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Intramolecular Reaction of Silanol and Triarylborane: Boron−Aryl Bond Cleavage and Formation of a Si−O−B Heterocyle

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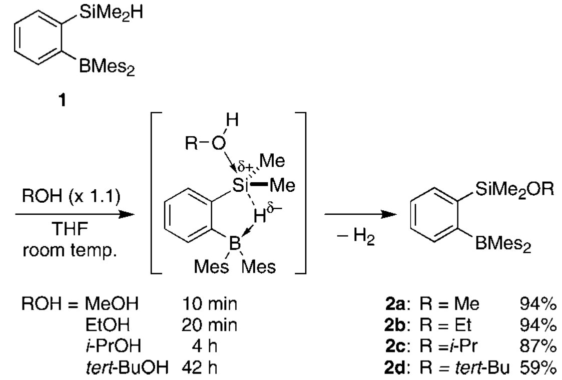
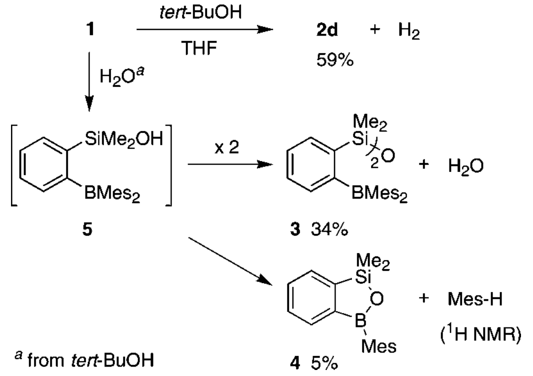
o-(Hydroxydimethylsilyl)(dimesitylboryl)benzene (**1**) underwent intramolecular cyclization to give 5,5-dimesityl-2,2-dimethyl-3,4-benzo-1,2,5-oxasilaboracyclopentene (**4**) and mesitylene by boron−aryl bond cleavage. Whereas triethylamine as an additive accelerated the cyclization, DBU stabilized a silyloxyborate complex, 1,8-diazabicyclo[5.4.0]-7-undecenium 5,5-dimesityl-2,2-dimethyl-3,4-benzo-1,2,5-oxasilaboratacyclopentene, which was characterized by X-ray crystallographic analysis and HF calculations. The deuterium-labeling experiments revealed that the hydrogen migrated from the hydroxyl group in **1** to the leaving mesitylene.

We have reported recently the dehydrogenative condensation reaction of *o*-(dimesitylboryl)(dimethylsilyl)benzene (**1**) with alcohols: hydrosilane **1** reacted with methanol, ethanol, and isopropyl alcohol in THF at room temperature in a short time, giving the corresponding alkoxysilanes **2** in excellent yields, as shown in Scheme 1.[1] The efficiency of this reaction is ascribed to the electrophilic activation of the Si−H bond[2] by the *o*-boryl group in **1**, because of which the silicon center tends to be receptive toward nucleophiles. The reaction of **1** with *tert*-butyl alcohol also proceeded to give **2d**, but the yield was rather low (59%) (Scheme 1). Precise identification of the byproduct revealed that disiloxane **3** (34% yield), 3,4-benzo-1,2,5-oxasilaboracyclopentene **4** (5% yield), and mesitylene (confirmed by ^{1}H NMR spectroscopy) were formed in the reaction, as shown in Scheme 2. We are interested in the formation of the unexpected products **4** and mesitylene and postulate their formation mechanism as follows (Scheme 2). (i) Hydrosilane **1** reacts with water in a manner similar to its reaction with alcohols, giving hydroxysilane **5**. Although *tert*-butyl alcohol used in the present reaction might contain only a trace amount of H_2O,[3] the reaction of **1** with bulky *tert*-butyl alcohol is so slow that the reaction of **1** with H_2O becomes competitive. (ii) While bimolecular condensation of **5** gives disiloxane **3**, intramolecular cyclization of **5** together with boron−mesityl bond cleavage results in the formation of **4** and mesitylene.

