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A Mechanism for the Palladium-Catalyzed Regioselective Silaboration of Allene: A Theoretical Study

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A mechanism for the regioselective silaboration of terminal allene by a palladium catalyst has been studied theoretically. The overall reaction scheme has been examined in particular to determine the mechanism of the regioselectivity. The present catalytic reaction is exothermic and the rate-determining step is the insertion of allene into the Pd−B bond of the Pd complex. σ-Allylic and π-allylic complexes exist as intermediates and play an important role in the regioselectivity. Selective insertion of the unsubstituted C=C bond into the Pd−B bond produces the most stable σ-allylic complex, which converts to the π-allylic complex while maintaining the Pd−O coordination. The selective formation of the specific σ-allylic complex and the large activation barrier between two isomeric π-allylic complexes dominantly determines the regioselectivity of the present reaction. The major-product complex is less stable than the minor-product complex, and therefore kinetic control is predominant in the present reaction.

Introduction

Transition-metal catalyzed additions of silicon-containing σ-bonds to unsaturated bonds of organic molecules have been a major strategy for the synthesis of organosilicon compounds.[1–3] While Si−Si bond addition has been extensively studied,[4] addition reactions involving silicon−heteroatom bonds such as B, Sn, and Ge have become important topics in recent years. Many reactions of these interelement σ-bonds proceed regioselectively, leading to the effective syntheses of regiodefined organosilicon compounds. In particular, Suginome and co-workers have developed Si−B bond addition reactions using silylboranes with a variety of unsaturated organic compounds.[5–12] In these reactions, the otherwise stable Si−B bond is effectively activated by the group 10 metal complexes, exhibiting its broader applicability to the reactions with unsaturated compounds than other silicon-containing bonds such as Si−Si and Si−Sn. It has been shown that high selectivity is attainable by an appropriate choice of the metal as well as the ligands of the catalysts in the silaboration reactions.

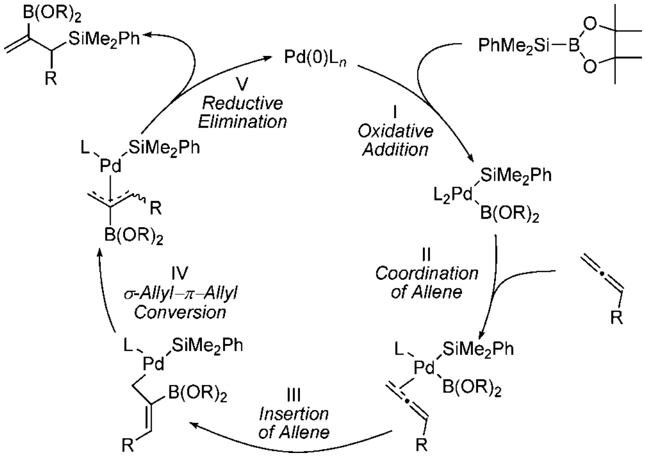
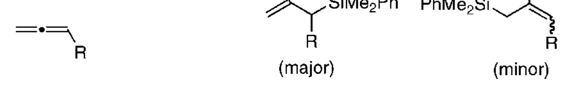


Figure 1. Reaction scheme of the palladium-catalyzed regioselective silaboration of allene.[12]

Recently, effective silaboration reactions of allenes with silylborane have been developed.[11,12] These reactions proceed in a regio- and stereoselective fashion in the presence of the palladium catalyst, producing synthetically useful β-borylallylsilanes in high yields as shown in eq 1.



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For this catalytic reaction, Suginome and co-workers proposed the reaction mechanism shown in Figure 1 and explained the

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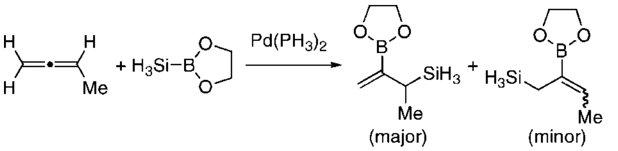
regio- and stereoselectivity.[12] In this mechanism, the Si−B bond oxidatively adds to the Pd(0) complex and then an allene coordinates and inserts into the Pd−B bond with the electron-deficient C═C bond. This selective formation of a B−C bond at the sp carbon of allene produces a σ-allylic Pd intermediate, in which the silyl group and the allylic carbon are located in a *trans* orientation. This σ-allylic Pd complex rapidly converts to the π-allylic Pd complex, which proceeds via facile reductive elimination of the silicon and the carbon atom located *cis* to the silyl group. Unfortunately, no intermediates were isolated for the present catalytic reactions, and therefore theoretical investigations are required to examine the possible mechanism of this reaction.

