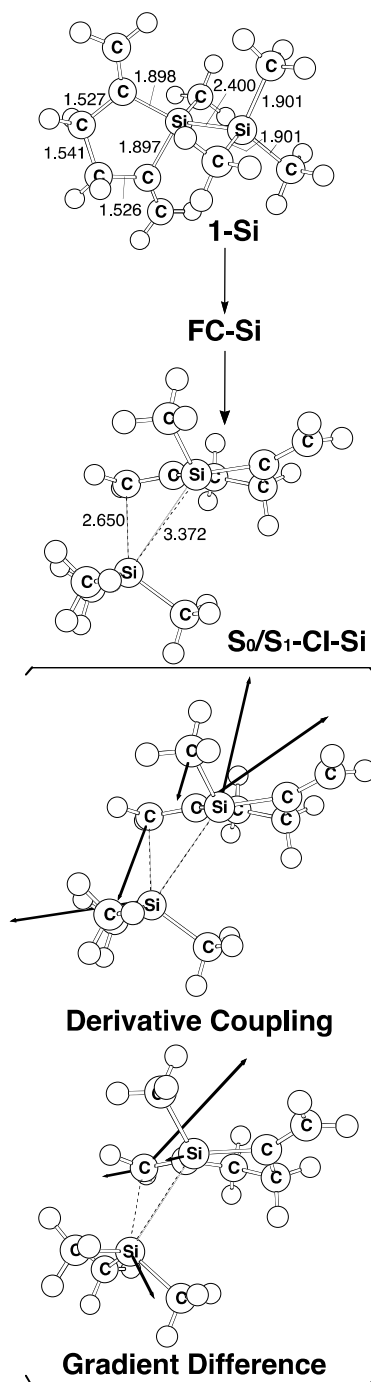


Figure 3: The CASSCF geometries (in Å and deg) for divinyldisilane (**1-Si**) and conical intersection (**CI**). The derivative coupling and gradient difference vectors — those which lift the degeneracy — computed with CASSCF at the conical intersection. The corresponding CASSCF vectors are shown inset. For more information see the Supporting Information.

