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Palladium-catalyzed regioselective silaboration of 1,2-dienes

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Abstract

Palladium complexes catalyzed regioselective addition of the Si–B bond of (dimethylphenylsilyl)pinacolborane to allenes in good yields. In the silaboration of terminal allenes having electron-donating substituents such as alkyl and methoxy groups, the Si–B bond added to the internal C=C bond with regioselective B–C and Si–C bond formation at the central and substituted carbon atoms of the allene, respectively. In contrast, the silylborane preferably added to the terminal C=C bond with exclusive Si–C bond formation at the terminal carbon atom in the silaboration of allenes bearing electron-withdrawing groups such as perfluoroalkyl group. 1,3-Disubstituted allenes also underwent the silaboration in good yields with varying regio- as well as stereoselectivity. The silyl and boryl groups of the 2-borylallylsilanes thus prepared were selectively utilized for further synthetic elaboration. Palladium-catalyzed coupling of the 2-borylallylsilanes with aryl iodides afforded the corresponding 2-arylallylsilanes in fair-to-good yields. 2-Boryl-π-allylpalladium complexes were successfully prepared by the reaction of the 2-borylallylsilanes with $PdCl_2(CH_3CN)_2$.

Keywords: Silylborane; Silaboration; Allene; Palladium catalyst; Platinum catalyst; Regioselection; Isocyanide; 2-Borylallylsilane; 2-Boryl(π-allyl)palladium complex; Cross-coupling

1. Introduction

Transition-metal catalyzed additions of silicon-containing inter-element σ-bonds to unsaturated organic molecules have provided an attractive strategy for the synthesis of organosilicon compounds which are otherwise inaccessible [1,2]. While the additions of Si–Si bond have been studied most extensively [3], interest has also been focused on the addition reactions of silicon–heteroatom bonds such as tin and germanium. It has been shown that many of the additions of those inter-element σ-bonds proceed regioselectively to lead to effective synthesis of regio-defined organosilicon compounds.

We have developed addition reactions of Si–B bond of silylboranes to unsaturated organic compounds [4–9]. In these reactions, an otherwise stable Si–B bond is effectively activated by group 10 metal complexes and exhibits its broader applicability to the reaction with unsaturated compounds than other silicon-containing σ-bonds such as Si–Si and Si–Sn. In the course of our exploitation of new reactions, we have centered our attention on regio- and stereoselectivity of the silaboration reactions. It has been found that high selectivity is attainable by appropriate choice of the metal as well as the ligand of the catalysts in the silaboration reactions.

Recently, we reported preliminarily that silaboration of allenes proceeded in a regio- and stereoselective fashion in the presence of palladium catalysts [10,11]. Although related transition-metal catalyzed addition reactions of Si–Si [12], Si–Sn [13], and B–B [14] bonds to allene have been documented [15], the new addition reaction is unique in that synthetically useful 2-borylallylsilanes are produced regioselectively in good yields. Herein, we describe a full detail of the silaboration of allenes, including mechanistic consideration and synthetic application.

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2. Results and discussion

2.1. Silaboration of monosubstituted allenes

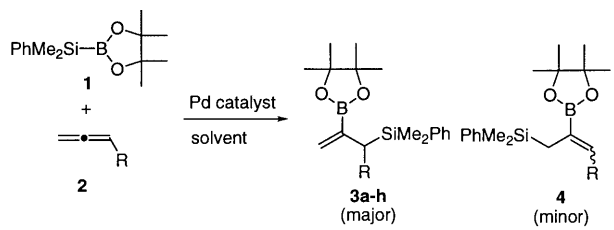
Reactions of 5-phenylpenta-1,2-diene (**2a**, 1.5 equiv) with (dimethylphenylsilyl)pinacolborane **1** were carried out in octane in the presence of various palladium catalysts (Scheme 1, Table 1). Initially, we employed a catalyst **A′** generated from $Pd(acac)_2$ (2 mol%) with 1,1,3,3-tetramethylbutyl isocyanide (*t*-Oc-NC, 30 mol%), which was developed for highly effective catalyst for the activation of Si–Si [16] as well as Si–B bonds [4]. Catalyst **A′** afforded silaboration product **3a** in 77% yield at 120°C for 2 h (Table 1; entry 1). It should be noted that only a single regioisomer, in which the boryl and the silyl groups were exclusively attached to 2- and 3-positions of the allene, respectively, was formed in the reaction. As we previously reported in the silaboration of alkynes, the silaboration of the allene was catalyzed by palladium catalysts bearing a wide range of ligands such as isonitriles and phosphines [4]. We found that use of 2,6-dimethylphenyl isocyanide (Xy-NC, 8 mol%) with $Pd(acac)_2$ (2 mol%) (catalyst **B**) gave the highest yields (99%) in the reaction of **2a** with **1** (entry 2). The use of Xy-NC as the ligand enables to reduce the amounts of the palladium complex (0.4 mol%) and allene **2a** (1.2 equiv) without decrease in yield and selectivity (entry 3). $PdCl_2(PPh_3)_2$ also served as an effective catalyst to afford **3a** in 90% yield (entry 4). It may be worth mentioning that use of a platinum catalyst resulted in the highly selective formation of a regioisomeric product **4a** albeit in low yield (ca. 10%) without formation of any other regioisomers (Scheme 2). Similar preference for the terminal addition was also reported in the related platinum-catalyzed additions to allenes [14,15]. Silaboration of hepta-1,2-diene (**2b**) was also catalyzed by the palladium catalyst with Xy-NC as well as *t*-Oc-NC to give 2-boryl-3-silylhept-1-en (**3b**) exclusively in high yield (entries 5 and 6). Ethyl penta-3,4-dienoate (**2c**) also underwent the silaboration with **1** in the presence of the Xy-NC-based catalyst in high yield and regioselectivity (entry 7).

Unlike the exclusive formation of the internal addition products (**3**) in the silaboration of the allenes with primary alkyl substituents, minor formation of a terminal addition product **4d** was observed in the reaction of cyclohexyl-1,2-propadiene (**2d**) in the presence of $Pd(acac)_2$ (2 mol%)/*t*-Oc-NC (8 mol%) (entry 8). Nevertheless, no regioisomer bearing a silyl group at the central carbon was detected in the reaction mixture. While the selectivity for the internal addition product **3d** was only slightly improved by carrying out the reaction at room temperature (entry 9), the amount of *t*-Oc-NC employed as a ligand on palladium dramatically affected the regioselectivity. In the presence of 30 and 100 mol% of *t*-Oc-NC with 2 mol% of $Pd(acac)_2$, the terminal addition product **4d** was formed as a major isomer in ratios of 26:74 and 22:78, respectively (entries 10 and 11). On the other hand, the regioisomeric ratio also varied with the ligand on palladium. Although 1-adamantyl isocyanide gave slightly lower ratio than that for *t*-Oc-NC (entry 15), use of other isonitriles such as Cy-NC, Xy-NC, and Dip-NC resulted in exclusive formation of internal addition product **3d** in good yields (entries 12–14). Some other palladium complexes including $Pd(PPh_3)_4$ and $PdCl_2$(BINAP) (BINAP: 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl) similarly afforded **3d** as a single regioisomer (entries 16 and 17). However, $Pd_2(dba)_3(CHCl_3)$ resulted in the formation of 53:47 mixture of **3d** and **4d** in lower yield (entry 18).

