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Palladium-Catalyzed β-Elimination of Aminoboranes from (Aminomethylsilyl)boranes Leading to the Formation of Silene Dimers

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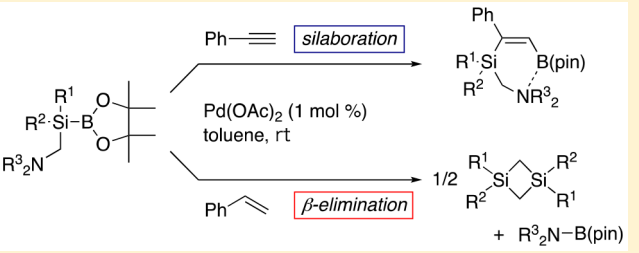
Supporting Information

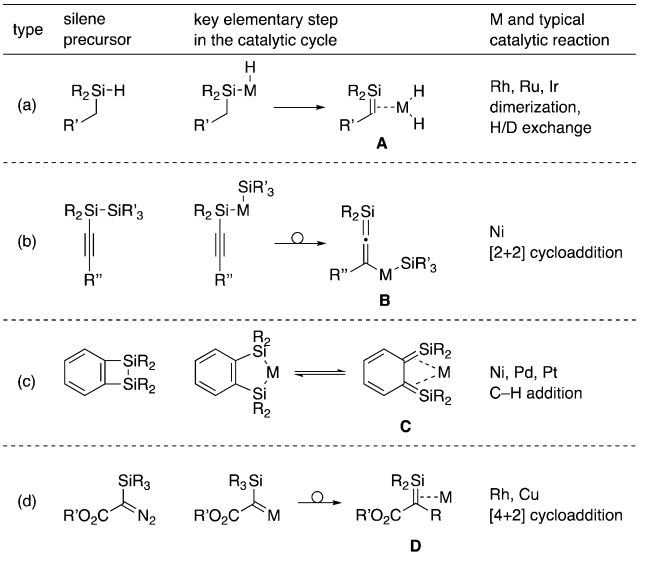
ABSTRACT: Silylboronic esters bearing a *N*,*N*-dialkylaminomethyl group on the silicon atoms were synthesized and used in palladium-catalyzed reactions. Five silylboronic esters were synthesized through a reaction of the [(*N*,*N*-dialkylaminomethyl)diorganosilyl]lithiums with *i*-PrOB(pin). An addition reaction of the silylboronic ester to ethynylbenzene (silaboration) took place efficiently by a phosphine- and isocyanide-free palladium catalyst to give (*E*)-1-silyl-2-boryl-1-phenylethene in a regio- and stereoselective manner. On the other hand, the silylboronic esters underwent β-elimination reactions in the presence of a palladium catalyst and styrene to afford 1,3-disilacyclobutanes and aminoboranes in good yields. This may be due to the generation of silene intermediates during the reaction. It should be noted that use of styrene as a ligand was essential for the generation of the silene species.



INTRODUCTION

Since a report on the first experimental evidence in 1967,[1] there has been much interest in the isolation, structure, reactivity, and synthetic application of silene derivatives ($R_2Si{=}CR'_2$), which contain a highly reactive silicon−carbon double bond.[2] With a view to the synthetic utilization of silene species, various thermal and photochemical reactions have been utilized for the generation of silene species under rather harsh reaction conditions, including the use of strong bases or UV irradiation, which often make their selective reaction difficult. Use of transition-metal catalysis for the generation of silene species or their equivalents has also attracted much interest, because these catalysts may promote not only silene generation but also subsequent reactions through the formation of transition-metal−silene complexes. Several transition-metal-catalyzed reactions involving the generation of silene have been reported to date.[3−6] They can be classified into four categories on the basis of the reaction mechanism (Scheme 1): (a) oxidative addition of the Si−H bond of alkylsilane followed by β-H elimination to afford η²-silene complex **A**,[3] (b) oxidative addition of the Si−Si bond of alkynyldisilane and subsequent 1,3-rearrangement to 3-sila-1,2-propadienyl complex **B**,[4] (c) oxidative addition of the Si−Si bond of 3,4-benzo-1,2-disilacyclobutene to give *o*-quinodisilane **C**,[5] and (d) formation of a silyl-substituted carbene complex from an α-diazocarbonyl compound followed by 1,2-rearrangement of one of the substituents on the silicon atom to afford **D**.[6] Reaction types a−c, which rely on Si−E (E = H, Si) bond activation, require high reaction temperatures (generally 150−220 °C). Although reaction type d can be carried out under rather mild conditions, the accessible silene is limited to that stabilized with carbonyl. For wider utilization of silene or its equivalents in the synthesis of organosilicon compounds, new catalytic reactions for the generation of silene under mild conditions are highly desirable.

Scheme 1. Mechanistic Classification of Transition-Metal-Catalyzed Generation of Silene Intermediate



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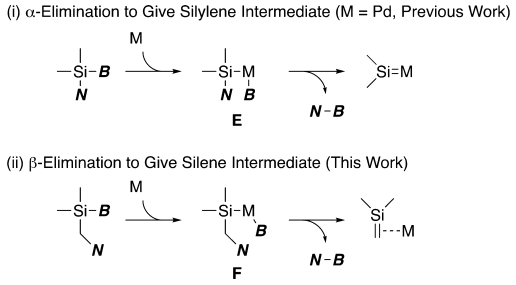
Organometallics XXXX, XXX, XXX−XXX

In this regard, we have focused our attention on the use of Si−B bond activation for mild generation of silene species.