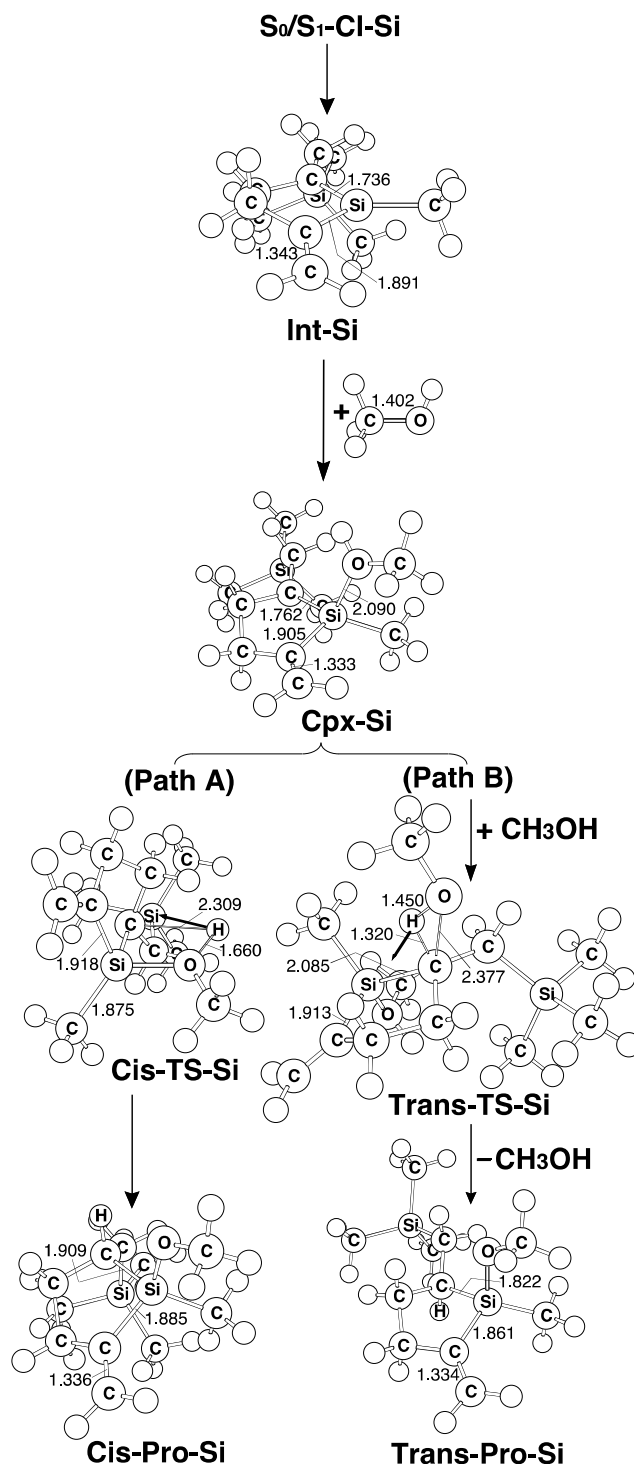


Figure 4: The CASSCF geometries (in Å and deg) for path A and path B of intermediate (**Int**), transition state (**TS**), and isomer products. The heavy arrows indicate the main atomic motions in the transition state eigenvector. For more information see the Supporting Information.

(1) When the $S_0 \rightarrow S_1$ vertical excitation occurs, the system relaxes from the **FC-Si** point ($S_1(S_0 \text{ geom.})$) to the conical intersection point (**$S_1/S_0\text{-CI}$**), as already predicted in Figure 2. The derivative coupling and the gradient difference vectors at the conical intersection for **1-Si** are shown in Figure 3. The gradient difference vector for **$S_1/S_0\text{-CI-Si}$** corresponds to an anti-symmetric stretching motion, which leads to a vibrationally hot species in the S_0 configuration. However, its derivative coupling vector corresponds to the intramolecular migration of a silyl group. The intriguing feature of the geometry of **$S_1/S_0\text{-CI-Si}$** is that one SiMe_3 group lies outside the plane of the five-membered ring, as predicted in the previous section. Planarity is lost in the formation of this conical intersection structure and the C-SiMe_3 and Si-SiMe_3 bond distances are respectively predicted to be 2.650 Å and 3.372 Å. Therefore, the structure at the **$S_1/S_0\text{-CI-Si}$** point shows that the nature of the relaxation on the S_1 potential surface can be regarded as the cleavage of a Si-SiMe_3 bond and as the formation of a C-SiMe_3 bond. This calculation demonstrates that the reactant, **1-Si**, undergoes an intramolecular 1,3-silyl migration through the conical intersection point, **$S_1/S_0\text{-CI}$** , to the cyclic silene (**Int-Si**). This theoretical result is the same as that for the assumed molecule, **2-Si**, as anticipated (Figure 1). It is also noteworthy that the **$S_1/S_0\text{-CI-Si}$** geometry that is shown in Figure 3 strongly indicates that the silyl-migration occurs supra-facially and the configuration of the migrating silyl group is retained, which is consistent with the prediction based on Woodward-Hoffmann rules.¹³

(2) As seen in Table 1, the MP2-CAS results indicate that **$S_1/S_0\text{-CI-Si}$** is 27 kcal/mol lower in energy than **FC-Si**, but 87 kcal/mol higher in energy than the

corresponding reactant, **1**. The existence of a low-lying conical intersection means that there is a highly effective radiationless decay channel.⁸ The computations also predict that the photochemical rearrangement reaction for **1-Si** should be a barrierless process. The supporting clue comes from the fact that a potential energy surface scan (CAS(6,6)/6-311G(d)) for the ground-state (S_0) and the first excited state (S_1) along the reaction coordinate (Figure SA, Supporting Information) shows no apparent energy barrier occurs during the formation of conical intersection. That is, starting from the **FC-Si** point, reactant **1-Si** enters an extremely efficient decay channel, **S₁/S₀-CI-Si**. After decay at this conical intersection point, the intermediate, **Int-Si** (cyclic conjugated silene), and the initial reactant, **1-Si**, can be reached via a barrier-less ground-state relaxation pathway.

