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Theoretical study on the consecutive 1,2-hydroboration and 1,1-organoboration reactions of alkyn-1-yl(vinyl)silane with borane

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ABSTRACT

The detailed pathway of the consecutive 1,2-hydroboration and 1,1-organoboration reactions of alkyn-1-yl(vinyl)silane with borane were studied theoretically by DFT calculations. It is found that the 1,2-hydroboration will occur at the C=C moiety when the alkynyl end is substituted, and give the anti-Markovnikov adduct as a result of steric hindrance. From the 1,2-hydroboration intermediate, the intramolecular 1,1-organoboration is a concerted asynchronous process, in which the ≡C–Si cleavage precedes 1,2-alkyl migration, with activation energy about 25 kcal/mol. Calculations reveal the electronic property of the substituent at the alkyne end has quite limited effect on the 1,1-organoboration activation energy. The ring constrain is found to influence the weak Si–H–B interactions in the 1-silacyclopent-2-ene product most, and similar C–H–B interactions were predicted for the corresponding carbon analogues.

1. Introduction

The insertion of an unsaturated moiety into B–H bond, namely hydroboration, has been one of the most important organic reactions due to its wide applications [1]. Previous studies show that the hydroboration reactions of borates should be catalyzed by transition metals [2]; however, borane (HBR_2, R = alkyl) or boron halide (HBX_2, X = Cl or Br) are more reactive hydroborating reagents, which could undergo hydroboration with alkyne or alkene under mild conditions without using any catalyst [3].

The chemo-, stereo- and regioselectivities in the hydroboration process have been widely studied [4]. Generally, the anti-Markovnikov addition is more favorable in the uncatalyzed hydroboration reactions [5]. However, both the steric and electronic properties of the substrates have notable effects on the regiochemistry. For reversing the regioselecitivity of the hydroboration, one efficient strategy is the introduction of fluorinated substituent to the C=C bond. Initial work of this method was reported by Ramachandran and coworkers [6], who found the hydroboration of perfluoro alkyl and aryl substituted ethylenes with borane or haloborane would give the Markovnikov products almost exclusively (Eq. 1, Scheme 1). Another remarkable strategy for regioselectivity control is the introduction of silyl group [7,8]. In most cases, the reactions of alkenylsilane and alkynylsilane with borane undergo the Markovnikov addition and give mainly the branched product (Eq. 2, Scheme 1), unless bulky boron reagent, such as 9-borabicyclo[3.3.1]nonane (9-BBN), is used [9].

Not only the 1,2-hydroboration of unsaturated moieties, has the 1,1-organoboration of alkyn-1-ylmetal compounds also been well studied in organoboron chemistry, ever since the seminal work of Wrackmeyer et al. [10,11]. As shown in Eq. 3, Scheme 2, the reaction is initiated with the cleavage of the polar metal–carbon bond by the electron-deficient boron atom to form an alkynylborate-like zwitterionic intermediate (**A**), followed by the 1,2-shift of one organyl group from boron to the neighbored alkynyl carbon atom, leading to the organometallic-substituted alkene product. This method is highly stereoselective, as in most cases, the boryl moiety and the metal fragment are in *cis* position at the C=C bond. Remarkably, if another alkynyl group is linked to the metal fragment, the second 1,1-organoboration will occur through an intramolecular activation of the next M–C≡ bond (Eq. 4, Scheme 2) [12]. Employment of this multiple 1,1-organoboration sequence has opened a novel access to various metallacyclopentadienes and spirocyclic metalloles, including all the group 14 metals as well as examples of Ti and Pt [13].

Due to the easiness of boryl introduction by 1,2-hydroboration of alkene and efficiency of ring construction by intramolecular 1,1-organoboration of alkynylmetal compounds, the combination of these two methods for organometallic synthesis has been studied by Wrackmeyer and coworkers in recent years [14], and four-, five-, and six-membered silacycles, namely 1-silacyclobutene,

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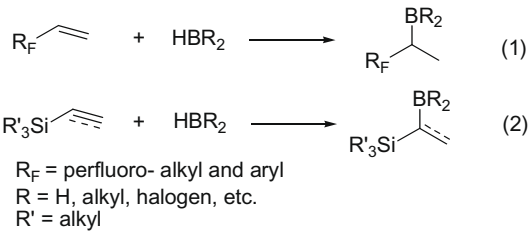


Scheme 1. Markovnikov 1,2-hydroboration.