In this paper, we theoretically investigate this catalytic reaction, the silaboration of allene catalyzed by the Pd complex, to clarify the reaction mechanism and the origin of the regioselectivity. We examined the reaction scheme shown in Figure 1 and calculated the intermediates and the transition states that appear in the course of the reaction. We expect that the mechanism of this particular reaction is generally applicable to the addition reactions of silicon−heteroatom bonds to allenes and is useful for the theoretical design and control for the regio- and stereoselectivities of these reactions. Recently, highly enantioface-selective silaboration of allenes has been achieved by refining the present reaction by inducing chirality in silylborane and/or the Pd catalyst.[13–15] The present system is also of particular interest in relation to our previous theoretical work[16] on the silastannation reactions of acetylenes with the Pd catalyst.

Computational Model and Details

In the present calculations, the silaboration of allene was modeled as shown in eq 2. Two isomers are represented by the positions of the boryl and silyl groups inserted into the allene.



(2)

$SiH_3-B(OCH_2)_2$ was adopted as a model of silylpinacolborane. The coordination of a lone pair on oxygen to the Pd complex was found to be important for the regioselectivity of the reaction as discussed later, and therefore $SiH_3-B(OH)_2$ is not satisfactory in the present system. As a model of the Pd catalyst, we adopted $Pd(PH_3)_2$, which has a much smaller steric effect than $Pd(PPh_3)_2$. This model is sufficient to simulate the present catalytic reaction and to clarify the mechanism of the reactivity and regioselectivity.

Density functional theory (DFT) was employed with the B3LYP functional for the exchange correlation term[17,18] to calculate the equilibrium structures and the energetics of all the intermediates and transition states that appear along the reaction path. The basis sets were [3s3p2d] and [3s2p] sets with the effective core potential[19] for the Pd, Si, and P atoms, [3s2p] of Dunning[20] for the C, O, and B atoms, and [2s] for the H atom. Geometry optimizations were performed without restricting the point group; all calculations were done under C_1 symmetry. The DFT calculations were performed with the Gaussian98 suite of programs.[21] It was confirmed that all the intermediates are true local minima and vibrational analysis showed that all the transition states have only one imaginary frequency. The solvent effect was not included in the present calculations; however, the present reaction is not substantially affected by the solvent effect as can be deduced from the experimental facts.

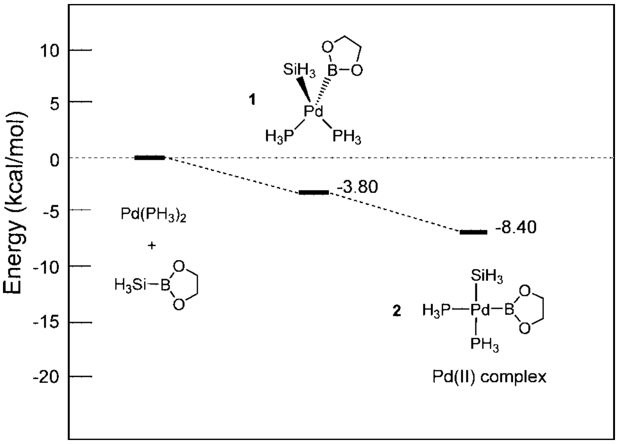


Figure 2. Energy diagram for the oxidative addition. Values are the energies relative to the reactant in kcal/mol.

Results and Discussion

We investigated the reaction mechanism according to the reaction scheme proposed previously[12] by examining possible regioisomers of the intermediates and the transition states. The reaction scheme is conventionally grouped into five steps as shown in Figure 1: (I) oxidative addition of the Si−B bond of silylborane into $Pd(PH_3)_2$, (II) coordination of allene to the Pd(II) complex, (III) insertion of allene to form a σ-allylic complex, (IV) conversion from the σ-allylic complex to a π-allylic complex, and (V) reductive elimination of silane and allene to form borylallylsilane. We discuss the mechanism of these reactions in the following sections.

A. Oxidative Addition. The energy diagram for the oxidative addition of the Si−B bond into the Pd(0) complex is shown in Figure 2. The (boryl)(silyl)Pd(II) complex **2** exothermically forms from the reactants, $SiH_3-B(OCH_2)_2$ and $Pd(PH_3)_2$. This Pd(II) complex **2** is stable by 8.4 kcal/mol relative to the reactants and the equilibrium structure is nearly square planar. This energy stabilization is caused by the strong Pd−B bond,

