



# Synthesis and structures of *o*-(dihydrosilyl)(dimesitylboryl)benzenes

Atsushi Kawachi\*, Hiroshi Morisaki, Masatoshi Zaima, Takuya Teranishi, Yohsuke Yamamoto

Department of Chemistry, Graduate School of Science, Hiroshima University, Kagamiyama 1-3-1, Higashi-Hiroshima 739-8526, Japan

## ARTICLE INFO

### Article history:

Received 27 April 2010

Received in revised form

31 May 2010

Accepted 3 June 2010

Available online 15 June 2010

### Keywords:

Dimethoxysilane

Dihydrosilane

Triarylborane

Reduction

## ABSTRACT

*O*-(Dihydrosilyl)(dimesitylboryl)benzenes **1** were prepared in 6 steps. *o*-Dibromobenzene was mono-lithiated with *n*-BuLi and reacted with chloro(dimethoxy)silanes to afford *o*-C<sub>6</sub>H<sub>4</sub>(Br)[SiR(OMe)<sub>2</sub>] (**2**) (R = Ph, Me). Bromine–lithium exchange between **2** and *tert*-BuLi produced *o*-C<sub>6</sub>H<sub>4</sub>(Li)[SiR(OMe)<sub>2</sub>] (**3**), which were reacted with fluoro(dimesityl)borane to give *o*-C<sub>6</sub>H<sub>4</sub>(BMe<sub>2</sub>)[SiR(OMe)<sub>2</sub>] (**4**). Reduction of **4** with LiAlH<sub>4</sub> in THF yielded [*o*-C<sub>6</sub>H<sub>4</sub>(BMe<sub>2</sub>H)(SiRH<sub>2</sub>)]<sup>−</sup>Li<sup>+</sup>(thf)<sub>*n*</sub> (**9**). Treatment of **9** with BF<sub>3</sub>·OEt<sub>2</sub> afforded the target compounds **1**. The structures of **1** were determined by NMR spectroscopy and X-ray crystallographic analysis.

© 2010 Elsevier B.V. All rights reserved.

## 1. Introduction

Reactions of hydrosilanes in the presence of Lewis acids are extensively studied in organic chemistry and widely used in organic transformations. Recently much attention has been paid to boron Lewis acids, especially B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> [1]. Incorporation of a boron Lewis acid moiety into a hydrosilane framework is expected to make a synergetic effect on reactivity of hydrosilanes [2].

We have recently prepared *o*-(dimesitylboryl)(dimethylsilyl)benzene (**I**), in which a hydrosilane moiety and an arylborane moiety are linked through an *o*-phenylene skeleton [3a]. The hydrosilane **I** readily underwent the dehydrogenative condensation reaction with alcohols to produce alkoxysilanes **II** in moderate to excellent yields (Scheme 1). It is plausible that the Si–H bond is activated by the *ortho*-boryl group in an electrophilic manner and thus the silicon center tends to be receptive toward nucleophiles. Reaction of **I** with H<sub>2</sub>O afforded *o*-[(hydroxy)silyl](dimesitylboryl)benzene **III** (R = H), which underwent the intramolecular cyclization to give 3,4-benzo-1,2,5-oxasilaboracyclopentene **IV** and mesitylene by the boron–aryl bond cleavage [3b].

In order to get further insight into reaction modes of *o*-(boryl)(silyl)benzene compounds, we turned our attention to dihydrosilyl derivatives, which were expected to be more labile than **I**. On searching for synthetic routes to *o*-(boryl)(dihydrosilyl)benzenes, SciFinder Scholar database [4] showed no example of *o*-(boryl)

(dihydrosilyl)arenes. Furthermore, Cambridge Crystallographic database [5] emphasized the structural novelty of *o*-(boryl)(dihydrosilyl)benzenes because no hits were found for dihydrosilanes linked with a boryl group via *o*-phenylene, ethylene, ethynylene, and ethynylene units. This situation encouraged us to report our results on the unique synthetic approach to *o*-(dimesitylboryl)(phenylsilyl)benzene (**1a**) and *o*-(dimesitylboryl)(methylsilyl)benzene (**1b**) and their crystal structures prior to studies on reactivity of **1a** and **1b**.

## 2. Results and discussion

### 2.1. Synthesis of *o*-(dihydrosilyl)(dimesitylboryl)benzenes

#### 2.1.1. *o*-Bromo(dimethoxysilyl)benzenes

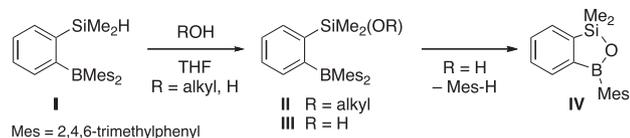
(*o*-Bromophenyl)lithium was prepared by bromine–lithium exchange between *o*-dibromobenzene and *n*-BuLi in THF–Et<sub>2</sub>O at –110 °C according to the reported procedure (Scheme 2) [6]. The phenyllithium was allowed to react with chloro(dimethoxy)phenylsilane and chloro(dimethoxy)methylsilane at –110 °C to give *o*-bromo[(dimethoxy)phenylsilyl]benzene (**2a**) in 87% yield and *o*-bromo[(dimethoxy)methylsilyl]benzene (**2b**) in 80% yield, respectively.

#### 2.1.2. *o*-(Dimesitylboryl)(dimethoxysilyl)benzenes

[*o*-(Dimethoxysilyl)phenyl]lithiums **3**, the key reactive intermediates in the present transformations, were prepared in a manner similar to the procedure by which we previously prepared [*o*-(fluorodimethylsilyl)phenyl]lithium [7]. Treatment of

\* Corresponding author.