1-silacyclopent-2-ene, and 1-silacyclohex-2-ene, respectively, were prepared via consecutive 1,2-hydroboration and 1,1-organoboration of the corresponding precursors with 9-BBN [14].

The reaction of alkyne-1-yl(vinyl)silane with 9-BBN is remarkable, however, there are still several unknowns about these consecutive 1,2-hydroboration and 1,1-organoboration reactions. First of all, the 1,2-hydroboration step is highly chemoselective and regioselective. Only the anti-Markovnikov addition of the alkene moieties occurs, even though the reactants possess both C=C and C≡C functionalities. The origin of the high selectivity is still unrevealed. Secondly, the 1,1-organoboration reaction is very interesting, yet no research about the detailed reaction pathway has been carried out. Thirdly, different substituents could be tolerated at the alkyne end, such as alkyl, phenyl, and silyl, and the functional effects of these groups on the energetics of the 1,2-hydroboration and 1,1-organoboration have not been addressed. In addition, the Si–H–B interaction in the product is quite rare, and the nature and properties of this novel interaction also need to be investigated [15].

In this report, we aim at revealing the above-mentioned unknowns by carrying hybride density functional theory (DFT) calculations. The mechanistic insights from these combined 1,2-hydroboration and 1,1-organoboration reactions would shed new light on the substituent effects, selectivities, and energetics of the 1,2-hydroboration and 1,1-organoboration reactions, which are very important synthetic methodologies in organic and organometallic chemistry.

2. Computational details

All DFT calculations were carried out by using GAUSSIAN 03 software package [16]. The stationary points along the reaction pathway were fully optimized at B3LYP/6-31G* level of theory [17,18], and were confirmed as minima (no imaginary frequency) or transition states (only one imaginary frequency) by frequency analysis. Previous studies indicate this method is reliable for the study of the hydroboration reaction mechanism [19]. IRC calculation was used to confirm the transition state located connects the right intermediates.

To validate the computational method used, calculations at B3LYP/6-311+G** level were carried out, and the results indicate that the relative energies are not sensitive to the basis set. For example, when calculated with B3LYP/6-311+G** method, the relative energies in Fig. 1 should be 0.0, 13.4, −24.2, −24.0, 2.0, and −38.4 kcal/mol, respectively, which are quite close to the relative energies reported herein. Unless otherwise stated, all the relative energies given in the figures and tables are the relative electronic energies with zero-point energy corrections at the B3LYP/6-31G* level.

The model reaction is shown in Scheme 3, in which **1** is used as the representation of alkyne-1-yl(vinyl)silane, and **2** is used as a simplified model of 9-BBN. So as to investigate the effects of the silyl functionalities in **1** on each step of the reactions, these silyl groups in **1** will be replaced by other substituents for comparisons. As in experiments the bulky 9-BBN was used as the hydroboration reagent, the reliability of the model reaction was tested. When 9-BBN is used in calculations, the relative energies in Fig. 1 are 0.0, 9.6, −27.0, −26.6, 0.6, and −43.5, respectively, showing the reported energetic values are reliable.

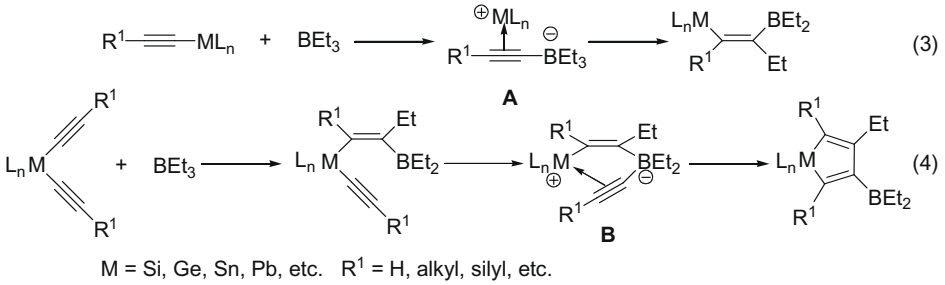
3. Results and discussion

3.1. Overall reaction pathway

The potential energy surface for the reaction of **1** with **2** is depicted in Fig. 1, and IRC analysis and geometries of selected transition states are given in Figs. 2 and 3, respectively. The details of each step of the reaction will be discussed in followed subsections.

