



Silylenes and germylenes: The activation of H–H bond in hydrogen molecule

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ABSTRACT

Possible mechanisms of activation reactions of H₂ with a variety of acyclic and cyclic silylenes and germylenes have been investigated by using the density functional theory (DFT), the second order Møller–Plesset perturbation theory (MP2), and the complete active space self-consistent field (CASSCF) method. Calculation results demonstrate the facile occurrence of the H₂ activation reaction through a concerted mechanism. The relative reactivity of H₂ splitting is closely related to the HOMO–LUMO or the singlet–triplet gaps of silylenes and germylenes. The activation energies of H₂ split by silylenes are smaller than those by germylenes. For N-heterocyclic silylenes and germylenes with the larger singlet–triplet energy gaps, the higher activation barriers are required to reach the transition states. The cyclopenta-2,4-dienylidene silylenes and germylenes are better candidates for activation reaction of H₂ with lower activation barriers. It is also shown that the halogen (F, Cl, Br) substitutions on different ring positions of the cyclopenta-2,4-dienylidene silylenes and germylenes have little influence on the activation energies and the exothermic energies of the insertion reactions with H₂.

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1. Introduction

The activation, adsorption, and regeneration of H₂ are important processes in hydrogen storage applications [1–10]. Transition metal complexes were widely adopted to split or liberate H₂. However, the reactions of H₂ with main group compounds have less been explored yet [11–19]. The reversible activation reactions of H₂ with boron and phosphorus centers are regarded as Lewis acid–base adduct reactions, in which the Lewis acidic B center and Lewis basic P center interact with H₂ synchronously [13]. Recently, H₂ was demonstrated to be split by nucleophilic activation at a single carbon center in the carbenes [20–26]. Theoretical calculations with the density functional theory (DFT) at the B3LYP/6-311G** level displayed that the hydrogen bounds to the carbon center irreversibly, generating a hydride-like hydrogen, which subsequently reacts with the positively polarized carbon atom [23].

Silylenes [27–70] and germylenes [71–84], the heavier analogues of carbenes [85–87], are important species in numerous thermal and photochemical reactions [88–113]. Similar to carbenes, most of silylenes and germylenes can function as Lewis acid or Lewis base, in which the vacant p orbital is responsible for electrophilic character (Lewis acid), while the non-bonding electron pair can act as the nucleophilic (Lewis base) attack region [77]. The activation reactions of some small inorganic and organic compounds by Lewis acid–base addition reactions, such as NO [91,98], NH₃ [103,110], CO [93], CO₂ [94,108], O₂ [91,102], Cl₂ [91] H₂O

[95,96,103–105,110], C₂H₄ [106,112], and C₂H₂ [107] with silylenes and germylenes have been investigated experimentally. The insertion reactions of silylenes or germylenes into C–H, C–Cl, C–Br, and O–H bonds of small molecules, for example, CH₄ [110,111], CCl₄ [100,101], and CBr₄ [100] etc., have also been studied by the density functional theory (DFT). Among those works, the concerted mechanism has been widely accepted. The reactions of silylenes and germylenes with alcohols have been reported to take place via the activation of O–H bond to generate the corresponding alkoxyhydrosilane [33,35,46]. In fact, activation of O–H of water molecule can also proceed with silylenes [67,95,96,103]. Similar mechanism exists for carbenes as well [20–26]. The isodesmic reactions of silylenes and germylenes with dihydrogen were employed to discuss the relative stability of cyclic silylenes and germylenes at the level of Hartree–Fock (HF) [27,71]. The unsaturated cyclic germylene is lower in energy than that of saturated cyclic germylene by 41 kcal/mol [71], while the reaction of unsaturated silylene with H₂ is about 11 kcal/mol less exothermic than that of saturated cyclic species [27]. However, the possible reaction paths and electronic structures of transition states for the activation reaction of H₂ with silylenes and germylenes have not been explored yet.

In the present work, we study the possible pathways of the activation reaction of H₂ with silylenes and germylenes (Fig. 1). The selected 36 reactants cover a wide range of silylenes and germylenes, as shown in Fig. 1b. The studied systems include both the acyclic silylenes and germylenes and cyclic species. The effect of ring size of cyclic silylenes (germylenes) can be seen from the comparison between the three-membered (**3**_{Si,Ge}) and five-membered rings (**4**_{Si,Ge}). The 2- and 3-mono-halo-substituted and

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Table 1

The energy differences between the lowest singlet (S) and triplet (T) states, ΔE_{S-T} , of acyclic and cyclic silylenes **1**_{Si}–**10**_{Si} and germylenes **1**_{Ge}–**10**_{Ge} calculated at the level of B3LYP/6-31G^{**}, B3LYP/6-311+G^{**}, MP2/6-31G^{**}, CASSCF(6, 6)/6-31G^{**}, and CASPT2(6, 6)/6-31G^{**}, respectively.