Scheme 1. Dehydrogenative Condensation Reaction of Hydrosilane 1 with Alcohols



Scheme 2. Formation and Reaction of Hydroxysilane 5



The intramolecular interaction between boryl groups and heteroatom-functionalized silyl groups has been precisely investigated by Wrackmeyer et al. with multinuclear NMR spectroscopy.[4] They prepared a number of compounds in which a heteroatom-functionalized silyl group and a boryl group were bonded to an alkene skeleton in a cis fashion and revealed that such compounds formed unique silicon−heteroatom−boron bridges. Because of intramolecular interaction between the oxygen atom and the boron atom, *cis*-2-boryl-1-(hydroxy)silylalkene **I** underwent intramolecular cyclization via hydrogen migration or ethane elimination to give 1,2,5-oxasilaborolane **II** or 1,2,5-oxasilaborole **III**, respectively (eq 1).[4c] *cis*-2-Boryl-1-[(diethylamino)silyl]alkene **IV** underwent hydrolysis to yield 1,2,5-oxasilaborolane **V** via the postulated hydroxysilyl intermediate **VI** (eq 2).[4d]

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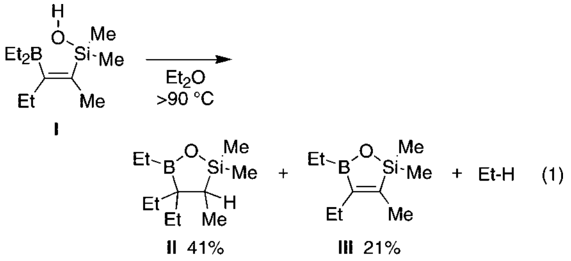
(1) Kawachi, A.; Zaima, M.; Tani, A.; Yamamoto, Y. *Chem. Lett.* **2007**, *36*, 362.

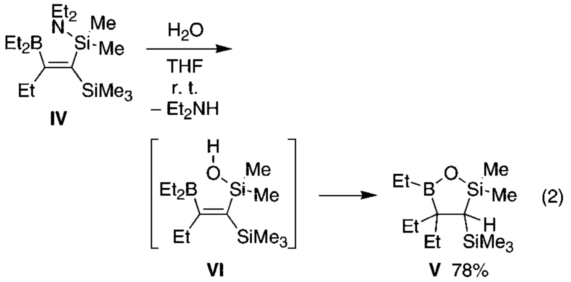
(2) For other examples of electrophilic activation of Si−H bonds: (a) Blackwell, J. M.; Foster, K. L.; Beck, V. H.; Piers, W. E. *J. Org. Chem.* **1999**, *64*, 4887. (b) Gevorgyan, V.; Liu, J.-X.; Rubin, M.; Benson, S,.; Yamamoto, Y. *Tetrahedron Lett.* **1999**, *40*, 8919. (c) Gevorgyan, V.; Rubin, M.; Benson, S.; Liu, J.-X.; Yamamoto, Y. *J. Org. Chem.* **2000**, *65*, 6179.

(3) *tert*-Butyl alcohol was dried with CaH_2 and distilled under a nitrogen atmosphere.

(4) (a) Wrackmeyer, B.; Milius, W.; Tok, O. L. *Chem. Eur. J.* **2003**, *9*, 4732. (b) Wrackmeyer, B.; Tok, O. L. *Magn. Reson. Chem.* **2002**, *40*, 406. (c) Köster, R.; Seidel, G.; Wrackmeyer, B. *Chem. Ber.* **1991**, *124*, 1003. (d) Wrackmeyer, B.; Süss, J.; Milius, W. *Chem. Ber.* **1996**, *129*, 147.

10.1021/om8004405 CCC: $40.75





In this work, we prepared hydroxysilane **5** and investigated whether **5** actually affords **4** and mesitylene under the appropriate reaction conditions. We also performed deuterium-labeling experiments to obtain further information on the boron−mesityl bond cleavage. In the course of our study, a silyloxyborate−amine complex was isolated. The results of the characterization of this complex by NMR spectroscopy, X-ray crystallographic analysis, and HF calculations are reported herein.

Results and Discussion

Formation of 3,4-Benzo-1,2,5-oxasilaboracyclopentene 4. Hydroxysilane **5** was prepared in 90% yield by hydrolysis of **1** with H_2O (1 molar equiv) in THF at room temperature for 10 min. Precipitation of **5** from acetonitrile yielded its pure form as white powder (mp 115−117 °C). The Si−OH functionality in **5** was confirmed by ^1H NMR spectroscopy (δ(Si−O*H*) 1.53 in C_6D_6) and IR spectroscopy (ν(O−H) 3579 cm^{-1}). The ^{11}B NMR signal was observed at δ 74 in the typical region for triarylboranes. These spectral data indicate that there is no significant intramolecular interaction between the hydroxyl oxygen and the boron center in **5** itself, unlike in **I** and **IV**, in which the coordination of the heteroatoms to the boron is evident from the ^{11}B NMR shifts (δ(**I**) 16,[4c] δ(**IV**) 6[4d]). This may be due to that the *o*-phenylene skeleton is rigid compared to the alkene skeleton, as well as the fact that the boron center is sterically crowded by the *o*-methyl groups.

