

Theoretical study on the mechanism of cycloaddition reaction between silylene silylene ($\text{H}_2\text{Si}=\text{Si}:$) and acetaldehyde

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Abstract The mechanism of the cycloaddition reaction between singlet silylene silylene ($\text{H}_2\text{Si}=\text{Si}:$) and acetaldehyde has been investigated with CCSD(T)//MP2/6-31G* and CCSD(T)//MP2/6-31G** method, from the potential energy profile, we could predict that the reaction has three competitive dominant reaction pathways. The present rule of this reaction is that the 3p unoccupied orbital of the Si: atom in silylene silylene ($\text{H}_2\text{Si}=\text{Si}:$) inserts on the π orbital of acetaldehyde from oxygen side, resulting in the formation of an intermediate. Isomerization of the intermediate further leads to the generation of a four-membered ring silylene (the $\text{H}_2\text{Si}-\text{O}$ in the opposite position). In addition, the [2+2] cycloaddition reaction of the two π -bonds in silylene silylene and acetaldehyde generates another four-membered ring silylene (the $\text{H}_2\text{Si}-\text{O}$ in the syn-position). Because of the unsaturated property of Si: atom in the two four-membered ring silylenes, they could further react with acetaldehyde, resulting in the generation of two spiro-heterocyclic ring compounds with Si. Simultaneously, the ring strain of the four-membered ring silylene (the $\text{H}_2\text{Si}-\text{O}$ in the syn-position) makes it isomerize to a twisted four-membered ring product.

Keywords Cycloaddition reaction · Potential energy profile · Silylene silylene ($\text{H}_2\text{Si}=\text{Si}:$)

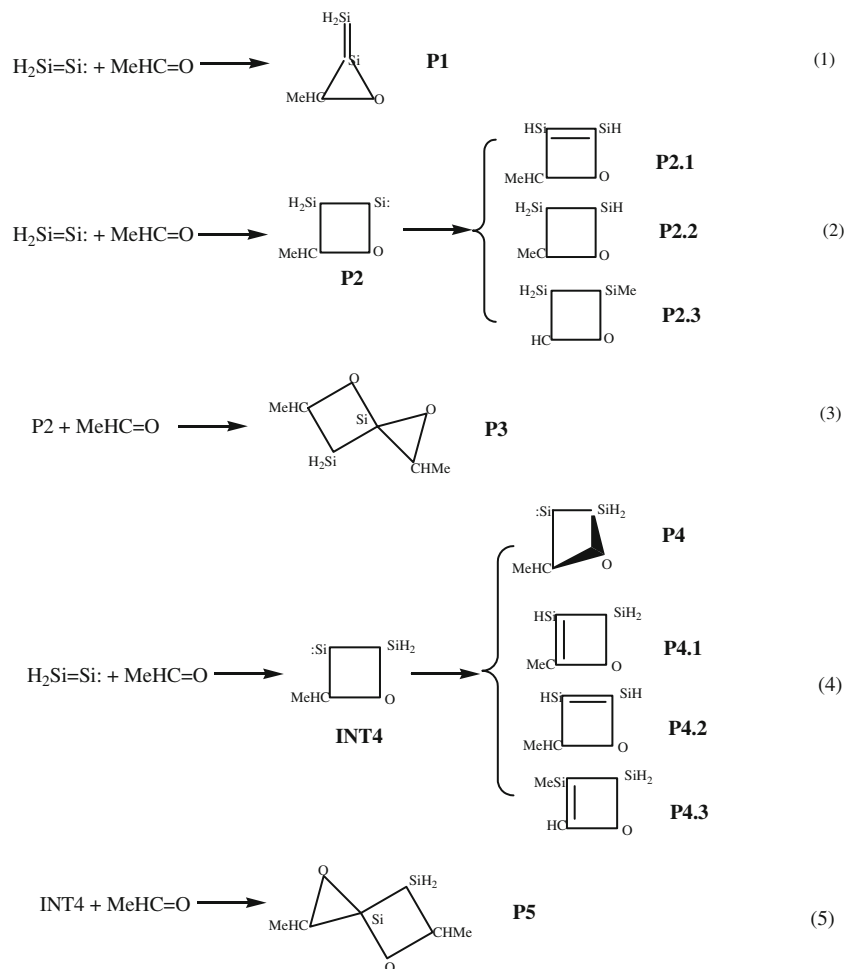
Introduction

Unsaturated silylene is a kind of important intermediate. The simplest unsaturated silylene, $\text{H}_2\text{C}=\text{Si}:$ was first observed experimentally by Leclercq and Dubois in 1979 [1]. Srinivas et al. [2] have used neutralization–reionization mass spectrometry to show that $\text{H}_2\text{C}=\text{Si}:$ is a viable molecule in the low-pressure gas phase. According to theoretical study, the ground state of $\text{H}_2\text{C}=\text{Si}:$ is singlet state. The energy of $\text{H}_2\text{C}=\text{Si}:$ is 84 kcal mol^{-1} lower than silacetylide. So $\text{H}_2\text{C}=\text{Si}:$ is the one isomer of the lowest energy [3]. We have studied the unsaturated silylenes cycloaddition reaction preliminarily [4–8], but these studies are always limited to the cycloaddition reaction of silylidene and its derivatives [$\text{R}_1, \text{R}_2\text{C}=\text{Si}:$ ($\text{R}_1, \text{R}_2 = \text{H}, \text{Me}, \text{F}, \text{Cl}, \text{Br}, \text{Ph}, \text{Ar}, \dots$)]. There are no reports on the cycloaddition reaction of silylene silylene and its derivatives [$\text{R}_1, \text{R}_2\text{Si}=\text{Si}:$ ($\text{R}_1, \text{R}_2 = \text{H}, \text{Me}, \text{F}, \text{Cl}, \text{Br}, \text{Ph}, \text{Ar}, \dots$)] till now, so it is a new field of study for unsaturated silylene cycloaddition reaction. In order to explore the rules of cycloaddition reactions between silylene silylene (include its derivatives) and the asymmetric π -bonded compound, silylene silylene ($\text{H}_2\text{Si}=\text{Si}:$) and acetaldehyde were selected as model molecules, and its mechanism (considering the hydrogen transfer and methyl transfer simultaneously) was investigated and analyzed