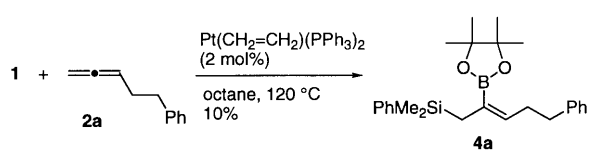
Silaboration of *t*-butylpropadiene (**2e**) also afforded the internal addition product **3e** in good yield. While the use of *t*-Oc-NC as well as Xy-NC as ligands on palladium resulted in the formation of a minor amount of a terminal addition product **4e** (entries 19 and 20), $PdCl_2(PPh_3)_4$ and $Pd(PPh_3)_4$ afforded the internal addition product **3e** exclusively (entries 21 and 22).

We carried out reactions of phenylpropadiene (**2f**) under various reaction conditions. As seen from Table 1, the minor formation of the terminal addition product **4f** could not be avoided by changing the ligand, solvent, and reaction temperature. However, the regioselectivity of the silaboration catalyzed by $Pd(acac)_2$/*t*-Oc-NC depended upon the reaction temperature: an 84:16 ratio for **3f** and **4f** was obtained at 80°C, while ratios of 66:34 and 81:19 were attained at room temperature and 120°C, respectively (entries 23–25). In the presence of palladium catalysts bearing isonitriles, phosphines, and phosphite as ligands, regioselectivity ranged from 81:19 to 90:10 (entries 27–38). The highest selectivity was obtained for the reaction in the presence of a catalyst generated from cyclopentadienyl(π-allyl)palladium with $P(OEt)_3$ (entry 38).

Further experiments using *p*-substituted arylpropadienes indicated that the regioselectivity of the silabora-



Scheme 1.



Scheme 2.

Table 1
Palladium-catalyzed silaboration of terminal allenes [a]

Entry	Allene (R)	Catalyst [b]	Temp. (°C)	Yield (%) [c]	Regioselectivity (**3**:**4**)
1	**2a** (CH_2CH_2Ph)	**A′**	120	77	100:0
2	**2a**	**B**	120	99	100:0
3 [d]	**2a**	**B**	120	96	100:0
4	**2a**	**F**	120	90	100:0
5	**2b** (*n*-Bu)	**A**	80	98	100:0
6	**2b**	**B**	120	99	100:0
7	**2c** (CH_2CO_2Et)	**B**	120	98	97:3
8	**2d** (Cy)	**A**	120	(92)	82:18
9	**2d**	**A**	r.t.	(74)	84:16
10	**2d**	**A′**	120	90 (92)	26:74
11	**2d**	**A″**	120	(82)	22:78
12	**2d**	**B**	120	76 (92)	100:0
13	**2d**	**C**	120	(95)	100:0
14	**2d**	**D**	120	81 (95)	100:0
15	**2d**	**E**	120	(93)	76:24
16	**2d**	**G**	120	(92)	100:0
17	**2d**	**O**	120	78 (84)	100:0
18	**2d**	**Q**	120	(64)	53:47
19	**2e** (*t*-Bu)	**A**	120	79	85:15
20	**2e**	**B**	120	88	94:6
21	**2e**	**F**	120	74	100:0
22	**2e**	**G**	120	51	100:0
23	**2f** (Ph)	**A′**	r.t.	(92)	66:34
24	**2f**	**A′**	80	86 (93)	84:16
25	**2f**	**A′**	120	(94)	81:19
26	**2f**	**B**	120	95	86:14
27 [e]	**2f**	**B**	120 in EDC	(95)	86:14
28 [f]	**2f**	**B**	120 in DMF	(95)	87:13
29	**2f**	**F**	120	73 (84)	84:16
30	**2f**	**G**	120	(73)	82:18
31	**2f**	**H**	120	(85)	87:13
32	**2f**	**I**	120	(96)	85:15
33	**2f**	**J**	120	(99)	87:13
34	**2f**	**K**	120	(54)	85:15
35	**2f**	**L**	120	(89)	86:14
36	**2f**	**M**	120	(84)	81:19
37	**2f**	**N**	120	(84)	84:16
38	**2f**	**P**	120	(91)	90:10
39	**2g** (p-$MeOC_6H_4$)	**B**	120	76	94:6
40	**2h** (p-$CF_3C_6H_4$)	**B**	120	81	36:64
41	**2i** (OMe)	**A′**	r.t.	(59)	70:30
42	**2i**	**A′**	80	(90)	86:14
43	**2i**	**A**	80	91 (94)	99:1
44	**2i**	**B**	120	92 (87)	100:0
45	**2j** (H)	**A**	80	93	
46	**2j**	**B**	120	79	
47	**2j**	**F**	120	65	

[a] Silylborane 1, allenes **2** (1.5 equiv), and palladium catalyst (2 mol%) were used unless otherwise noted. Abbreviations: *t*-Oc: 1,1,3,3-tetramethylbutyl; Xy: 2,6-dimethylphenyl; Cy: cyclohexyl; Dip: 2,6-diisopropylphenyl; 1-Adm: 1-adamantyl; dppe: 1,2-bis(diphenylphosphino)ethane; dppb: 1,4-bis(diphenylphosphino)butane; binap: 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl; dba: dibenzalacetone.

[b] **A**: $Pd(acac)_2$/*t*-Oc-NC (1/4); **A′**: $Pd(acac)_2$/*t*-Oc-NC (1/15); **A″**: $Pd(acac)_2$/*t*-Oc-NC (1/50); **B**: $Pd(acac)_2$/Xy-NC (1/4); **C**: $Pd(acac)_2$/Cy-NC (1/4); **D**: $Pd(acac)_2$/Dip-NC (1/4); **E**: $Pd(acac)_2$/1-Adm-NC (1/4); **F**: $PdCl_2(PPh_3)_2$; **G**: $Pd(PPh_3)_4$; **H**: (η^5-Cp)(η^3-allyl)Pd/PPh_3 (1/2); **I**: (η^5-Cp)(η^3-allyl)Pd/$PMePh_2$ (1/2); **J**: (η^5-Cp)(η^3-allyl)Pd/PMe_2Ph (1/2); **K**: (η^5-Cp)(η^3-allyl)Pd/PBu_3 (1/2); **L**: (η^5-Cp)(η^3-allyl)Pd/$PCyPh_2$ (1/2); **M**: (η^5-Cp)(η^3-allyl)Pd/dppe (1/1); **N**: (η^5-Cp)(η^3-allyl)Pd/dppb (1/1); **O**: $PdCl_2$(binap); **P**: (η^5-Cp)(η^3-allyl)Pd/$P(OEt)_3$ (1/2); **Q**: $Pd_2(dba)_3(CHCl_3)$.

[c] Isolated yield (GC yield in parentheses).

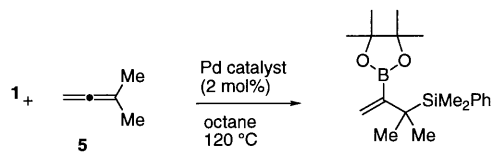
[d] 1.2 equiv of allene **2a** and 0.4 mol% of $Pd(acac)_2$ were used.

[e] A reaction in 1,2-dichloroethane.

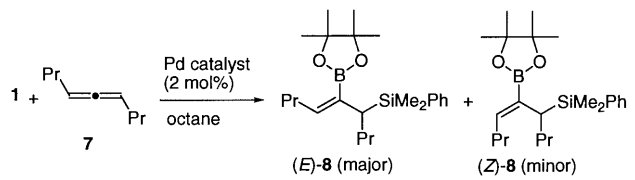
[f] A reaction in DMF.

tion reaction significantly depended on the electronic nature of the *p*-substituent. Thus, higher regioselectivity for the internal addition product **3g** was attained in the reaction of *p*-methoxyphenylpropadiene (**2g**) with **1** in the presence of $Pd(acac)_2$/Xy-NC (1/4) (catalyst **B**), whereas terminal addition product **4h** was predominantly formed in the reaction of *p*-(trifluoromethyl)-phenylpropadiene (**2h**) under the same reaction conditions (entries 26, 39 and 40).