We and other groups have developed various catalytic reactions of silylboronic esters through activation of Si−B bonds by transition-metal catalysts.[7−9] In addition to simple addition reactions including asymmetric variants, silaborative C−C bond forming reactions have also been established.[9] The Si−B bond can be activated by palladium catalysts under mild reaction conditions.[7a−i,l] Most notably, we have reported that silylboronic esters bearing a dialkylamino group on the silicon atom reacts as a synthetic equivalent of silylene (R_2Si:) under palladium-catalyzed reaction conditions.[10] In this conversion, elimination of aminoborane from the boryl(aminosilyl) palladium intermediate **E**, which is formed by oxidative addition of the Si−B bond of silylborane to the Pd(0) species, is involved as the key step (Scheme 2i). Upon looking at the generation of silylene species via the formal α-elimination of aminoborane from (aminosilyl)borane, we envisioned that silene species could be similarly generated via formal β-elimination of aminoborane from (aminomethylsilyl)boronic ester through activation of the Si−B bond to form **F** (Scheme 2ii).[11] Herein, we describe the synthesis of (aminomethylsilyl)-boronic esters and their reactivities in the presence of palladium catalysts.

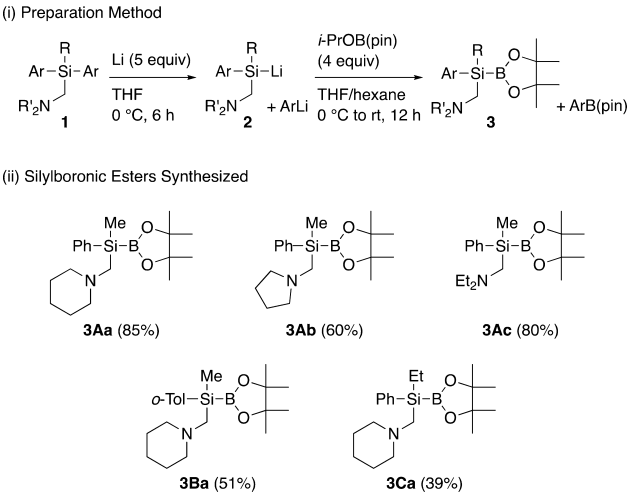
Scheme 2. Concept of Catalytic Generation of Silylene and Silene: α- and β-Elimination Reactions of Amino-Substituted Silylboronic Esters



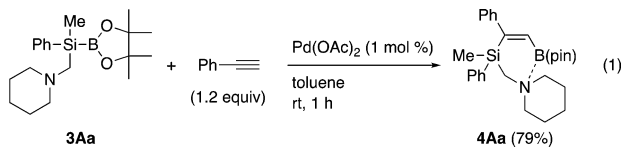
RESULTS AND DISCUSSION

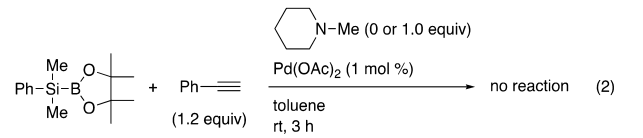
Preparation of Silylboronic Esters Bearing an *N,N*-Dialkylaminomethyl Group on Silicon. According to the procedure reported by Strohmann and co-workers,[12] silyllithium **2** bearing a *N,N*-dialkylaminomethyl group on the silicon atom was prepared from diaryldiorganosilanes **1** by reductive cleavage of the Si−Ar bond using Li (Scheme 3i). Reaction of **1** with Li (5 equiv) in THF at 0 °C gave a mixture of **2** and ArLi after 6 h. The solution was then treated with *i*-PrOB(pin) (4 equiv) in THF/hexane at 0 °C.[13] Silylboronic esters **3** and ArB(pin) were formed and then separated by distillation. Piperidino-, pyrrolidino-, and diethylamino-substituted **3Aa−c** were prepared in 60−85% yields (Scheme 3ii). (Piperidinomethyl)silane derivatives **3Ba** and **3Ca**, bearing *o*-tolyl and ethyl groups, respectively, were also synthesized. ^{11}B NMR chemical shifts of **3Aa−c**, **3Ba**, and **3Ca** (δ 35−36 ppm) indicated no coordination of the nitrogen atom to the boron center. Compounds **3Aa−c**, **3Ba**, and **3Ca** were thermally stable and storable at room temperature under an atmosphere of nitrogen for several months.

Scheme 3. Preparation of Silylboronic Esters 3 Bearing an *N,N*-Dialkylaminomethyl Group on Silicon



Reaction of 3Aa with Ethynylbenzene: Silaboration Catalyzed by Phosphine- and Isocyanide-Free Palladium. The reaction of **3Aa** with ethynylbenzene was examined in the presence of a palladium catalyst. We envisioned that if "MePhSi=CH_2" is formed through β-elimination, it is spontaneously trapped by ethynylbenzene. Indeed, **3Aa** reacted with ethynylbenzene (1.2 equiv) efficiently in toluene at room temperature in the presence of $Pd(OAc)_2$ (1 mol %) (eq 1).





However, the reaction gave (*Z*)-1-boryl-2-silylethene **4Aa** in 79% yield, indicating that silaboration of alkyne took place instead of β-elimination.[7] ^{11}B NMR chemical shifts of **4Aa** (δ 11.9 ppm) indicated coordination of the nitrogen atom to the boron center. It should be noted that the silaboration proceeded efficiently without the use of tertiary phosphines or isocyanides as ligands, which have been essential in palladium-catalyzed silaboration of alkynes with Me_2PhSi−B(pin).[7a−i,l] Indeed, silaboration of ethynylbenzene with Me_2PhSi−B(pin) did not proceed under identical conditions even in the presence of *N*-methylpiperidine (1.0 equiv) (eq 2). These results indicate that coordination of the nitrogen atom of **3Aa** to palladium promotes activation of the intramolecular Si−B bond.