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theoretically. The results show that cycloaddition reaction consists of five possible pathways, as follows:



Calculation methods

MP2/6-31G* and MP2/6-31G** [9] implemented in the Gaussian 98 package [10] is employed to locate all the stationary points along the reaction pathways. Full optimization and vibrational analysis are done for the stationary points on the reaction profile. Zero point energy and CCSD(T) single point calculation corrections [CCSD(T)/MP2/6-31G* and CCSD(T)/MP2/6-31G**] are included for the energy calculations. In order to explicitly establish the relevant species, the intrinsic reaction coordinate (IRC) [11, 12] is also calculated for all the transition states appearing on the cycloaddition energy profile.

Results and discussion

Theoretical calculations indicate that the geometric parameters, which appear in the cycloaddition reactions (1)–(5)

between silylene-silylene ($H_2Si=Si:$) and acetaldehyde, are almost the same at the MP2/6-31G* and MP2/6-31G** levels, so are the mechanisms of cycloaddition reaction between silylene-silylene ($H_2Si=Si:$) and acetaldehyde with both MP2/6-31G* and MP2/6-31G** methods. Considering the accuracy of CCSD(T)/MP2/6-31G** method in energy calculation, the following discussions therefore are based on the results from MP2/6-31G** and CCSD(T)/MP2/6-31G** with respect to geometric parameters and energy, respectively.

Reaction (1): channel of forming the three-membered ring product (P1)

The geometrical parameters of silylene-silylene (R1), acetaldehyde (R2), intermediate (INT1), transition state (TS1) and product (P1) appearing in reaction (1) between silylene-silylene and acetaldehyde are given in Fig. 1. The energies are listed in Table 1, and the potential energy profile for the

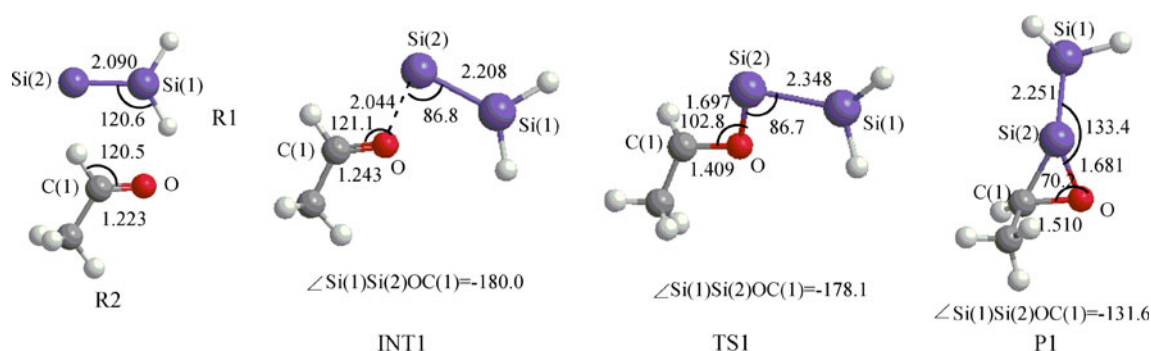


Fig. 1 Optimized MP2/6-31G** geometrical parameters and the atomic numbering for the species in cycloaddition reaction(1). Bond lengths and bond angles are in angstrom and degree, respectively

cycloaddition reaction is shown in Fig. 2. The unique imaginary frequency of the transition state (TS1) is 210.6i, consequently, the transition state can be affirmed as the real one. According to the calculations of the IRC of TS1 and further optimization for the primary IRC results, TS1 connects INT1 with P1.

According to Fig. 2, it can be seen that reaction (1) consists of two steps: the first one is that the two reactants (R1, R2) first form an intermediate (INT1), which is a barrier-free exothermic reaction of 90.0 kJ mol⁻¹; in the second step, intermediate (INT1) is isomerized to a three-membered ring product (P1) through the transition state (TS1) with an energy barrier of 75.0 kJ mol⁻¹.

Reaction (2): channels of forming four-membered ring silylene (P2), hydrogen transfer products (P2.1, P2.2) and methyl transfer product (P2.3)

The geometrical parameters of intermediate (INT2), transition states (TS2, TS2.1, TS2.2, TS2.3) and products (P2, P2.1, P2.2, P2.3) appearing in reaction(2) between silylene silylene and acetaldehyde are given in Fig. 3. The energies are listed in Table 1, and the potential energy profile for the cycloaddition reaction is shown in Fig. 2. The unique imaginary frequencies of the transition states TS2, TS2.1, TS2.2 and TS2.3 are 265.2i, 636.4i, 855.3i and 514.6i, respectively, consequently, these transition states can be affirmed as the real ones. According to the calculations of the IRC of TS2, TS2.1, TS2.2 and further optimization for the primary IRC results: TS2 connects INT2 with P2. TS2.1 connects P2 with P2.1. TS2.2 connects P2 with P2.2. TS2.3 connects P2 with P2.3.