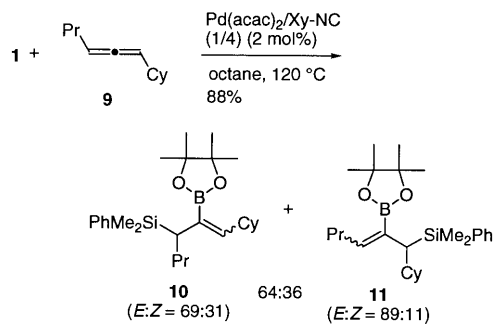
Silaboration of methoxypropadiene (**2i**) also proceeded regioselectively to afford internal addition product **3i**. As seen in the reactions of **2f**, the regioselectivity of the $Pd(acac)_2$/*t*-Oc-NC catalyzed reactions depended upon the reaction temperature as well as the amount of the ligand employed. Thus, the reaction at 80°C in the presence of $Pd(acac)_2$/*t*-Oc-NC (1/4) provided better selectivity and yield (entry 43) than those for the reactions at room temperature (entry 41) or in the presence of $Pd(acac)_2$/*t*-Oc-NC (1/15) (entry 42). The reaction of **2i** was best catalyzed by $Pd(acac)_2$/Xy-NC (1/4) at 120°C to give **3i** exclusively in high yield (entry 44).



Scheme 3.



Scheme 4.



Scheme 5.

Gaseous allene (**2j**, 1 atm) also underwent the silaboration in the presence of palladium catalyst bearing isonitrile or phosphine ligands, giving 2-boryl-3-silylpropene (**3j**) in good yields (entries 45–47).

2.2. Silaboration of 1,1-disubstituted allenes

Reaction of 3-methylbuta-1,2-diene (**5**) with **1** in the presence of the $Pd(acac)_2$/Xy-NC resulted in the formation of a complex mixture. On the other hand, internal addition product **6** was selectively obtained in low yield by use of $Pd(acac)_2$ with *t*-Oc-NC as ligand (Scheme 3). It was found that the $PdCl_2(PPh_3)_2$ catalyst was most effective for the silaboration of **5** to give **6** without any detectable formation of a terminal addition product.

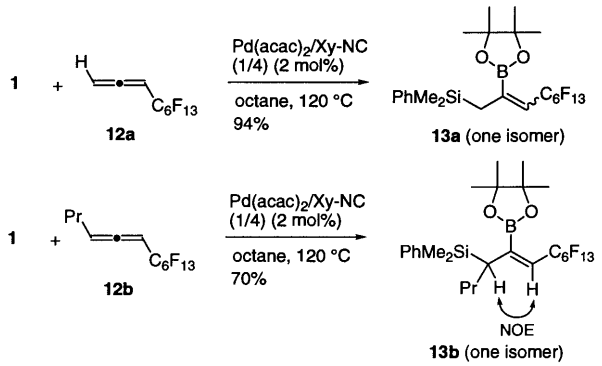
2.3. Silaboration of 1,3-disubstituted allenes

Reaction of nona-4,5-diene (**7**) with **1** in the presence of $Pd(acac)_2$/Xy-NC afforded a mixture of *E* and *Z*-addition products (*E*)-**8** and (*Z*)-**8** in a 62:38 ratio in 88% total yield (Scheme 4). While the reaction of **7** with **1** at 80°C in the presence of $Pd(acac)_2$/*t*-Oc-NC also afforded a 62:38 mixture of the *E* and *Z* isomers, the ratio was improved to 89:11 by raising the reaction temperature to 120°C. $PdCl_2(PPh_3)_2$ also catalyzed the reaction in good yield, but gave a 66:34 mixture of (*E*)-**8** and (*Z*)-**8**.

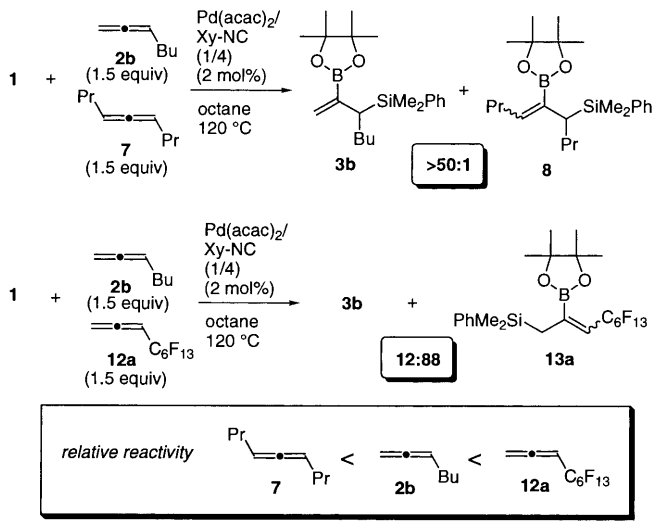
We also carried out a reaction of unsymmetrical 1,3-disubstituted allene **9** in the presence of $Pd(acac)_2$/Xy-NC at 120°C. The reaction afforded all of the four possible isomers (*E*)-**10**, (*Z*)-**10**, (*E*)-**11**, and (*Z*)-**11** in 88% total yield (Scheme 5). The structure of each isomer was identified by NMR experiments including NOE measurements. They showed that the silyl group was preferentially introduced to the allylic carbon atom adjacent to the propyl group (**10**) rather than to that adjacent to the cyclohexyl group (**11**) in a 64:36 ratio with the corresponding (*E*)-isomers predominating.

2.4. Silaboration of perfluoroalkylated allenes

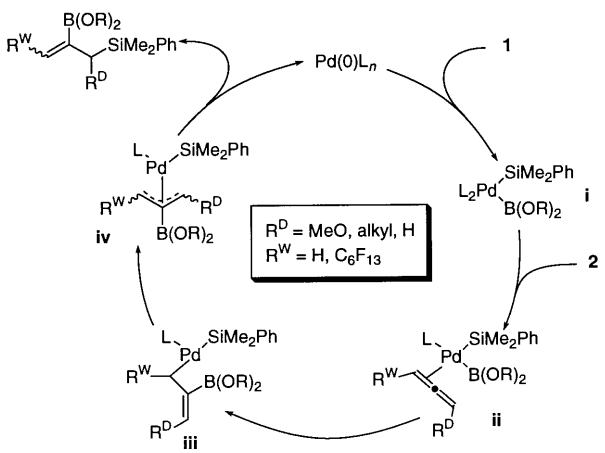
Some comments may be deserved on the remarkable effect of perfluoroalkyl group on the regioselectivity of the silaboration reaction. Perfluorohexylallene (**12a**) was reacted with **1** in the presence of $Pd(acac)_2$/Xy-NC at 120°C, providing terminal addition product **13a** in high yield as a single isomer with regioselectivity completely opposite to that for primary-alkyl substituted allenes (Scheme 6). A similar effect on the regioselectivity was also found in the reaction of 1-perfluorohexylhexa-1,2-diene (**12b**), which afforded a single product **13b** bearing the silyl group at the carbon remote from the perfluorohexyl group. Although the geometry of the C=C bond in **13a** could not be determined by an NOE experiment, NOE between allylic and vinylic protons was observed for **13b**, being indicative of (*E*)-geometry of the C=C bond.



Scheme 6.



Scheme 7.



Scheme 8.

2.5. Mechanism

A regiochemical trend of the silaboration reaction of allenes can be summarized as follows: (1) the boryl group is generally attached to the central (*sp*) carbon of the allenes and (2) the silyl group is preferentially attached to more electron-rich sp^2 carbon of the allenes. The same regiochemical outcome for the internal additions has also been reported for the palladium-catalyzed bis-silylation and silastannation of terminal allenes bearing alkyl groups.