E-mail address: [kawachi@sci.hiroshima-u.ac.jp](mailto:kawachi@sci.hiroshima-u.ac.jp) (A. Kawachi).



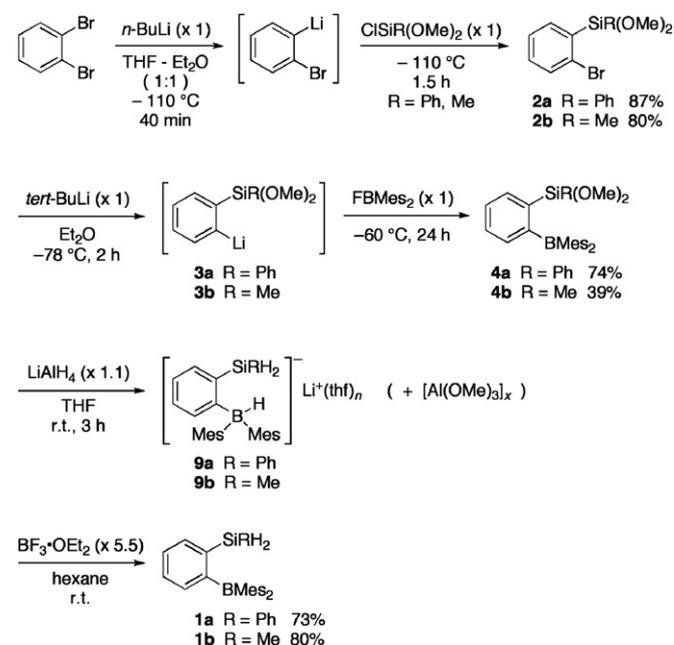
Scheme 1.

bromobenzenes **2** with *tert*-BuLi (1 mol equiv.) in Et<sub>2</sub>O at –78 °C for 2 h produced **3**, which were reacted with fluoro(dimesityl)borane at –60 °C for 24 h to provide *o*-(dimesitylboryl)(dimethoxysilyl)benzenes **4a** in 74% yield and **4b** in 39% yield (Scheme 2).

The choice of methoxy functionality is a key point for obtaining stable silicon-bifunctionalized (*o*-silylphenyl)lithiums available to the following reactions with electrophiles. [*o*-[Difluoro(methyl)silyl]phenyl]lithium (**5**) prepared under the same reaction conditions readily underwent dimerization even at –78 °C to give 9,10-disila-9,10-dihydroanthracene **6** prior to the reaction with fluoro(dimesityl)borane. [*o*-(methylsilyl)phenyl]lithium (**7**) was also afforded the dimerized product **8** under the same reaction conditions [8] (Chart 1).

### 2.1.3. *o*-(dihydrosilyl)(dimesitylboryl)benzenes

Reduction of *o*-dimethoxysilyl(boryl)benzenes **4** with LiAlH<sub>4</sub> in THF provided lithium borohydrides **9** instead of the neutral compounds **1**: the boryl group as well as the dimethoxysilyl group was reacted with a hydride (Scheme 1) [9]. (Dimethoxy)phenylsilyl derivative **4a** was exposed to LiAlH<sub>4</sub> (1 mol equiv.) in THF at room temperature. Without conventional aqueous workup, which could hydrolyze the dihydrosilyl moiety, the reaction mixture was concentrated in vacuo to yield highly viscous oil of lithium borohydride **9a**. The high viscosity of the reaction mixture **9a** might be attributed to the incorporation of the resulting aluminum methoxide [Al(OMe)<sub>3</sub>]<sub>x</sub>, which was present in some polymeric form [9]. Although **9a** could not be isolated in a pure form, characteristics of a lithium borohydride were confirmed by NMR spectroscopy. The <sup>11</sup>B NMR spectra exhibited a doublet at δ –15.4 (<sup>1</sup>J<sub>B–H</sub> = 71 Hz). The shift and the coupling constant are consistent with those for borohydrides reported so far [9]. The <sup>7</sup>Li NMR spectra showed



Scheme 2.

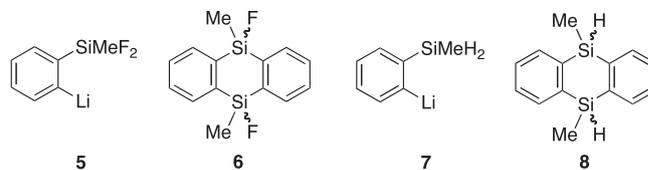


Chart 1.

a peak at δ –3.7, falling in the region observed for lithium borate species [10]. In the <sup>1</sup>H NMR spectra, however, a peak for the B–H moiety was not observed perhaps due to quadrupole relaxations of <sup>10</sup>B (*I* = 3) and <sup>11</sup>B (*I* = 3/2) nuclei [10]. In the IR spectra, **9a** displayed a broad absorption around 2120 cm<sup>–1</sup>, which makes a striking contrast to a sharp absorption arising from the Si–H stretching in **1a** at 2168 cm<sup>–1</sup> [11]. Thus, this absorption may be attributed to both of the Si–H bond and B–H bond stretchings [9].

Conversion of lithium borohydride **9a** into boron **1a** was successful by using BF<sub>3</sub>·OEt<sub>2</sub>. Treatment of **9a** with BF<sub>3</sub>·OEt<sub>2</sub> (5 mol equiv.) in hexane for 2 h produced **1a** in 73% yield (two steps from **4a**), as shown in Scheme 2. Similarly, **4b** afforded **1b** via **9b** in 80% yield (two steps from **4b**).