Reaction of 3 in the Presence of Styrene: Palladium-Catalyzed β-Elimination Reaction. Styrene was then examined as a reaction partner of **3Aa**. The reaction was carried out in toluene at room temperature in the presence of $Pd(OAc)_2$ (1 mol %) and styrene (0.5−2.2 equiv) (entries 1−3, Table 1). In sharp contrast to the reaction with ethynylbenzene, this reaction gave aminoboronate **6a** in 46−93% yields within 5 min, indicating that β-elimination took place efficiently under the mild conditions. The reaction also afforded 1,3-dimethyl-1,3-diphenyl-1,3-disilacyclobutane (**5A**),

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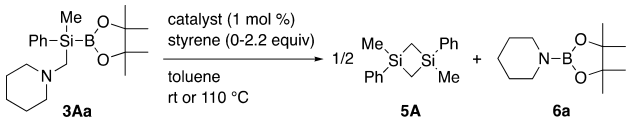
Organometallics XXXX, XXX, XXX−XXX

Table 1. Reaction of 3a in the Presence of Styrene[a]



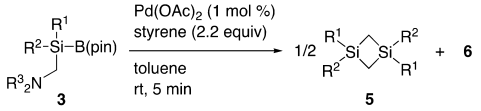
entry	catalyst	styrene (equiv)	temp (°C)	time	yield (%)[b] 5A	6a
1	$Pd(OAc)_2$	0.5	room temp	5 min	28[c]	46
2	$Pd(OAc)_2$	1.0	room temp	5 min	68[c]	85
3	$Pd(OAc)_2$	2.2	room temp	5 min	88[c]	93
4	$Pd(dba)_2$	2.2	room temp	5 min	85[c]	88
5[d]	$Pd(OAc)_2$	0	110	24 h	0	14
6	–	2.2	110	24 h	0	0
7	–	0	110	24 h	0	0
8[d]	$Ni(cod)_2$	2.2	110	24 h	0	19
9[d]	$Pt_2(dba)_3$	2.2	110	24 h	0	14
10[d]	$[RhCl(cod)]_2$	2.2	110	24 h	0	6

[a]Conditions unless specified otherwise: a catalyst (0.0010 mmol), an additive (0–0.22 mmol), and **3Aa** (0.10 mmol) were reacted in toluene (0.1 mL) at the indicated temperature. [b]^{1}H NMR yield. [c]*cis*:*trans* = 1:1. [d]5 mol % of catalyst was used.

a cyclic dimer of "MePhSi=CH_2", in 28–88% yields, while styrene remained unreacted. $Pd(dba)_2$ was equally effective as a catalyst precursor in the reaction (entry 4), indicating that the catalytic cycle involves Pd(0). In the absence of styrene, the reaction did not give **5A**, even after increasing the loading of $Pd(OAc)_2$ (5 mol %) with heating to 110 °C and a longer reaction time, although a small amount of **6a** was formed (entry 5). No reaction took place in the absence of palladium catalyst (entries 6 and 7), indicating that both palladium and styrene are essential for the formation of **5A**. No formation of **5A** was observed when using $Ni(cod)_2$, $Pt_2(dba)_3$, and $[RhCl(cod)]_2$ as catalysts (entries 8–10).

Silylboronic esters **3** were subjected to the β-elimination reaction (Table 2). The reactions of **3Aa–c**, bearing different dialkylamino groups, were complete within 5 min at room temperature to give **5A** in 73–74% yields (entries 1–3). *o*-Tolyl-substituted **3Ba** reacted efficiently to afford **5B** in high yield (96%, entry 4). The conversion of ethyl-substituted **3Ca** to give **5C** was sluggish at room temperature; it required forcing reaction conditions (50 °C, 24 h) with use of an increasing amount of styrene (4.4 equiv) (entry 5). In contrast, aminosilane **7** and hydrosilane **8** did not undergo β-elimination, even when the reaction was carried out at 50 °C using 5 mol % of $Pd(OAc)_2$ (Scheme 4). This indicated that both cleavage of the Si–B bond by Pd(0) and formation of the thermodynamically stable N–B bond are essential to achieve successful β-elimination.

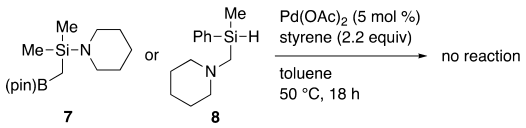
Table 2. Palladium-Catalyzed β-Elimination Reaction to Give 1,3-Disilacyclobutanes 5[a]



entry	Si–B	product	yield (%)[b]
1	**3Aa**	**5A** (R^1 = Me, R^2 = Ph)	73
2	**3Ab**	**5A** (R^1 = Me, R^2 = Ph)	73
3	**3Ac**	**5A** (R^1 = Me, R^2 = Ph)	74
4	**3Ba**	**5B** (R^1 = Me, R^2 = *o*-Tol)	96
5[c]	**3Ca**	**5C** (R^1 = Et, R^2 = Ph)	65

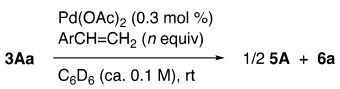
[a]Conditions unless specified otherwise: $Pd(OAc)_2$ (0.0020 mmol), styrene (0.44 mmol), and **3** (0.20 mmol) were reacted in toluene (0.2 mL) at room temperature for 5 min. [b]Isolated yield. [c]At 50 °C for 24 h with styrene (4.4 equiv).