Before assuming a plausible catalytic cycle of the silaboration, we compared relative reactivity of 1,2-heptadiene (**2b**), 4,5-nonadiene (**7**), and perfluoroalkylpropadiene (**12a**) by competitive reactions, in which silylborane **1** was reacted with a mixture of two of the three allenes (1.5 equiv each) in the presence of $Pd(acac)_2$/Xy-NC (1/4) at 120°C in octane (Scheme 7). The competitive reaction revealed much higher reactivity of **2b** than that of **7**, indicating the presence of the terminal C=C bond enhanced the reactivity, although addition of Si–B bond took place only at the internal C=C bond. On the other hand, **12a** showed higher reactivity than **2b**, indicating the silaboration of C=C bond bearing electron-withdrawing group was accelerated in spite of the fact that the addition took place at the terminal C=C bond of **12b**.

Taking the results of the competitive reactions into consideration, we may propose the following catalytic cycle for the palladium-catalyzed silaboration of allenes (Scheme 8). A (boryl)(silyl)palladium(II) complex (**i**) may be initially formed by oxidative addition of the Si–B bond of **1** onto the palladium(0) complex. The activation of the Si–B bond is followed by the formation of **ii** with coordination of allenes. Subsequently, migratory insertion of more electron-deficient C=C bond may take place. As we have proposed for many silaboration reactions using group 10 metal complexes, the C=C bond may preferentially be inserted into the Pd–B bond rather than the Pd–Si bond [4–8]. Thus, selective B–C bond formation may proceed at the *sp* carbon of allene to give σ-allylic palladium intermediate **iii**, in which the silyl group and the allylic carbon are located in a trans fashion. Intermediate **iii** is rapidly converted to the corresponding π-allylic palladium intermediate **iv**, which then undergoes facile reductive elimination of the silicon and the carbon atom located *cis* to the silyl group.

The proposed mechanism is interestingly compared with that of $Pd(PPh_3)_4$-catalyzed reaction of cinnamyl acetate with hexamethyldisilane, in which a closely related (organosilyl)(π-allyl)palladium(II) intermediate may be involved [17]. The reaction exclusively provides (*E*)-1-phenyl-3-trimethylsilyl-1-propene, which arises from reductive elimination at the terminal allylic carbon. The highly contrasted regiochemistry may indicate that the reductive elimination of the Si–C bond is so facile that the regioselectivity of the Si–C bond formation is determined by the configuration of the primarily formed (organosilyl)(π-allyl)palladium intermediate prior to a possible *cis-trans* equilibrium of the intermediate.

Although it is still difficult to explain the formation of the minor regioisomers in the reactions of the terminal allenes with bulky substituents, they may be formed through *cis-trans* isomerization of **iii** as well as **iv** followed by reductive elimination at the less substituted allylic carbon.

2.6. Synthetic application

The silaboration products, which possess vinylic boryl as well as allylic silyl moiety, are widely utilized in organic synthesis for carbon-carbon bond formation. A series of the silaboration products served as useful precursors for the synthesis of 2-arylallylsilanes. For instance, selective replacement of the boryl group by phenyl group took place, giving dimethylphenyl(2-phenylallyl)silane (**14a**) in 75% yield (Scheme 9) [18].

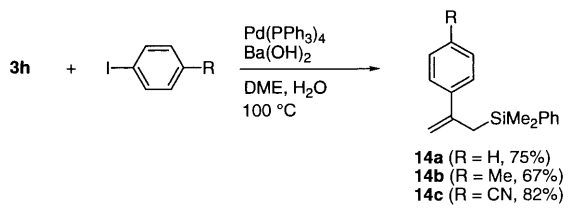
On the other hand, the silaboration products could also be utilized for the synthesis of 2-boryl π-allylpalladium complexes, which may be otherwise inaccessible. Treatment of **3a** with $PdCl_2(CH_3CN)_2$ in MeOH at room temperature gave 2-boryl substituted π-allylpalladium chloride dimer **15a** in 97% yield (Scheme 10). Similar quantitative formations of π-allylpalladium complexes were also observed in the reactions of **3j** and **8** with $PdCl_2(CH_3CN)_2$ in MeOH, although the corresponding products **15b** and **15c** could not be purified so as to give satisfactory elemental analysis.

3. Conclusion

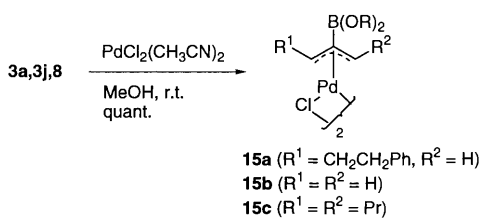
Regioselective additions of the Si–B bond of silylborane to allenes were effectively catalyzed by various palladium complexes with isonitrile, phosphine, and phosphite ligands. The reactions generally proceeded with highly regioselective B–C bond formation at the central *sp* carbon of the allene. Furthermore, the silaboration of the terminal allenes proceeded with highly regioselective Si–C bond formation either at the terminal or internal carbon atom of the allene. Exclusive internal addition took place for the terminal allenes with electrondonating substituents such as methoxy and alkyl groups, while terminal addition is preferred in the reactions of the allenes with electronegative groups such as perfluoroalkyl group. A platinum-catalyst was also found to catalyze the silaboration of the terminal allene in much inferior yield than the palladium catalyst but with opposite regioselectivity, i.e. the terminal addition.

A mechanism of the silaboration reaction has not been clarified yet. However, insertion of less substituted C=C bond of the terminal allenes into the B–Pd of **i** may be involved in the catalytic cycle, resulting in the observed regioselective B–C bond formation at the central carbon of the allene.

As shown in some examples, the 2-borylallylsilanes prepared by the silaboration of allenes may serve as a useful building block in synthetic organic chemistry.



Scheme 9.



Scheme 10.

4. Experimental

^1H, ^{13}C, and ^{19}F-NMR spectra were recorded on a Varian Gemini 2000 spectrometer (7.0 T magnet) at ambient temperature. ^{11}B NMR spectra were recorded on a JEOL JNM-GX400 spectrometer (9.3 T magnet) at ambient temperature. ^1H-NMR data are reported as follows: chemical shift in ppm downfield from tetramethylsilane (δ scale), multiplicity (s=singlet, d=doublet, t=triplet, q=quartet, and m=multiplet), coupling constant (Hz), and integration. ^{13}C-NMR chemical shifts are reported in ppm downfield from tetramethylsilane (δ scale). All ^{13}C-NMR spectra were obtained with complete proton decoupling. ^{11}B-NMR chemical shifts are reported in ppm downfield from $BF_3{\cdot}OEt_2$ (δ scale). ^{19}F-NMR chemical shifts are reported in ppm downfield from $CFCl_3$ (δ scale). IR spectra were obtained on a Hitachi 270-30 spectrometer. High resolution mass spectra were recorded on a JEOL JMS-SX102A spectrometer.

Solvents were distilled from the indicated drying agents: octane (CaH_2); DME ($LiAlH_4$); DMF (CaH_2); MeOH (MgOMe); 1,2-dichloroethane (CaH_2).