(3) As shown in Figure 2, **Int-Si** then reacts with the methanol molecule to form the local minimum, **Cpx-Si**. The MP2-CAS computational results indicate that the energy of **Cpx-Si** relative to the ground state minimum (**1-Si** + CH₃OH) is 0.41 kcal/mol, but this is 17 kcal/mol lower than **Int-Si**.¹⁵ When the local minimum, **Cpx-Si**, is produced on the S_0 potential energy surface, there are two possible reaction pathways (path A and path B) by which the final products, **Cis-Pro-Si** and **Trans-Pro-Si**, are produced. Figure 2 clearly shows that the transition state, **Cis-TS-Si**, for the intermediate **Cpx-Si** that leads to product **Cis-Pro-Si**, lies about 5.0 kcal/mol above the energy of **Trans-TS-Si**, which connects the intermediate, **Cpx-Si**, and the product, **Trans-Pro-Si**. Because a large excess energy (114 kcal/mol) is produced by the decay from **FC-Si**, both barriers are easily surmounted, so it is probable that the relaxation energy is sufficient to

provoke effective photo-isomerization reactions (paths A and B) for **1-Si**. However, since path B involves a second molecule of CH₃OH, the quantum yields of both final products (**Cis-Pro-Si** and **Trans-Pro-Si**) depend, not only on energy barriers, but also on concentrations of CH₃OH.¹⁶ Nevertheless, the present theoretical findings given in Table 1 indicate that path B is more favorable than path A, from an energetic viewpoint. The reason for this could be due to the fact that the steric hindrance for the former is less than that for the latter (see Scheme 1 and Figure 4). It is therefore predicted that the product of path B (**Trans-Pro-Si**) is produced in a larger quantum yield than that of path A (**Cis-Pro-Si**). Supporting evidence comes from the fact that, as shown experimentally,³ one major product (**Trans-Pro-Si**) and one minor product (**Cis-Pro-Si**) are observed with the addition of methanol to a cyclic conjugated silene.^{17,18}

(4) For comparison, the methanol addition reaction for the **1-C** molecule is considered. Its reaction pathways for both the photochemical reaction and the methanol insertion reaction are quite similar to those for **1-Si**, which are shown in Figure 2. The relative energies of the crucial points, at the MP2-CAS level of theory, are shown in Table 1. The most significant difference between the **1-C** and **1-Si** systems is that the energy of the **S₁/S₀-CI-C** point is 5.2 kcal/mol higher than that of **FC-C**, which strongly implies that the singlet excited energy of **1-C** (91 kcal/mol) is not sufficient to produce the final methanol addition photoproducts (i.e., **Cis-Pro-C** and **Trans-Pro-C**) via the conical intersection channel. This theoretical observation indicates that no photochemical reactions are possible for the **1-C** system. Since there have been no experimental studies of the alcohol

addition reaction to **1-C** via the photochemical route, these theoretical conclusion are a prediction.

(5) Corrections for solvation (single-point calculations on gas-phase optimized structures) in dielectric medium with the *i*-PrOH dielectric constant ($\epsilon = 19.92$) were made using the self-consistent reaction field (SCRF) method (SCRF = PCM)¹⁹ in Gaussian 09,⁹ whose computational results are given in Table 1. Remarkably, the relative energies calculated with different approaches for different systems, MP2-CAS/6-311++G(3df,3pd)//CAS/6-311G(d) and CAS/6-311G(d) + PCM(solvent = *i*-PrOH)//CAS/6-311G(d), are quite close. In consequence, it is felt that the present theoretical conclusions from the gas-phase study should be reliably for the same systems on the solvent effects.³

It is interesting that the photochemical reaction for **1-Si** in Scheme 1 is a barrier-less reaction process and poses no difficulty, but the energy of **FC-C** is insufficient to allow **1-C** to undergo the alcohol addition reaction. This may be due to the fact that the atomic radius of carbon (77 pm) is smaller than that of silicon (117 pm),²⁰ so the conformation for **1-C** is more sterically congested than that for **1-Si**, along the 1,3-silyl migration pathway. Therefore, it is expected that the CI point of **1-C** should exist at the high-energy point. The supporting information comes from the theoretical evidence shown in Figure 1, in which the S_0 and S_1 energy surfaces for **1-C** are much steeper than those for **1-Si**, which suggests that the S_1/S_0 -CI-C point should appear on the high energy pathway, which is confirmed by the MP2-CAS computations that are shown in Table 1. This, in turn, means that the vertical excitation energy of **1-C** would be insufficient to surmount

this high-energy barrier so it could not undergo a photochemical rearrangement, let alone the alcohol addition reactions.