Scheme 4. Structure Requirements for β-Elimination



The palladium-catalyzed reaction of **3Aa** was carried out using electronically and sterically different styrene derivatives as additives (Table 3). To slow down the reaction rates for tracing by ^{1}H NMR, the reaction was carried out in dilute C_6D_6 solution (ca. 0.1 M) using a smaller amount of $Pd(OAc)_2$ (0.3 mol %). When the reaction was carried out with styrene (2.2 equiv), the time required for 50% conversion of **3Aa** ($t_{1/2}$) was 54 min (entry 1). No induction period was observed (see the Supporting Information). Consumption of **3Aa** and formation of **5A** and **6a** proceeded in a parallel manner, and no intermediates were observed (see the Supporting Information). The conversion yields of **5A** and **6a** after 60 min (43% and 71%, respectively) indicated that the formation of **5A** from the silene intermediate was less efficient than the reaction under the optimized conditions (88% and 93%, respectively; entry 3 in Table 1). Styrenes having electron-rich aryls led to slower reactions (entries 2 and 3), whereas rate acceleration was observed in the reactions with electron-deficient styrenes (entries 4 and 5). Sterically demanding *o*-methylstyrene resulted in a slow reaction (entry 6). It is noted that slow conversion of **3Aa** resulted in a decrease in conversion yield of

Table 3. Reaction of 3Aa in the Presence of Electronically and Sterically Different Styrenes[a]



entry	Ar	*n*	$t_{1/2}$ (min)[b]	conversn yield (%)[c] 5A	6a
1	Ph	2.2	54	43	71
2	4-$MeOC_6H_4$	2.2	>300	23	58
3	4-MeC_6H_4	2.2	190	30[d]	61[d]
4	4-$CF_3C_6H_4$	2.2	11	46[e]	74[e]
5	4-ClC_6H_4	2.2	<5	57	81
6	2-MeC_6H_4	2.2	>300	17	46
7	Ph	4.4	<5	68	84
8	Ph	6.5	<5	71[f]	87[f]

[a]Conditions: $Pd(OAc)_2$ (0.00021 mmol), styrene (0.154–0.455 mmol), **3Aa** (0.070 mmol), and dibenzyl ether (0.10 mmol, internal standard) were reacted in C_6D_6 (0.7 mL) at room temperature. [b]The time required for 50% conversion of **3Aa**. [c]Conversion yield after 60 min. [d]Conversion yield after 55 min. [e]Conversion yield after 45 min. [f]Conversion yield after 30 min.

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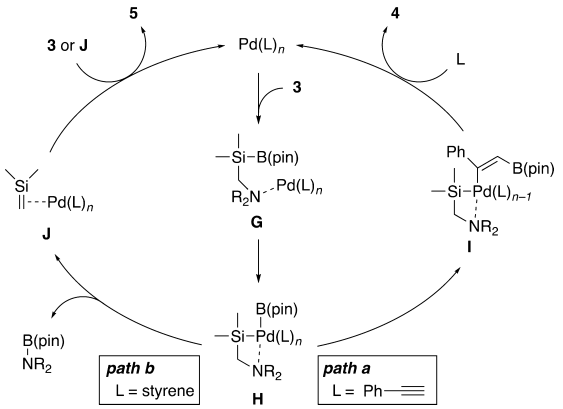
Organometallics XXXX, XXX, XXX–XXX

5A after 60 min (entries 2, 3, and 6), indicating that a high concentration of silene species leads to the more efficient formation of **5A**. Indeed, when the reaction was carried out with an increased amount of styrene (4.4 and 6.5 equiv), $t_{1/2}$ was reduced (<5 min) and the conversion yield of **5A** was improved (entries 7 and 8). On the basis of these results, we assume that styrene coordinates to the palladium center as a spectator ligand, which stabilizes a (η^2-silene)Pd intermediate.[14]

A possible mechanism for the palladium-catalyzed reaction of **3** is shown in Scheme 5. The first step is oxidative addition of

Scheme 5. Possible Mechanism



the Si–B bond of **3** to Pd(0) to give **H**, in which the bond activation is facilitated by preceding coordination of the nitrogen atom of **3** to the palladium center (**G**). In the reaction with ethynylbenzene, insertion of the C–C triple bond into the Pd–B bond takes place in a regio- and stereoselective manner to afford **I**, which undergoes reductive elimination to give **4** and Pd(0) (path a).[15] In contrast, the reaction in the presence of styrene leads to β-amino elimination, which is followed by reductive elimination of aminoborane to give (η^2-silene)Pd complex **J** (path b). The following reaction of **J** with either **3** or **J** results in the formation of silene dimer **5**. Dissociation of free silene from **J** followed by dimerization to form **5** is unlikely because no products derived from styrene are formed, even though styrene is one of the typical trapping reagents of free silene.[16,17]

■ CONCLUSION

We synthesized silylboronic esters bearing a *N*,*N*-dialkylaminomethyl group on the silicon atoms and successfully established the palladium-catalyzed silaboration of ethynylbenzene and the β-elimination reaction in the presence of styrene. Remarkably, the latter reaction proceeds efficiently under mild conditions (within 5 min at room temperature) to give silene dimers. We found that the use of styrene as a ligand is essential for the generation of silene species. Our findings open up new possibilities for the development of new catalytic reactions involving silene intermediates. Application of the catalytic system described here to the synthesis of new organosilicon compounds is underway in our laboratory.

■ EXPERIMENTAL SECTION

General Considerations. Column chromatography was performed with Ultra Pure Silica Gel (SILICYCLE, pH 7.0, 40–63 μm, 60 Å). Gas chromatography (GC) was performed with a Shimadzu GC-2014 instrument with Agilent J&W GC Column DB-1 (i.d. 0.32 mm × 15 m). ^{1}H NMR spectra were recorded on a Varian 400-MR (399.89 MHz) spectrometer. ^{13}C NMR spectra were recorded on a Varian 400-MR (100.55 MHz) spectrometer. ^{11}B NMR spectra were recorded on a Varian 400-MR (128.30 MHz) spectrometer. ^{1}H NMR data were reported as follows: chemical shifts in ppm downfield from tetramethylsilane, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet), coupling constant (J), and integration. ^{13}C and ^{11}B NMR data were reported in ppm downfield from tetramethylsilane (^{13}C) and BF_3·OEt_2 (^{11}B), respectively. High-resolution mass spectra were recorded on JEOL JMS-MS700 (EI) or Thermo Scientific Exactive (MALDI, APCI) spectrometers.