Activation barrier indicates the 1,2-hydroboration step is quite facile, and the 1,1-organoboration is the rate-limiting step with an activation barrier of 24.8 kcal/mol. Thermodynamic data show both steps are irreversible with an overall exothermicity of 42.7 kcal/mol for the formation of **3** from **1** and **2**. When entropy contribution is included, the activation free energies of the intermolecular 1,2-hydroboration and intramolecular 1,1-organoboration steps are 22.9 and 27.9 kcal/mol, respectively.

The stabilities of both conformers **4** and **5** of the intermediate from the 1,2-hydroboration are almost the same, and no intramolecular interaction of the electrophilic boryl with C≡C moiety of intermediate **5** was calculated, as implied by the relative long B–C4 and B–C5 distances of 3.63 and 4.05 Å, respectively. Geometry shows that the internal Si–C is cleaving and a new C–B bond is forming in the 1,1-organoboration transition state **TS2**, in which the Si3–C4 and C4–B distances are 1.99 and 1.74 Å, respectively (Fig. 3). Although the zwitterionic intermediates were characterized for the intermolecular 1,1-organoboration processes of Sn–C_{sp} and Pb–C_{sp} [13], no intermediate of type **A** or **B** (Scheme 2) was located for the Si–C_{sp} system, and IRC calculation indicates the 1-silacyclopent-2-ene product **3** would be formed directly via **TS2**. Details about this will be discussed in Section 3.3.



Scheme 2. 1,1-Organoboration of alkyn-1-ylmetal compounds.

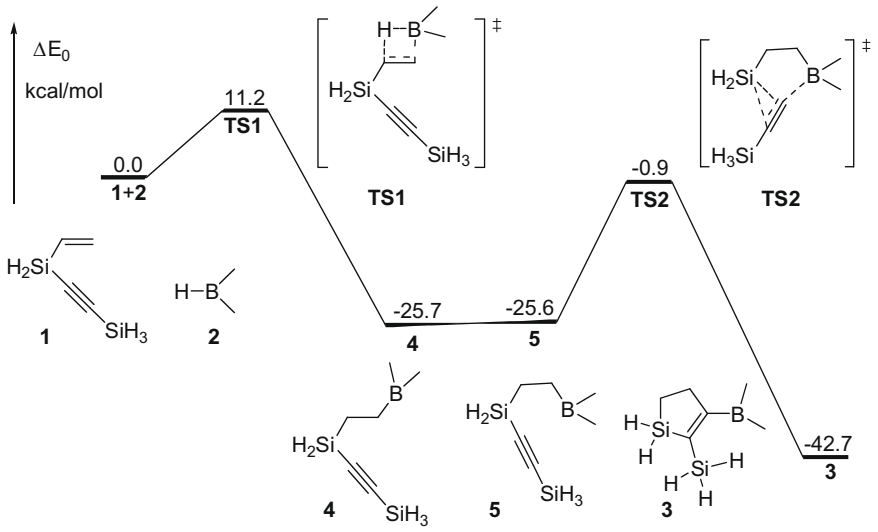
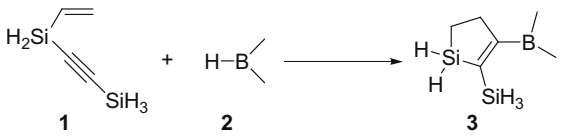


Fig. 1. Potential energy surface for the 1,2-hydroboration and 1,1-organoboration reactions of **1** with **2**.



Scheme 3. Model reaction.