2a, **2b**, **2d**, **2f**, **2g**, **2h** [19], **2c** [20], **2e** [21], **2I** [22], **7**, **9**[23], **12a**, **12b** [24], $Pd(PPh_3)_4$ [25], $PdCl_2(PPh_3)_2$ [26], Cp(allyl)Pd [27], and $PdCl_2(CH_3CN)_2$ [28] were prepared by the literature methods. Isonitriles were prepared by dehydration of the corresponding formamides with $POCl_3$ in the presence of triethylamine [29]. 1,1,3,3-Tetramethylbutyl isocyanide (Aldrich) and 2,6-

dimethylphenyl isocyanide (Aldrich) were also obtained from the indicated commercial source. Triphenylphosphine (Wako), dimethylphenylphosphine (Aldrich), methyldiphenylphosphine (Aldrich), cyclohexyldiphenylphosphine (Strem), tributylphosphine (Wako), and triethylphosphite (Nacalai) were purchased and purified by distillation or recrystallization before use. 1,2-Propadiene (**2j**, Oakwood Products), 3-methyl-1,2-butadiene (**5**, Aldrich), dppe (Kanto), dppb (Kanto) and $Pd(acac)_2$ (Mitsuwa) were used as received.

All reactions were carried out under an argon or nitrogen atmosphere.

4.1. General procedure for the silaboration of allenes

A solution of $Pd(acac)_2$ (2.3 mg, 0.0076 mmol) and 2,6-dimethylphenyl isocyanide (4.0 mg, 0.031 mmol) in octane (0.2 ml) was heated at 120°C for 30 s with stirring and then cooled to room temperature. To the red solution were added **1** (100 mg, 0.38 mmol) and allene (0.58 mmol) at room temperature. The mixture was heated at the indicated temperature with stirring. After cooling to room temperature, the mixture was subjected to bulb-to-bulb distillation to afford silaboration product.

4.2. Synthesis of 3-(dimethylphenylsilyl)-5-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-pentene (3a)

The title compound was prepared by the general procedure. ^{1}H-NMR ($CDCl_3$) δ 0.23 (s, 3H), 0.27 (s, 3H), 1.22 (s, 12H), 1.71–1.82 (m, 1H), 1.89–2.06 (m, 1H), 2.14 (dd, $J = 3.3$, 12.0 Hz, 1H), 2.32–2.42 (m, 1H), 2.64–2.74 (m, 1H), 5.45 (d, $J = 3.0$ Hz, 1H), 5.92 (d, $J = 3.0$ Hz, 1H), 7.08–7.35 (m, 8H), 7.46–7.49 (m, 2H); ^{13}C-NMR ($CDCl_3$) δ −5.3, −3.9, 24.7, 30.9, 33.4, 35.2, 83.3, 125.5, 127.3, 127.5, 128.2, 128.6, 128.8, 134.3, 138.4, 143.1; ^{11}B-NMR ($CDCl_3$) δ 30.0; IR (neat) 3036, 1604, 1310, 1112, 736 cm^{-1}. Anal. Calc. for $C_{25}H_{35}BO_2Si$: C, 73.88; H, 8.68. Found: C, 73.71; H, 8.88%.

4.3. Synthesis of (E)-1-(dimethylphenylsilyl)-5-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-pentene (4a)

The title compound was prepared by platinum-catalyzed silaboration of **2a** (Scheme 2). A mixture of $Pt(CH_2{=}CH_2)(PPh_3)_2$ (5.7 mg, 7.6×10^{-3} mmol), **1** (101 mg, 0.38 mmol), and **2a** (85 mg, 0.59 mmol) in octane (0.1 mL) was heated at 120°C for 3 h with stirring. After evaporation of volatile materials, resultant residue was subjected to preparative TLC (hexane/ether = 19/1) to give **4a** (16 mg, 10%). ^{1}H-NMR ($CDCl_3$) δ 0.21 (s, 6H), 1.20 (s, 12H), 1.81 (s, 2H), 2.60–2.72 (m, 4H), 5.90 (t, $J = 6.9$ Hz, 1H), 7.15–7.42 (m, 8H), 7.46–7.57 (m, 2H); ^{13}C-NMR ($CDCl_3$) δ −3.2, 24.8, 29.6, 32.9, 36.8, 82.8, 125.6, 127.6, 128.2, 128.6, 128.7, 133.9, 139.7, 142.6, 144.6; IR (neat) 2984, 1624, 1406, 1146 cm^{-1}. HRFABMS Calc. for $C_{25}H_{36}BO_2Si$ (M + 1): 407.2576. Found: 407.2573. The geometry was determined by an NOE between protons at 1 and 3 positions.

4.4. Synthesis of 3-(dimethylphenylsilyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-heptene (3b)

The title compound was prepared by the general procedure. ^{1}H-NMR ($CDCl_3$) δ 0.23 (s, 3H), 0.27 (s, 3H), 0.80 (t, $J = 6.9$ Hz, 3H), 0.98–1.82 (m, 4H), 1.19 (s, 12H), 1.20–1.34 (m, 1H), 1.37–1.51 (m, 1H), 2.06 (dd, $J = 3.6$, 11.7 Hz, 1H), 5.36 (d, $J = 3.0$ Hz, 1H), 5.81 (d, $J = 3.0$ Hz, 1H), 7.30–7.41 (m, 3H), 7.49–7.55 (m, 2H); ^{13}C-NMR ($CDCl_3$) δ −5.2, −3.9, 13.9, 22.4, 24.6, 28.2, 31.1, 33.4, 83.1, 126.8, 127.5, 128.7, 134.3, 138.8; IR (neat) 2968, 1600, 1308, 1144 cm^{-1}. Anal. Calc. for $C_{21}H_{35}BO_2Si$: C, 70.38; H, 9.84. Found: C, 70.11; H, 9.71%.

4.5. Synthesis of ethyl 3-(dimethylphenylsilyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-pentenoate (3c)

The title compound was prepared by the general procedure. ^{1}H-NMR ($CDCl_3$) δ 0.27 (s, 3H), 0.28 (s, 3H), 1.16 (t, $J = 7.2$ Hz, 3H), 1.20 (s, 6H), 1.21 (s, 6H), 2.33–2.45 (m, 1H), 2.58–2.70 (m, 2H), 3.91–4.12 (m, 2H), 5.36 (d, $J = 2.4$ Hz, 1H), 5.79 (d, $J = 2.4$ Hz, 1H), 7.28–7.38 (m, 3H), 7.45–7.55 (m, 2H); ^{13}C-NMR ($CDCl_3$) δ −5.5, −4.0, 14.1, 24.6, 24.7, 29.8, 34.4, 60.0, 83.3, 127.2, 127.6, 129.1, 134.3, 137.3, 173.4; IR (neat) 2988, 1738, 1604, 1142, 702 cm^{-1}. Anal. Calc. for $C_{21}H_{33}BO_4Si$: C, 64.94; H, 8.56. Found: C, 64.87; H, 8.80%.

4.6. Synthesis of 3-cyclohexyl-3-(dimethylphenylsilyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-propene (3d)

The title compound was prepared by the general procedure. ^{1}H-NMR ($CDCl_3$) δ 0.20 (s, 3H), 0.37 (s, 3H), 0.69–0.88 (m, 2H), 0.95–1.41 (m, 3H), 1.23 (s, 12H), 1.47–1.83 (m, 6H), 1.97 (d, $J = 10.2$ Hz, 1H), 5.43 (d, $J = 3.3$ Hz, 1H), 5.79 (d, $J = 3.3$ Hz, 1H), 7.25–7.40 (m, 3H), 7.45–7.60 (m, 2H); ^{13}C-NMR ($CDCl_3$) δ −3.8, −1.3, 24.5, 24.7, 26.5, 26.6, 33.5, 34.2, 38.9, 41.5, 83.2, 127.4, 127.6, 128.3, 134.1, 140.9; IR (neat) 2932, 1602, 1308, 1146 cm^{-1}. Anal. Calc. for $C_{23}H_{37}BO_2Si$: C, 71.86; H, 9.70. Found: C, 71.64; H, 9.63%.