According to Fig. 2, it can be seen that reaction (2) consists of five steps: the first step is that the two reactants (R1, R2) form an intermediate (INT2), which is a barrier-free exothermic reaction of 91.0 kJ mol⁻¹; the second step is that the intermediate (INT2) isomerizes to a four-membered ring silylene (P2) via transition state (TS2) with an energy barrier of 13.0 kJ mol⁻¹; in the third, fourth and fifth step, P2 undergoes Si-Si and C-Si(2) hydrogen transfer and C-Si(2) methyl

transfer, via transition states TS2.1, TS2.2 and TS2.3 with energy barriers of 149.0, 128.0 and 204.0 kJ mol⁻¹ respectively, resulting in the formation of products (P2.1, P2.2 and P2.3). Because the energy of P2.1, P2.2 and P2.3 is 67.0, 82.0 and 85.0 kJ mol⁻¹ higher than the energy of P2, so the reactions of P2→P2.1, P2→P2.2 and P2→P2.3 is prohibited in thermodynamics, and reaction (2) will be end with product P2. According to the comparison of reaction (2) with reaction (1), the energy of TS1 is 61.0 kJ mol⁻¹ higher than that of TS2, so reaction (2) is the dominant channel.

Reaction (3): channel of forming a spiro-heterocyclic ring compound with Si (P3)

In reaction (3), the four-membered ring silylene (P2) further reacts with acetaldehyde to form a spiro-heterocyclic ring compound with Si (P3). The geometrical parameters of intermediate (INT3), transition state (TS3) and product (P3) appearing in reaction (3) are given in Fig. 4. The energies are listed in Table 1, and the potential energy profile for the cycloaddition reaction is shown in Fig. 2. The unique imaginary frequency of the transition state (TS3) is 354.1i, consequently, the transition state can be affirmed as the real one. According to the calculation of the IRC of TS3 and further optimization for the primary IRC results, TS3 connects INT3 with P3.

According to Fig. 2, it can be seen that processes of reaction (3) are as follows: on the basis of P2 formed from reaction (2), P2 further reacts with acetaldehyde to form an intermediate (INT3), which is a barrier-free exothermic reaction of 41.0 kJ mol⁻¹; and then, the intermediate (INT3) is isomerized to a spiro-heterocyclic ring compound with Si (P3) via a transition state (TS3) with an energy barrier of 121.0 kJ mol⁻¹.

Reaction (4): the channels of forming four-membered ring silylene (INT4) and its isomer(P4), H-transfer products (P4.1and P4.2) and Me-transfer product (P4.3)

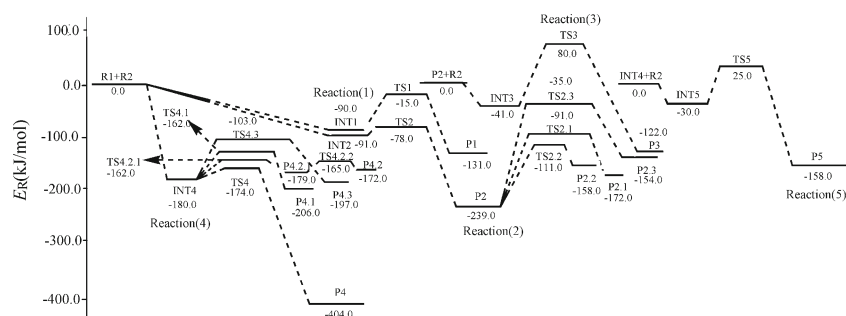
The geometrical parameters of the four-membered ring silylene (INT4), transition states (TS4, TS4.1, TS4. 2.1,TS4.2.2,

Table 1 Total energies(E_T /hartree)and relative energies(E_R /kJ mol⁻¹)for the species from various theoretical methods