3.2. 1,2-hydroboration

It is consistent with the experimental results that the addition of **2** to the C═C moiety (1, 2-addition) of **1** is more favorable than addition to the C≡C moiety (4,5-addition) (Entry 1, Table 1) [14]. So as to reveal the effects of the two silyl functionalities of **1** on the chemoselectivity, additional calculations have been done on

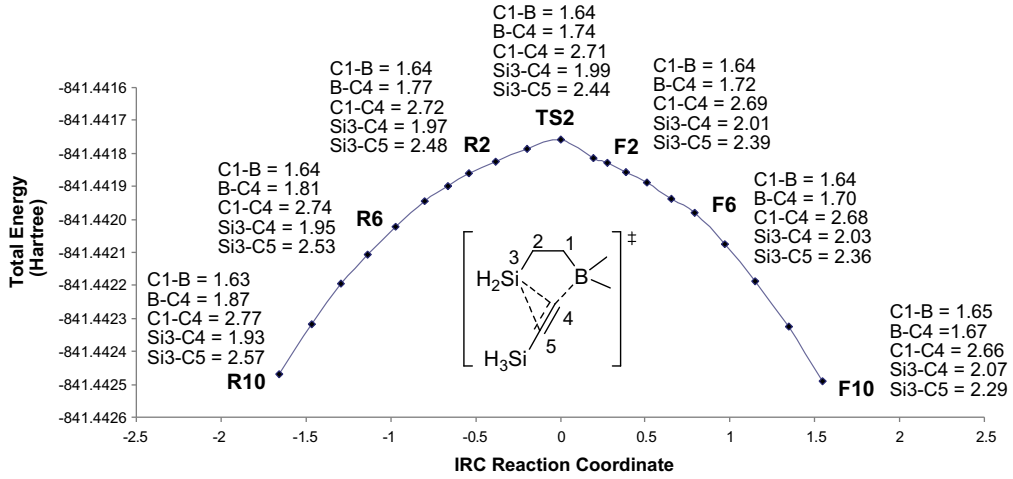


Fig. 2. IRC analysis of **TS2**, distances are in Å.

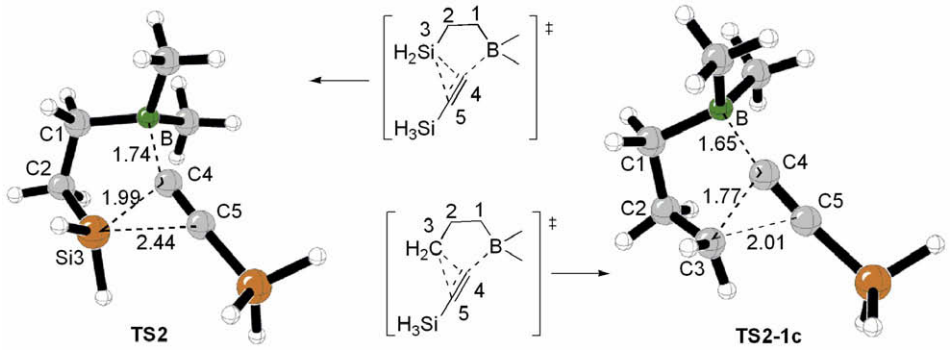
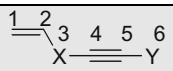


Fig. 3. Geometries for **TS2** and **TS2-1c** (Distances are in Å).

Table 1
Activation barriers for the 1,2-addition and 4,5-addition of 1,4-enyne derivatives with **2** (in kcal/mol)

Entry		1,2-addition[a]	4,5-addition[b]
1	**1** (X = SiH_2, Y = SiH_3)	11.2	12.1
2	**1a** (X = SiH_2, Y = CH_3)	10.6	12.1
3	**1b** (X = SiH_2, Y = H)	11.0	10.3
4	**1c** (X = CH_2, Y = SiH_3)	9.2	9.8

[a] Activation barriers for the anti-Markovnikov addition of **2** to the 1,4-enynes.
[b] Boron atom of **2** is adding to C5 of the 1,4-enynes. The barriers for the addition of boron to C4 are given in Supplementary Material.

the hydroboration reactions of 1,4-enyne substrates **1a**, **1b**, and **1c**, in which the silyl groups of **1** are replaced by other groups. Comparing the reaction barriers in Table 1 we can find the internal silylene functionality (X = SiH_2) affects the activation barriers most, and both the 1,2- and 4,5-addition activation barriers of substrate **1** (X = SiH_2) will be about 2 kcal/mol higher than those of **1c** (X = CH_2), respectively, which may be the results of deactivation of the π systems of **1** by the electron-deficient silyl group. If replacing the terminal silyl group to a methyl (**1a**) (Entry 2, Table 1), no change of the barrier of the 4,5-addition was calculated, but slightly lowering of the 1,2-addition barrier was obtained. Generally, the 1,2-addition is more kinetically favorable when the alkyne terminal is substituted (**1**, **1a**, and **1c**), accounting for the necessity of an attachment at the alkyne end for controlling of the chemoselectivity.

