

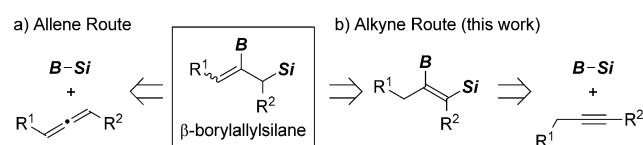
(E)- and (Z)-β-Borylallylsilanes by Alkyne Silaboration Followed by Regio- and Stereoselective Double-Bond Migration**

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Allylic boranes and silanes bearing additional boryl or silyl groups on their double bonds serve as useful building blocks in organic synthesis.^[1–3] These reagents allow the nucleophilic introduction of modifiable allylic groups possessing boryl or silyl groups, which can be converted into a variety of functional groups through oxidation, cross-coupling, halogenation, etc. It is hence highly desirable to develop efficient methods for their synthesis. β-Borylallylsilanes are one such class of useful allylation reagents in organic synthesis.^[4,5] These compounds are utilized not only in simple Lewis acid promoted allylation,^[4] but also in cyclizative allylations^[4] and three-component reactions to form a decalin-type skeleton by a Prins-type cyclization.^[5] These particular β-borylallylsilanes are best synthesized by the catalytic silaboration of terminal allenes, in which the internal C=C bond undergoes an addition reaction in a highly regioselective manner (Scheme 1, left).^[6–8] This system was extended to asymmetric

bismetallation is synthetically much more accessible than allene bismetallation,^[1] therefore a synthetic pathway involving alkyne bismetallation followed by controlled C=C bond migration would be attractive (Scheme 1, right). We have recently found that (Z)-1-boryl-2-silyl-1-alkenes, which were prepared by palladium-catalyzed silaboration of terminal alkynes, underwent selective Z-to-E isomerization rather than C=C bond migration.^[12] However, our recent study on catalysts for the regiocomplementary silaboration of terminal alkynes^[13] prompted us to examine the possibility of the conversion of the 2-boryl-1-silyl-1-alkenes into β-borylallylsilanes by catalytic C=C bond migration. Herein, we report on the successful synthesis of β-borylallylsilanes by controlled C=C bond migration. It should be noted that the isomerization led ultimately to the thermodynamically favored stereoisomers through selective formation of the kinetically favored isomerization products, which were also isolable when a modified catalyst system was used.

The double-bond migration of β-borylallylsilane (E)-**1a** was examined in toluene at 50 °C in the presence of a palladium catalyst (1.0 mol %; Table 1).^[14] No reaction took place in the presence of [Pd(dba)₂] with or without PPh₃



Scheme 1. Synthetic strategies for β-Borylallylsilane.

silaboration giving β-borylallylsilanes with high diastereo- and enantioselectivities and these compounds were successfully utilized for asymmetric cyclization reactions.^[9] Terminal-selective silaboration of terminal allenes using a platinum catalyst has also been developed.^[7b,8] However, in these syntheses, the use of allenes as the starting material is not ideal because of their low availability and high cost. It would be preferable to synthesize them using more readily available starting materials.

We were interested in utilizing the transition-metal-catalyzed C=C bond migration in the synthesis of boryl- and the silyl-substituted allylic boranes and silanes.^[10,11] Alkyne

Table 1: Palladium-catalyzed double-bond migration of (E)-**1a**.^[a]