Species	ΔE_{S-T} (kcal/mol)			
	B3LYP/6-31G ^{**}	B3LYP/6-311+G ^{**}	MP2/6-31G ^{**}	CAS/6-31G ^{**} (CASPT2) ^a
1 _{Si}	–19.97	–20.39	–13.54	–16.38 (–13.18)
2 _{Si}	–25.81	–26.72	–21.24	–18.95 (–20.09)
3 _{Si}	–54.18	–52.59	–75.32	–52.28 (–77.73)
4a _{Si}	–15.05	–20.39	–50.51	–22.66 (–15.64)
5b _{Si}	–19.24	–19.10	–30.35	–16.86 (–29.35)
6b _{Si}	–21.69	–22.31	–24.54	–21.64 (–22.56)
7b _{Si}	–23.80	–21.04	–27.46	–16.49 (–23.96)
8 _{Si}	–55.06	–56.35	–53.78	–43.83 (–54.66)
9a _{Si}	–58.04	–58.81	–13.54	–64.69 (–69.01)
10 _{Si}	–62.13	–63.05	–95.99	–77.99 (–76.36)
1 _{Ge}	–25.66	–26.80	–16.88	–19.99 (–16.49)
2 _{Ge}	–29.64	–31.49	–22.38	–37.85 (–21.42)
3 _{Ge}	–79.59	–78.69	–42.90	–33.04 (–45.49)
4a _{Ge}	–20.57	–26.80	–34.92	–25.12 (–19.23)
5b _{Ge}	–24.83	–26.68	–34.09	–37.20 (–42.24)
6b _{Ge}	–10.51	–13.40	–22.19	–24.01 (–17.91)
7b _{Ge}	–27.65	–28.70	–35.48	–27.08 (–29.98)
8 _{Ge}	–56.12	–59.00	–54.61	–50.80 (–54.67)
9a _{Ge}	–48.98	–46.60	–16.88	–55.71 (–59.15)
10 _{Ge}	–53.81	–51.70	–60.34	–51.25 (–65.78)

^a The CASPT2/6-31G^{**} results are given in parentheses.

Table 2

Values of the activation energy, E_a , and the exothermic energy, E_{exo} , of insertion reactions of acyclic and cyclic silylenes, **1**_{Si}–**10**_{Si}, and germylenes, **1**_{Ge}–**10**_{Ge}, with H₂ calculated at the level of B3LYP/6-31G^{**}, B3LYP/6-311+G^{**}, MP2/6-31G^{**}, CASSCF(6, 6)/6-31G^{**}, and CASPT2(6, 6)/6-31G^{**}, respectively.

Species	Activation energy (E_a) ^a , kcal/mol				Exothermic energy (E_{exo}) ^b , kcal/mol			
	B3LYP/6-31G ^{**}	B3LYP/6-311+G ^{**}	MP2/6-31G ^{**}	CAS/6-31G ^{**} (CASPT2) ^c	B3LYP/6-31G ^{**}	B3LYP/6-311+G ^{**}	MP2/6-31G ^{**}	CAS/6-31G ^{**} (CASPT2) ^c
1 _{Si}	4.88	4.82	6.12	16.87 (5.43)	–51.28	–50.71	–56.54	–52.99 (–60.21)
2 _{Si}	13.25	13.31	16.97	42.15 (13.95)	–51.58	–50.89	–53.59	–24.89 (–59.49)
3 _{Si}	55.18	53.15	63.55	80.50 (64.27)	–17.77	–18.65	–16.98	3.49 (–21.68)
4a _{Si}	6.07	5.87	10.86	26.47 (9.94)	–50.53	–49.60	–50.16	–46.83 (–55.30)
5b _{Si}	10.29	8.27	11.95	26.23 (13.67)	–47.64	–48.55	–50.98	–47.43 (–53.32)
6b _{Si}	9.05	9.56	11.52	24.44 (14.19)	–48.34	–46.98	–50.42	–55.54 (–52.57)
7b _{Si}	10.45	11.77	17.68	24.51 (22.57)	–49.34	–46.76	–46.97	–48.78 (–52.54)
8 _{Si}	45.37	45.59	53.09	62.93 (50.76)	–23.86	–23.34	–25.20	–14.83 (–29.80)
9a _{Si}	66.40	63.46	75.03	81.81 (76.05)	–5.10	–6.65	–3.90	9.61 (–7.02)
10 _{Si}	62.12	59.88	70.30	80.09 (69.88)	–10.27	–11.39	–10.09	4.95 (–13.69)
1 _{Ge}	12.74	14.68	15.37	20.25 (14.07)	–37.92	–34.69	–41.77	–38.99 (–45.98)
2 _{Ge}	18.32	22.82	20.87	47.71 (18.67)	–38.60	–32.61	–42.12	–11.56 (–47.32)
3 _{Ge}	62.84	65.42	68.25	80.91 (69.74)	0.70	1.77	–3.28	4.35 (–7.15)
4a _{Ge}	16.26	19.23	18.84	34.21 (18.59)	–35.07	–30.82	–37.18	–38.10 (–41.11)
5b _{Ge}	19.48	22.63	21.69	29.21 (23.40)	–32.95	–28.58	–35.78	–37.96 (–38.65)
6b _{Ge}	19.44	23.61	22.27	29.95 (23.07)	–32.65	–27.54	–35.11	–42.87 (–39.04)
7b _{Ge}	23.26	24.32	21.76	25.77 (16.29)	–30.78	–28.52	–37.60	–43.20 (–32.59)
8 _{Ge}	55.07	59.74	58.80	72.83 (59.52)	–7.06	–1.78	–10.92	3.76 (–15.27)
9a _{Ge}	76.40	78.35	82.11	99.31 (83.70)	14.33	17.10	13.73	29.81 (10.96)
10 _{Ge}	72.48	74.69	71.51	75.40 (78.23)	8.52	11.71	–0.03	8.99 (3.76)

^a $E_a = E_{TS} - E_{Re}$, in unit of kcal/mol.