With hydroxysilane **5** in hand, we examined the formation of **4** under several reaction conditions. The results are summarized in Table 1. Actually, **5** in THF underwent intramolecular cyclization, as expected. When the reaction was conducted at room temperature for 240 h, **5** was completely consumed to give **3**, **4**, and mesitylene in 10%, 86%, and 81% yields, respectively (Table 1, entry 1).[5] Furthermore, **4** was isolated in 64% yield by bulb-to-bulb distillation as a colorless oil that solidified to a white solid on standing. The formation of **4** was largely accelerated by heat: the reaction was completed after 24 h at 80 °C (Table 1, entry 2). The addition of triethylamine (1 molar equiv) also effectively accelerated the reaction, even at room temperature (Table 1, entry 3). In contrast, a highly polar solvent such as acetonitrile completely inhibited the formation of **4** (Table 1, entry 4).

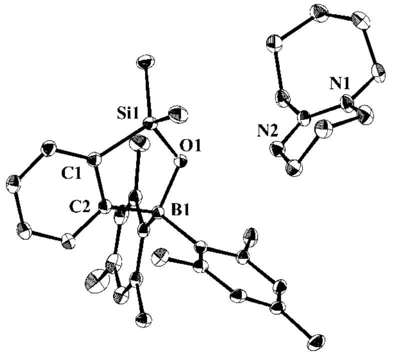
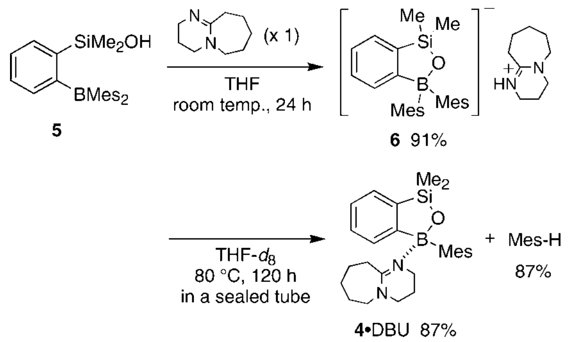


Figure 1. Crystal structure of **6** at the 30% probability level. One of the two independent molecules is shown. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): C1−C2, 1.414(3)/1.415(3); Si1−C1, 1.852(2)/1.848(2); Si1−O1, 1.6399(15)/1.6377(14); B1−O1, 1.561(2)/1.567(2); B1−C2, 1.654(3)/1.654(3); O1···N2, 2.769(2)/2.920(2); C2−C1−Si1, 107.07(14)/108.28(14); C1−Si1−O1, 97.58(8)/97.69(8); Si1−O1−B1, 114.71(12)/114.82(11); O1−B1−C2, 103.27(15)/103.47(14); C1−C2−B1, 115.42(16)/114.71(16).

Scheme 3. Cyclization Reaction of Hydroxysilane 5 in the Presence of DBU



In order to gain further insights into the effect of amines, we used a stronger base, DBU (1,8-diazabicyclo[5.4.0]undec-7-ene), in place of triethylamine. Stirring of **5** and DBU (1 molar equiv) in THF at room temperature afforded the silyloxyborate−[DBU·H^+] complex **6** in 91% yield as a white solid after precipitation from hexane, as shown in Scheme 3. The silyloxyborate complex **6** was identified by NMR spectroscopy. In ^{11}B NMR spectra, a signal (δ 6) appears in the typical region for tetracoordinate borates. In ^1H NMR spectra, a broad signal for the amidinium proton in [DBU·H^+] was observed at δ 12. As far as we know, there is only one example of a silyloxyborate−[R_3NH^+] complex in the literature. The complex was prepared by treatment of a silica surface ((−O−)$_3$Si−OH) with $B(C_6F_5)_3$ and Et_2NPh and characterized by IR and multinuclear solid-state NMR spectroscopy.[6]