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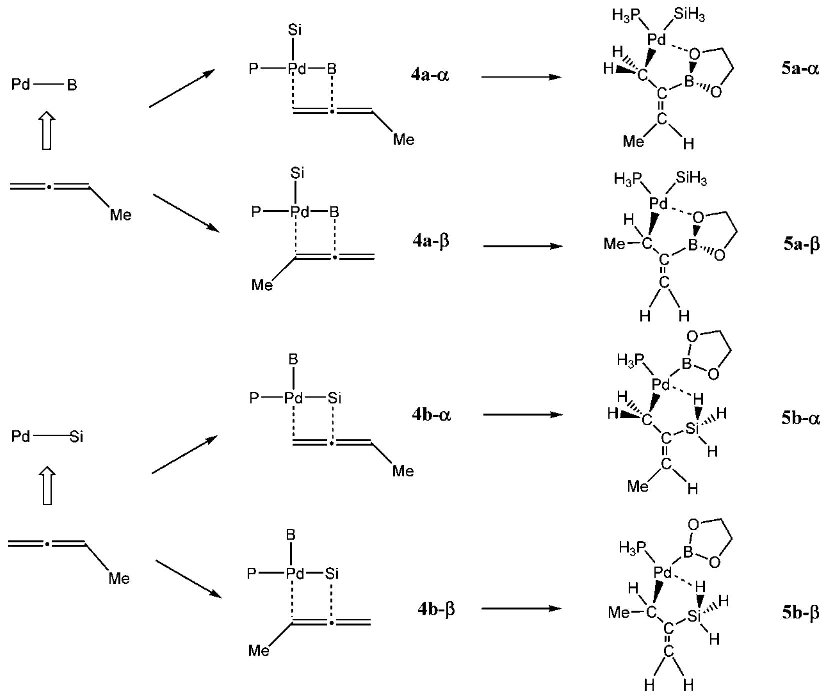

Figure 3. Four possible reaction paths for the insertion of allene; the coordinated complexes **4a**-**x**, **4b**-**y** (**x**, **y** = **α**, ***β***) and *σ*-allylic complexes **5a**-**x**, **5b**-**y** (**x**, **y** = **α**, ***β***).

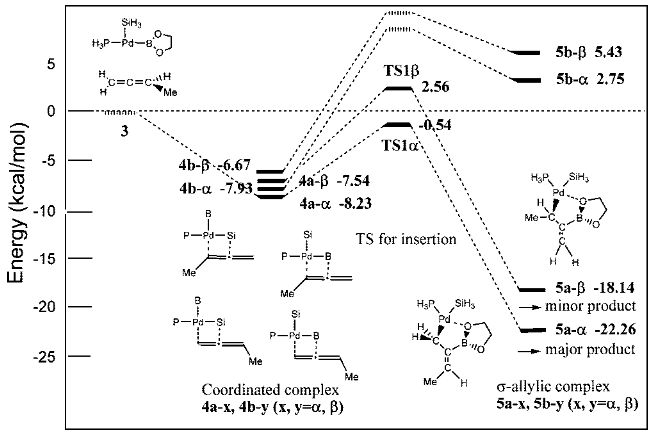

Figure 4. Energy diagram for the coordination and insertion of allene into the Pd complex. Values are the energies relative to the tricoordinated Pd complex **3** in kcal/mol.

which is ascribed to the orbital interaction of the back-donation from the d orbital of Pd to an unoccupied p orbital of B.[22] This reaction proceeds with no activation barrier via the nonplanar tetrahedral precursor complex **1** with a broken Si–B bond as an intermediate. For the $B(OH)_2SiH_3 + Pd(PH_3)_2$ system, a very low activation barrier was obtained from the MP2-MP4(SDQ) and CCSD(T) calculations, where the transition state was predicted to be nonplanar.[22] In the present calculations, we failed to obtain the transition state around the precursor complex **1**, whose total energy is 3.8 kcal/mol below that of the reactants. We also examined the possibility of a square-planar coordination of this intermediate **1**; however, a large activation barrier was calculated. This reaction path via a nonplanar structure is caused by the steric effect between $SiH_3{-}B(OCH_2)_2$ and the phosphine ligands. The structure of the precursor complex is determined by the electronic and steric factors, which favor planar and nonplanar structures, respectively. The B–X *σ*-bond activation (X = C, Si, Ge, Sn) of $(HO)_2B{-}XH_3$ by $M(PH_3)_2$ (M = Pd, Pt) was systematically investigated by Sakaki et al.[22] For the structure of complex **2**, we also observed that the $B(OCH_2)_2$ ligand shows as strong a *trans* influence for the Pd–P bond length as the $B(OH)_2$ ligand;[22] Pd–P at a *trans* position to B is longer by 0.05 Å than the Pd–P distance at a *trans* position to Si.