*4.7. Synthesis of (E)-1-cyclohexyl-3-(dimethylphenylsilyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-propene (**4d**)*

The title compound was prepared by use of *t*-Oc-NC/$Pd(acac)_2$ (1/15) as a catalyst (Table 1; entry 10) and separated from **3d** by HPLC (silica gel). ^{1}H-NMR ($CDCl_3$) δ 0.24 (s, 6H), 0.87–1.07 (m, 2H), 1.07–1.36 (m, 2H), 1.19 (s, 12H), 1.56–1.72 (m, 6H), 1.78 (s, 2H), 2.60–2.73 (m, 1H), 5.63 (d, $J = 9.3$ Hz, 1H), 7.30–7.35 (m, 3H), 7.48–7.54 (m, 2H); ^{13}C-NMR ($CDCl_3$) δ −3.3, 24.3, 24.8, 25.9, 26.0, 34.0, 39.4, 82.7, 127.5, 128.7, 133.9, 139.8, 151.7; IR (neat) 2936, 1624, 1146, 836 cm^{-1}. Anal. Calc. for $C_{23}H_{37}BO_2Si$: C, 71.86; H, 9.70. Found: C, 71.85; H, 9.90%. The geometry was determined by an NOE between protons at 1 and 3 positions.

*4.8. Synthesis of 4,4-dimethyl-3-(dimethylphenylsilyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-pentene (**3e**)*

The title compound was prepared by the general procedure. ^{1}H-NMR ($CDCl_3$) δ 0.28 (s, 3H), 0.45 (broad s, 3H), 0.89 (s, 9H), 1.20 (s, 12H), 2.15 (broad s, 1H), 5.56 (broad s, 1H), 5.89 (broad s, 1H), 7.26–7.32 (m, 3H), 7.50–7.58 (m, 2H); ^{13}C-NMR ($CDCl_3$) δ −0.7, −0.4, 24.5, 31.1, 34.9, 83.3, 127.4, 128.2, 131.0, 134.2, 141.8; IR (neat) 2980, 1604, 1308, 1136 cm^{-1}. HRMS Calc. for $C_{21}H_{35}BO_2Si$: 358.2497. Found: 358.2495.

*4.9. Synthesis of 3-(dimethylphenylsilyl)-3-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-propene (**3f**)*

The title compound was prepared by the general procedure and separated from **4f** by HPLC. ^{1}H-NMR ($CDCl_3$) δ 0.27 (s, 3H), 0.31 (s, 3H), 1.15 (s, 6H), 1.17 (s, 6H), 3.55 (s, 1H), 5.66 (d, $J = 2.7$ Hz, 1H), 5.88 (d, $J = 2.7$ Hz, 1H), 7.04–7.15 (m, 3H), 7.15–7.22 (m, 2H), 7.24–7.39 (m, 3H), 7.39–7.44 (m, 2H); ^{13}C-NMR ($CDCl_3$) δ −3.5, −3.1, 24.56, 24.62, 42.2, 83.5, 124.8, 127.4, 127.9, 128.9, 129.1, 134.5, 138.3, 142.7; IR (neat) 2988, 1602, 1252, 704 cm^{-1}. Anal. Calc. for $C_{23}H_{31}BO_2Si$: C, 73.01; H, 8.26. Found: C, 72.85; H, 8.54%.

*4.10. Synthesis of 3-(dimethylphenylsilyl)-1-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-propene (**4f**)*

The title compound was isolated from a mixture of **3f** and **4f** (86:14) by HPLC (Table 1; entry 26). ^{1}H-NMR ($CDCl_3$) δ 0.19 (s, 6H), 1.24 (s, 12H), 2.31 (s, 2H), 7.12 (s, 1H), 7.12–7.33 (m, 8H), 7.44–7.50 (m, 2H); ^{13}C-NMR ($CDCl_3$) δ −2.5, 19.2, 24.8, 83.5, 126.7, 127.7, 128.1, 128.8, 129.0, 133.8, 138.6, 139.3, 139.5; IR (neat) 2988, 1600, 1374, 1142 cm^{-1}. Anal. Calc. for $C_{23}H_{31}BO_2Si$: C, 73.01; H, 8.26. Found: C, 72.89; H, 8.51%. No NOE was observed for the protons at 1 and 3 positions.

*4.11. Synthesis of 3-(dimethylphenylsilyl)-3-(4-methoxyphenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-propene (**3g**)*

The title compound was prepared by the general procedure. ^{1}H-NMR ($CDCl_3$) δ 0.27 (s, 3H), 0.30 (s, 3H), 1.15 (s, 3H), 1.17 (s, 6H), 3.48 (s, 1H), 3.76 (s, 3H), 5.61 (d, $J = 2.4$ Hz, 1H), 5.84 (d, $J = 2.4$ Hz, 1H), 6.69–6.80 (m, 2H), 6.97–7.04 (m, 2H), 7.21–7.35 (m, 3H), 7.38–7.44 (m, 2H); ^{13}C-NMR ($CDCl_3$) δ −3.5, −3.0, 24.6, 24.7, 41.1, 55.1, 83.5, 113.3, 127.4, 128.7, 128.8, 130.1, 134.5, 134.8, 138.4, 157.2; IR (neat) 3076, 1610, 1514, 1250 cm^{-1}. Anal. Calc. for $C_{24}H_{33}BO_3Si$: C, 70.58; H, 8.14. Found: C, 70.34; H, 8.26%.

*4.12. Synthesis of 3-(dimethylphenylsilyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(4-trifluoromethylphenyl)-1-propene (**3h**)*

The title compound was prepared by the general procedure. The regioisomers **3h** and **4h** were separated by silica gel HPLC. ^{1}H-NMR ($CDCl_3$) δ 0.29 (s, 3H), 0.31 (s, 3H), 1.15 (s, 6H), 1.18 (s, 6H), 3.59 (s, 1H), 5.66 (d, $J = 2.4$ Hz, 1H), 5.92 (d, $J = 2.4$ Hz, 1H), 7.16 (d, $J = 8.1$ Hz, 2H), 7.25–7.44 (m, 7H); ^{13}C-NMR ($CDCl_3$) δ −3.5, −3.4, 24.57, 24.62, 42.7, 83.7, 124.7 (q, $J = 3.5$ Hz), 127.0 (q, $J = 32.3$ Hz), 127.6, 128.2, 129.05, 129.15, 130.0, 134.4, 137.6, 147.2; IR (neat) 2936, 1620, 1326, 1126 cm^{-1}. Anal. Calc. for $C_{24}H_{30}BF_3O_2Si$: C, 64.58; H, 6.77. Found: C, 64.65; H, 6.74%.

*4.13. Synthesis of 3-(dimethylphenylsilyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(4-trifluoromethylphenyl)-1-propene (**4h**)*

The title compound was prepared by the general procedure. ^{1}H-NMR ($CDCl_3$) δ 0.21 (s, 6H), 1.27 (s, 12H), 2.28 (s, 2H), 7.09 (s, 1H), 7.23–7.34 (m, 5H), 7.38–7.48 (m, 4H); ^{13}C-NMR ($CDCl_3$) δ −2.6, 19.7, 24.8, 83.7, 124.3 (q, $J = 270.9$ Hz), 125.0 (q, $J = 3.5$ Hz), 127.7, 128.3 (q, $J = 32.3$ Hz), 129.0, 133.7, 137.5, 138.9, 142.1; IR (neat) 2988, 1612, 1326, 1126 cm^{-1}. Anal. Calc. for $C_{24}H_{30}BF_3O_2Si$: C, 64.58; H, 6.77. Found: C, 64.33; H, 6.74%. No NOE was observed for the protons at 1 and 3 positions.