^b $E_{\text{exo}} = E_{Pr} - E_{Re}$, in unit of kcal/mol.

^c The CASPT2/6-31G^{**} results are given in parentheses.

3.1. Reactants: geometries and relative stabilities

The silylenes and germylenes are reactive and easily react with another molecule or themselves [91–111]. Drahnak et al. reported that dimethylsilylene, (CH₃)₂Si (**2**_{Si}), was stable in hydrocarbon glasses at 77 K or below [116]. In 1992, the stable germylene, Ge[N(Bu^t)CHCHNBu^t] (**9b**_{Ge}), was isolated at 298 K under inert gas [71]. Shortly afterward, the first stable silylene, Si[N(Bu^t)CHCHNBu^t] (**9b**_{Si}), was reported to be distilled at a temperature of 358 K [27]. The relative stabilities of silylenes and germylenes are also closely related to the energy gap between singlet and triplet states, ΔE_{S-T} , ($\Delta E_{S-T} = E_S - E_T$). The B3LYP, MP2, CASSCF, and CASPT2 energies of the lowest singlet (S) and triplet (T) states

and the singlet–triplet energy gaps, ΔE_{S-T} , of acyclic (**1**_{Si}–**3**_{Si}, **1**_{Ge}–**3**_{Ge}) cyclic (**4**_{Si}–**7**_{Si}, **4**_{Ge}–**7**_{Ge}) and amino-containing (**8**_{Si}, **8**_{Ge}, **9**_{Si}, **10**_{Si}, **9**_{Ge}, **10**_{Ge}) systems are listed in Tables 1 and S2. All the singlet silylenes and germylenes, **1**_{Si}–**10**_{Si} and **1**_{Ge}–**10**_{Ge}, are more stable than the corresponding triplet states, indicating the distinct singlet preference in ground states. Especially, N-heterocyclic silylenes (**9**_{Si}, **10**_{Si}) and germylenes (**9**_{Ge}, **10**_{Ge}) are distinguished by the large S–T splitting energies (**9a**_{Si}: –69.01 kcal/mol, **10**_{Si}: –76.36 kcal/mol, **9a**_{Ge}: –59.15 kcal/mol, **10**_{Ge}: –65.78 kcal/mol, at the level of CASPT2/6-31G^{**}).

Some selected geometric parameters of singlet silylenes and germylenes, **1**_{Si}–**10**_{Si} and **1**_{Ge}–**10**_{Ge}, are listed in Table S3. For the experimentally observed N-heterocyclic **9b**_{Si}, **10**_{Si}, **9b**_{Ge}, **10**_{Ge}, the