B. Coordination and Insertion of Allene. Next, we discuss the coordination and insertion of allene to the (boryl)(silyl)Pd(II) complex producing a *σ*-allylic complex. In the coordination step, the reaction proceeds so that phosphine of tetracoordinated complex **2** is substituted with allene. Although the primary substitution in these types of reactions is associative (S_N2), there are cases where dissociative substitution takes place with Pd complex.[23] In the present case, the determination of the transition state of the associative reaction was difficult and we adopted the dissociative mechanism with tricoordinated Pd complex, $Pd(PH_3)(SiH_3)B(OCH_2)_2$ (**3**). We examined two types of tricoordinated complex with the phosphine trans to Si or B, although the boron has a larger trans influence. The tricoordinated complex **3** with a loss of phosphine trans to Si is located at ~13 kcal/mol above the tetracoordinated complex **2**: this gives the *upper bond energy* of this coordination step. This energy difference of 13 kcal/mol is attributed to the $Pd{-}PH_3$ coordination energy, structure relaxation, and the gas phase nature of the calculation. For this step, we also examined the reaction scheme via pentacoordinated intermediates, $Pd(PH_3)_2(SiH_3)B(OCH_2)_2(C_4H_6)$; however, neither stable intermediates nor a plausible reaction path were obtained. Possible reaction schemes for the coordination and insertion are shown in Figure 3. We have considered those reaction schemes in which either Si or B attacks the central carbon of allene, otherwise the reaction does not produce the product. Four intermediates **4a-x** and **4b-y** (**x**, **y** = **α**, ***β***) that lead to *σ*-allylic complexes **5a-x** and **5b-y** (**x**, **y** = **α**, ***β***), respectively, were examined: either the Pd–B or

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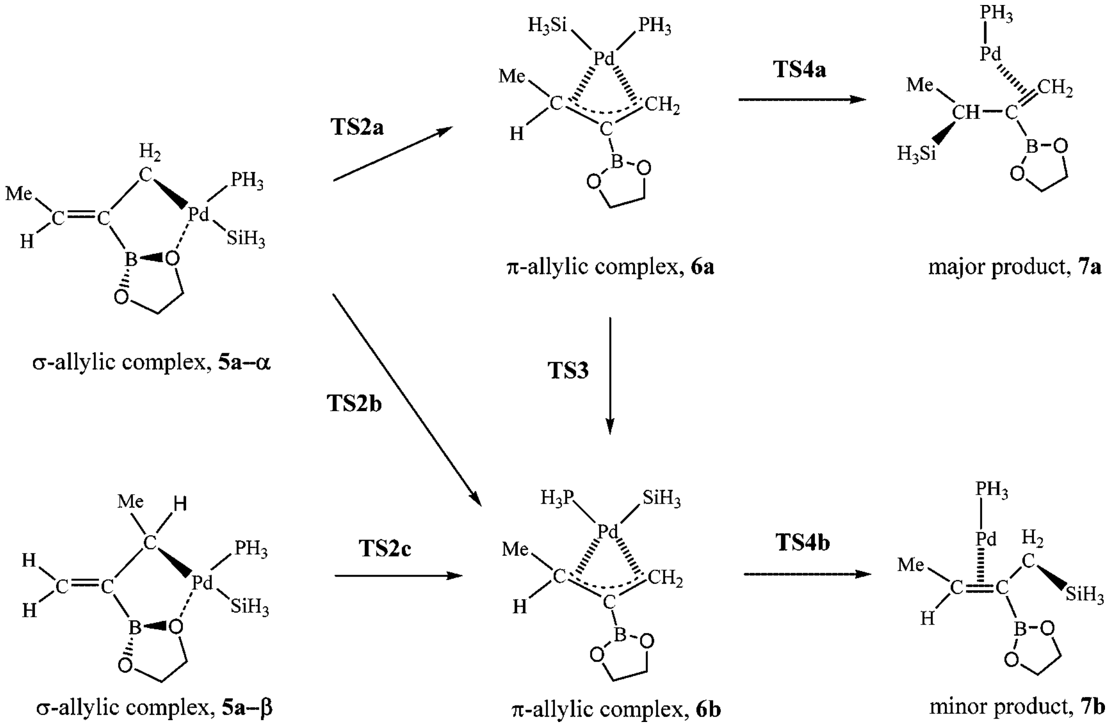

Figure 5. Reaction path for the σ-allyl$-\pi$-allyl conversion and reductive elimination from σ-allylic complexes **5a-α/5a-*β*** to the products **7a/7b** via π-allylic complexes **6a/6b**.