So as to investigate the regiochemistry of the 1,2-hydroboration step, we calculated the relative activation barriers of the Markovnikov and anti-Markovnikov additions of the hydroborations of monosubstituted alkenes with BH_3, **2**, and 9-BBN, respectively. As given in Table 2, the anti-Markovnikov addition has lower barrier than the Markovnikov addition in all cases of alkyl-substituted alkenes (Entries 2 and 4, Table 2). However, when substituted with silyl group (Entries 1 and 3, Table 2), the energy gaps between the Markovnikov and anti-Markovnikov additions will be reduced. The relative barriers indicate the Markovnikov addition is more favorable in the reaction of **1d** with BH_3, as result of the electronic effect of the silyl group. However, the function of the silyl group is quite limited when increasing the steric hindrance of either the hydroborating reagent or the silyl group. The Markovnikov addition will be still more favorable in the reactions of **1d** with **2** and **1f** with BH_3, but the energy gaps between the Markovnikov addition and anti-Markovnikov addition are reduced to 0.5 and 0.7 kcal/mol, respectively. As result of the steric hindrance, the anti-Markovnikov additions are more favorable by several kcal/mol in all reactions of 9-BBN, no matter which alkene is used.

3.3. 1,1-Organoboration

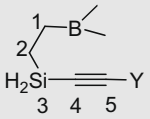
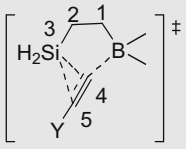
As aforementioned, only one transition state (**TS2**) was located for the 1,1-organoboration step. To gain more insight about this process, the IRC analysis of **TS2** is shown in Fig. 2. The geometry variation along the reaction coordinate indicates this transition state is a transition structure for the migration of alkylnyl group

Table 2
Relative barriers for the Markovnikov and anti-Markovnikov additions of alkyl and silyl substituted alkenes (in kcal/mol)

Entry	BH_3			$HBMe_2$ (**2**)		9-BBN	
		M-addition[a]	AM-addition[b]	M-addition[a]	AM-addition[b]	M-addition[a]	AM-addition[b]
1	H_3Si **1d**	−1.7	0.0	−0.5	0.0	2.7	0.0
2	H_3C **1e**	2.4	0.0	3.0	0.0	5.2	0.0
3	Me_3Si **1f**	−0.7	0.0	1.6	0.0	5.4	0.0
4	Me_3C **1g**	1.5	0.0	6.1	0.0	10.8	0.0

[a] Markovnikov addition, energies are relative to that of the AM-addition.
[b] Anti-Markovnikov addition.

Table 3
Activation barriers and selected geometric parameters of the transition states for the intramolecular 1,1-organoborations

Entry	Intermediate[a]	TS	Activation energy (kcal/mol)	TS geometry (Å)		
				Si3–C4	Si3–C5	C4–B
1	**4** (Y = SiH_3)	**TS2**	24.8	1.99	2.44	1.74
2	**4-1a** (Y = CH_3)	**TS2-1a**	23.4	2.09	2.23	1.67
3	**4-1b** (Y = H)	**TS2-1b**	25.0	1.99	2.43	1.76
4	**4-1h** (Y = F)	**TS2-1h**	28.1	2.18	2.17	1.66
5	**4-1i** (Y = Cl)	**TS2-1i**	27.3	2.14	2.22	1.66
6	**4-1j** (Y = CF_3)	**TS2-1j**	28.6	2.01	2.42	1.74
7	**4-1k** (Y = CN)	**TS2-1k**	30.8	2.14	2.30	1.64
8	**4-1l** (Y = CHO)	**TS2-1l**	24.4	2.03	2.44	1.70
9	**4-1m** (Y = NO_2)	**TS2-1m**	27.7	2.11	2.35	1.66
10	**4-1n** (Y = OH)	**TS2-1n**	26.2	2.35	2.07	1.59
11	**4-1o** (Y = OMe)	**TS2-1o**	25.9	2.30	2.08	1.61
12	**4-1p** (Y = $OSiH_3$)	**TS2-1p**	26.6	2.32	2.08	1.60
13	**4-1q** (Y = NH_2)	**TS2-1q**	26.0	2.33	2.06	1.59

[a] Intermediates of type **5** are higher in energies.