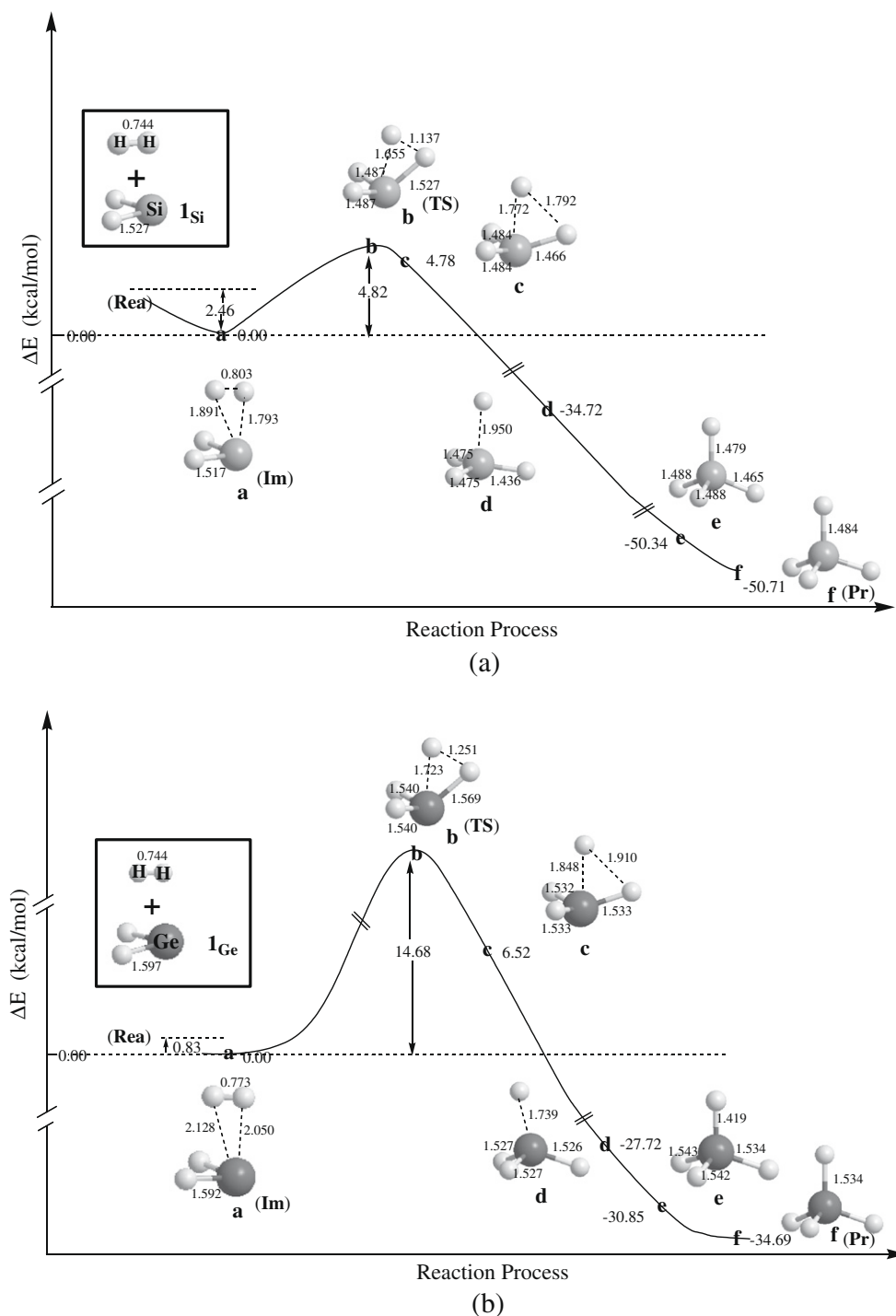


Fig. 2. Some selected structures along the intrinsic reaction coordinate (IRC) of the insertion reaction of (a) silylene, $\mathbf{1}_{\text{Si}}$, and (b) germylene, $\mathbf{1}_{\text{Ge}}$, with H_2 , calculated at the B3LYP/6-311+G^{*} level. Bond distances in angstrom (Å) are also given, in accompany with the relative energies to reactants, in units of kcal/mol.

calculated N–Si (or N–Ge) bond lengths are slightly longer by 0.02–0.05 Å than those obtained by X-ray crystallography [28–32,71,87]. The theoretical bond angles of $\angle\text{N–Si(Ge)–N}$ at the silylenes (germylenes) center are 87.5° ($\mathbf{9b}_{\text{Si}}$), 83.8° ($\mathbf{10}_{\text{Si}}$), 86.1° ($\mathbf{9b}_{\text{Ge}}$), and 82.6° ($\mathbf{10}_{\text{Ge}}$), respectively, in good agreement with X-ray data (90.5° , 84.8° , 88.2° , and 84.9° , respectively). The calculated results in the present work are also close to previous theoretical results [69,90,107].

It has been demonstrated that silylene ($\mathbf{1}_{\text{Si}}$) and germylene ($\mathbf{1}_{\text{Ge}}$) and their derivatives have relatively low-lying doubly-occupied

orbital and a higher-lying π -type vacant orbital [69,99–101,109–112]. In Table S4, the energies of the highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs) of silylenes ($\mathbf{1}_{\text{Si}}\text{--}\mathbf{10}_{\text{Si}}$) and germylenes ($\mathbf{1}_{\text{Ge}}\text{--}\mathbf{10}_{\text{Ge}}$), together with those of H_2 molecule, are listed. It can be found that the HOMOs of silylenes and germylenes may play the role of an electron donor whereas the LUMO of H_2 molecule functions as an electron acceptor, because of the smaller gap ($\text{HOMO}_{\text{silylenes(or germylenes)}} \rightarrow \text{LUMO}_{\text{H}_2}$: 0.122–0.198 au) between the HOMOs of silylenes (or germylenes) and the LUMO of the H_2 molecule than that