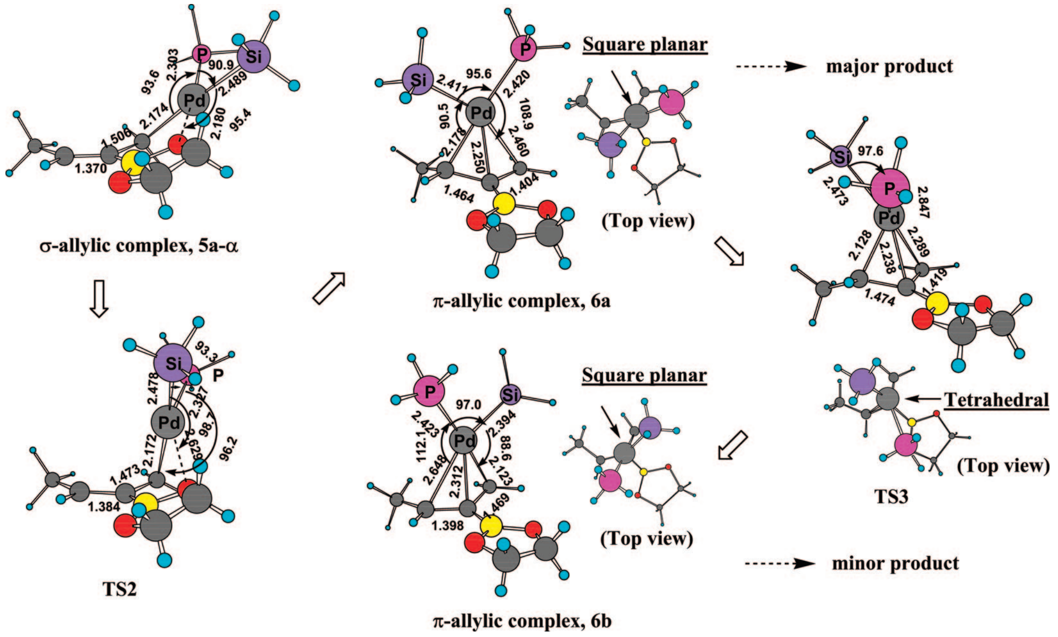

Figure 6. Geometrical change from σ-allylic complex to π-allylic complex. Bond lengths are in Å and bond angles are in degrees.

the Pd−Si bond coordinates to allene in **4a** and **4b**, respectively, and either the electron-deficient C=C bond or the electron-rich C=C bond of allene coordinates to the Pd complex for **α** and ***β***, respectively. We examined the energetics for all of these reaction paths that lead to four regioisomeric σ-allylic complexes.

The energy diagram of these four reactions is shown in Figure 4. Energies are relative to the tricoordinated complex **3**. Four intermediates **4a-x** and **4b-y** (**x**, **y** = α, ***β***) in which the (silyl)(boryl)Pd(II) complex coordinates to allene are true local minima, with nearly the same thermodynamic stability; the calculated stabilization energies are 6.7–8.2 kcal/mol relative to the tricoordinated complex **3**. The σ-allylic complexes **5a-x** and **5b-y** (**x**, **y** = α, ***β***) energetically split into two groups. Two complexes **5a-x** (**x** = α, ***β***), which form via insertion of allene into the Pd−B bond, are stable by 18.1 and 22.3 kcal/mol relative to the initial complex **3** of the present step, while the other two complexes **5b-y** (**y** = α, ***β***) are unstable by 2.8 and 5.4 kcal/mol, respectively. From these relative energies, the reaction pathways via **5b-y** (**y** = α, ***β***) are ruled out. The stable nature of complex **5a** compared with **5b** is partly attributed to the B−C and Si−C bond energies, while Pd−B and Pd−Si bond breaking has the opposite effect.[24] The Pd−O coordination and conjugation over the allyl and B(OCH_2)$_2$ units stabilize the intermediates **5a-x** (**x** = α, ***β***): this stabilization energy for **5a-α**

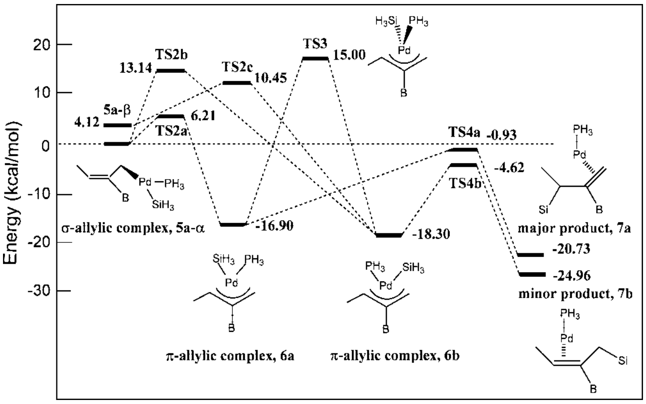

Figure 7. Energy diagram for the σ-allyl−π-allyl conversion and reductive elimination. Values are the energies relative to σ-allylic complex **5a-α** in kcal/mol.

is estimated as ∼24 kcal/mol by rotating the $B(OCH_2)_2$ unit at the optimized structure, while the Pd−H coordination energy for **5a-*β*** is ∼15 kcal/mol. In the real system, no Pd−H coordination exists because of the $-SiMe_3$ unit and the energy difference between **5a** and **5b** should be much larger than in the present model system.