### 2.1.4. Spectroscopic and crystallographic analyses of *o*-(dihydrosilyl)(dimesitylboryl)benzenes

The spectroscopic data of **1a** are as follows. The <sup>11</sup>B chemical shift (δ 75) falls in the region for typical triarylboranes [10]. The <sup>29</sup>Si resonance was observed at δ –34.5 with the <sup>1</sup>J(Si–H) coupling constant of 202 Hz, which is almost consistent with that of Ph<sub>2</sub>SiH<sub>2</sub>

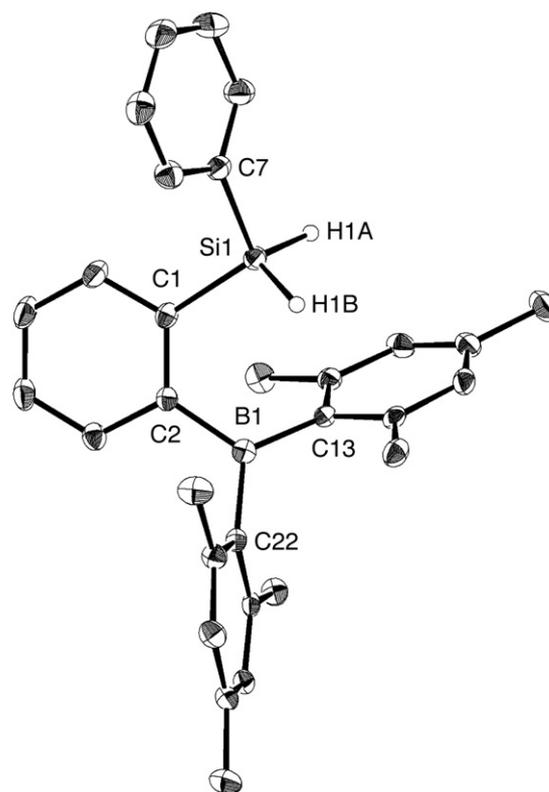
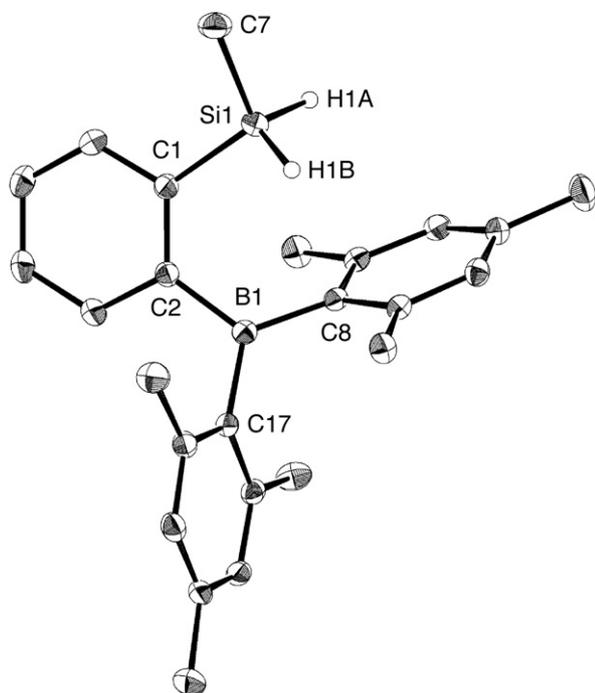


Fig. 1. Molecular structure of **1a** with thermal ellipsoids at the 30% probability level. Hydrogen atoms except for those attached to the silicon atom are omitted for clarity. Selected bond lengths (Å) and angles (°): Si1–H1A, 1.42(2); Si1–H1B, 1.40(2); Si1–C1, 1.882(2); Si1–C7, 1.871(2); B1–C2, 1.570(3); B1–C13, 1.574(3); B1–C22, 1.579(3); Si1–C2, 123.44(15); C1–C2–B1, 124.04(17); C2–B1–C13, 120.10(18); C13–B1–C22, 122.19(18); C22–B1–C2, 117.68(17); Si1–C1–C2–B1, –14.1(3).



**Fig. 2.** Molecular structure of **1b** with thermal ellipsoids at the 30% probability level. Hydrogen atoms except for those attached to the silicon are omitted for clarity. Selected bond lengths (Å) and angles (°): Si1–H1A, 1.417(19); Si1–H1B, 1.446(17); Si1–C1, 1.879(2); Si1–C7, 1.860(2); B1–C2, 1.566(3); B1–C8, 1.577(3); B1–C17, 1.576(3); Si1–C1–C2, 125.06(15); C1–C2–B1, 125.11(18); C2–B1–C8, 120.68(17); C8–B1–C17, 121.88(17); C17–B1–C2, 117.39(17); Si1–C1–C2–B1, –6.3(3).

( $^1J(\text{Si–H}) = 198 \text{ Hz}$ ) [11]. The IR spectra showed the  $\nu(\text{Si–H})$  absorption at  $2166 \text{ cm}^{-1}$  [12].