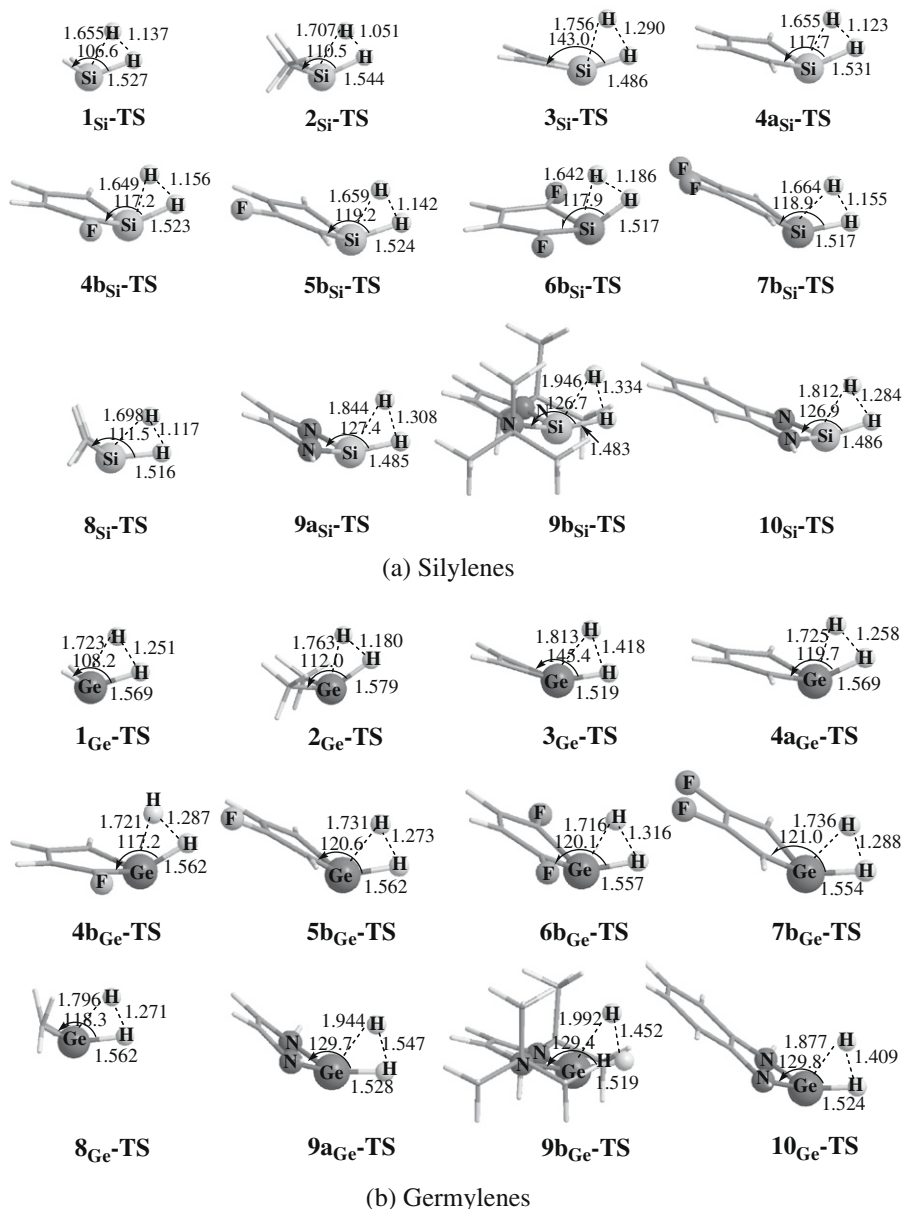


Fig. 3. Transition states (TS) of the activation reaction of hydrogen with (a) silylenes and (b) germynes obtained at the level of B3LYP/6-311+G^{**}. The distances are in angstrom (Å).

(HOMO_{H₂} → LUMO_{silylenes(or germynes)}: 0.194–0.399 au) between the HOMO of the H₂ molecule and the LUMOs of silylenes (or germynes) (Table S4).

As already been noticed before [63], the energy differences between the HOMO and LUMO, $\Delta E(\text{HOMO-LUMO})$, of the studied silylenes (germylenes) are nearly in linear correlation with their S-T splitting energies (Fig. S4). It will be demonstrated in the following subsections that the HOMO-LUMO and S-T gaps are the major factors for affecting the reactivity of silylenes (germylenes) towards the H₂ splitting.

3.2. Precursor complexes and transition states

The precursor complexes (**Im**) for the reactants **1_{Si}**–**10_{Si}** and **1_{Ge}**–**10_{Ge}** are located at various computational levels (Table S5). Within the frameworks of B3LYP, MP2, and CASSCF, the stable precursor complexes in most reaction systems can be easily located, except for **2_{Si}**, **3_{Si}** (**2_{Ge}**, **3_{Ge}**), amino-containing species, **8_{Si}**–**10_{Si}**

(**8_{Ge}**–**10_{Ge}**). As shown in Fig. 2, there is the three-centered interaction in **Im** between the two hydrogen atoms of H₂ and the silicon (germanium) center of silylenes (germylenes), with the Si···H distances of 1.89 and 1.79 Å (**1_{Si}**), and Ge···H distances of 2.13 and 2.05 Å (**1_{Ge}**) at the level of B3LYP/6-311+G^{**}, respectively (Fig. 2). For other derivatives, the average distances between the silicon center and two H atoms of H₂ gas in these precursor complexes are lengthened to around 2.02 Å for silylenes and 2.14 Å for germynes, respectively.

As illustrated in Fig. 1a, the activation reaction of H₂ with silylenes and germynes R₂X (X = Si, Ge) are expected to reach R₂XH₂ products via a concerted transition state (TS). We located the transition states (**1_{Si}**–**TS**–**10_{Si}**–**TS** and **1_{Ge}**–**TS**–**10_{Ge}**–**TS**) at B3LYP/6-311+G^{**}, MP2/6-31G^{**}, and CASSCF/6-31G^{**} levels, respectively. The optimized geometries of transition states for other silylenes and germynes at the B3LYP/6-311+G^{**} level are given in Fig. 3. The imaginary frequencies of transition states are about 1200i cm⁻¹ at the B3LYP/6-311+G^{**} level, 1400i cm⁻¹ at the MP2/

6-31G** level, and 1100i cm⁻¹ at the CASSCF(6,6)/6-31G** level. The imaginary vibrational motion for the activation of H₂ with silylenes (or germylenes) does involve the bond formation between silicon (or germanium) and H₂ in concert with H–H bond breaking.

In all these transition states, both H atoms of H₂ molecule interact with silicon (or germanium) center with a concomitant activation of H₂. The H–H bond is nearly breaking, and simultaneously, two new Si–H (or Ge–H) bonds are forming, similar to those observed in the H₂-activation by carbenes [20–23]. The lengths of the nearly formed Si–H (or Ge–H) bonds in transition states are predicted to be around 1.48–1.54 Å for silylenes and 1.52–1.58 Å for germylenes. Like what has been found in the splitting of hydrogen by singlet carbenes [20–23], another H atom is still far away from the Si and Ge centers with long Si···H and Ge···H distances of around 1.66–1.95 Å (**1_{Si}-TS-10_{Si}-TS**) and 1.72–1.99 Å (**1_{Ge}-TS-10_{Ge}-TS**), respectively (Fig. 3). At the same time, the H–H bond is significantly elongated to 1.05–1.55 Å, almost twice of the bond distance (0.74 Å) in gas phase [117].