Next, we discuss the stable σ-allylic complexes **5a-x** (**x** = **α**, ***β***). These two complexes differ in the position of the methyl group. Energetically, σ-allylic complex **5a-α**, in which Pd bonds to an unsubstituted carbon atom, is more stable by 4.1 kcal/mol than the complex **5a-*β***. For the reactions from **4a-x** to **5a-x** (**x** = **α**, ***β***), the transition states **TS1α** and **TS1*β*** were located, the calculated activation energies being 7.7 and 10.1 kcal/mol for **5a-α** and **5a-*β***, respectively. The intermediate **5a-α** is favorable considering both the thermodynamic stability and activation barrier, and therefore the reaction should proceed via this intermediate. The transition state **TS1α** of this step is located highest in energy as well as the intermediates **3** in the entire energy diagram, therefore this step would be the rate-determining step in the present reaction. Note that when intermediate **5a-*β*** is produced in this step, the reaction leads to the minor product. Therefore, this step is one of the key steps controlling the regioselectivity of the reaction. If we use PPh_3 instead of PH_3, the energy difference between **5a-α** and **5a-*β*** would become larger because of the steric hindrance effect, which is in good agreement with the regioselectivity of the experiment. The *terminal* addition produces the most stable intermediate in this step, although the present catalytic reaction results in the *internal* addition. We will discuss this issue in Section E.

C. *σ*-Allyl−*π*-Allyl Conversion. The most stable σ-allylic complex **5a-α** formed by the insertion of allene into the Pd complex has an approximately planar structure, where the silyl group and the terminal allylic carbon are located in a *trans* orientation. A rapid conversion from this σ-allylic complex to the π-allylic complex, which then undergoes facile reductive elimination, was proposed.[12] Figure 5 shows the reaction scheme from the σ-allylic complexes to the final products. The major product is generated via π-allylic complex **6a** in which Si and α-C are located in the *trans* orientation, while the minor product is produced via π-allylic complex **6b** in which Si and α-C are located in the *cis* orientation. It was found that during the conversion, a lone pair on oxygen maintains the tetrahedral coordination to Pd, namely, Si and α-C are located *trans*, otherwise a large activation barrier exists. Thus, π-allylic complex **6a** is produced from the most stable σ-allylic complex **5a-α** and this reaction path is most favorable, as shown below. Another possible structure of **5a-α**, where PH_3 is in a *cis* orientation relative to O, could lead to π-allylic complex **6b**. However, the conversion to such a structure requires the breaking of the planar coordination of the Pd complex, and therefore such a process has a large activation barrier; this is similar to the high rotation barrier between π-allylic complexes (**TS3**), as seen later. This rotation barrier for the real system with a PPh_3 ligand is much larger than that for the model system with PH_3. In the real system, the reaction from the σ-allylic complex to the π-allylic complex proceeds very rapidly because of the smooth energy path, and thus the formation of another structure with PH_3 being *cis* to O would be very minor.

The intermediates and transition states involved in this σ-allyl−π-allyl conversion have been examined. The optimized structures and the energy diagram are shown in Figures 6 and 7, respectively. From the σ-allylic complex **5a-α**, the $Pd(PH_3)(SiH_3)$ group rises from the plane of the allylic group maintaining a square-planar coordination around Pd (**TS2a**). $Pd(PH_3)(SiH_3)$ then rotates on the plane of the allylic group and **TS2a** converts to π-allylic complex **6a**. The calculated energy barrier for this step was only 6.2 kcal/mol. Conversion from π-allylic complex **6a** to π-allylic complex **6b**, on the other hand, involves a very large activation barrier, such as $E_a = 32$ kcal/mol. This conversion occurs via the unstable structure **TS3**, in which the complex has tetrahedral coordination around Pd. This large activation barrier prevents the reaction to π-allylic complex **6b**, hence, the regioselectivity of the reaction is retained.

Other reaction paths to π-allylic complex **6b** that lead to minor product have also been examined. The reaction path from σ-allylic complex **5a-α** to π-allylic complex **6b** requires the breaking of the planar coordination of Pd. Therefore, a high activation barrier (**TS2b**) exists and the calculated energy barrier is 13.1 kcal/mol. The reaction path from σ-allylic complex **5a-*β*** to π-allylic complex **6b** may also be possible. This **5a-*β*** is located above **5a-α** by 4.1 kcal/mol. The reaction path to **5a-*β*** is also unfavorable compared with the path to **5a-α**; the activation barrier from **4a-*β*** to **5a-*β*** is larger by 2.4 kcal/mol than the barrier from **4a-α** to **5a-α**. The transition state of this path (**TS2c**) from **5a-*β*** to **6b** is located 10.5 kcal/mol above the most stable σ-allylic complex **5a-α**, and the activation barrier is 6.3 kcal/mol from **5a-*β***. In the real system, this unfavorable nature of the path via **5a-*β*** would be enhanced because of the steric hindrance effect. On the basis of all these calculations, we conclude that the reaction path from σ-allylic complex **5a-α** to π-allylic complex **6a** is the most favorable.