Molecular structures of **1a** and **1b** are shown in Figs. 1 and 2. Crystallographic data are summarized in Table 1. The geometries of **1a** and **1b** are almost similar to each other. The Si–H bond lengths

**Table 1**  
Crystallographic data for compounds **1a** and **1b**.

	<b>1a</b>	<b>1b</b>
Formula	C <sub>33</sub> H <sub>33</sub> BSi	C <sub>25</sub> H <sub>31</sub> BSi
Formula weight	432.46	370.40
Temp/K	173(2)	173(2)
Wavelength/Å	0.71075	0.71075
Cryst color	Colorless	Colorless
Cryst size/mm	0.30 × 0.20 × 0.30	0.50 × 0.20 × 0.10
Cryst syst	Triclinic	Monoclinic
Space group	<i>P</i> -1	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> /Å	9.3167(8)	8.4033(3)
<i>b</i> /Å	10.7012(9)	21.6032(7)
<i>c</i> /Å	14.1187(12)	12.0940(4)
$\alpha$ /deg	70.591(3)	90
$\beta$ /deg	76.240(3)	92.5425(10)
$\gamma$ /deg	73.742(2)	90
<i>V</i> /Å <sup>3</sup>	1258.14(19)	2193.36(13)
<i>Z</i>	2	4
$\rho_{\text{calc}}/\text{g cm}^{-3}$	1.142	1.122
$\mu$ (Mo <i>K</i> $\alpha$ )/mm <sup>-1</sup>	0.108	0.114
<i>F</i> (0 0 0)	464	800
$\theta$ range/°	3.10–27.48	3.02–27.48
Reflections collected	13307	22584
Independent reflections	5743	5026
<i>R</i> (int)	0.0387	0.0573
Data/restraints/parameters	5743/0/356	5026/0/259
Goodness of fit on <i>F</i> <sup>2</sup>	1.060	1.054
Final <i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	0.0563, 0.1309	0.0580, 0.1392
Final <i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> (all data)	0.0838, 0.1450	0.0814, 0.1537
Large diff. peak and hole/e Å <sup>-3</sup>	0.304, –0.248	0.295, –0.219

(**1a**: 1.42(2) and 1.40(2) Å; **1b**: 1.417(19) and 1.446(17) Å) are in the range of normal values of Si–H bonds in tetracoordinate dihydrosilanes (1.290–1.508 Å), [5] and slightly shorter than those for monohydro derivative **1** (1.47(2) and 1.55(2) Å in the two independent molecules) [3a]. The Si–H···B atomic distances (**1a**: 3.15(2) and 3.85(2) Å; **1b**: 3.247(17) and 3.881(19) Å) are almost equal to or longer than the sum of the van der Waals radii of hydrogen atom and boron atom (3.28 Å) [13], and the shorter ones are similar to the corresponding distances in **1** (3.22(2) and 3.25(2) Å) [3a]. There seems to be no noticeable intramolecular Si–H···B interaction. Thus, the anticipated high reactivity of the Si–H bond in **1** was not confirmed in the crystal structures.

### 3. Conclusion

*o*-(Dihydrosilyl)(dimesitylboryl)benzenes **1a** and **1b** were prepared starting from *o*-dibromobenzene. The key steps are (i) preparation of [*o*-(dimethoxysilyl)phenyl]lithiums **3**, (ii) reduction of *o*-(dimethoxysilyl)(boryl)benzenes **4** with LiAlH<sub>4</sub>, and (iii) treatment of borohydride **9** with BF<sub>3</sub>·OEt<sub>2</sub>. Structures of **1** were revealed by spectroscopic and X-ray crystallographic analyses. Reactivity of **1** toward alcohols and ketones is currently under investigation and will be reported elsewhere in the near future.

### 4. Experimental

#### 4.1. General procedure

<sup>1</sup>H (400 MHz), <sup>11</sup>B (128.3 MHz), <sup>13</sup>C (100 MHz), and <sup>29</sup>Si (79.4 MHz) NMR spectra were recorded with a JEOL EX-400 or AL-400 spectrometer. <sup>1</sup>H and <sup>13</sup>C chemical shifts were referenced to internal CDCl<sub>3</sub> (<sup>1</sup>H  $\delta = 7.26$ ; <sup>13</sup>C  $\delta = 77.00$ ) and benzene-*d*<sub>6</sub> (<sup>1</sup>H  $\delta = 7.20$ ; <sup>13</sup>C  $\delta = 128.0$ ). <sup>11</sup>B chemical shifts were referenced to external BF<sub>3</sub>·OEt<sub>2</sub> ( $\delta = 0$ ). <sup>29</sup>Si chemical shifts were referenced to external tetramethylsilane ( $\delta = 0$ ). Mass spectra (EI) were measured at 70 eV with a JEOL SX-102A mass spectrometer at the Natural Science Center for Basic Research and Development (N-BARD), Hiroshima University. Melting points were measured with a Yanaco Micro Melting Point Apparatus and were uncorrected. Elemental analyses were performed with a Perkin–Elmer 2400CHN elemental analyzer at our laboratory. Column chromatography on silica gel was performed using Kieselgel 60 (230–400 mesh) (Merck). Thin-layer chromatography was performed on plates of Silica gel 60/Kieselguhr F254 (Merck).

1,2-Dibromobenzene was purchased from Tokyo Chemical Industry Co., Ltd. and dried over molecular sieves 4 Å prior to use. *n*-Butyllithium in hexane and *tert*-butyllithium in pentane were purchased from Kanto Chemical Co., Inc. Chloro(dimethoxy)(methyl)silane was purchased from Sin-Etsu Chemical Co., Ltd. Phenylsilane was purchased from Tokyo Chemical Industry Co., Ltd. Palladium(II) dichloride and lithium aluminum hydride were purchased from Wako Pure Chemical Industries, Ltd. Carbon tetrachloride was distilled over sodium hydride under nitrogen atmosphere. Mesityl bromide was purchased from Sigma–Aldrich. Fluoro(dimesityl) borane was prepared according to the literature method [14]. BF<sub>3</sub>·OEt<sub>2</sub> was purchased from Sigma–Aldrich and distilled over sodium hydride.