Materials. $Pd(OAc)_2$ (Aldrich) and $Ni(cod)_2$ (Strem) were used as received from commercial sources. $Pd(dba)_2$,[18] $Pt_2(dba)_3$,[19] and $[RhCl(cod)]_2$[20] were synthesized by the method reported previously. Toluene (Kanto) and tetrahydrofuran (THF, Wako) were degassed by purging with argon (15 min + 10 min) and then dried by The Ultimate Solvent System (GlassContour). 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (*i*-PrOB(pin)) was synthesized by the reported method.[21] Styrene (Wako), 4-methoxystyrene (Wako), 4-methylstyrene (TCI), 4-chlorostyrene (Wako), and 2-methylstyrene (TCI) were distilled prior to use. Compounds **1** were synthesized through a reaction of secondary amines with alkyldiaryl(chloromethyl)silanes.[22] **7** was prepared via iridium-catalyzed C–H borylation of chlorotrimethylsilane.[22] **8** was synthesized through a reaction of piperidine with (chloromethyl)methylphenylsilane.[22]

Preparation of 3 (Scheme 3). Compounds **3** were synthesized by the reaction of *i*-PrOB(pin) with silyllithiums **2** according to the reported procedure.[13] Silyl lithiums **2** were generated from **1** according to the method reported by Strohmann.[12] A typical procedure is given for the preparation of **3Aa**.

*2-[Methylphenyl(piperidinomethyl)silyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3Aa**).* A 100 mL two-necked, round-bottomed flask, equipped with a magnetic stirring bar, was charged with cut lithium (nacalai, 0.69 g, 100 mmol). The flask was evacuated and backfilled with argon. THF (15 mL) and methyldiphenyl(piperidinomethyl)silane (**1Aa**; 5.91 g, 20 mmol) were placed in the flask. After a color change of the solution (colorless to pale yellow), the mixture was cooled to 0 °C and stirred for 6 h. The solution color changed during the reaction (red, green, and then black). An another 100 mL two-necked, round-bottomed flask, equipped with a magnetic stirring bar, was charged with *i*-PrOB(pin) (1.49 g, 80 mmol) and hexane (17 mL). The flask was cooled to 0 °C by ice-water bath, and the black solution including silyl lithium was added slowly to the flask. The mixture as stirred for 12 h at room temperature. Volatiles were removed in vacuo, and the residue was filtered through Celite. **3Aa** (5.85 g, 85%) was obtained as a colorless liquid after bulb-to-bulb distillation (120–130 °C/0.17 mmHg). Data for **3Aa** are as follows. ^{1}H NMR (400 MHz, C_6D_6): δ 7.86–7.91 (m, 2H), 7.23–7.29 (m, 2H), 7.17–7.22 (m, 1H), 2.37–2.52 (m, 4H), 2.42 [d (AB pattern), J = 14.0 Hz, 1H], 2.33 [d (AB pattern), J = 14.0 Hz, 1H], 1.50–1.58 (m, 4H), 1.24–1.33 (m, 2H), 1.07 (s, 12H), 0.61 (s, 3H). ^{13}C NMR (101 MHz, C_6D_6): δ 138.3, 135.1, 129.0, 128.1, 83.5, 58.7, 50.4, 26.8, 25.06 [CH_3 of B(pin), 2C], 25.01 [CH_3 of B(pin), 2C], 24.3, −4.9. ^{11}B NMR (128 MHz, C_6D_6): δ 35.6. HRMS (MALDI): m/z calcd for $C_{19}H_{33}BNO_2Si^+$ [M + H]$^+$, 346.2368; found, 346.2377.

*2-[Methylphenyl(pyrrolidinomethyl)silyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3Ab**).* According to the procedure given for **3Aa**, methyldiphenyl(pyrroridinomethyl)silane (**1Ab**; 2.81 g, 10 mmol), lithium (0.35 g, 50 mmol), and *i*-PrOB(pin) (0.75 g, 40 mmol) were reacted. **3Ab** (1.99 g, 60%) was obtained as a colorless liquid after bulb-to-bulb distillation (120–130 °C/0.17 mmHg). Data for **3Ab** are as follows. ^{1}H NMR (400 MHz, C_6D_6): δ 7.86–7.92 (m, 2H), 7.23–7.29 (m, 2H), 7.16–7.22 (m, 1H), 2.47–2.58 (m, 4H), 2.52 [d (AB pattern), J = 14.0 Hz, 1H], 2.47 [d (AB pattern), J = 14.0 Hz, 1H], 1.58–1.67 (m, 4H), 1.06 (s, 12H), 0.63 (s, 3H). ^{13}C NMR (101 MHz, C_6D_6): δ 138.1, 135.1, 129.0, 128.1, 83.4, 58.1, 46.0, 25.03 [CH_3 of B(pin), 2C], 24.97 [CH_3 of B(pin), 2C], 24.5, −5.0. ^{11}B NMR (128 MHz, C_6D_6): δ 35.7. HRMS (MALDI): m/z calcd for $C_{18}H_{31}BNO_2Si^+$ [M + H]$^+$, 332.2212; found, 332.2221.