D. Reductive Elimination. It is generally accepted that π-allylic complexes are key intermediates[25,26] in transition-metal-catalyzed reactions and react via facile reductive elimination. As we showed in Section C, we also obtained the π-allylic complex as an intermediate in the present reaction. However, the two π-allylic complexes **6a** and **6b** produce major and minor

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(24) Typical B−C and Si−C bond energies are known to be 90 and 76 kcal/mol, respectively (Sanderson, R. T. *Chemical bonds and bond energy*; Academic Press: New York, 1971). The Pd−B and Pd−Si bonds have opposite effects; their bond energies were estimated as 52.8 and 44.1 kcal/mol, respectively, by the MP4(SDQ) calculation.[22] This trend has also been confirmed in the present intermediates by the natural bond orbital analysis.

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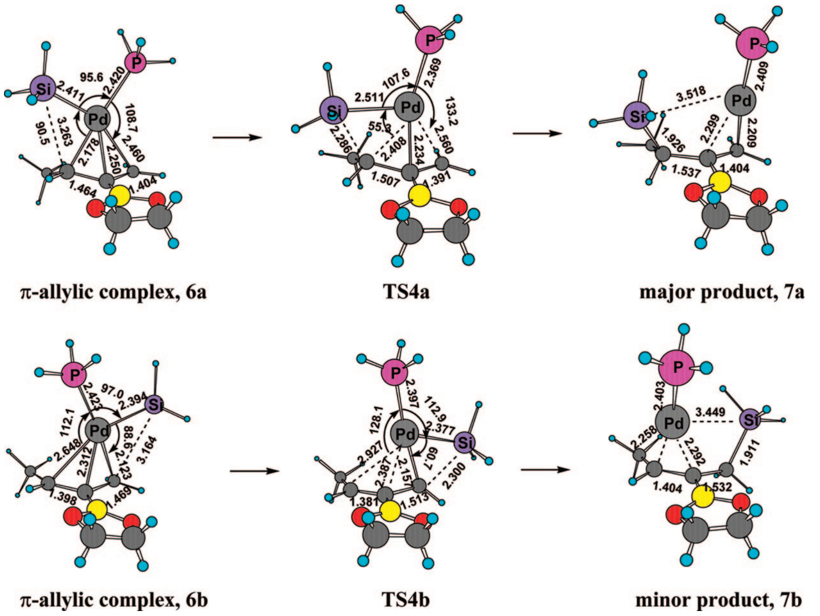

Figure 8. Geometrical change in the reductive elimination. Bond lengths are in Å and bond angles are in degrees.

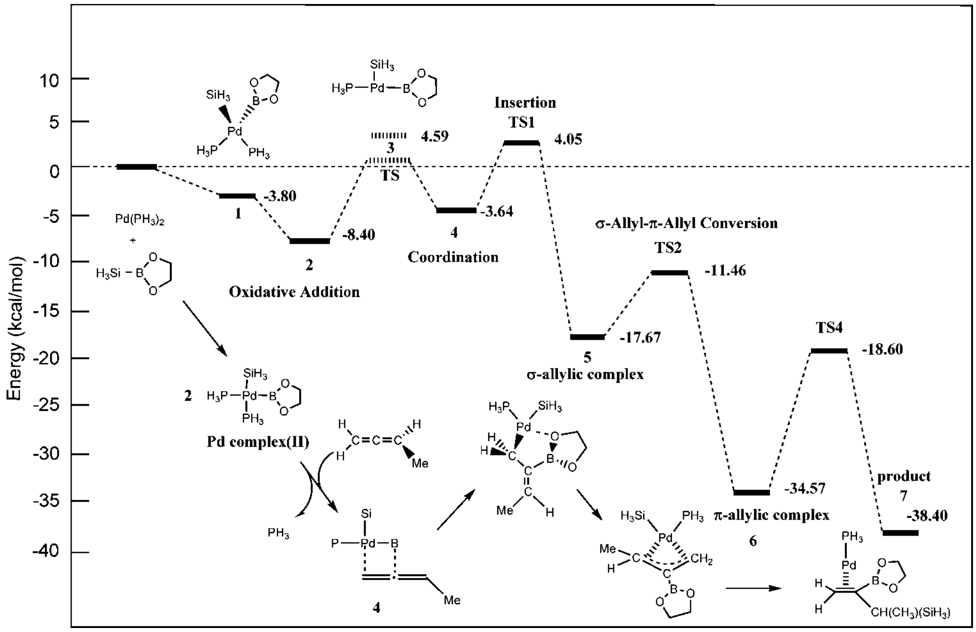

Figure 9. Energy diagram for the overall reaction. Values are the energies relative to the reactant in kcal/mol.