THF and Et<sub>2</sub>O were distilled over sodium diphenylketyl under nitrogen atmosphere, or dehydrated solvents (<10 ppm for THF and <50 ppm for Et<sub>2</sub>O; Kanto Chemical Co., Inc.) were dried through a Solvent Dispensing System (Glass Contour) under nitrogen atmosphere. Benzene and toluene were distilled over sodium diphenylketyl under nitrogen atmosphere. Hexane was distilled over sodium under nitrogen atmosphere, or a dehydrated solvent (<10 ppm; Kanto Chemical Co., Inc.) was dried through a Solvent

Dispensing System (Glass Contour) under nitrogen atmosphere. All reactions were carried out under inert gas atmosphere.

## 4.2. Synthesis

### 4.2.1. Chloro(dimethoxy)phenylsilane

To a solution of palladium(II) dichloride (25 mg) and phenylsilane (6.2 mL, 50 mmol) in benzene (100 mL) was added methanol (4.1 mL, 100 mmol) at 0 °C over 2 min. A gas evolution immediately occurred. The reaction mixture was stirred at 0 °C until the gas evolution ceased, resulting in formation of (dimethoxy)phenylsilane. Carbon tetrachloride (5.0 mL, 52 mmol) was added to the reaction mixture at room temperature over 2 min. Palladium(II) dichloride (30 mg, 0.17 mmol) was added by one portion to the reaction mixture at room temperature, and the reaction mixture was heated at 50 °C for 30 min. Further palladium(II) dichloride (29 mg, 0.16 mmol) was added to the reaction mixture at 50 °C, resulting in a gas evolution. After the gas evolution ceased, the reaction mixture was cooled to room temperature. Then the solvents were removed in vacuo. The residue (11.0 g) was subjected to bulb-to-bulb distillation (64–66 °C (bath temp.)/3.5 mmHg) to afford chloro(dimethoxy)phenylsilane (9.78 g, 96% yield) as a colorless oil.

### 4.2.2. *o*-Bromo(dimethoxy(phenyl)silyl)benzene (**2a**)

A solution of *n*-BuLi in hexane (1.54 M, 32.0 mL, 49 mmol) was added dropwise to a solution of 1,2-dibromobenzene (5.1 mL, 42 mmol) in THF–Et<sub>2</sub>O (80 mL/80 mL) over 1 h at –110 °C (ethanol/liq. N<sub>2</sub> slush bath). After the reaction mixture was stirred at the same temperature for 40 min, chloro(dimethoxy)(phenyl)silane (8.59 g, 42 mmol) was added dropwise to the reaction mixture over 15 min at –110 °C. The reaction mixture was stirred at the same temperature for further 1.5 h and then allowed to warm to ambient temperature. After the solvents were removed in vacuo, the residue was diluted with hexane (70 mL) and filtered through a glass fiber pad to remove inorganic salts. The filtrate was concentrated in vacuo to give an oil (15.4 g). The oil was subjected to column chromatography on silica gel using hexane–AcOEt (20/1) as eluent (*R<sub>f</sub>* = 0.30) to give **2a** (11.9 g, 87% yield) as a colorless oil.

<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, δ) 3.51 (s, 6H), 6.84 (ddd, <sup>3</sup>*J* = 8 Hz and 8 Hz, <sup>4</sup>*J* = 2 Hz, 1H), 7.07 (dd, <sup>3</sup>*J* = 8 Hz and 8 Hz, 1H), 7.22–7.24 (m, 3H), 7.36 (d, <sup>3</sup>*J* = 8 Hz, 1H), 7.89 (m, 2H), 8.08 (dd, <sup>3</sup>*J* = 8 Hz, <sup>4</sup>*J* = 2 Hz, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ) 50.79 (OMe), 126.36 (CH), 127.75 (CH), 129.57 (C), 130.27 (CH), 131.71 (C), 132.13 (CH), 132.67 (CH), 134.18 (C), 134.83 (CH), 138.58 (CH). <sup>29</sup>Si{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, δ) –32.0. Anal. Calc. for C<sub>14</sub>H<sub>15</sub>BrO<sub>2</sub>Si: C, 52.02; H, 4.68. Found: C, 51.82; H, 5.01%.

### 4.2.3. *o*-Bromo(dimethoxy(methyl)silyl)benzene (**2b**)

A solution of *n*-BuLi in hexane (1.55 M, 20.0 mL, 31 mmol) was added dropwise to a solution of 1,2-dibromobenzene (3.6 mL, 30 mmol) in THF–Et<sub>2</sub>O (60 mL/60 mL) over 30 min at –110 °C (ethanol/liq. N<sub>2</sub> slush bath). After the reaction mixture was stirred at the same temperature for 40 min, chloro(dimethoxy)(methyl)silane (4.3 mL, 32 mmol) was added dropwise to the reaction mixture over 30 min at –110 °C. The reaction mixture was stirred at the same temperature for further 1.5 h and then allowed to warm to ambient temperature. After the solvents were removed in vacuo, the residue was diluted with hexane (70 mL) and filtered through a glass fiber pad to remove inorganic salts. The filtrate was concentrated in vacuo to give an oil (7.56 g). The oil was subjected to bulb-to-bulb distillation (57–62 °C (bath temp.)/0.15 mmHg) to give **2b** (6.29 g, 80% yield) as a colorless oil.