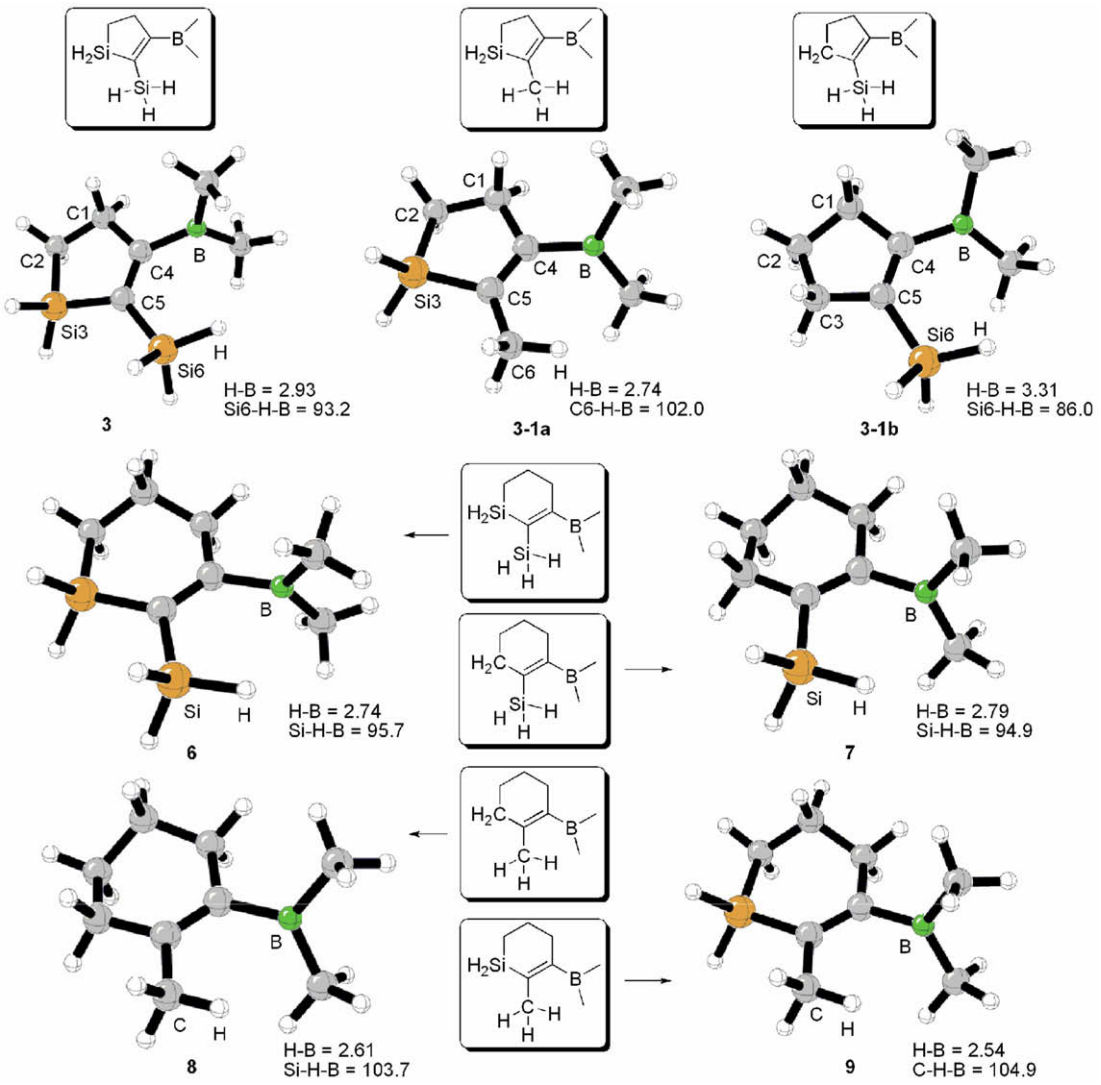


Fig. 4. X–H–B (X = Si and C) interactions in five- and six-membered rings. Distances and angles are in angstrom and degree, respectively.

from Si3 to B, which is consistent with the vibrational model of **TS2** (from frequency calculation). However, as the IRC plots in Fig. 2 do not reach the related minima for both the forward and reverse reactions, optimizations starting from the points **F10** and **R10** (Fig. 2) were carried out, which were found to lead to intermediate **5** and product **3**, respectively. The energy and geometry variations in the optimizations starting from **F10** suggest that no zwitterionic intermediate existed in the process, and the migration of the alkynyl group from Si3 to B precedes the migration of C1 from B to C4 [20]. Thus, the 1,1-organoboration could be better described as a concerted asynchronous reaction, in which no intermediate is involved but several chemical evens that do not occur simultaneously are contained [21].