products, respectively. We therefore examined the reductive eliminations from these two π-allylic complexes. Figure 7 shows the energy diagram from these two π-allylic complexes to the products. Products **7a** and **7b** are calculated as the Pd complexes that directly lead to the products by Pd(PH_3) decoordination. As shown in Figure 7, the major product **7a** is calculated to be energetically less stable by 4.2 kcal/mol compared with the minor product **7b**. The stabilities of the transition states **TS4a/TS4b** relative to the products also show the same trend: **TS4a** is less stable by 3.7 kcal/mol than **TS4b**. Therefore, the stable nature of the specific σ-allylic complex **5a-α** and the large activation barrier (**TS3**) between **6a** and **6b** dominantly determine the selectivity of this reaction. Thus, the reaction leads to the major product, although internal addition complex **7a** is less stable than the terminal addition complex **7b**. The π-allylic complex was not observed experimentally, although the complex was calculated to be in a deep well.

Figure 8 shows the detailed structure of the intermediates, transition states, and products of this reductive elimination step. In this step, formation of the C−Si bond precedes the Si−Pd bond cleavage. The C−Si distances drastically change from **6a/6b** to **TS4a/TS4b**: the C−Si distances of **6a/6b** are 3.26/3.16 Å, while those of **TS4a/TS4b** are 2.29/2.30 Å. On the other hand, the Si−Pd bond lengths of **6a/6b** (2.41/2.39 Å) do not change so much from those of **TS4a/TS4b** (2.51/2.38 Å). This is because Si constructs a hypervalent bond, as discussed in other studies.[25,26]

E. Reaction Mechanism. Figure 9 presents the energy diagram and the reaction scheme for the overall reaction; only the main reaction path that leads to the major product is depicted. The present catalytic reaction proceeds exothermically to the product and the rate-determining step is the coordination and insertion step of allene into the Pd−B bond, generating the σ-allylic complex. **TS1** is located highest in energy as well as the intermediate **3** in the entire reaction. The intermediate **3** gives the *upper-bound energy* in the coordination of allene. As described in Section B, four regioisomeric intermediates are possible for the σ-allylic complex. The most stable σ-allylic complex is the terminal addition complex **5a-α** and the activation barrier for this complex is also lowest. Therefore, the reaction dominantly proceeds via this complex. Another important key for the regioselectivity is the large rotational barrier of the Pd(PH_3)(SiH_3) group that converts the two π-allylic complexes **6a/6b**. The major product **7a** is less stable than the minor product **7b**. Therefore, the reductive elimination step is kinetically controlled and the internal addition compound is the major product, although it is less stable than the terminal addition compound.

It is of interest to control the energetics and selectivity of this reaction based on the mechanism predicted in the present calculations. For example, in the reductive elimination step, when we make the metal−Si bond stronger, the regioselectivity is expected to be reversed. The activation barrier for the reductive elimination at **TS4a/TS4b** becomes larger than the other barriers. In such a case, thermodynamic control becomes dominant and the reaction would produce the terminal addition complex as the major product because that is energetically more stable than the internal addition complex.

Summary and Conclusions

We have investigated the reaction mechanism for the regioselective silaboration of allene with a palladium catalyst using theoretical calculations. We have examined the energetics of the overall reaction and located the intermediates and transition states. In particular, we confirmed the existence of σ-allylic and π-allylic complexes as the intermediates that were suggested experimentally in our previous work.[12] The energy diagram of the overall reaction has been presented and the results are summarized as follows.

(1) The present reaction proceeds exothermically and the rate-determining step is the coordination and insertion of allene into the Pd−B bond of the Pd complex that generates the σ-allylic complex. In this step, the selective insertion of the electron-deficient C═C bond into the Pd−B bond provides the most stable σ-allylic complex.

(2) The σ-allylic complex converts into the π-allylic complex while maintaining the coordination of O to Pd so that the *trans* orientation of Si and the terminal C of allene is retained. This π-allylic complex facilitates the reductive elimination, which leads to the regioselective product.

(3) A large activation barrier has been predicted for isomerization between the two π-allylic isomeric complexes, which prevents the reaction to the minor product.

(4) Energetically, the major-product complex is less stable than the minor-product complex; this indicates that kinetic control is dominant in the present reaction.

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