<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, δ) 0.53 (s, 3H), 3.45 (s, 6H), 6.83 (ddd, <sup>3</sup>*J* = 8 Hz and 8 Hz, <sup>4</sup>*J* = 2 Hz, 1H), 7.03 (ddd, <sup>3</sup>*J* = 8 Hz and 8 Hz, <sup>4</sup>*J* = 1 Hz, 1H), 7.41 (d, <sup>3</sup>*J* = 8 Hz, 1H), 7.88 (dd, <sup>1</sup>*J* = 8 Hz, <sup>4</sup>*J* = 1 Hz, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ)

–4.49 (Me), 50.38 (OMe), 126.29 (CH), 129.07 (C), 131.73 (CH), 132.49 (CH), 135.64 (C), 137.57 (CH). <sup>29</sup>Si{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, δ) –17.5. Anal. Calc. for C<sub>9</sub>H<sub>13</sub>BrO<sub>2</sub>Si: C, 41.39; H, 5.02. Found: C, 41.04; H, 5.14%.

### 4.2.4. *o*-(Dimesitylboryl)[dimethoxy(phenyl)silyl]benzene (**4a**)

*tert*-BuLi in pentane (1.59 M, 6.80 mL, 10.8 mmol) was added dropwise to a solution of **2a** (3.58 g, 11.1 mmol) in Et<sub>2</sub>O (20 mL) at –78 °C over 25 min. The reaction mixture was stirred at the same temperature for 2 h to form a yellow suspension of **3a**. To the suspension was added a solution of fluorodimesitylborane (3.10 g, 11.6 mmol) in Et<sub>2</sub>O (10 mL) at –78 °C over 35 min. The reaction mixture was stirred at –60 °C for 24 h and then allowed to warm to ambient temperature over 1.5 h. Then the solvents were removed in vacuo. The residue was diluted in hexane (100 mL) and filtered through a glass fiber pad to remove inorganic salts. The filtrate was concentrated in vacuo. The residue (5.22 g) was subjected to column chromatography on silica gel using hexane–CH<sub>2</sub>Cl<sub>2</sub> (3/1) as eluent (*R<sub>f</sub>* = 0.33) to give **4a** (3.53 g, 74% yield) as white solids.

m.p. 117–118.5 °C (in air). <sup>1</sup>H NMR (C<sub>6</sub>H<sub>6</sub>, δ) 1.4–2.6 (br, 18H), 3.33 (s, 6H), 6.3–6.9 (br, 4H), 7.14–7.22 (m, 5H), 7.36 (d, <sup>3</sup>*J* = 8 Hz, 2H), 7.49 (d, <sup>3</sup>*J* = 8 Hz, 1H), 7.91 (d, <sup>3</sup>*J* = 8 Hz, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ) 21.20 (CH<sub>3</sub>), 23.0–24.0 (br, CH<sub>3</sub>), 50.48 (OMe), 127.24 (CH), 127.6–129.0 (C), 128.27 (CH), 128.33 (CH), 129.36 (CH), 129.55 (CH), 132.93 (CH), 133.01 (C), 134.16 (CH), 135.75 (CH), 136.83 (C), 138.2–139.3 (br, C), 141.0–142.8 (br, C), 157.38 (C). <sup>11</sup>B{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, δ) 74 (br). <sup>29</sup>Si{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, δ) –28.2. Anal. Calc. for C<sub>32</sub>H<sub>37</sub>BO<sub>2</sub>Si: C, 78.03; H, 7.57. Found: C, 77.84; H, 7.90%.

### 4.2.5. *o*-(Dimesitylboryl)[dimethoxy(methyl)silyl]benzene (**4b**)

*tert*-BuLi in pentane (1.58 M, 3.50 mL, 5.5 mmol) was added dropwise to a solution of **2b** (1.40 g, 5.4 mmol) in Et<sub>2</sub>O (10 mL) at –78 °C over 15 min. The reaction mixture was stirred at the same temperature for 2 h to form a yellow suspension of **3b**. To the suspension was added a solution of fluorodimesitylborane (1.47 g, 5.5 mmol) in Et<sub>2</sub>O (5 mL) at –78 °C over 12 min. The reaction mixture was stirred at –60 °C for 24 h and then allowed to warm to ambient temperature over 1.5 h. Then the solvents were removed in vacuo. The residue was diluted in hexane (30 mL) and filtered through a glass fiber pad to remove inorganic salts. The filtrate was concentrated in vacuo. The residue (2.38 g) was subjected to column chromatography on silica gel using hexane–CH<sub>2</sub>Cl<sub>2</sub> (2/1) as eluent (*R<sub>f</sub>* = 0.35) to give crude **4b** (961 mg), which was again subjected to column chromatography on silica gel using hexane–CH<sub>2</sub>Cl<sub>2</sub> (2.5/1) as eluent (*R<sub>f</sub>* = 0.15) to give pure **4b** (829 mg, 39% yield) as white solids.

m.p. 112.0–114.0 °C (in air). <sup>1</sup>H NMR (C<sub>6</sub>H<sub>6</sub>, δ) –0.10 (s, 3H), 1.6–2.5 (br, 18H), 3.1–3.4 (br, 6H), 6.6–6.9 (br, 4H), 7.27 (ddd, <sup>3</sup>*J* = 7 Hz and 7 Hz, <sup>4</sup>*J* = 1 Hz, 2H), 7.51 (d, <sup>3</sup>*J* = 7 Hz, 1H), 7.90 (d, <sup>3</sup>*J* = 7 Hz, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ) –4.98 (Me), 21.23 (CH<sub>3</sub>), 22.0–24.1 (CH<sub>3</sub>), 48.9–50.3 (br, OMe), 127.2–127.9 (br, CH), 128.53 (CH), 129.43 (CH), 133.26 (CH), 134.95 (CH), 138.19 (C), 138.0–144.0 (br, C), 157.07 (C). <sup>11</sup>B{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, δ) 74 (br). <sup>29</sup>Si{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, δ) –12.4. Anal. Calc. for C<sub>27</sub>H<sub>35</sub>BO<sub>2</sub>Si: C, 75.34; H, 8.20. Found: C, 75.39; H, 8.46%.