Reaction	Species	MP2/6-31G*		CCSD(T)//MP2/6-31G*		MP2/6-31G**		CCSD(T)//MP2/6-31G**	
		^a E_T	E_R	^a E_T	E_R	^a E_T	E_R	^a E_T	E_R
^b Reaction(1)	R1+R2	-732.11039	0.0	-732.24953	0.0	-732.15668	0.0	-732.42938	0.0
	INT1	-732.33527	-590.0	-732.41519	-435.0	-732.38184	-591.0	-732.46365	-90.0
	TS1(INT1-P1)	-732.29889	-495.0	-732.38658	-360.0	-732.34587	-496.0	-732.43525	-15.0
	P1	-732.35519	-643.0	-732.43006	-474.0	-732.40285	-646.0	-732.47938	-131.0
^b Reaction(2)	R1+R2	-732.11039	0.0	-732.24953	0.0	-732.15688	0.0	-732.42938	0.0
	INT2	-732.33591	-592.0	-732.41547	-436.0	-732.38269	-593.0	-732.46407	-91.0
	TS2(INT2-P2)	-732.33175	-581.0	-732.40988	-421.0	-732.37895	-583.0	-732.45899	-78.0
	P2	-732.39624	-751.0	-732.47058	-580.0	-732.44423	-754.0	-732.52047	-239.0
	TS2.1 (P2-P2.1)	-732.3361	-593.0	-732.41426	-433.0	-732.38451	-598.0	-732.46386	-91.0
	P2.1	-732.3714	-685.0	-732.44529	-514.0	-732.41941	-689.0	-732.49499	-172.0
	TS2.2 (P2-P2. 2)	-732.34836	-625.0	-732.42049	-449.0	-732.39824	-634.0	-732.47174	-111.0
	P2. 2	-732.37075	-684.0	-732.44028	-501.0	-732.41843	-687.0	-732.48983	-158.0
	TS2. 3 (P2-P2.3)	-732.3197	-550.0	-732.39189	-374.0	-732.36820	-555.0	-732.4428	-35.0
P2.3	-732.36984	-681.0	-732.43815	-495.0	-732.41802	-686.0	-732.48820	-154.0	
^c Reaction(3)	P2+R2	-885.6862	0.0	-885.79901	0.0	-885.76558	0.0	-885.88188	0.0
	INT3	-885.70371	-46.0	-885.81442	-41.0	-885.78333	-47.0	-885.89752	-41.0
	TS3(INT3-P3)	-885.6549	82.0	-885.76875	79.0	-885.73468	81.0	-885.85155	80.0
	P3	-885.74233	-147.0	-885.84503	-121.0	-885.82218	-149.0	-885.92836	-122.0
^b Reaction(4)	R1+R2	-732.11039	0.0	-732.24953	0.0	-732.15688	0.0	-732.42938	0.0
	INT4	-732.37386	-692.0	-732.44767	-520.0	-732.42209	-696.0	-732.49804	-180.0
	TS4(INT4-P4)	-732.37124	-685.0	-732.4453	-514.0	-732.41947	-689.0	-732.49577	-174.0
	P4	-732.38253	-715.0	-732.45383	-536.0	-732.43076	-719.0	-732.58323	-404.0
	TS4.1 (INT4-P4.1)	-732.36593	-671.0	-732.44007	-500.0	-732.41541	-679.0	-732.49109	-162.0
	P4.1	-732.38642	-725.0	-732.45826	-548.0	-732.43380	-727.0	-732.50769	-206.0
	TS4.2.1 (INT4-P4.2.1)	-732.3675	-675.0	-732.44078	-502.0	-732.41615	-681.0	-732.49124	-162.0
	P4.2.1	-732.37361	-691.0	-732.44556	-515.0	-732.42404	-701.0	-732.49769	-179.0
	TS4.2.2 (P4.2.1-P4.2)	-732.36894	-679.0	-732.44201	-505.0	-732.41759	-685.0	-732.49218	-165.0
	P4.2	-732.3714	-685.0	-732.44529	-514.0	-732.41941	-689.0	-732.49499	-172.0
	TS4.3 (INT4-P4.3)	-732.34566	-618.0	-732.41811	-443.0	-732.39410	-623.0	-732.46849	-103.0
	P4.3	-732.38282	-715.0	-732.45383	-536.0	-732.43114	-720.0	-732.50423	-197.0
^d Reaction(5)	INT4+R2	-885.66383	0.0	-885.7761	0.0	-885.74344	0.0	-885.85945	0.0
	INT5	-885.68081	-45.0	-885.78752	-30.0	-885.76067	-45.0	-885.87083	-30.0
	TS5(INT5-P5)	-885.65433	25.0	-885.76667	25.0	-885.73445	24.0	-885.85005	25.0
	P5	-885.73343	-183.0	-885.83592	-157.0	-885.81350	-184.0	-885.91973	-158.0

^a $E_T = E(\text{Species}) + \text{zero point energy}$, b: $E_R = E_T - E_{(R1+R2)}$, c: $E_R = E_T - E_{(P2+R2)}$, d: $E_R = E_T - E_{(INT4+R2)}$

Fig. 2 The potential energy profile for the cycloaddition reactions between $H_2Si=Si$ and acetaldehyde with CCSD (T)//MP2/6-31G**