$ \begin{array}{c} \text{B(pin)} \\ \\ n\text{C}_5\text{H}_{11}\text{CH}_2\text{CH}=\text{CHSiMe}_2(\text{O}i\text{Pr}) \\ \text{(E)-1a} \end{array} \xrightarrow[\text{toluene, 50 }^\circ\text{C, 24 h}]{\text{Pd cat. (1 mol \%), additive (0–2 mol \%)}} \begin{array}{c} \text{B(pin)} \\ \\ n\text{C}_5\text{H}_{11}\text{CH}_2\text{CH}=\text{CHSiMe}_2(\text{O}i\text{Pr}) \\ \text{(E)-2a} \end{array} + \begin{array}{c} \text{B(pin)} \\ \\ n\text{C}_5\text{H}_{11}\text{CH}=\text{CHSiMe}_2(\text{O}i\text{Pr}) \\ \text{(Z)-2a} \end{array} $				
Entry	Pd cat	Additive	Yield [%] ^[b]	E/Z ^[c]
1	[Pd(dba) ₂]	–	no reaction	–
2	[Pd(dba) ₂]	PPh ₃ ^[d]	no reaction	–
3	[Pd{P(<i>t</i> Bu) ₃ }] ₂	–	95	83:17
4	[Pd{P(<i>t</i> Bu) ₃ }] ₂	P(<i>t</i> Bu) ₃ ^[e]	94	95:5
5	[Pd{P(<i>t</i> Bu) ₃ }] ₂	<i>o</i> -bromotoluene ^[d]	94	9:91

[a] A palladium complex (1.0 mol %), additive (0–2.0 mol %), and **1a** (0.20 mmol) in toluene (0.2 mL) was stirred at 50 °C for 24 h. [b] Yield of the isolated product. [c] Determined by GC analysis of the crude mixture. [d] 2.0 mol %. [e] 1.0 mol %. dba = dibenzylideneacetone, pin = pinacolato.

(Table 1, entries 1 and 2), whereas [Pd{P(*t*Bu)₃}]₂^[15] catalyzed the double-bond migration efficiently to give β-borylallylsilane **2a** in quantitative yield as a mixture of stereoisomers (E/Z=83:17; Table 1, entry 3). To improve the stereoselectivity, we tested several additives with [Pd{P(*t*Bu)₃}]₂. We found that the stereoselective formation of the E isomer was

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[**] This work was supported by Grant-in-Aid for Scientific Research on Priority Areas (No. 20037031, “Chemistry of Concerto Catalysis”) from the Ministry of Education, Culture, Sports, Science and Technology (Japan). K.O. acknowledges JSPS for fellowship support.

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.201106077>.

achieved when the reaction was carried out with additional $\text{P}(\text{tBu})_3$ (1.0 mol %; $E/Z = 95:5$; Table 1, entry 4). It is interesting to note that the stereoselectivity of the reaction was switched in the presence of catalytic amounts of aryl bromides, such as *o*-bromotoluene (2.0 mol %; Table 1, entry 5).^[16] In this case, the reaction proceeded with high *Z* selectivity to give **2a** in high yield with an E/Z ratio of 9:91.

Various β -borylalkenylsilanes (**E**)-**1** were subjected to the *E*- and *Z*-selective double-bond migrations (Table 2). To obtain (*E*)- β -borylallylsilanes, the double-bond migration was

high isomeric purity by the isomer-selective Suzuki–Miyaura coupling (see Scheme 2).

The nature of the substituents on the silicon atom of the starting alkenylsilane is not critical in the double-bond migration. Dimethylphenylsilyl-substituted (*E*)-**3** underwent isomerization under both conditions A and B to lead to the selective formation of (*E*)- and (*Z*)-**4**, respectively (Table 2, entry 7).

The double-bond migration under conditions B was also effective for the isomerization of cyclohexyl-substituted (*E*)-**1h** [Eq. (1)]. The reaction gave β -borylallylsilane **2h**, which has a tetrasubstituted $\text{C}=\text{C}$ bond, in 91 % yield.

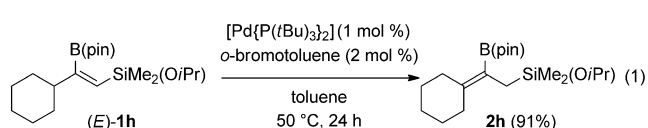
Table 2: Stereoselective synthesis of (*E*)- and (*Z*)- β -borylallylsilanes **2** and **4** by palladium-catalyzed double-bond migration.