### 4.2.6. *o*-(Dimesitylboryl)(phenylsilyl)benzene (**1a**)

A solution of **4a** (514 mg, 1.0 mmol) in THF (3 mL) was added dropwise to a suspension of LiAlH<sub>4</sub> (41 mg, 1.1 mmol) in THF (1 mL) at 0 °C over 4 min, and the reaction mixture was stirred at room temperature for 3 h. The reaction mixture was concentrated in vacuo to yield milky oil of **9a**. The oil was vigorously stirred in hexane (5 mL) to form a white suspension. BF<sub>3</sub>·OEt<sub>2</sub> (0.70 mL, 5.5 mmol) was added to the white suspension at room temperature, and the reaction mixture was stirred at the same temperature for 2 h. Then the

solvents were removed in vacuo. The resulting white solids were heated at 75 °C under reduced pressure (ca. 1 mmHg) overnight to remove volatile materials. The residual white solids (388 mg) were dissolved in hexane (30 mL), and insoluble inorganic salts were removed by filtration. The filtrate was cooled to –30 °C to give **1a** (328 mg, 73% yield based on **4a**) as white solids.

m.p. 155–156 °C (in a sealed tube). <sup>1</sup>H NMR (C<sub>6</sub>H<sub>6</sub>, δ) 1.8–2.4 (br, 18H), 4.6–5.0 (br, 2H), 6.5–6.9 (br, 4H), 7.09–7.17 (m, 5H), 7.39 (dt, <sup>3</sup>J = 7 Hz, <sup>4</sup>J = 1 Hz, 2H), 7.55 (1H), 7.64 (1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ) 21.27 (CH<sub>3</sub>), 21.7–24.4 (br, CH<sub>3</sub>), 127.56 (CH), 128.5 (br, CH), 129.18 (CH), 129.39 (CH), 132.58 (C), 134.57 (CH), 135.50 (CH), 137.05 (C), 137.65 (CH), 138.9 (br, C), 140.1 (br, C), 141.5 (br, C), 156.41 (C). <sup>11</sup>B {<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, δ) 75 (br). <sup>29</sup>Si NMR (C<sub>6</sub>D<sub>6</sub>, δ) –34.2 (t, <sup>1</sup>J<sub>Si–H</sub> = 202 Hz). Anal. Calc. for C<sub>30</sub>H<sub>33</sub>BSi: C, 83.32; H, 7.69. Found: C, 83.05; H, 8.07%. IR (KBr, cm<sup>–1</sup>) 2166 (ν<sub>Si–H</sub>). MS (EI, *m/z*) 432 (M<sup>+</sup>, 25), 417 (M<sup>+</sup> – Me, 30), 339 (12), 312 (M<sup>+</sup> – Mes – H, 71), 297 (100).

#### 4.2.7. Lithium [*o*-(phenylsilyl)phenyl](dimesityl)borohydride (**9a** (*n* = 2))

The milky oil of **9a** prepared from **4a** (2.19 mmol) in the same manner as above was heated at 50 °C under reduced pressure (ca. 1 mmHg) for 1 h gave bis-solvated **9a** (*n* = 2) (996 mg) as white solids. The number of the included THF molecules was determined by <sup>1</sup>H NMR analysis.

<sup>1</sup>H NMR (C<sub>6</sub>H<sub>6</sub>, δ) 1.03 (m, 8H, *thf*), 2.27 (s, 6H), 2.36 (s, 12H), 2.98 (m, 8H, *thf*), 4.97 (s, 2H), 6.90 (s, 4H), 7.11 (dd, <sup>3</sup>J = 7 Hz and 7 Hz, 1H), 7.26 (m, 4H), 7.60 (d, <sup>3</sup>J = 7 Hz, 1H), 7.76 (m, 2H). <sup>11</sup>B NMR (C<sub>6</sub>D<sub>6</sub>, δ) –15.4 (d, <sup>1</sup>J<sub>B–H</sub> = 71 Hz). <sup>29</sup>Si NMR (CDCl<sub>3</sub>, δ) –39.1 (t, <sup>1</sup>J<sub>Si–H</sub> = 185 Hz). IR (KBr, cm<sup>–1</sup>) 2125 (ν<sub>Si–H</sub>).

#### 4.2.8. *o*-(Dimesitylboryl)(methylsilyl)benzene (**1b**)

A solution of **4b** (780 mg, 1.8 mmol) in THF (8 mL) was added dropwise to a suspension of LiAlH<sub>4</sub> (74 mg, 2.0 mmol) in THF (3 mL) at 0 °C over min, and the reaction mixture was stirred at 0 °C for 2 h. The reaction mixture was concentrated in vacuo to yield milky oil of **9b**. The oil was vigorously stirred in hexane (5 mL) to form a white suspension. BF<sub>3</sub>·OEt<sub>2</sub> (1.20 mL, 9.5 mmol) was added to the white suspension at room temperature, and the reaction mixture was stirred at the same temperature for 2 h. Then the solvents were removed in vacuo. The resulting white solids were heated at 75 °C under reduced pressure (ca. 1 mmHg) overnight to remove volatile materials. The residual white solids (859 mg) were dissolved in hexane (15 mL), and insoluble inorganic salts were removed by filtration. The filtrate was cooled to –30 °C to give **1b** (536 mg, 80% yield based on **4b**) as white solids.