*2-[(N,N-diethylaminomethyl)methylphenylsilyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3Ac**).* According to the procedure given

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Organometallics XXXX, XXX, XXX–XXX

for **3Aa**, (*N*,*N*-diethylaminomethyl)methyldiphenylsilane (**1Ac**; 2.83 g, 10 mmol), lithium (0.35 g, 50 mmol), and *i*-PrOB(pin) (0.75 g, 40 mmol) were reacted. **3Ac** (2.67 g, 80%) was obtained as a colorless liquid after by bulb-to-bulb distillation (120−130 °C/0.17 mmHg). Data for **3Ac** are as follows. ^{1}H NMR (400 MHz, C_6D_6): δ 7.86−7.91 (m, 2H), 7.23−7.30 (m, 2H), 7.17−7.23 (m, 1H), 2.45−2.61 (m, 4H), 2.46 [d (AB pattern), J = 14.4 Hz, 1H], 2.38 [d (AB pattern), J = 14.4 Hz, 1H], 1.06 (s, 12H), 0.99 (t, J = 7.2 Hz, 6H), 0.62 (s, 3H). ^{13}C NMR (101 MHz, C_6D_6): δ 138.4, 135.1, 129.0, 128.1, 83.4, 50.4, 44.1, 25.08 [CH_3 of B(pin), 2C], 25.00 [CH_3 of B(pin), 2C], 12.1, −5.1. ^{11}B NMR (128 MHz, C_6D_6): δ 35.7. HRMS (MALDI): m/z calcd for $C_{18}H_{33}BNO_2Si^+$ [M + H]$^+$, 334.2368; found, 334.2375.

*2-[Methyl(piperidinomethyl)-o-tolylsilyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3Ba**).* According to the procedure given for **3Aa**, methyl(piperidinomethyl)di-*o*-tolylsilane (**1Ba**; 3.24 g, 10 mmol), lithium (0.35 g, 50 mmol), and *i*-PrOB(pin) (0.75 g, 40 mmol) were reacted. After bulb-to-bulb distillation (120−130 °C/0.17 mmHg), **3Ba** was obtained with a small amount of unreacted **1Ba** (2.16 g, **3Ba**:**1Ba** = 85:15). The yield of **3Ba** was estimated as 51%. Data for **3Ba** are as follows. ^{1}H NMR (400 MHz, C_6D_6): δ 7.88−7.96 (m, 1H), 7.07−7.21 (m, 3H), 2.61 (s, 3H), 2.50 [d (AB pattern), J = 14.0 Hz, 1H], 2.38−2.50 (m, 4H), 2.39 [d (AB pattern), J = 14.0 Hz, 1H], 1.47−1.57 (m, 4H), 1.24−1.36 (m, 2H), 1.06 (s, 12H), 0.64 (s, 3H). ^{13}C NMR (101 MHz, C_6D_6): δ 144.1, 136.7, 135.7, 129.8, 129.4, 125.4, 83.4, 58.7, 49.9, 26.8 [CH_3 of B(pin), 2C], 26.7 [CH_3 of B(pin), 2C], 25.0, 24.4, 23.4, −4.1. ^{11}B NMR (128 MHz, C_6D_6): δ 35.7. HRMS (MALDI): m/z calcd for $C_{20}H_{35}BNO_2Si^+$ [M + H]$^+$, 360.2525; found, 360.2531.

*2-[Ethylphenyl(piperidinomethyl)silyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3Ca**).* According to the procedure given for **3Aa**, ethyldiphenyl(piperidinomethyl)silane (**1Ca**; 1.54 g, 5 mmol), lithium (0.17 g, 25 mmol), and *i*-PrOB(pin) (3.7 g, 20 mmol) were reacted. **3Ca** (0.70 g, 39%) was obtained as a colorless liquid after bulb-to-bulb distillation (120−130 °C/0.17 mmHg). Data for **3Ca** are as follows. ^{1}H NMR (400 MHz, C_6D_6): δ 7.89−7.95 (m, 2H), 7.24−7.31 (m, 2H), 7.16−7.24 (m, 1H), 2.36−2.53 (m, 4H), 2.44 [d (AB pattern), J = 14.0 Hz, 1H], 2.40 [d (AB pattern), J = 14.0 Hz, 1H], 1.49−1.51 (m, 4H), 1.23−1.33 (m, 5H), 1.10−1.15 (m, 2H), 1.09 (s, 12H). ^{13}C NMR (101 MHz, C_6D_6): δ 137.4, 135.5, 129.0, 128.0, 83.4, 58.8, 48.8, 26.8, 25.04 [CH_3 of B(pin), 2C], 25.03 [CH_3 of B(pin), 2C], 24.3, 8.8, 5.1. ^{11}B NMR (128 MHz, C_6D_6): δ 35.7. HRMS (MALDI): m/z calcd for $C_{20}H_{35}BNO_2Si^+$ [M + H]$^+$, 360.2525; found, 360.2532.

Reaction of 3Aa with Ethynylbenzene (Eq 1). In a glovebox, a 4 mL screw cap vial, equipped with a magnetic stirring bar, was charged with $Pd(OAc)_2$ (1.1 mg, 0.0047 mmol) and **3Aa** (173 mg, 0.50 mmol). Ethynylbenzene (63 mg, 0.62 mmol) and toluene (0.5 mL) were added, and the resulting mixture was stirred at room temperature for 1 h. After removal of the volatiles in vacuo, the residue was purified by bulb-to-bulb distillation (110−130 °C/0.17 mmHg). (*Z*)-1-[Methylphenyl(piperidinomethyl)silyl]-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-phenylethene (**4Aa**; 176 mg, 79%) was obtained as a viscous liquid. Data for **4Aa** are as follows. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65−7.73 (m, 2H), 7.29−7.41 (m, 3H), 7.16−7.26 (m, 4H), 7.08−7.16 (m, 2H), 2.84−3.04 (m, 4H), 2.72 [d (AB pattern), J = 14.4 Hz, 1H], 2.68 [d (AB pattern), J = 14.4 Hz, 1H], 1.42−1.62 (m, 6H), 1.23 (s, 12H), 0.49 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 157.5 (broad, *C*−B), 145.4, 137.5, 134.6, 129.1, 128.0, 127.8, 126.2, 125.8, 80.4, 54.1, 41.7, 27.4, 27.1, 23.2, 20.3, −3.2. ^{11}B NMR (128 MHz, $CDCl_3$): δ 11.9. HRMS (ESI): m/z calcd for $C_{27}H_{39}BNO_2Si$ [M + H]$^+$, 448.2838; found, 448.2828.