B(pin)	
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[a] Conditions A: $[\text{Pd}\{\text{P}(\text{tBu})_3\}_2]$ (1.0 mol %), $\text{P}(\text{tBu})_3$ (1.0 mol %), and **1** (0.20 mmol) in toluene (0.2 mL) was stirred at 50 °C for 24 h. [b] Conditions B: $[\text{Pd}\{\text{P}(\text{tBu})_3\}_2]$ (1.0 mol %), *o*-bromotoluene (2.0 mol %), and **1** (0.20 mmol) in toluene (0.2 mL) was stirred at 50 °C for 24 h. [c] Yield of the isolated product. [d] Determined by GC.

carried out in the presence of $[\text{Pd}\{\text{P}(\text{tBu})_3\}_2]$ (1.0 mol %) and $\text{P}(\text{tBu})_3$ (1.0 mol %; conditions A). The reactions of **1b–1g** took place smoothly at 50 °C to give (*E*)-**2b–2g** in 88–94 % yields with high *E* selectivities ($E/Z = 95:5$ – $91:9$; Table 2, entries 1–6). The reactions of substrates **1f** and **1g**, which bear chlorine and cyano groups, respectively, were not affected by those functional groups (Table 2, entries 5 and 6), whereas the *E* selectivities dropped slightly in the reactions of ester **1d** and silyl ether **1e** (Table 2, entries 3 and 4).

To synthesize (*Z*)- β -borylallylsilanes, the double-bond migration of **1b–1g** was carried out in the presence of $[\text{Pd}\{\text{P}(\text{tBu})_3\}_2]$ (1.0 mol %) and *o*-bromotoluene (2.0 mol %; conditions B). The reaction proceeded smoothly at 50 °C under these reaction conditions. The reactions of **1b–1f** gave (*Z*)-**2b–2f** in 84–95 % yields with E/Z ratios of 10:90–14:86 (Table 2, entries 1–5). Slightly lower stereoselectivity was observed in the reaction of nitrile **1g** ($E/Z = 18:82$; Table 2, entry 6). Further enrichment of the isomeric purity of the allylic silanes could be achieved either by chromatographic separation or by kinetic separation. The pure *E* and *Z* isomers of **2d** and **2g**, which bear relatively polar acetyl and cyano groups, respectively, were easily obtained by column chromatography on silica gel. It was even possible to convert β -borylallylsilanes that do not have polar functional groups, such as **2a**, into the corresponding β -arylallylsilanes with a



To get an insight into the catalyst-controlled stereoselectivity, the course of the reaction over time was monitored (Figure 1). In the double-bond migration of (*E*)-**1a** in the absence of any additives, it took 4 h for 100 % conversion

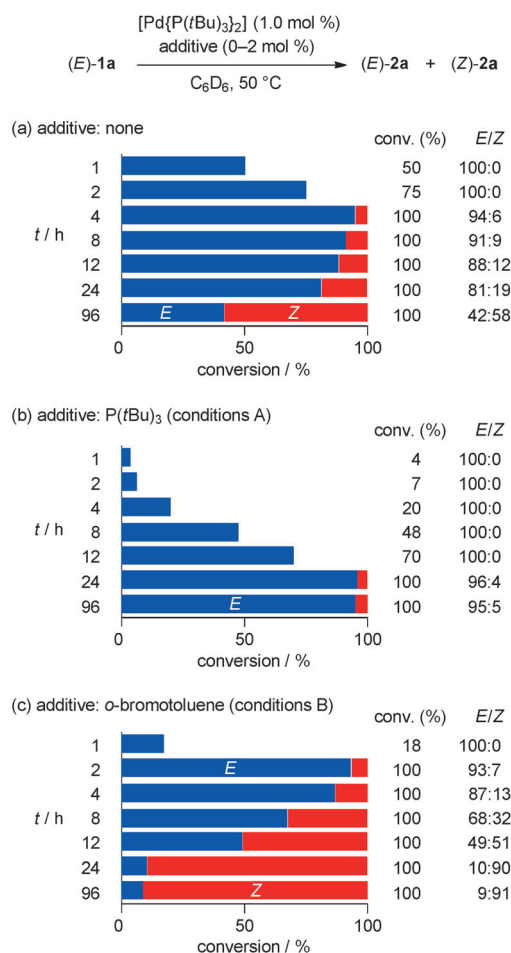
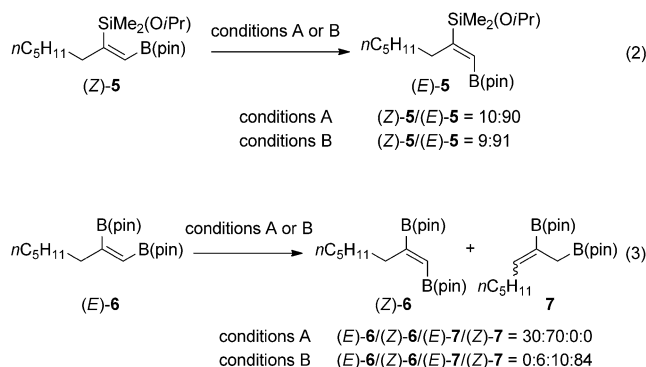