3.3. Activation energies: silylenes vs. germylenes

Although the activation reactions of H₂ with silylenes and germylenes, **1_{Si}-10_{Si}** and **1_{Ge}-10_{Ge}**, proceed via the similar pathways, the relative activation barriers are different. At the level of B3LYP/6-311+G**, the activation barrier decreases in the order: **9a_{Si}** (63.46 kcal/mol) > **10_{Si}** (59.88 kcal/mol) > **3_{Si}** (53.15 kcal/mol) > **8_{Si}** (45.59 kcal/mol) > **2_{Si}** (13.31 kcal/mol) > **7b_{Si}** (11.77 kcal/mol) > **6b_{Si}** (9.56 kcal/mol) > **5b_{Si}** (8.27 kcal/mol) > **4b_{Si}** (7.76 kcal/mol) > **4a_{Si}** (5.87 kcal/mol) > **1_{Si}** (4.82 kcal/mol) for silylenes. A similar sequence of **9a_{Ge}** > **10_{Ge}** > **3_{Ge}** > **8_{Ge}** > **2_{Ge}** > **7b_{Ge}** > **6b_{Ge}** > **5b_{Ge}** > **4b_{Ge}** > **4a_{Ge}** > **1_{Ge}** is found for germylenes. The MP2 and CASSCF results follow the same trend as that from B3LYP/6-311+G** calculations (cf., Tables 2 and S6–S8). Interestingly, the activation barriers and Gibbs free activation barriers for silylenes are relatively lower than those for corresponding germylenes, as shown in Fig. 4, and also lower than that for carbene [20–23].

In order to understand the more facile activation of H₂ by silylenes relative to germylenes and carbenes, the natural bond orbital (NBO) analysis of the orbital interactions between silylenes (germylenes) and H₂ in the transition state (**1_{Si}-TS-10_{Si}-TS** and **1_{Ge}-TS-10_{Ge}-TS**) has been carried out at the B3LYP/6-311+G** level. The selected donor–acceptor interactions in Table S9 are the most

significant ones with appreciable second-order stabilization energies $E^{(2)}$. As expected, the effective orbital interactions between the adjacent bonding $\sigma_{\text{Si-H}}$ ($\sigma_{\text{Ge-H}}$) and anti-bonding $\sigma_{\text{Si-H}}^*$ ($\sigma_{\text{Ge-H}}^*$) orbitals in transition states correlate well with the reactivity of the splitting of H₂ by silylenes and germylenes. From Table S9, one can find that for all the studied systems the stabilization energy of $\sigma_{\text{Si-H}} \rightarrow \sigma_{\text{Si-H}}^*$ interaction in silylenes are slightly larger than $\sigma_{\text{Ge-H}} \rightarrow \sigma_{\text{Ge-H}}^*$ in germylenes. This may originate from the longer Ge···H distance than the Si···H separations by about 0.70–0.80 Å (Fig. 3).

It is interesting to see from Fig. 5 the close relationship between the activation energies and the HOMO–LUMO gaps. According to Fig. 5, the studied systems are clearly cut into two groups. The silylenes (germylenes) that contain the highly-strained three-membered ring (**3**) or nitrogen atoms (**8-10**) are much more inert than the others towards H₂-breaking reactions. The relevant discussions will be given in Section 3.5.

3.4. Exothermic energies

As mentioned before, the splitting of H₂ with silylenes or germylenes is initiated by the reactants **Rea** or the precursor complexes **Im**. The concerted transition state **TS** is then reached by overcoming the activation barrier of around 4.82–78.35 kcal/mol at the level of B3LYP/6-311+G**. Finally, the addition product (**Pr**) is generated upon the formation of two covalent Si–H (Ge–H) bonds, releasing a large amount of energy, E_{exo} ($E_{\text{exo}} = E_{\text{pr}} - E_{\text{rea}}$), of around –18.65 to –50.89 kcal/mol for the most of studied systems. The exothermic energies are quite small for the insertion products of **8_{Ge}** (–1.78 kcal/mol), **3_{Ge}** (–1.77 kcal/mol), and turn to endothermic for **9_{Ge}** (17.1 kcal/mol) and **10_{Ge}** (11.71 kcal/mol) at the level of B3LYP/6-311+G**. In the case of the reaction of H₂ with **9a_{Si}**, the exothermic energy is predicted to be –1.75 kcal/mol (MP2/6-31G**//RHF/6-31G*) [27]. Here, we found that the calculated values of the exothermic energy significantly depend on the theory levels. Take **9a_{Si}** as an example, B3LYP/6-311+G**, MP2/6-31G**, and CASSCF/6-31G** calculations give predictions on the exothermic energy of –0.65, –3.90, and 9.61 kcal/mol, respectively.