Structure of the Silyloxyborate−[DBU·H$^+$] Complex 6. Recrystallization of **6** from THF−hexane afforded colorless crystals that were used in X-ray crystallographic analysis. The crystal structure of **6** is shown in Figure 1. Two independent molecules are present in the asymmetric unit: their geometries are similar to each other, except for the direction of tilt of the mesityl groups. The borate geometry in **6** is clearly demonstrated by the sum of the three C−B−C angles of 336.2(25)/336.9(25)° and the B−O bond length of 1.561(2)/1.567(2) Å. The three B−C bond lengths are almost the same, and their average is

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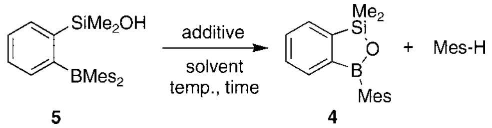
(5) The yields were estimated in ^1H NMR spectra by use of anisole as an internal standard.

(6) Millot, N.,.; Cox, A.; Santini, C. C.; Molard, Y.; Basset, J.-M. *Chem. Eur. J.* **2002**, *8*, 1438.

Table 1. Cyclization of Hydroxysilane 5



entry	solvent	temp	time (h)	additive	NMR yield (%)[a] (isolated yield (%))	
					4	mesitylene
1	THF	room temp	240		86 (64)	81
2	THF	80 °C	24		91 (86)	89
3	THF	room temp	24	Et_3N (×1)	93 (91)	91
4	CH_3CN	room temp	48		no reacn	

[a] Estimated by use of anisole as an internal standard in ^1H NMR spectra.

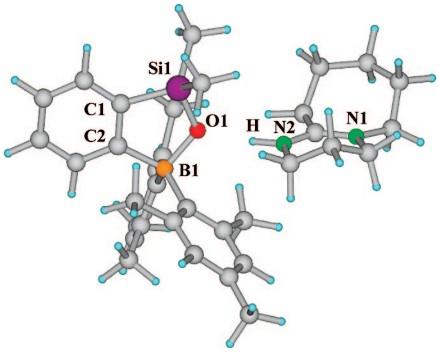


Figure 2. Optimized structure of **6** at the HF/6-31+G(d) level. Selected bond lengths (Å) and angles (deg): C1−C2, 1.4042; Si1−C1, 1.8357; Si1−O1, 1.6449; B1−O1, 1.5745; B1−C2, 1.6721; O1···N2, 2.8605; O1···H, 1.8451; C2−C1−Si1, 107.85; C1−Si1−O1, 97.78; Si1−O1−B1, 114.98; O1−B1−C2, 102.37; C1−C2−B, 115.88.

1.661(3)/1.661(3) Å. The distance between the oxygen atom in the borate part and the amidinium nitrogen atom in [DBU·H$^+$] is 2.769(2)/2.920(2) Å (average 2.845 Å), which falls in the typical distances of O···(H)N hydrogen bonds (2.6−3.1 Å).[7] Since the proton bonded to the nitrogen could not be observed by X-ray crystallographic analysis, the structure of **6** was computationally generated at the HF/6-31+G(d) level of theory[8] to determine the location of the proton. The O···N distance was well reproduced, and the proton was found between the two atoms, as shown in Figure 2: O···N = 2.8605 Å; O···H = 1.8451 Å; H−N = 1.0194 Å; O···H−N = 174°. Thus, the borate moiety in **6** forms a contact ion pair with the countercation [DBU·H$^+$] through the O···(H)N hydrogen bond.

For the reaction from **6** to **4** to proceed, **6** needs to be activated at high temperature. A solution of **6** in THF-d_8 was heated at 80 °C for 120 h in a sealed tube to afford the DBU adduct of **4** (**4**·DBU) in 87% yield and mesitylene also in 87% yield (Scheme 3).[5] Formation of the DBU adduct of **4** was confirmed by the facts that (i) its ^{11}B NMR signal (δ 42) exhibited an upfield shift compared to that of **4** itself (δ 50) and (ii) a small change in the ^1H NMR signals corresponding to the DBU part was observed in comparison to those of DBU itself, although the ^1H NMR signals corresponding to the part of **4** were almost identical.