Reaction of 3a in the Presence of Styrene (Table 1). *Procedure for the Reaction at Room Temperature (Entries 1−4, Table 1).* In a glovebox, a 4 mL screw cap vial, equipped with a magnetic stirring bar, was charged with $Pd(OAc)_2$ (0.0010 mmol), toluene (0.1 mL), additive (0.05−0.22 mmol), dibenzyl ether (20 mg, 0.10 mmol, internal standard), and **3Aa** (0.10 mmol). The mixture was stirred at room temperature for 5 min. The resulting mixture was analyzed by ^{1}H NMR to determine the yield of **5A** and **6a**.

Procedure for the Reaction at 110 °C (Entries 5−10, Table 1). In a glovebox, a glass tube (outside diameter 20 mm) having PTFE stopcock (J. Young), equipped with a magnetic stirring bar, was charged with a catalyst precursor (0.0010 mmol for metal), toluene (0.1 mL), additive (0 or 0.22 mmol), dibenzyl ether (20 mg, 0.10 mmol, internal standard), and **3Aa** (0.10 mmol). The tube was sealed with a stopcock and was taken out from the glovebox. The mixture was stirred at 110 °C for 24 h by a heating magnetic stirrer with an aluminum heating block (hole size 21 mm diameter × 33 mm depth). The resulting mixture was analyzed by ^{1}H NMR to determine the yield of **5A** and **6a**. For 1,3-dimethyl-1,3-diphenyl-1,3-disilacyclobutane (**5A**), the structure was confirmed by comparison of the ^{1}H and ^{13}C NMR data with an authentic sample, which was prepared by treatment of (chloromethyl)methylphenylsilyl chloride with Mg.[23] In all reactions that gave **5A** (entries 1−4), **5A** was obtained as a *cis*/*trans* mixture (1/1). The isomers could be separated by HPLC (nacalai COSMOSIL 5SL-II, 20 × 250 mm, 10 mL/min, UV 254 nm, eluent hexane). Data for *cis*-**5A** are as follows. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54−7.60 (m, 4H), 7.32−7.38 (m, 6H), 0.66−0.74 (m, 2H), 0.59 (s, 6H), 0.42−0.49 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 139.7, 133.3, 129.1, 127.8, 2.3, 1.0. HRMS (EI): m/z calcd for $C_{16}H_{20}Si_2^+$ [M]$^+$ 268.1098; found, 268.1091. Data for *trans*-**5A** are as follows. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62−7.69 (m, 4H), 7.38−7.46 (m, 6H), 0.57 (s, 4H), 0.46 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 139.9, 133.3, 129.1, 127.9, 2.0, 1.3. HRMS (EI): m/z calcd for $C_{16}H_{20}Si_2^+$ [M]$^+$, 268.1098; found, 268.1098. Data for 2-piperidino-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**6a**) are as follows.[24] ^{1}H NMR (400 MHz, C_6D_6): δ 3.14−3.26 (m, 4H), 1.30−1.42 (m, 6H), 1.14 (s, 12H). ^{11}B NMR (128 MHz, C_6D_6): δ 24.0.

Palladium-Catalyzed Reaction of 3 To Give 1,3-Disilacyclobutanes 5 (Table 2). *General Procedure.* In a glovebox, a 4 mL screw cap vial, equipped with a magnetic stirring bar, was charged with $Pd(OAc)_2$ (0.01 M solution in toluene, 0.20 mL), styrene (0.44 mmol), and **3** (0.20 mmol). The mixture was stirred at room temperature for 5 min. The resulting mixture was analyzed by ^{1}H NMR to determine the *cis*/*trans* ratio. **5** was purified by column chromatography on silica gel.

*Reaction of **3Aa** To Give **5A** (Entry 1, Table 2).* According to the general procedure, **3Aa** (70 mg, 0.20 mmol) was reacted in toluene (0.2 mL) at room temperature in the presence of $Pd(OAc)_2$ (0.0020 mmol) and styrene (46 mg, 0.44 mmol). **5A** (20 mg, 73%) was obtained as a *cis*/*trans* mixture (1/1) after column chromatography on silica gel (eluent hexane/Et_2O = 10/1). For characterization data of *cis*- and *trans*-**5A**, see above.

*Reaction of **3Ab** To Give **5A** (Entry 2, Table 2).* According to the general procedure, **3Ab** (68 mg, 0.20 mmol) was reacted in toluene (0.2 mL) at room temperature in the presence of $Pd(OAc)_2$ (0.0020 mmol) and styrene (46 mg, 0.44 mmol). **5A** (20 mg, 73%) was obtained as a *cis*/*trans* mixture (1/1) after column chromatography on silica gel (eluent hexane/Et_2O 10/1). For characterization data of *cis*- and *trans*-**5A**, see above.