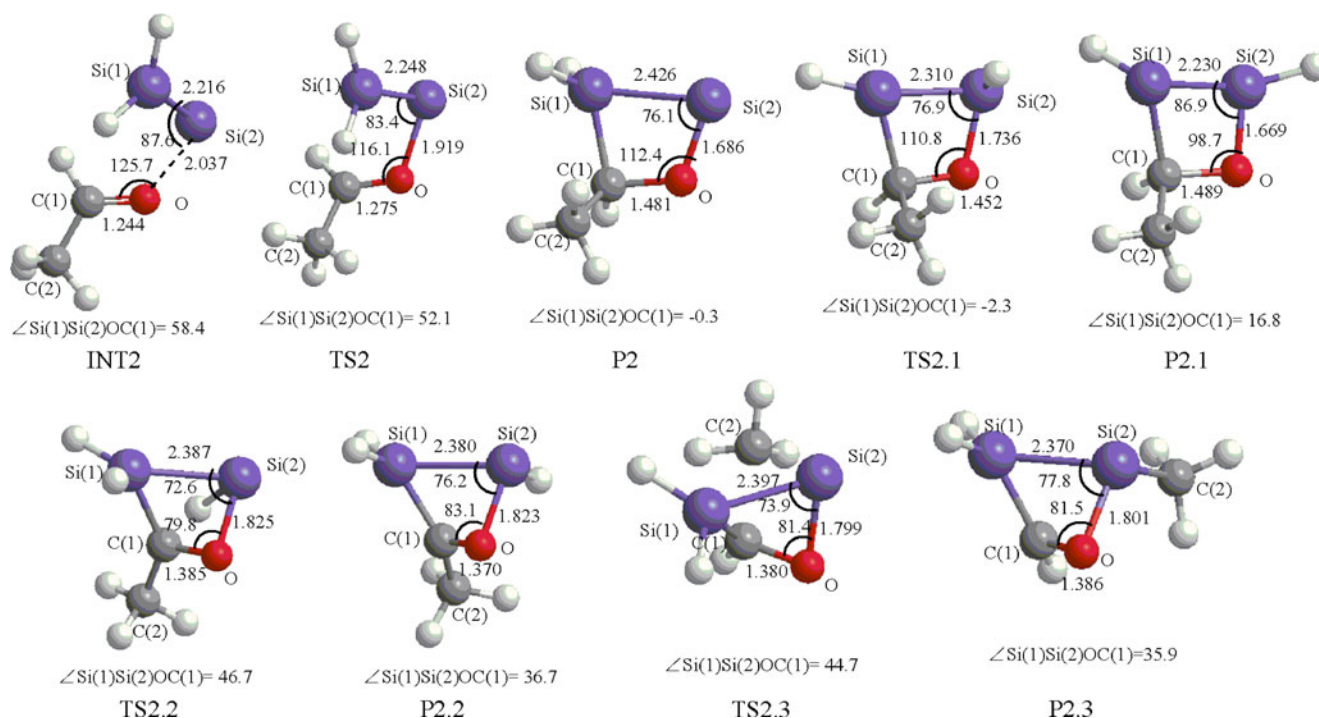


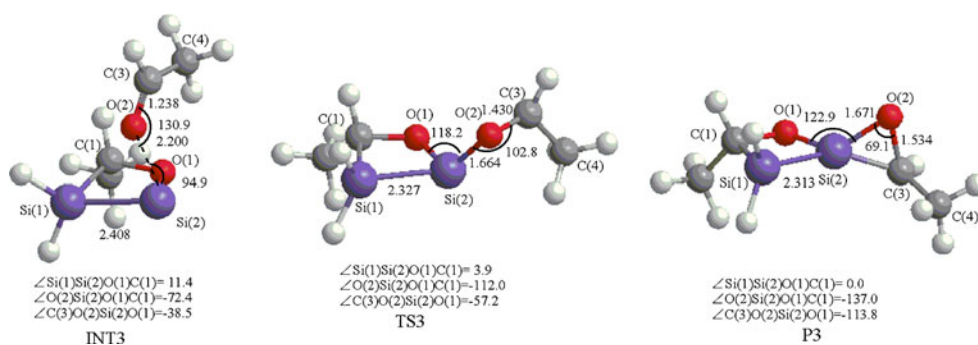
Fig. 3 Optimized MP2/6-31G** geometrical parameters of INT2, TS2, TS2.1, TS2.2, TS2.3, P2, P2.1, P2.2, P2.3 and the atomic numbering for the species in cycloaddition reaction (2). Bond lengths and bond angles are in angstrom and degree, respectively

TS4.3) and products (P4, P4.1, P4.2.1, P4.2, P4.3) appearing in reaction (4) between silylene silylene and acetaldehyde are given in Fig. 5. The energies are listed in Table 1, and the potential energy profile for the cycloaddition reaction is shown in Fig. 2. The unique imaginary frequencies of the transition states TS4, TS4.1, TS4.2.1, TS4.2.2 and TS4.3 are 186.5i, 706.5i, 406.3i, 256.4i and 324.8i respectively, consequently, these transition states can be affirmed as the real ones. According to the calculations of the IRC of TS4, TS4.1, TS4.2.1, TS4.2.2 and TS4.2 and further optimization for the primary IRC results: TS4 connects INT4 with P4. TS4.1 connects INT4 with P4.1. TS4.2.1 connects INT4 with P4.2.1. TS4.2.2 connects P4.2.1 with P4.2. TS4.3 connects INT4 with P4.3.

According to Fig. 2, it can be seen that reaction (4) consists of five steps: in the first step, the two reactants form

a four-membered ring silylene (INT4), which is a barrier-free exothermic reaction of 180.0 kJ mol⁻¹; in the second step, the INT4 is isomerized to a distorted four-membered ring product (P4) through transition state (TS4) with energy barrier of 6.0 kJ mol⁻¹; in the third step, INT4 undergoes C-Si(2) hydrogen transfer via transition state (TS4.1) with energy barrier of 18.0 kJ mol⁻¹, resulting in the formation of product (P4.1); in the fourth step, INT4 undergoes Si-Si hydrogen transfer via transition state (TS4.2.1) with energy barrier of 18.0 kJ mol⁻¹, resulting in the formation of product (P4.2.1); and then, P4.2.1 undergoes Si-Si hydrogen transfer via transition state (TS4.2.2) with energy barrier of 14.0 kJ mol⁻¹, resulting in the formation of product (P4.2). In the fifth step, INT4 undergoes C-Si(2) methyl transfer via transition state (TS4.3) with energy barrier of 78.0 kJ mol⁻¹, resulting in the formation of product (P4.3). Because the

Fig. 4 Optimized MP2/6-31G** geometrical parameters of INT3, TS3, P3 and the atomic numbering for the species in cycloaddition reaction (3). Bond lengths and bond angles are in angstrom and degree, respectively