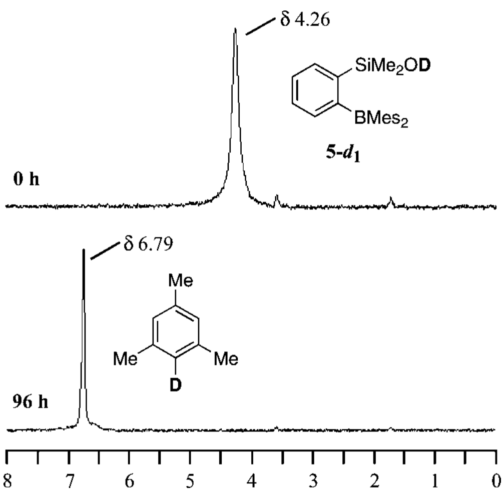
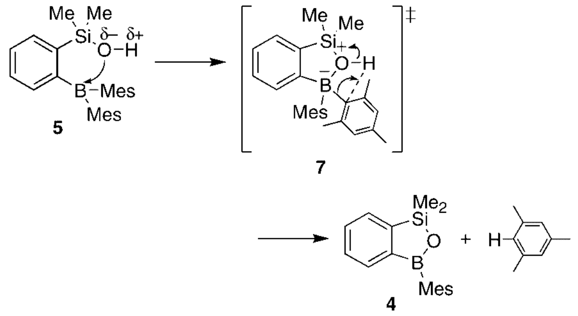


Figure 3. ^2H NMR monitoring of reaction of **5-*d*** in THF.

Scheme 4. Postulated Mechanism of Cyclization Reaction of Hydroxysilane 5



Hydrogen Source of Mesitylene. Next, we performed deuterium-labeling experiments with the aid of ^2H NMR spectroscopy to determine the hydrogen source of mesitylene formed in the reaction. The deuterated hydroxysilane **5-*d*** was prepared by treatment of **4** with D_2O in a manner similar to the preparation of **5**: the atom % D of **5-*d*** was estimated to be 83% from ^2H NMR spectra using CD_3CN as an internal standard. ^2H NMR monitoring of **5-*d*** in THF at 80 °C for 96 h showed that the O−D signal at δ 4.26 disappeared and a new signal appeared at δ 6.79 in the aromatic region, as shown in Figure 3. A quantitative experiment demonstrated that **4** was formed in 92% yield[5] and deuterated mesitylene (mesitylene-*d*) was formed in 100% yield (based on the atom % D of **5-*d***).[9] It is clear that hydrogen/deuterium of mesitylene comes from OH/OD bonded to silicon in **5**/**5-*d***.

Mechanistic Considerations. A mechanistic overview of the formation of **4** is postulated, as shown in Scheme 4. First, intramolecular nucleophilic attack of the hydroxyl oxygen on the boron center occurs in **5**. In transition state **7**, the boron−mesityl bonds are activated by formation of the borate complex and the proton on the oxygen migrates to the ipso carbon of one of the mesityl groups, resulting in elimination of

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(7) Stout, G. H.; Jensen, L. H. In *X-ray Structure Determination: A Practical Guide*; Macmillan: New York, 1968.

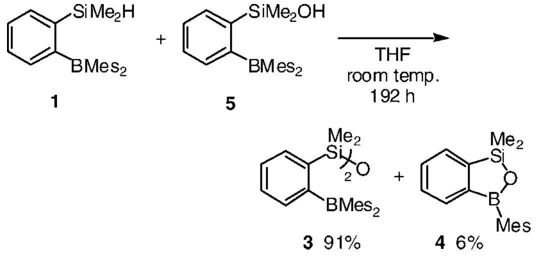
(8) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Oritz, J. V.; Stefanov, J. V.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, M. W.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. Gaussian 98; Gaussian, Inc.: Pittsburgh, PA, 1998.

(9) The yield was estimated from ^2H NMR spectra by use of CD_3CN as an internal standard.

the mesitylene. A similar reaction mechanism was discussed by Eisch et al. in the reaction of trimesitylborirene and an alcohol: one boron−carbon (ring) bond in trimesitylborirene was cleaved by prior coordination of the alcohol to the boron center and subsequent intramolecular proton transfer.[10] Kawashima and Okazaki et al. reported that a boron−mesityl bond in a borate complex was easily cleaved by hydrolysis.[11,12]

Triethylamine polarizes the O−H bond in **5** by forming an OH···N hydrogen bond, which enhances nucleophilicity of the hydroxyl oxygen and accelerates the cyclization. DBU, a stronger base than triethylamine, completely abstracts the proton from the hydroxyl group in **5**, resulting in the formation of the stable silyloxyborate−DBU·H$^+$ complex **6**. On the other hand, the effect of CH_3CN remains unclear. Initially we postulated that CH_3CN coordinates to a vacant p orbital on the boron center in **5**, which inhibits the nucleophilic attack of the oxygen on the boron. However, the ^{11}B NMR resonance of **5** in CD_3CN exhibited no shift change compared to that in C_6D_6.