V. Conclusion

The excited state and the ground state reaction pathways for a cyclic divinylsilane (**1-Si**) and a related carbon molecule (**1-C**) are studied using ab initio calculations at the CASSCF and MP2-CAS levels of theory. These theoretical findings for **1-Si** definitively support the mechanism that was proposed by Kira et al.³

The computational results of this study demonstrate that the reactant, **1**, is initially excited to the first singlet excited state ($^1\pi \rightarrow ^1\pi^*$). The photo-chemically active relaxation from the $S_1(^1\pi^*)$ to the ground state then leads to an S_1/S_0 conical intersection, from where the photo-excited system undergoes radiation-less decay to the ground state (S_0). Relaxation on the S_1 surface causes the migration of intramolecular 1,3-silyl, which results in the formation of the five-membered ring conjugated silene (**Int-Si**). This theoretical study also indicates that for a photo-excited cyclic divinylsilane (**1-Si**) with an alcohol, there must exist two reaction pathways (path A and path B) that lead to adducts with different stereochemistry. The theoretical results show that these two reaction pathways must compete with each other, since the energetics for their transition states (**Cis-TS-Si** and **Trans-TS-Si**) are similar. Therefore, both steric effects and the concentrations of CH_3OH should play a major role in determining the quantum yields of the final products. Indeed, as seen in Figure 3, since the steric intersections in **Trans-TS-Si** is less congested than those in **Cis-TS-Si**, the quantum yield of the former is larger than that in the latter, which is consistent with the available experimental findings.³ However, these theoretical conclusions anticipate that the carbon derivative

molecule (**1-C**) should not undergo the alcohol addition reaction via the photochemical pathway because its energy of conical intersection (S_1/S_0 -CI-C) is above that of its FC (FC-C) by about 6 kcal/mol. The reason for these phenomena could be due to the fact that the atomic radius of carbon is much smaller than that of silicon (77 and 117 pm, respectively). In consequence, it would cause the conformation for **1-C** is more sterically congested than that for **1-Si**, along the 1,3-silyl migration pathway.

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- (15) A similar process might be that of converting 1,4-pentadiene to 1,3-*trans*-pentadiene for which ΔH^0 is known to be -6.6 kcal/mol. However, our model study shown in Figure 2 and Table 1 reveals that for **1-C** case the step from reactants to **Int-C** involves formation of a conjugated diene and ought to be downhill in energy. For comparison, the author have used the MP2-CAS/6-311++G(3df,3pd)//CAS(6,6)/6-311G(d) level of theory to calculate the enthalpy from 1,4-pentadiene to 1,3-*trans*-pentadiene, which was computed to be -7.1 kcal/mol rather than the reported value (-6.6 kcal/mol). It seems that the electron correlation effect should play an

- important role in such calculations.
- (16) However, several related thermal and photochemical 1,3-silyl migrations of allylsilanes have been reported to occur with inversion stereochemistry. See: (a) Slutsky, J.; Kwart, H. *J. Am. Chem. Soc.* **1973**, *95*, 8678. (b) Kira, M.; Taki, T.; Sakurai, H. *J. Org. Chem.* **1989**, *54*, 5647. (c) Takahashi, M.; Kira, M. *J. Am. Chem. Soc.* **1997**, *119*, 1948. (d) Zhang, L. C.; Kabuto, C.; Kira, M. *J. Am. Chem. Soc.* **1999**, *121*, 2925.
- (17) According to the available experimental work, it was found that the ratio **Cis-Pro-Si/Trans-Pro-Si** increased in the order: MeOH < *n*-PrOH < *i*-PrOH << *t*-BuOH. In particular, *tert*-Butyl alcohol gave only a cis adduct. See reference (3).
- (18) Many groups have theoretically investigated the mechanistic aspects of the reactions of silenes with alcohols under the thermal conditions. See: (a) Leigh, W. J.; Owens, T. R.; Bendikov, M.; Zade, S. S.; Apeloig, Y. *J. Am. Chem. Soc.* **2006**, *128*, 10772. (b) Li, B.-Y. Su, M.-D. *J. Phys. Chem. A* **2012**, *116*, 4222, and references therein.
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TOP

The Mechanistic Study of the Addition of Alcohol to a Five-Membered Ring Silene via the Photochemical Reaction

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The mechanisms for the alcohol addition reactions for a cyclic divinylsilane (**1-Si**) are theoretically studied using the CAS/6-311G(d) and MP2-CAS/6-311++G(3df,3pd) methods. The model computations show that the conical intersection mechanism plays an essential role in this photochemical reaction. The steric effects of alcohols also determine the final yields of the adducts. However, it is theoretically predicted that the carbon derivative (**1-C**) does not undergo the alcohol addition reactions when it absorbs light.