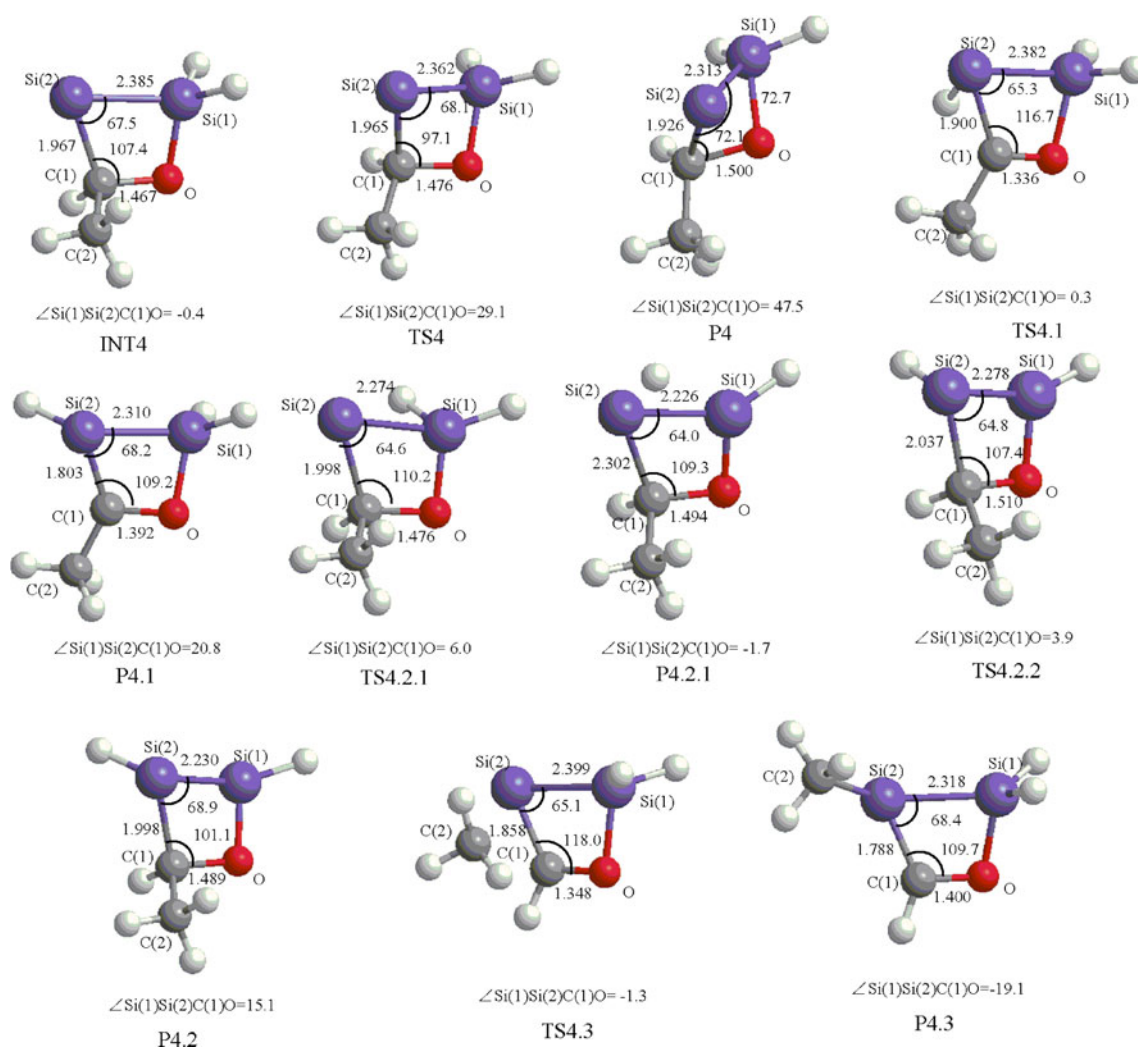
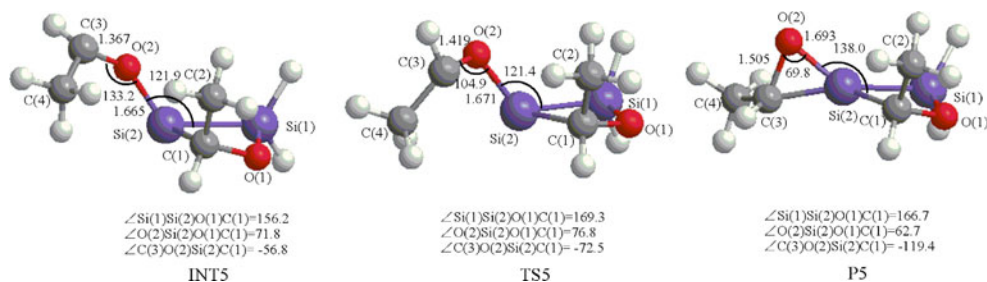


Fig. 5 Optimized MP2/6-31G** geometrical parameters of INT4, TS4, P4, TS4.1, P4.1, TS4.2.1, P4.2.1, TS4.2.2, P4.2, TS4.3, P4.3 and the atomic numbering for the species in cycloaddition reaction (4). Bond lengths and bond angles are in angstrom and degree, respectively

energy of P4.2.1 is 1.0 kJ mol^{-1} higher than INT4, INT4→P4.2 is prohibited in thermodynamics at normal temperature and pressure. Because the energy of TS4 is 12.0 and 72.0 kJ mol^{-1} lower than TS4.1 and TS4.3, INT4→P4 is a dominant reaction pathway of reaction (4). According to the comparison of reaction (3) with reaction (4), there is only an energy barrier difference of 7.0 kJ mol^{-1} between TS2 and TS4, so reaction (3) and INT4→P4 in reaction (4) are the two competitive dominant channels.

Fig. 6 Optimized MP2/6-31G** geometrical parameters of INT5, TS5, P5 and the atomic numbering for the species in cycloaddition reaction (5). Bond lengths and bond angles are in angstrom and degree, respectively



Reaction (5): channel of forming a spiro-heterocyclic ring compound with Si (P5)

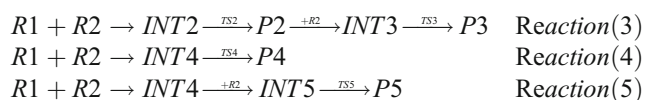
In reaction (5), the four-membered ring intermediate (INT5) further reacts with acetaldehyde (R2) to form a spiro-heterocyclic ring compound with Si (P5). The geometrical parameters of intermediate (INT5), transition state (TS5) and product (P5) appearing in reaction (5) are given in Fig. 6. The energies are listed in Table 1,

and the potential energy profile for the cycloaddition reaction is shown in Fig. 2. The unique imaginary frequency of the transition state (TS5) is 308.5i, consequently, the transition state (TS5) can be affirmed as the real one. According to the calculations of the IRC of TS5 and further optimization for the primary IRC results, TS5 connects INT5 with P5.