It can be also found that the splitting of H₂ with mono-halogen (F, Cl, Br) substituents on cyclic silylenes (**4_{Si}**, **5_{Si}**) and germylenes (**4_{Ge}**, **5_{Ge}**) and di-halogen substituted silylenes (**6_{Si}**, **7_{Si}**) and germylenes (**6_{Ge}**, **7_{Ge}**) are more exothermic (–28.58 to –49.78 kcal/mol, at

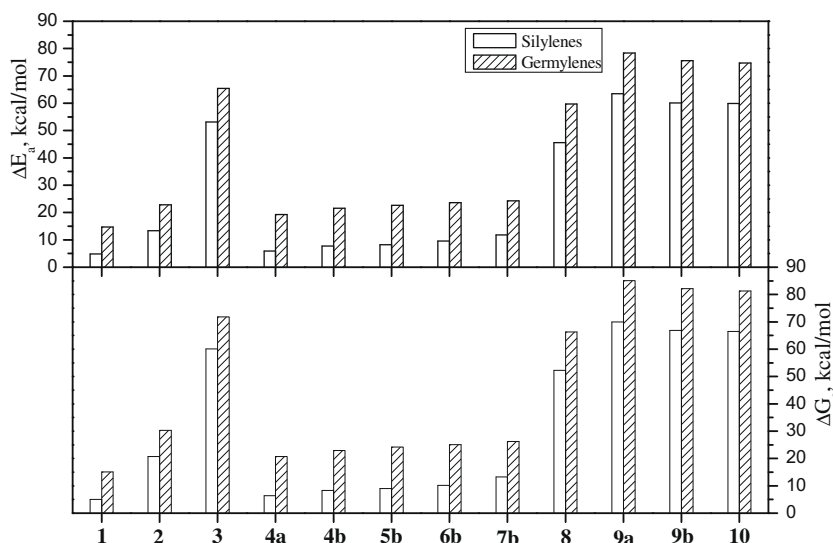


Fig. 4. Energies of (a) the activation energy, E_a ($E_a = E_{\text{TS}} - E_{\text{Re}}$), and (b) the Gibbs free activation energy, G_a ($G_a = G_{\text{TS}} - G_{\text{Re}}$), of insertion reactions of silylenes, **1_{Si}-10_{Si}**, and germylenes, **1_{Ge}-10_{Ge}**, with H₂, calculated at the level of B3LYP/6-311+G**.

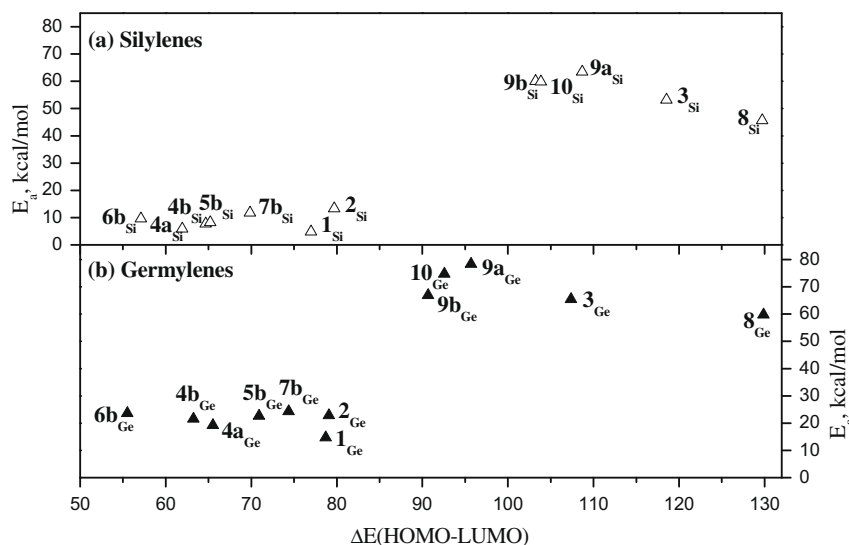


Fig. 5. Correlation of activation energies, E_a , of (a) silylenes and (b) germylenes with the energy differences between the HOMO and LUMO calculated at the level of B3LYP/6-311+G**.

the B3LYP/6-311+G** level) with lower activation barriers (5.87–9.56 kcal/mol, at the B3LYP/6-311+G** level) than those N-heterocyclic silylenes (**9_{Si}**–**10_{Si}**) and germylenes (**9_{Ge}**–**10_{Ge}**). This trend is in agreement with the early conclusion drawn from the reactivity of silylenes with CCl₄ [101], that the smaller singlet–triplet gap, the lower activation barrier and the larger exothermicity.

3.5. Factors that affect the reactivity of H₂ splitting

3.5.1. Acyclic vs. cyclic reactants

The activation energies (4.88 kcal/mol) for the acyclic silylene (**1_{Si}**) is close to those (6.07 kcal/mol) of the cyclic species **4a_{Si}**, which contains a five-membered ring. From Table S3, one can find that the five-membered ring in the cyclic silylenes (**4_{Si}**–**7_{Si}**) does not introduce much difference in geometry at the silylene center and electronic structure properties in comparison with the acyclic silylenes. For example, the H–Si–H bond angle in **1_{Si}** is 90.5°, quite close to the C–Si–C bond angles (**4a_{Si}**: 87.6°; **6b_{Si}**: 83.3°; **7b_{Si}**: 89.3°) at the silylene center of the five-membered ring systems. In addition, the acyclic **1_{Si}** has similar HOMO–LUMO and S–T gaps to those of the five-membered-ring-containing **4_{Si}** (cf. Tables S2 and S4). Similarities between the N-heterocyclic silylenes, **9_{Si}** and **10_{Si}**, and acyclic nitrogen-containing counterpart **8_{Si}** are also revealed in aspects of geometry, S–T gap, and hence, the activation energy. The benzo-annulated heterocyclic diamino silylene **10_{Si}** has nearly identical N–Si bond length and N–Si–N angle to its parent N-heterocyclic **9_{Si}**, suggesting little perturbation was caused by ring fusing.