*4.14. Synthesis of 3-(dimethylphenylsilyl)-3-methoxy-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-propene (**3i**)*

The title compound was prepared by the general procedure. ^{1}H-NMR ($CDCl_3$) δ 0.25 (s, 3H), 0.28 (s,

3H), 1.15 (s, 6H), 1.17 (s, 6H), 3.25 (s, 3H), 3.97 (t, $J=$ 1.2 Hz, 1H), 5.69 (dd, $J=1.2$, 3.6 Hz, 1H), 5.88 (dd, $J=1.2$, 3.6 Hz, 1H), 7.30–7.37 (m, 3H), 7.54–7.63 (m, 2H); ^{13}C-NMR ($CDCl_3$) δ −6.0, −5.1, 24.7, 58.4, 78.3, 83.3, 126.4, 127.6, 129.0, 134.5, 137.5; IR (neat) 2988, 1604, 1314, 1144, 736 cm^{-1}. Anal. Calc. for $C_{18}H_{29}BO_3Si$: C, 65.06; H, 8.80. Found: C, 65.23; H, 8.95%.

4.15. Synthesis of 3-(dimethylphenylsilyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-propene (3j)

The reaction was carried out under an atmosphere of propadiene (1 atm). ^{1}H-NMR ($CDCl_3$) δ 0.27 (s, 6H), 1.20 (s, 12H), 1.92 (s, 2H), 5.38 (d, $J=3.3$ Hz, 1H), 5.67 (d, $J=3.3$ Hz, 1H), 7.31–7.57 (m, 5H); ^{13}C-NMR ($CDCl_3$) δ −3.4, 24.1, 24.7, 83.4, 127.6, 128.8, 133.9, 139.3; IR (neat) 2988, 1608, 1312, 1146 cm^{-1}. Anal. Calc. for $C_{17}H_{27}BO_2Si$: C, 67.55; H, 9.00. Found: C, 67.31; H, 9.21%.

4.16. Synthesis of 3-(dimethylphenylsilyl)-3-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-butene (6)

The title compound was prepared by use of $PdCl_2(PPh_3)_2$ as a catalyst (Scheme 3). ^{1}H-NMR ($CDCl_3$) δ 0.28 (s, 6H), 1.12 (s, 6H), 1.20 (s, 12H), 5.29 (d, $J=2.4$ Hz, 1H), 5.74 (d, $J=2.4$ Hz, 1H), 7.29–7.51 (m, 5H); ^{13}C NMR ($CDCl_3$) δ −5.3, 24.2, 24.6, 28.5, 83.0, 125.9, 127.3, 128.7, 134.9, 138.0; IR (neat) 2936, 1582, 1302, 1146 cm^{-1}. Anal. Calc. for $C_{19}H_{31}BO_2Si$: C, 69.08; H, 9.46. Found: C, 68.80; H, 9.68%.

4.17. Synthesis of (E)-6-(dimethylphenylsilyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-nonene ((E)–8)

The title compound was prepared by the general procedure. The stereoisomers (*E*)-**8** and (*Z*)-**8** were separated by silica gel HPLC. ^{1}H-NMR ($CDCl_3$) δ 0.22 (s, 3H), 0.27 (s, 3H), 0.78 (t, $J=7.2$ Hz, 3H), 0.86 (t, $J=$ 7.2 Hz, 3H), 1.01–1.21 (m, 2H), 1.21 (s, 12H), 1.23–1.45 (m, 4H), 1.97 (dd, $J=3.3$, 11.7 Hz, 1H), 2.29 (q, $J=7.5$ Hz, 2H), 5.75 (t, $J=7.8$ Hz, 1H), 7.30–7.36 (m, 3H), 7.47–7.55 (m, 2H); ^{13}C-NMR ($CDCl_3$) δ −4.9, −3.3, 13.6, 13.7, 21.9, 23.5, 24.7, 24.8, 31.6, 33.2, 33.7, 82.6, 127.4, 128.5, 134.3, 139.7, 144.0; ^{11}B-NMR ($CDCl_3$) δ 30.4; IR (neat) 2968, 1620, 1408, 1144 cm^{-1}. Anal. Calc. for $C_{23}H_{39}BO_2Si$: C, 71.48; H, 10.17. Found: C, 71.49; H, 10.39%. The geometry was determined by an NOE between protons at 4 and 6 positions.

4.18. Synthesis of (Z)–6-(dimethylphenylsilyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-nonene ((Z)-8)

^{1}H-NMR ($CDCl_3$) δ 0.20 (s, 3H), 0.34 (s, 3H), 0.77 (t, $J=6.9$ Hz, 3H), 0.85 (t, $J=7.2$ Hz, 3H), 0.90–1.08 (m, 1H), 1.20–1.40 (m, 4H), 1.21 (s, 6H), 1.22 (s, 6H), 1.72–2.09 (m, 3H), 2.22 (dd, $J=3.3$, 12.0 Hz, 1H), 6.22 (t, $J=6.9$ Hz, 1H), 7.30–7.36 (m, 3H), 7.48–7.57 (m, 2H); ^{13}C-NMR ($CDCl_3$) δ −4.3, −3.3, 13.8, 14.1, 22.3, 22.9, 24.3, 24.9, 29.7, 30.7, 31.1, 82.6, 127.5, 128.5, 134.1, 140.1, 144.8; IR (neat) 2968, 1608, 1376, 1140 cm^{-1}. Anal. Calc. for $C_{23}H_{39}BO_2Si$: C, 71.48; H, 10.17. Found: C, 71.42; H, 10.25%. No NOE was observed for the protons at 4 and 6 positions.

4.19. Reaction of 9 with 1 (Scheme 5)

According to the general procedure, **9** (83 mg, 0.50 mmol) was reacted with **1** (98 mg, 0.37 mmol) in the presence of $Pd(acac)_2$ (2.3 mg, 7.6×10^{-3} mmol) with Xy-NC (4.0 mg, 0.031 mmol) in octane. After 2 h, the mixture was subjected to bulb-to-bulb distillation to give a mixture of **10** and **11** (141.1 mg, 88%). The regioisomeric ratio of 44:32:20:4 for (*E*)-**10**, (*E*)-**11**, (*Z*)-**10**, and (*Z*)-**11** was determined by ^{1}H-NMR with the vinylic signals at 5.30 (d, $J=9.3$ Hz), 5.82 (t, $J=7.5$ Hz), 6.00 (d, $J=9.8$ Hz), and 6.17 (t, $J=6.0$ Hz), respectively. The geometry was assumed by NOE experiments. A mixture of (*Z*)-**10** and (*Z*)-**11** was separated from a mixture of (*E*)-**10** and (*E*)-**11** by HPLC and subjected to the elemental analysis. Anal. Calc. for $C_{26}H_{43}BO_2Si$: C, 73.22; H, 10.16. Found: C, 72.92; H, 10.39%.

4.20. Synthesis of 1-(dimethylphenylsilyl)-4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluoro-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-nonene (13a)

The title compound was prepared by the general procedure. ^{1}H-NMR ($CDCl_3$) δ 0.31 (s, 6H), 1.19 (s, 12H), 2.27 (t, $J=3.6$ Hz, 2H), 6.03 (t, $J=16.5$ Hz, 1H), 7.31–7.39 (m, 3H), 7.48–7.58 (m, 2H); ^{13}C-NMR ($CDCl_3$) δ −2.8, 21.7, 24.6, 84.4, 122.0 (t, $J=21.3$ Hz), 127.7, 129.1, 133.8, 138.5; ^{19}F-NMR ($CDCl_3$) δ −81.4, −106.5, −122.2, −123.4, −123.9, −126.7; IR (neat) 2992, 1630, 1240, 1144, 836 cm^{-1}. Anal. Calc. for $C_{23}H_{26}BF_{13}O_2Si$: C, 44.53; H, 4.23. Found: C, 44.33; H, 4.12%. No NOE was observed for the protons at 1 and 3 positions.