According to Fig. 2, it can be seen that the process of reaction (5) is as follows: on the basis of the two reactants (R1, R2) to form a four-membered ring silylene (INT4), INT4 further reacts with acetaldehyde (R2) to form an intermediate (INT5), which is a barrier-free exothermic reaction of 30.0 kJ mol⁻¹. And then intermediate (INT5) isomerizes to a spiro-heterocyclic ring compound with Si (P5) via a transition state (TS5) with an energy barrier of 55.0 kJ mol⁻¹. Comparing reaction (5) with reaction (4), it is realized that the two reactions compete mutually due to scrambling for INT4 together. In reaction (5), INT4+R2→INT5 can reduce the energy of 30.0 kJ mol⁻¹. In reaction (4), the energy barrier of INT4→P4 is only 6.0 kJ mol⁻¹. Therefore, reaction (5) and reaction (4) are two competitive dominant reaction channels.

Theoretical analysis and explanation of the dominant reaction channels

According to the above analysis, there are three competitive dominant reaction channels of the cycloaddition reaction between singlet state silylene silylene and acetaldehyde as follows:



The mechanism of reaction (3) can be explained with the frontier molecular orbital diagram (Figs. 7 and 8) and Figs. 1,

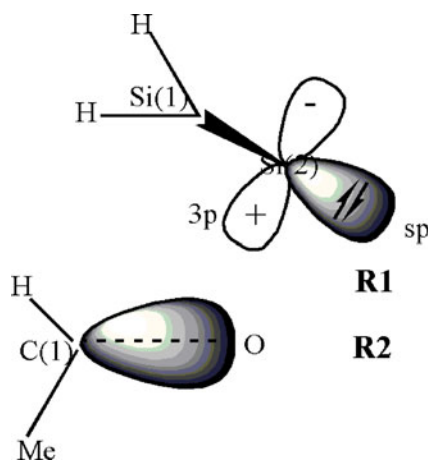


Fig. 7 A schematic interaction diagram for the frontier orbitals of H₂Si=Si:(R1) and MeHC=O (R2)

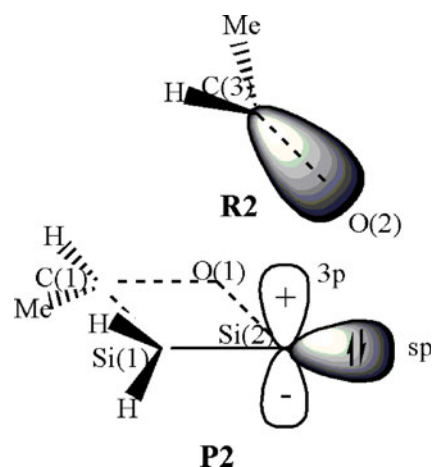


Fig. 8 A schematic interaction diagram for the frontier orbitals of P2 and MeHC=O(R2)

3 and 4. According to Figs. 1, 3 and 7, because the carbonyl of aldehyde is a polar group, the electron clouds of the π -bond gather around the side of oxygen, when the silylene silylene interacts with acetaldehyde, so the 3p unoccupied orbital of the Si(2) atom in silylene silylene will insert the π orbital of acetaldehyde from oxygen side. Then the shift of π -electrons to the p unoccupied orbital gives a π →p donor–acceptor bond, leading to the formation of intermediate INT2. As the reaction goes on, due to the \angle Si(1)Si(2)OC(1)(INT2: 58.4°, TS2: 52.1°, P2: -0.3°) decreases gradually, \angle Si(1)Si(2)O (INT2: 87.6°, TS2: 83.4°, P2: 76.1°) decreases gradually, the length of Si(2)–O bond (INT2: 2.037 Å, TS2: 1.919 Å, P2: 1.686 Å) shortens gradually, length of Si(1)–Si(2) bond (INT2: 2.216 Å, TS2: 2.248 Å, P2: 2.426 Å) and the bond of C(1)–O (INT2: 1.244 Å, TS2: 1.275 Å, P2: 1.481 Å) elongates gradually. And finally intermediate (INT2) transforms to a more stable four-membered ring silylene (P2) via the transition state (TS2). Because P2 is still an active product, P2 may further react with acetaldehyde to form spiro-heterocyclic ring

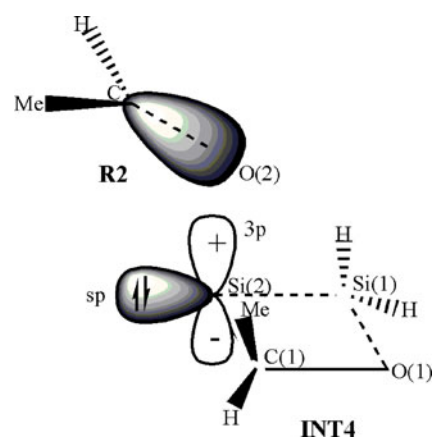


Fig. 9 A schematic interaction diagram for the frontier orbitals of INT4 and MeHC=O(R2)