Results of Wrackmeyer and co-workers found the polarity of the M–C_{sp} is crucial for the 1,1-organoboration. As expected, the activation energy for the 1,1-organoboration step of substrate **1c**, in which the internal Si atom of **1** is replaced by a C atom, is over 20 kcal/mol higher than that of **1**. Partially because the strength of a C–C bond is stronger than that of a Si–C bond [22], and also as result of a more fused 1,1-organoboration transition state (**TS2-1c**, Fig. 3) is calculated for **1c**, as geometrical structure shows the C3 has closer interactions with both C4 and C5 in **TS2-1c**, and a shorter C4–B distance is observed, compared with their counterparts in **TS2**.

Previous experimental studies mainly focused on the cleavage of different M–C_{sp} bonds; however, effect of the functional group at the alkyne end on the 1,1-organoboration has not been addressed. So as to evaluate the effect of the electronic structure of the C≡C moiety on the energetics of the 1,1-hydroboration, the activation barriers for the intramolecular 1,1-hydroboration of the 1,2-hydroboration intermediates of various 1,4-enynes have been calculated, and the results are summarized in Table 3. The activation barriers indicate the 1,1-organoboration is the most efficient when the alkyne end is substituted by an alkyl group (Entry 2, Table 3). The calculations also give the prediction that the CN group will make the intramolecular 1,1-organoboration more unfavorable (Entry 7, Table 3), with a highest activation barrier of 30.8 kcal/mol among the reactions. Although the electronic effect of the substituent is not dramatic in terms of activation energy, in general, the substrates with electron-donating groups attached to the alkyne is slightly more reactive than those of the electron-withdrawing group substituted ones, with an exception of the CHO case (Entry 8, Table 3), which needs an activation barrier of only 24.4 kcal/mol.

The computational results in Table 3 are understandable, as the 1,1-organoboration reaction would be both influenced by the electronic structure of the C≡C moiety and the intensity of the Si–C_{sp} bond. When an electron-withdrawing group (X = F, Cl, CF_3, CN,

CHO, and NO_2) is attached to the alkyne, as results of decreasing the electron density of the C≡C moiety, the Si–C_{sp} bond intensity will be weakened, and the electrophilic attack of the boryl will also be less favorable. On the other hand, the electron-donating group (X = CH_3, OH, OMe, $OSiH_3$, and NH_2) will favor the electrophilic attack of the boryl, but also enhance the intensity of the Si–C_{sp} at the same time.

While the activation barriers for these 1,1-organoborations are similar, the geometries of the transition states differ a lot (Table 3). Generally, when substituted with electron-withdrawing groups, early transition states with shorter Si3–C4 and longer Si3–C5 and C4–B distances are calculated, compared with their counterparts in electron-donating group substituted transition states. For example, in **TS2-1j**, which is substituted by the strong electron-withdrawing group CF_3, the Si3–C4, Si3–C5, and C4–B distances are 2.01, 2.42, and 1.74 Å, respectively. When the CF_3 is replaced by a weaker electron-withdrawing group, such as Cl in **TS2-1i**, these three parameters are changed to 2.14, 2.21, 1.66 Å, respectively. These distances will be further changed to 2.35, 2.07, and 1.59 Å, respectively, in **TS2-1n**, in which an electron-donating OH group is substituted.

The geometry variation of the transition states is consistent with the electronic effect of the terminal substituents (Mulliken charge populations of the transition states are given in Supplementary Material). When substituted by the electron-withdrawing groups, more negative charge will be populated on C4 in the transition states, thus shorter Si3–C4 distances are calculated. On the contrary, the electron-donating groups will make the C5 more negative, and shorter Si3–C5 distances are obtained.