Formation of Disiloxane. The reaction pathway to disiloxane **3** deserves some comments. We initially postulated that disiloxane **3** was formed by condensation of two molecules of **5** during the reaction of **1** with *tert*-butyl alcohol (Scheme 2).[13] However, we found that stirring of **5** in THF at room temperature for 240 h gave rise to disiloxane **3** in only 10% yield, as described earlier. In contrast, treatment of **5** with an equimolar amount of **1** in THF at room temperature for 192 h gave **3** in 91% yield and **4** in 6% yield, as shown in eq 3. These results indicate that the main pathway to **3** in the present reaction is condensation of **5** with **1**, rather than condensation of two molecules of **5**.[14] A similar type of disiloxane formation involving a hydrosilane was reported by Chojnowski et al. They disclosed that a hydrosilane (R_3SiH) underwent $(C_6F_5)_3B$-mediated condensation reaction with an alkoxysilane (R'_3SiOR'') to yield a mixed disiloxane ($R_3SiOSiR'_3$) with elimination of alkane $R''H$.[15]



(3)

Conclusion

We prepared hydroxysilane **5** by hydrolysis of hydrosilane **1** and confirmed that **5** underwent intramolecular cyclization to give 3,4-benzo-1,2,5-oxasilaboracyclopentene **4** with elimination of mesitylene. The cyclization was accelerated by heating or in the presence of triethylamine. The cyclization involves formation of a transient silyloxyborate complex and subsequent hydrogen migration from the hydroxyl group to the ipso carbon of one of the mesityl groups. The former was supported by isolation of the silyloxyborate−DBU·H$^+$ complex **6**, and the latter was confirmed by ^2H NMR monitoring of the reaction of deuterium-labeled **5**.

Experimental Section

General Considerations. ^1H (400 MHz), ^2H (61.4 MHz), ^{11}B (128.3 MHz), ^{13}C (100 MHz), and ^{29}Si (79.4 MHz) NMR spectra were recorded with a JEOL EX-400 or AL-400 spectrometer. ^1H and ^{13}C chemical shifts were referenced to the residual proton (for $CDCl_3$, $\delta(^1H)$ 7.26 ppm, $\delta(^{13}C)$ 77.0 ppm; for C_6D_6, $\delta(^1H)$ 7.20 ppm, $\delta(^{13}C)$ 128.0 ppm). ^1H and ^{13}C chemical shifts in THF-d_8 were referenced to external tetramethylsilane ($\delta(^1H)$ 0 ppm; $\delta(^{13}C)$ 0 ppm). ^{11}B chemical shifts were referenced to external $BF_3 \cdot Et_2O$ (δ 0 ppm). ^{29}Si chemical shifts were referenced to external tetramethylsilane (δ 0 ppm). 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. Recycling preparative HPLC was performed with an LC918 instrument equipped with a JAIGEL SIL SH-043-15 column.

Hexane was distilled under a nitrogen atmosphere over calcium hydride, or the dehydrated solvent (<10 ppm; Kanto Chemical Co., Inc.) was dried through a Solvent Dispensing System (GlassContour) under a nitrogen atmosphere (99.999%). THF and Et_2O were distilled under a nitrogen atmosphere over sodium diphenylketyl, or the dehydrated solvents (<10 ppm for THF and <50 ppm for Et_2O; Kanto Chemical Co., Inc.) were dried through the Solvent Dispensing System (GlassContour) under a nitrogen atmosphere (99.999%). C_6D_6, toluene, and THF-d_8 were distilled under a nitrogen atmosphere over sodium diphenylketyl. $CDCl_3$, CH_3CN, CD_3CN, triethylamine, and 1,8-diazabicyclo[5.4.0]-7-undecene (DBU) were distilled under a nitrogen atmosphere over calcium hydride. All reactions were carried out under an inert gas atmosphere.