compound with Si (P3). The mechanism of this reaction can be explained with Figs. 4 and 8. According to the rule of molecular orbital symmetry adaptation, when P2 interacts with acetaldehyde (R2), the 3p unoccupied orbital on Si(2) atom of P2 will insert on the π orbital of acetaldehyde from the oxygen side. Then the shift of π -electrons to the p unoccupied orbital gives a $\pi \rightarrow p$ donor–acceptor bond, leading to the formation of intermediate INT3. As the reaction goes on, due to $\angle O(2)Si(2)O(1)$ (INT3: 94.9°, TS3: 118.2°, P3: 122.9°) and $\angle O(2)Si(2)O(1)C(1)$ (INT3: -72.4°, TS3: -112.0°, P3: -137.0°) increases gradually, $\angle C(3)O(2)Si(2)$ (INT3: 130.9°, TS3: 102.8°, P3: 69.1°) decreases gradually, the length of C(3)–O(2) (INT3: 1.238 Å, TS3: 1.430 Å, P3: 1.534 Å) elongates gradually. Finally the Si(2) atom in INT3 hybridizes to sp^3 hybrid orbital after the transition state TS3, forming the more stable spiro-heterocyclic ring compound with Si (P3).

The mechanism of reaction (4) and reaction (5) can be explained with the molecular orbital diagram (see Fig. 9 and Figs. 5 and 6). According to Fig. 5, as silylene silylene (R1) initially interacts with acetaldehyde (R2), the [2+2] cycloaddition of the bonding π -orbitals first results in a four-membered ring silylene (INT4). Because of the four-membered ring silylene (INT4) has a larger tensility, so INT4 is at a higher energy state, under the energy driven, the INT4 is isomerized into a distorted four-membered ring product (P4) via transition state (TS4). Otherwise, Si(2) atom in INT4 is unsaturated. So, INT4 further reacts with acetaldehyde to form a spiro-heterocyclic ring compound with Si (P5). The mechanism of reaction can be explained with Figs. 6 and 9. When INT4 interacts with acetaldehyde (R2), the 3p unoccupied orbital of the Si(2) atom in INT4 will insert on the π orbital of acetaldehyde from the oxygen side. Then the shift of π -electrons to the p unoccupied orbital gives a $\pi \rightarrow p$ donor–acceptor bond, leading to the formation of intermediate INT5. As the reaction goes on, due to $\angle C(3)O(2)Si(2)$ (INT5: 133.2°, TS5: 104.9°, P5: 69.8°) decreases gradually and the length of C(3)–O(2) bond (INT5: 1.367 Å, TS5: 1.419 Å, P5: 1.505 Å) elongates gradually. Finally the Si(2) atom in INT5 hybridizes to sp^3 hybrid orbital after the transition state TS5, forming the more stable spiro-heterocyclic ring compound with Si (P5).

Comparing the dominant reaction channels of the cycloaddition reaction between silylene silylene ($H_2Si=Si:$) and acetaldehyde with the cycloaddition reaction between germylene silylene ($H_2Ge=Si:$) and acetone [13], the cycloaddition reaction between silylidene ($H_2C=Si:$) and formaldehyde [5], the result indicated that the mechanism of cycloaddition reaction between germylene silylene ($H_2Ge=Si:$) and acetone is similar to that of cycloaddition reaction between silylene silylene ($H_2Si=Si:$) and acetaldehyde, and there are three dominant reaction channels similar to that of cycloaddition reaction between silylene silylene ($H_2Si=Si:$) and acetaldehyde. The cycloaddition reaction between silylidene ($H_2C=Si:$) and

formaldehyde has only one dominant reaction channel, the mechanism of the reaction channel is similar to that of the cycloaddition reaction (3) between silylene silylene ($H_2Si=Si:$) and acetaldehyde. The cycloaddition reactions (4) and (5) between silylene silylene ($H_2Si=Si:$) and acetaldehyde are not the dominant reaction channels for the cycloaddition reaction between silylidene ($H_2C=Si:$) and formaldehyde.

Conclusions

On the basis of the potential energy profile the cycloaddition reaction between singlet silylene silylene and acetaldehyde was obtained with the CCSD(T)/MP2/6-31G** method, it can be predicted that the reaction has three competitive dominant reaction channels. The first dominant reaction channel consists of four steps: (1) two reactants form an intermediate (INT2), which is a barrier-free exothermic reaction of 91.0 kJ mol⁻¹. (2) Intermediate (INT2) is isomerized to a four-membered ring silylene (P2) via a transition state (TS2) with an energy barrier of 13.0 kJ mol⁻¹. (3) Four-membered ring silylene (P2) further reacts with acetaldehyde to form an intermediate (INT3), which is also a barrier-free exothermic reaction of 41.0 kJ mol⁻¹; (4) Intermediate (INT3) is isomerized to a spiro-heterocyclic ring compound with Si (P3) via a transition state (TS3) with an energy barrier of 121.0 kJ mol⁻¹. The second dominant reaction channel consists of two steps: (1) the two reactants form a four-membered ring silylene (INT4), it is a barrier-free exothermic reaction of 180.0 kJ mol⁻¹. (2) INT4 is isomerized to a distorted four-membered ring product (P4) via a transition state (TS4) with an energy barrier of 6.0 kJ mol⁻¹. The third dominant reaction channels are as follows: on the basis of INT4 formed from reaction (4), INT4 further reacts with acetaldehyde to form an intermediate (INT5), which is also a barrier-free exothermic reaction of 30.0 kJ mol⁻¹; and then intermediate (INT5) is isomerized to a spiro-heterocyclic ring compound with Si (P5) via a transition state (TS5) with an energy barrier of 55.0 kJ mol⁻¹.

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