m.p. 120.0–121.0 °C (decomposed, in a sealed tube). <sup>1</sup>H NMR (C<sub>6</sub>H<sub>6</sub>, δ) 0.06 (t, <sup>3</sup>J = 4 Hz, 3H), 1.7–2.5 (br, 18H), 4.1–4.5 (br, 2H), 6.79 (br, 4H), 7.17 (ddd, <sup>3</sup>J = 8 and 8 Hz, <sup>4</sup>J = 2 Hz, 1H), 7.22 (ddd, <sup>3</sup>J = 8 and 8 Hz, <sup>4</sup>J = 2 Hz, 1H), 7.52 (dd, <sup>3</sup>J = 8 Hz, <sup>4</sup>J = 2 Hz, 1H), 7.62 (dd, <sup>3</sup>J = 8 Hz, <sup>4</sup>J = 2 Hz, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ) –7.14 (Me), 21.29 (CH<sub>3</sub>), 22.0–24.2 (br, CH<sub>3</sub>), 128.44 (br, CH), 129.09 (CH), 129.38 (CH), 134.18 (CH), 136.13

(CH), 138.89 (C), 139.0–144.0 (br, C), 156.35 (C). <sup>11</sup>B NMR (C<sub>6</sub>D<sub>6</sub>, δ) 75 (br). <sup>29</sup>Si NMR (C<sub>6</sub>D<sub>6</sub>, δ) –36.8 (triplet of septet, <sup>1</sup>J<sub>Si–H</sub> = 194 Hz and 7 Hz). Anal. Calc. for C<sub>25</sub>H<sub>31</sub>BSi: C, 81.06; H, 8.44. Found: C, 81.07; H, 8.74%. IR (KBr, cm<sup>–1</sup>) 2169, 2156 (ν<sub>Si–H</sub>). MS (EI, *m/z*) 370 (M<sup>+</sup>, 14), 355 (M<sup>+</sup> – Me, 10), 250 (M<sup>+</sup> – Mes – H, 41), 235 (100).

#### Acknowledgments

This work was partly supported by a Grant-in-Aid for Scientific Research (No. 19020048) from the Ministry of Education, Culture, Sports, Science and Technology, Japan. We thank Mr. Daisuke Kajiya, the Natural Science Center for Basic Research and Development (N-BARD), Hiroshima University for the measurement of the mass spectra (EI).

#### Appendix A. Supplementary material

CCDC No. – 774820 and – 774821 contain the supplementary crystallographic data for complexes **1a** and **1b**, respectively. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

#### References

- [1] Recent examples of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>-catalyzed reactions of hydrosilanes: (a) D.J. Parks, J.M. Blackwell, W.E. Piers, *J. Org. Chem.* 65 (2000) 3090; (b) V. Gevorgyan, M. Rubin, S. Benson, J.-X. Liu, Y. Yamamoto, *J. Org. Chem.* 65 (2000) 6179; (c) J. Chojnowski, S. Rubinsztajn, J.A. Cella, W. Fortuniak, M. Cypryk, J. Kurjata, K. Kázmierski, *Organometallics* 24 (2005) 6077; (d) S. Rendler, M. Ostreich, *Angew. Chem. Int. Ed.* 47 (2008) 5997.
- [2] For examples: (a) B. Wrackmeyer, O.L. Tok, Y.N. Bubnov, *Appl. Organomet. Chem.* 18 (2004) 43; (b) B. Wrackmeyer, O.L. Tok, *Z. Naturforsch.* 61b (2006) 243.
- [3] (a) A. Kawachi, M. Zaima, A. Tani, Y. Yamamoto, *Chem. Lett.* 36 (2007) 362; (b) A. Kawachi, M. Zaima, Y. Yamamoto, *Organometallics* 27 (2008) 4691.
- [4] SciFinder Scholar (2007).
- [5] The Cambridge Structural Database (Ver. 5.3).
- [6] L.S. Chen, G.J. Chen, C. Tamborski, *J. Organomet. Chem.* 193 (1980) 283.
- [7] (a) A. Kawachi, A. Tani, K. Machida, Y. Yamamoto, *Organometallics* 26 (2007) 4697; (b) A. Kawachi, A. Tani, J. Shimada, Y. Yamamoto, *J. Am. Chem. Soc.* 130 (2008) 4222.
- [8] (a) W.Z. McCarthy, J.Y. Corey, E.R. Corey, *Organometallics* 3 (1984) 255; (b) J.Y. Corey, W.Z. McCarthy, *J. Organomet. Chem.* 271 (1984) 319.
- [9] (a) H.C. Brown, S. Krishnamurthy, J.L. Hubbard, *J. Organomet. Chem.* 166 (1979) 271; (b) H.C. Brown, C.W. Kramer, J.L. Hubbard, S. Krishnamurthy, *J. Organomet. Chem.* 188 (1980) 1.
- [10] C. Elschenbroich, A. Salzer, *Organometallics 2nd Revised ed.*, VCH, Weinheim, 1992.
- [11] C. Shumann, H. Dreeskamp, *J. Magn. Reson.* 3 (1970) 204.
- [12] T.R. Crompton, in: S. Patai, Z. Rappoport (Eds.), *The Chemistry of Organic Silicon Compound*, John Wiley & Sons Ltd., New York, 1989, pp. 393–444 (Chapter 6).
- [13] J. Emsley, *The Elements*, second ed., Oxford University Press, Oxford, 1992, H, 1.20 Å; B, 2.08 Å; C, 1.85 Å.
- [14] J.J. Eisch, B. Shafii, J.D. Odom, A.L. Rheingold, *J. Am. Chem. Soc.* 112 (1990) 1847.