***o*-(Dimesitylboryl)(dimethylsilyl)benzene (1).** This compound was prepared in a manner similar to the procedure reported previously.[1]

Reaction of 1 with *t*-BuOH: Formation of 2d, 3, and 4. A mixture of **1** (155 mg, 0.40 mL) and *t*-BuOH (38 mg, 0.52 mmol) in THF (1.0 mL) was stirred at room temperature for 42 h. Then, the solvent was removed in vacuo. The resulting oil was diluted with hexane (1 mL), vigorously stirred for 5 min, and dried in vacuo to form a white solid containing **2d**, **3**, and **4**. The solid was dissolved in C_6D_6 (1.0 mL). The yields of **2d**, **3**, and **4** were estimated to be 59%, 34%, and 5%, respectively, by ^1H NMR analysis of the solution using anisole, which was added prior to the analysis, as an internal standard. Then, the solvent was removed in vacuo. The residue was washed with CH_3CN (1 mL) with vigorous stirring, and the resulting solid was filtered. The solid on the filter paper was washed with CH_3CN (total volume 4 mL) to give a mixture of **2d** and **3** (118 mg) as a white solid. The mixture was subjected to HPLC with hexane/CH_2Cl_2 (5:1) as eluent to give **3** (39 mg, 10% yield) (R_f = 0.58) and **2d**[1] (56 mg, 30% yield) (R_f = 0.5) as white solids.

[*o*-(Dimesitylboryl)phenyl]dimethyldisiloxane (3). Mp: 184−185 °C (decomposed in a sealed tube). ^1H NMR (C_6D_6, δ): 0.13 (br, 6H), 0.40 (br, 6H), 1.78−2.31 (br, 18H), 6.68−6.82 (br, 8H), 7.17

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[10] Eisch, J. J.; Shafii, B.; Odom, J. D.; Rheingold, A. L. *J. Am. Chem. Soc.* **1990**, *112*, 1847.

[11] Kawashima, T.; Kannabe, N.; Tokitoh, R.; Okazaki, *Organometallics* **1999**, *18*, 5180.

[12] For an example of an intermolecular reaction between triphenylborane and isopropyl alcohol: Domaille, P. J.; Druliner, J. D.; Gosser, L. W.; Read, J. M., Jr.; Schmelzer, E. R.; Stevens, W. R. *J. Org. Chem.* **1985**, *50*, 189.

[13] For a review of siloxanes and silanols: (a) Drake, R.; MacKinnon, I.; Taylor, R. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: Chichester, U.K., 1998; Vol. 2, pp 2217−2244. (b) Lickiss, P. D. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: Chichester, U.K., 2001; Vol. 3, pp 695−744.

[14] We cannot exclude the possibility that the alcohol serves as a Brønsted acid to facilitate the bimolecular condensation of **5**.

[15] Chojnowski, J.; Rubinsztajn, S.; Cella, J. A.; Fortuniak, W.; Cypryk, M.; Kurjata, K.; Kazmierski, K. *Organometallics* **2005**, *24*, 6077.

(ddd, ^3J = 8 Hz, ^3J = 8 Hz, ^4J = 1 Hz, 1H), 7.29 (ddd, ^3J = 8 Hz, ^3J = 8 Hz, ^4J = 1 Hz, 1H), 7.54 (d, ^3J = 8 Hz, 1H), 8.23 (d, ^3J = 8 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 2.80, 21.22, 22.73−24.03 (br), 128.67, 128.97, 127.92−129.20 (br), 133.86, 135.70, 138.49−144.92 (br), 145.21, 155.28. ^{11}B NMR (C_6D_6, δ): 74 (br). ^{29}Si{^{1}H} NMR (C_6D_6, δ): −0.49. MS (EI): *m/z* 768 ($M^+ - Me$, 5), 457 ($M^+ - BPhMes_2$, 44), 383 ($[Mes_2B(C_6H_4)SiMe_2]^+$, 85), 177 (100). Anal. Calcd for $C_{52}H_{64}B_2OSi_2$: C, 79.78; H, 8.24. Found: C, 79.68; H, 8.43.

Hydrolysis of 1 with H_2O: Formation of 5. To a solution of **1** (3.07 g, 7.99 mmol) in THF (16 mL) was added H_2O (145 μL, 8.02 mmol) dropwise via a syringe at room temperature. Gas was evolved immediately. After the reaction mixture was stirred at room temperature for 10 min, the solvent was removed in vacuo. In order to remove volatile materials completely, the resulting highly viscous oil was treated twice with the following procedures: (i) dilution with hexane (8 mL), (ii) vigorous stirring at room temperature for 5 min, and (iii) evaporation under reduced pressure, giving a white solid. Then, the white solid was suspended in CH_3CN (5 mL) by vigorous stirring for 20 min and the suspension filtered. The solid on the filter paper was washed with CH_3CN (total volume 20 mL) to give pure **5** (2.94 g, 90% yield) as a white solid.