3.4. Si–H–B interaction

Through IR and NMR spectroscopic study, the Si–H–B bridge was observed in the 1-silacyclopent-2-ene product (**3**) by Wrackmeyer and co-workers [14,15]. As depicted in Fig. 4, the computed geometry of **3** shows the Si–H–B interaction is rather weak in our model, as the H–B distance is about 2.93 Å and the Si6–H–B angle is 93.2°. To gain more information about the factors that influence this weak interaction, we optimized the geometries of **3-1a** and **3-1b**, which are the products of **1a** and **1b**, respectively. The geometries indicate when the external Si (silyl) is replaced by a C (methyl), stronger C–H–B interaction is calculated in **3-1a** than the Si–H–B interaction in **3**, evidenced by shorter H–B distance and greater C6–H–B angle, 2.74 Å and 102.0 degree, respectively, in **3-1a**. This should be the result of shorter C5–C6 distance (1.51 Å) in **3-1a** than C5–Si6 distance (1.86 Å) in **3**, which enables closer interaction of C6–H with B atom. However, when the internal Si atom (silylene) is changed to a C (methylene), no interaction will be observed in **3-1b**, with the H–B distance increased dramatically to 3.31 Å and the Si6–H–B angle decreased to 86.0°, implying the constrained cyclopentene ring may disfavor the Si–H–B interaction (C3–C2 = 1.54 Å, C3–C5 = 1.53 Å, C2–C3–C5 = 103.5° in **3-1b** vs. Si3–C2 = 1.90 Å, Si3–C5 = 1.88 Å, C2–Si3–C5 = 94.4° in **3**).

As expected, when expanding the 1-silacyclopent-2-ene (**3** and **3-1a**) and cyclopentene (**3-1b**) to 1-silacyclohex-2-ene and cyclohexene, such as **6**, **7**, **8**, and **9** (Fig. 4), the X–H–B (X = Si and C) will be stronger than that in the corresponding five-membered ring [14b]. The strongest X–H–B interaction was predicted for **9**, which is free of ring constraint and has a closer methyl boryl interaction, having a H–B distance of 2.54 Å and C–H–B angle of 104.9°. Compared **6** with **3**, a shorter H–B distance of 2.74 Å and a greater Si–H–B angle of 95.7 are calculated. Notable, changing the 1-silacyclopent-2-ene to its carbon analogues, such as **7** and **8**, still quite strong X–H–B interactions were calculated, showing that it is not the steric repulsion between the germinal silyl groups in **3** and **6**, but the relieve of the ring constraint, enhances the X–H–B interaction.

4. Conclusions

The consecutive 1,2-hydroboration and 1,1-organoboration reaction of alkyn-1-yl(vinyl)silane with trialkyl borane was studied by means of DFT calculation. Based on the computational results of each step, the following conclusions could be drawn:

(1) The 1,2-hydroboration of the double bond of alkyn-1-yl(vinyl)silane with HBR_2 is quite facile with activation barrier around 10 kcal/mol. The group attached at the alkyne end is crucial for controlling the chemoselectivity, otherwise, the hydroboration of the triple bond will be more favorable.
(2) The regiochemistry of the 1,2-hydroboration could be affected by the electronic effect of the silyl group of vinylsilanes, and the Markovnikov addition could be more favorable in some cases. However, the regioselectivity is more sensitive to the steric effect of the hydroborating reagent and the silyl group. The anti-Markovnikov addition will be much more favorable when 9-BBN is used.
(3) The intramolecular 1,1-organoboration of alkyn-1-ylsilane is a concerted asynchronous Si–C_{sp} cleavage and 1,2-organyl shift process with an activation barrier of about 25 kcal/mol. It is found that the electronic structure of the alkyne moiety has quite limited effect on the kinetic property of the 1,1-organoboration, and the activation energies for various group substituted alkyn-1-ylsilanes are similar.
(4) The weak Si–H–B interaction in the product was investigated by geometry optimization. Comparing the strength of the X–H–B interaction of 1-silacyclopent-2-ene and 1-silacyclohex-2-ene with their carbon analogues, the geometric constraint of the cyclic olefin was revealed as the major factor that affects the X–H–B bridge, and the C–H–B interactions would be stronger when the ring constraint is relieved, according to the predictions.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.09.016.

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