4.21. Synthesis of (E)-4-(dimethylphenylsilyl)-7,7,8,8,9,9,10,10,11,11,12,12,12-tridecafluoro-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-dodecene (13b)

The title compound was prepared by the general procedure. ^{1}H-NMR ($CDCl_3$) δ 0.30 (s, 3H), 0.37 (s, 3H), 0.80 (t, $J=6.9$ Hz, 3H), 1.03–1.25 (m, 2H), 1.24 (s, 6H), 1.25 (s, 6H), 1.40–1.56 (m, 2H), 2.03–2.10 (m, 1H), 5.49 (t, $J=14.4$ Hz, 1H), 7.28–7.41 (m, 3H), 7.47–7.57 (m, 2H); ^{19}F-NMR ($CDCl_3$) δ −81.4, −106.7, −122.4, −123.0, −123.4, −126.7; IR (neat) 2968, 1630, 1242,

1144 cm^{-1}. Anal. Calc. for $C_{26}H_{32}BF_{13}O_2Si$: C, 47.14; H, 4.87. Found: C, 47.25; H, 4.92%. The geometry was determined by an NOE between the protons at 4 and 6 positions.

4.22. Competitive silaboration of **2b** and **7**

A solution of $Pd(acac)_2$ (0.58 mg, 1.9×10^{-3} mmol) and 2,6-dimethylphenyl isocyanide (1.0 mg, 7.6×10^{-3} mmol) in octane (0.1 ml) was heated at 120°C for 30 s with stirring. To the red solution were added **1** (25 mg, 0.095 mmol), **2b** (14 mg, 0.14 mmol), and **7** (18 mg, 0.14 mmol) at room temperature. The mixture was heated at 120°C for 2 h with stirring. After evaporation of the solvent, the mixture was analyzed by ^{1}H-NMR, which showed the major formation of **3a** and a trace amount of **8** (>50:1).

4.23. Competitive silaboration of **2b** and **12a**

By using $Pd(acac)_2$ (0.58 mg, 1.9×10^{-3} mmol), 2,6-dimethylphenyl isocyanide (1.0 mg, 7.6×10^{-3} mmol), **1** (25 mg, 0.095 mmol), **2b** (14 mg, 0.14 mmol), and **12b** (51 mg, 0.14 mmol), the title experiment was carried out under a condition similar to that for the competitive silaboration of **2a** and **7**. A ^{1}H-NMR analysis showed the formation of **3a** and **13a** in 12:88 ratio.

4.24. General procedure for the cross-coupling of **3j** with aryl iodide

To a mixture of $Pd(PPh_3)_4$ (6.1 mg, 5.0×10^{-3} mmol) and $Ba(OH)_2 \cdot 8H_2O$ (78 mg, 0.25 mmol) in dimethoxyethane/water (0.9 ml/0.15 ml) under nitrogen were added aryl iodide (0.25 mmol) and **3j** (50 mg, 0.17 mmol) at room temperature. The mixture was heated at 100°C for 3 h with stirring. Extraction with ether followed by column chromatography on silica gel afforded the corresponding allylsilane **14**.

4.25. Synthesis of 2-phenyl-3-(dimethylphenylsilyl)-1-propene (**14a**)

The title compound was prepared by the general procedure (4.6.1.). ^{1}H-NMR (acetone-d_6) δ 0.13 (s, 6H), 2.31 (s, 2H), 4.86 (d, $J = 1.8$ Hz, 1H), 5.13 (d, $J = 1.8$ Hz, 1H), 7.20–7.65 (m, 10H); ^{13}C-NMR (acetone-d_6) δ −2.8, 25.6, 111.2, 127.3, 128.3, 128.6, 129.1, 129.9, 134.5, 134.7, 139.6, 147.2; IR (neat) 2968, 1618, 1252, 1114 cm^{-1}. HRMS Calc. for $C_{17}H_{20}Si$: 252.1334. Found: 252.1323.

4.26. Synthesis of 2-(4-methylphenyl)-3-(dimethylphenylsilyl)-1-propene (**14b**)

The title compound was prepared by the general procedure (4.6.1.). ^{1}H-NMR (acetone-d_6) δ 0.14 (s, 6H), 2.30 (d, $J = 1.2$ Hz, 2H), 2.31 (s, 3H), 4.81 (m, 1H), 5.12 (d, $J = 1.5$ Hz, 1H), 7.03–7.15 (m, 2H), 7.24–7.62 (m, 7H); ^{13}C-NMR (acetone-d_6) δ 2.7, 21.0, 25.5, 110.4, 127.2, 127.3, 128.6, 129.7, 129.9, 134.5, 139.8, 140.6, 147.0; IR (neat) 2968, 1612, 1252, 1116 cm^{-1}. HRMS Calc. for $C_{18}H_{22}Si$: 266.1491. Found: 266.1482.

4.27. Synthesis of 2-(4-cyanophenyl)-3-(dimethylphenylsilyl)-1-propene (**14c**)

The title compound was prepared by the general procedure (4.6.1.). ^{1}H-NMR ($CDCl_3$) δ 0.18 (s, 6H), 2.23 (s, 2H), 4.97 (d, $J = 1.2$ Hz, 1H), 5.20 (d, $J = 1.2$ Hz, 1H), 7.25–7.43 (m, 7H), 7.47–7.53 (m, 2H); ^{13}C-NMR ($CDCl_3$) δ −3.2, 25.0, 110.7, 113.6, 119.0, 127.0, 127.8, 129.2, 131.9, 133.5, 138.0, 144.7, 147.1; IR (neat) 2968, 2232, 1608, 1116 cm^{-1}. HRMS Calc. for $C_{18}H_{19}NSi$: 277.1287. Found: 277.1290.

4.28. Synthesis of π-allylpalladium complexes **15**

To a solution of **3a** (111 mg, 0.27 mmol) in MeOH (2 ml) was added $PdCl_2(CH_3CN)_2$ (73 mg, 0.28 mmol) under nitrogen. The orange suspension was stirred at room temperature for 12 h. Yellow precipitates were collected by filtration and washed with MeOH several times. After drying in vacuo, pale yellow powder (110 mg, 97%) was obtained. **15a**: ^{1}H-NMR ($CDCl_3$) δ 1.30 (s, 24H), 2.04–2.17 (m, 2H), 2.23–2.36 (m, 2H), 2.78–2.92 (m, 6H), 3.82 (dd, $J = 5.7$, 8.4 Hz, 2H), 4.14 (s, 2H), 7.15–7.30 (m, 10H); ^{13}C-NMR ($CDCl_3$) δ 24.5, 24.7, 33.6, 35.6, 65.1, 84.3, 90.7, 125.9, 128.3, 128.7, 141.6; ^{11}B-NMR ($CDCl_3$) δ 28.7; IR (neat) 3468, 2980, 1602, 1142, 858 cm^{-1}. Anal. Calc. for $C_{34}H_{48}B_2Cl_2O_4Pd_2$: C, 49.43; H, 5.86. Found: C, 49.60; H, 5.82%. Related complexes **15b** and **15c** were prepared by the same procedure, although they were identified only by NMR. **15b**: ^{1}H-NMR ($CDCl_3$) δ 1.30 (s, 24H), 3.10 (s, 4H), 4.33 (s, 4H). **15c**: ^{1}H-NMR ($CDCl_3$) δ 0.89 (t, $J = 7.0$ Hz, 12H), 1.35 (s, 24H), 1.43–1.75 (m, 16H), 3.69 (t, $J = 7.0$ Hz, 4H); ^{11}B-NMR ($CDCl_3$) δ 29.0.

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