Figure 1. The course of the isomerization of (*E*)-**1a** over time. The total bar size (blue + red) corresponds to the conversion of (*E*)-**1a** and the bar color indicates the E/Z (blue/red) ratio of **2a** formed.

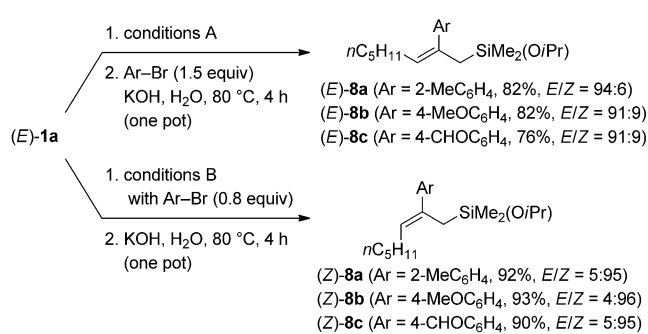
of **1a** (Figure 1 a). Selective formation of (*E*)-**2a** was observed during the reaction. A prolonged reaction time led to slow isomerization of the initially formed *E* isomer into the *Z* isomer, and the *E/Z* ratio reached 42:58 after 96 h. These results indicate that the reaction gave the *E* isomer as the kinetic product and the *Z* isomer as the thermodynamically favored product.^[17] The double-bond migration under conditions A (additive: P(*t*Bu)₃) was slower than for the reaction without additives; it required 24 h for full conversion (Figure 1 b). Selective formation of the *E* isomer was again observed, and only a little *E/Z* isomerization occurred over a period of 96 hours. In sharp contrast, the double-bond migration proceeded rather quickly under conditions B (additive: *o*-bromotoluene; Figure 1 c). It took only 2 hours for complete conversion of **1a** into **2a**, thus resulting in selective formation of the *E* isomer. Note that the *E/Z* isomerization proceeded faster than for the reaction without the additive, thus leading to selective formation of the *Z* isomer after 24 hours (*E/Z* = 10:90). These results indicate that the addition of P(*t*Bu)₃ slows the rate of both the double-bond migration and the *E/Z* isomerization, whereas the catalyst species formed in the presence of *o*-bromotoluene efficiently promotes both steps.^[18]

The palladium-catalyzed isomerization could be applied to the stereoselective conversion of other metallo-substituted alkenes. Thus, reactions of the alkyne silaboration product (*Z*)-**5**^[12] and the alkyne diboration product (*E*)-1,2-diboryl-1-octene (*E*)-**6**^[19] were examined under conditions A and B [Eqs. (2) and (3)]. Interestingly, the reaction courses of the isomerization of these compounds were totally different



from that of (*E*)-**1** shown above. The reaction of (*Z*)-**5** under conditions A gave (*E*)-**5** without positional isomerization of the double bond [Eq. (2)]. Almost identical results were obtained in the reaction of (*Z*)-**5** under conditions B. In contrast, the reaction of (*E*)-**6** gave (*Z*)-**6** under conditions A and the positional isomerization product (*Z*)-**7** under conditions B [Eq. (3)].^[20]

The synthetic application of the stereodefined β -borylallylsilanes is demonstrated by the stereoselective one-pot synthesis of allylic silanes **8** (Scheme 2). The *E*-selective double-bond migration of (*E*)-**1a** was carried out under conditions A (upper equation). The resulting solution containing *E*-enriched **2a** was then mixed with aryl bromide,



Scheme 2. One-pot synthesis of allylsilanes **8** by stereoselective double-bond migration of (*E*)-**1a** and a subsequent Suzuki–Miyaura coupling with aryl bromides.