However, **3_{Si}**, which contains a highly-strained three-membered ring, requires a high barrier (55.18 kcal/mol) in breaking a H₂ molecule. Such a small ring makes the silylene highly distorted. The C–Si–C angle in the three-membered ring is only 42.1°, almost half of those in the acyclic and five-membered-ring-containing cyclic silylenes. Similar conclusions can be drawn for germylenes.

It can be seen from the above discussions that the geometry feature of the silylene (germylene) center as well as electronic structure (HOMO–LUMO and S–T gaps) play important roles in controlling the reactivity of the activation of hydrogen molecule.

3.5.2. Halogen substitutions

The halogen substituted carbenes and heavier analogous have attracted intensive interest both experimentally and theoretically [62,100,101]. The mono-halogen (F, Cl, Br) substitution on cyclo-

penta-2,4-dienylidene silylenes (**4b_{Si}**–**4d_{Si}**, **5b_{Si}**–**5d_{Si}**) and germylenes (**4b_{Ge}**–**4d_{Ge}**, **5b_{Ge}**–**5d_{Ge}**) have been evaluated, with the B3LYP/6-311+G** results displayed in Fig. S5 and Tables S6 and S10. Both the 2- and 3-halo-substituted silylene derivatives have almost equal activation energies of 7.76 (**4b_{Si}**), 7.65 (**4c_{Si}**), 7.67 (**4d_{Si}**), 8.27 (**5b_{Si}**), 7.84 (**5c_{Si}**), 7.87 (**5d_{Si}**) kcal/mol. A similar trend is also held for germylenes. This implies that the halogen substitution on different positions of the five-membered ring have little influence on the activation energies. This is not surprising since the energy levels of HOMO and LUMO are almost unchanged upon the substitution by halogen.

The di-halogen on 2,5- and 3,4-halo-substituted cyclopenta-2,4-dienylidene silylenes (**6b_{Si}**–**6d_{Si}**, **7b_{Si}**–**7d_{Si}**) and germylenes (**6b_{Ge}**–**6d_{Ge}**, **7b_{Ge}**–**7d_{Ge}**) have also been studied. For example, the activation barriers of the insertion reactions of di-substituted silylenes with H₂ at the level of B3LYP/6-311+G** are 9.56 (**6b_{Si}**), 9.38 (**6c_{Si}**), 9.41 (**6d_{Si}**), 11.77 (**7b_{Si}**), 10.05 (**7c_{Si}**), and 9.96 (**7d_{Si}**) kcal/mol, respectively, a little higher than the mono-halogen-substituted derivatives. The same phenomenon is also obtained for the substituted germylenes, as shown in Table 2 and Fig. S5.

The halogen substituent effects on 2- and 3-halo-substituted cyclopenta-2,4-dienylidene silylenes and germylenes also have little influence on exothermic energies, similar to what was found for the activation energies (Fig. S5 and Tables S6 and S10).

3.5.3. N-heterocyclic systems

It has already been mentioned that the N-heterocyclic silylenes and germylenes are stabilized by the amino groups [27,71]. Our calculation results also displayed that the S–T or HOMO–LUMO gaps in the N-heterocyclic systems (**8_{Si}**–**10_{Si}**, **8_{Ge}**–**10_{Ge}**) are at least twice of those in unstabilized silylenes (**4_{Si}**–**7_{Si}**) and germylenes (**4_{Ge}**–**7_{Ge}**), although all of them have the common structural unit, a five-membered ring. Those unsaturated silylenes and germylenes contain five-membered rings were recognized as aromatic species, with the aromatic resonance energy up to 50–60% of that in benzene. The high stability of N-heterocyclic silylene (germylene) makes it rather inert in activation reaction of hydrogen molecule, as shown in Fig. 5. In addition, the introduction of nitrogen atom in N-heterocyclic silylene (germylene) shifts up the energy levels of both the HOMO and LUMO, but to a different degree. The LUMOs of N-containing systems are much highly lying in comparison with those silylene (germylene) without nitrogen atoms (Table S4).

Up to now, although a lot of singlet silylenes and germylenes have been reported [27–84], the triplet state of silylene is of increasing interest in experimental and theoretical works [118–123]. Further theoretical investigations on the stability and reactivity of triplet state of silylenes and germylenes are in progress.

4. Conclusions

Possible reaction pathways for activation reactions of H₂ with a series of silylenes and germylenes have been investigated through DFT, MP2, and CASSCF calculations. Similar to carbenes, the stable singlet silylenes and germylenes can mimic the reactivity of transition metals with H₂ to some extent. The activation reactions of H₂ can proceed via the concerted dissociation of H₂ and addition of two H atoms to silicon (or germanium) center, similar to the reported reactions with carbenes [20–23].

The 2- or 3-halo-substituted silylenes and germylenes are predicted to be better candidates for activation reaction of H₂ than those N-heterocyclic silylenes (**9_{Si}**, **10_{Si}**) and germylenes (**9_{Ge}**, **10_{Ge}**). The mono- and di-substitutions effects on cyclopenta-2,4-dienylidene silylenes (**4_{Si}**–**7_{Si}**) and germylenes (**4_{Ge}**–**7_{Ge}**) have little influence on the activation energies and exothermic energies of the insertion reactions with H₂. Our results may enrich the information of chemical reactions of silylene and germylene derivatives.

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Appendix A. Supplementary material

The optimized energies of reactants, transition states, and products by B3LYP, MP2, and CASSCF methods are listed in Tables S1–S12 of Supporting Information. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.03.051.

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