*Reaction of **3Ac** To Give **5A** (Entry 3, Table 2).* According to the general procedure, **3Ac** (65 mg, 0.20 mmol) was reacted in toluene (0.2 mL) at room temperature in the presence of $Pd(OAc)_2$ (0.0020 mmol) and styrene (46 mg, 0.44 mmol). **5A** (20 mg, 74%) was obtained as a *cis*/*trans* mixture (1/1) after column chromatography on silica gel (eluent hexane/Et_2O 10/1). For characterization data of *cis*- and *trans*-**5A**, see above.

*Reaction of **3Ba** To Give 1,3-Dimethyl-1,3-di-o-tolyl-1,3-disilacyclobutane (**5B**) (Entry 4, Table 2).* According to the general procedure, **3Ba** (**3Ba**:**1Ba** = 85:15, 70 mg, 0.17 mmol of **3Ba**) was reacted in toluene (0.2 mL) at room temperature in the presence of $Pd(OAc)_2$ (0.0020 mmol) and styrene (46 mg, 0.44 mmol). **5B** (24 mg, 96%) was obtained as a *cis*/*trans* mixture (1/1) by column chromatography on silica gel (eluent hexane/CH_2Cl_2 10/1). The isomers could be separated by HPLC (nacalai COSMOSIL 5SL-II, 20 × 250 mm, 10 mL/min, UV 254 nm, eluent: hexane). Data for *cis*-**5B** are as follows. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50−7.56 (m, 2H), 7.25 (dt, J = 7.6, 1.6 Hz, 2H), 7.10−7.18 (m, 4H), 2.46 (s, 6H), 0.75−0.84 (m, 2H), 0.55−0.64 (m, 2H), 0.55 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.1, 138.1, 134.1, 129.4 (two nonequivalent carbons overlapped), 124.9, 22.3, 3.7, 1.6. HRMS (EI): m/z calcd for

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Organometallics XXXX, XXX, XXX−XXX

$C_{17}H_{21}Si_2^+$ [M − CH_3]$^+$, 281.1176; found, 281.1180. Data for *trans*-**5B** are as follows. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, J = 7.6 Hz, 2H), 7.32 (dt, J = 7.6, 1.2 Hz, 2H), 7.17−7.27 (m, 4H), 2.51 (s, 6H), 0.69 (s, 4H), 0.37 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.4, 137.9, 134.3, 129.5 (two nonequivalent carbons overlapped), 124.9, 22.5, 3.2, 2.2. HRMS (EI): m/z calcd for $C_{17}H_{21}Si_2^+$ [M − CH_3]$^+$, 281.1176; found, 281.1182.

Reaction of ***3Ca*** *To Give 1,3-Diethyl-1,3-diphenyl-1,3-disilacyclobutane (****5C****) (Entry 5, Table 2).* According to the general procedure, **3Ca** (71 mg, 0.20 mmol) was reacted in toluene (0.2 mL) at 50 °C for 24 h in the presence of $Pd(OAc)_2$ (0.0020 mmol) and styrene (92 mg, 0.88 mmol). **5C** (19 mg, 65%) was obtained as a *cis*/*trans* mixture (1/1) by column chromatography on silica gel (eluent hexane/CH_2Cl_2 10/1). The isomers could be separated by HPLC (nacalai COSMOSIL 5SL-II, 20 × 250 mm, 10 mL/min, UV 254 nm, eluent: hexane). Data for *cis*-**5C** are as follows. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48−7.55 (m, 4H), 7.27−7.37 (m, 6H), 1.02−1.12 (m, 6H), 0.93−1.02 (m, 4H), 0.44−0.58 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 138.6, 133.6, 129.0, 127.7, 9.1, 7.2, −2.3. HRMS (EI): m/z calcd for $C_{16}H_{19}Si_2^+$ [M − CH_2CH_3]$^+$, 267.1020; found, 267.1018. Data for *trans*-**5C** are as follows. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60−7.67 (m, 4H), 7.37−7.45 (m, 6H), 0.88−0.95 (m, 6H), 0.79−0.87 (m, 4H), 0.51 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 138.8, 133.6, 129.1, 127.8, 9.3, 7.1, −2.3. HRMS (EI): m/z calcd for $C_{17}H_{21}Si_2^+$ [M − CH_2CH_3]$^+$, 267.1020; found, 267.1017.

Structure Requirements for β-Elimination (Scheme 4). *Reaction of* ***7****.* According to the general procedure given for Table 2, **7** (57 mg, 0.20 mmol) was reacted in toluene (0.2 mL) at 50 °C in the presence of $Pd(OAc)_2$ (0.010 mmol) and styrene (46 mg, 0.44 mmol). No reaction took place after 18 h.

Reaction of ***8****.* According to the general procedure given for Table 2, **8** (44 mg, 0.20 mmol) was reacted in toluene (0.2 mL) at 50 °C in the presence of $Pd(OAc)_2$ (0.010 mmol) and styrene (46 mg, 0.44 mmol). No reaction took place after 18 h.

Reaction of 3Aa in the Presence of Electronically and Sterically Different Styrenes (Table 3). In a glovebox, a 4 mL screw cap vial was charged with $Pd(OAc)_2$ solution (0.0010 M in C_6D_6, 0.21 mL), styrene (0.050−0.22 mmol), dibenzyl ether (19.8 mg, 0.10 mmol, internal standard), C_6D_6 (0.49 mL), and **3Aa** (0.070 mmol). The mixture was transferred into a NMR tube having a PTFE stopcock (J. Young). The reaction was monitored by ^{1}H NMR once every 5 min. For the time course plot for consumption of **3Aa** and formation of **5A** and **6a**, see the Supporting Information.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.7b00695.

Preparation of **1**, **7**, and **8**, time course in the reaction of **3Aa**, and NMR spectra of new compounds and key known compounds (PDF)

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Notes

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