KOH, and H₂O, and the mixture was reacted at 80 °C for 4 hours. The Suzuki–Miyaura coupling reaction took place efficiently to give aryl-substituted allylic silanes (*E*)-**8a–8c** in yields of 76–82 % with *E/Z* ratios of 91:9–94:6. The stereoselective synthesis of (*Z*)-**8** was also achieved in a one-pot manner under conditions B, in which the aryl bromides (80 mol %) used for the Suzuki–Miyaura coupling reaction were added in the isomerization step (lower equation). (*Z*)-**2a** reacted faster than the sterically demanding (*E*)-**2a** in the second step (Suzuki–Miyaura coupling), therefore the allylic silanes (*Z*)-**8a–8c** could be obtained in 90–93 % yields (based on the aryl bromides) with high *E/Z* ratios (4:96–5:95).

In conclusion, we have established efficient palladium catalyst systems for the double-bond migration of 2-boryl-1-silyl-1-alkenes. The reaction using [Pd{P(*t*Bu)₃}₂]/P(*t*Bu)₃ as the catalyst gave (*E*)-2-boryl-1-silyl-2-alkenes, whereas the corresponding *Z* isomer was formed selectively by the palladium catalyst generated from [Pd{P(*t*Bu)₃}₂] with *o*-bromotoluene. The stereoselectivity originates from a two-step reaction mechanism involving positional isomerization of the double bond and a subsequent *E/Z* isomerization. Further application of the palladium-catalyzed double-bond migration is underway in this laboratory.

Experimental Section

General procedure for the stereoselective synthesis of (*E*)- and (*Z*)-**2** by double-bond migration of (*E*)-**1**: [Pd{P(*t*Bu)₃}₂] (1.0 mg, 2.0 μ mol) and an additive [P(*t*Bu)₃] (0.40 mg, 2.0 μ mol) for conditions A and *o*-bromotoluene (0.70 mg, 4.0 μ mol) for conditions B] were placed in a screw-capped vial. Toluene (0.2 mL) and (*E*)-**1** (0.20 mmol) were added to the vial, and the mixture was stirred at 50 °C for 24 h. After cooling the solution, the volatiles were evaporated and the residue was purified by bulb-to-bulb distillation to afford *E*- or *Z*-enriched pure **2**.

Received: August 27, 2011

Published online: November 9, 2011

Keywords: boron · homogeneous catalysis · isomerization · palladium · silicon

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- [16] A similar effect was observed in the reaction with other aryl bromides such as bromobenzene, *m*- and *p*-bromotoluene, *p*-bromoanisole, and *p*-bromobenzotrifluoride.
- [17] DFT calculations [RB3LYP/6-311G(dp)] of a model product MeCH=C[B(pin)]CH₂SiMe₃ indicated that the *Z* isomer is 5.3 kJ mol⁻¹ more stable than the *E* isomer.
- [18] The reaction mechanisms for the double-bond migration and *E/Z* isomerization are not clear at this moment. A mechanism involving formation of a π -allyl palladium intermediate through oxidative addition of the allylic C–H bond to coordinatively unsaturated Pd⁰ is one of the plausible catalytic cycles. On the other hand, the reaction of [Pd(P(*t*Bu)₃)₂] with bromobenzene in toluene may give [Pd(H)(Br)(P(*t*Bu)₃)₂] as reported by Hartwig and co-workers. Thus a mechanism involving addition/elimination of Pd–H is also possible under the reported conditions: B. F. Barrios-Landeros, B. P. Carrow, J. F. Hartwig, *J. Am. Chem. Soc.* **2008**, *130*, 5842.
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