***o*-(Hydroxydimethylsilyl)(dimesitylboryl)benzene (5).** Mp: 115−117 °C (decomposed in a sealed tube). ^{1}H NMR (C_6D_6, δ): 0.14−0.37 (br, 6H), 1.51 (s, 1H), 1.79−2.36 (br, 18H), 6.74−6.78 (br, 4H), 7.14−7.26 (m, 2H), 7.52 (ddd, ^3J = 8 Hz, ^4J = 1 Hz, ^5J = 1 Hz, 1H), 7.57 (ddd, ^3J = 8 Hz, ^4J = 1 Hz, ^5J = 1 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 1.41 (br), 21.23, 22.64−23.84 (br), 127.76 (br), 128.60 (br), 128.83, 129.08, 129.58−129.72 (br), 134.11, 134.38, 138.76−144.23 (br), 144.73, 155.24 (br). ^{11}B NMR (C_6D_6, δ): 74 (br). ^{29}Si{^{1}H} NMR (C_6D_6, δ): 6.89. MS (EI): *m/z* 280 ($M^+ - Mes$, 100), 265 ($M^+ - 2Me$, 42), 161 ($M^+ - 2Mes$, 92). Anal. Calcd for $C_{26}H_{33}BOSi$: C, 77.98; H, 8.31. Found: C, 77.71; H, 8.25.

Cyclization of 5: Typical Procedure for Formation of 4. A solution of **5** (200 mg, 0.50 mmol) in THF-d_8 (1.0 mL) was stirred at room temperature for 240 h to afford **3**, **4**, and mesitylene. The yields of **3**, **4**, and mesitylene were estimated to be 10%, 86%, and 81%, respectively, by ^{1}H NMR analysis of the solution using anisole, which was added prior to the analysis, as an internal standard. Then, the solvent was removed in vacuo. In order to remove volatile materials completely, the resulting highly viscous oil was treated twice with the following procedures: (i) dilution with hexane (1 mL), (ii) vigorous stirring at room temperature for 5 min, and (iii) evaporation under reduced pressure. The obtained oil was washed with CH_3CN (1 mL) with vigorous stirring, and the resulting white solid was filtered. The solid on the filter paper was washed with CH_3CN (total volume 4 mL) to give **3** (10 mg, 5% yield) as a white solid. The filtrate was concentrated in vacuo to afford a highly viscous oil. The oil was subjected to bulb-to-bulb distillation (240−250 °C/0.3 mmHg) to give **4** (90 mg, 64% yield) as a highly viscous colorless oil, which solidified on standing.

5,5-Dimesityl-2,2-dimethyl-3,4-benzo-1,2,5-oxasilaboracyclopentene (4). Mp: 42.0−44.0 °C (in air). ^{1}H NMR (C_6D_6, δ): 0.39 (s, 6H), 2.29 (s, 6H), 2.37 (s, 12H), 6.90 (s, 2H), 7.23 (ddd, ^3J = 7 Hz, ^3J = 7 Hz, ^4J = 1 Hz, 1H), 7.31 (ddd, ^3J = 7 Hz, ^3J = 7 Hz, ^4J = 1 Hz, 1H), 7.54 (ddd, ^3J = 7 Hz, ^4J = 1 Hz, ^5J = 1 Hz, 1H), 7.70 (ddd, ^3J = 7 Hz, ^4J = 1 Hz, ^5J = 1 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): −0.75, 21.37, 22.09, 127.19 (2C), 129.66, 130.44, 131.03, 134.02, 137.90, 139.44, 149.66 (9 signals were observed in the aromatic region, although 10 signals were expected). ^{11}B NMR (C_6D_6, δ): 50 (br). ^{29}Si{^{1}H} NMR (C_6D_6, δ): 27.26. MS (EI): *m/z* 280 (M^+, 100), 265 ($M^+ - Me$, 66), 161 ($M^+ - Mes$, 21). Anal. Calcd for $C_{17}H_{21}BOSi$: C, 72.86; H, 7.55. Found: C, 72.46; H, 7.40.

Cyclization of 5 in the Presence of DBU: Formation of 6. A solution of **5** (398 mg, 0.99 mmol) and DBU (150 mL, 1.00 mmol) in THF (2.0 mL) was stirred at room temperature for 24 h to yield a white suspension. The solvent was removed in vacuo. In order to remove volatile materials completely, the resulting solid was treated twice with the following procedures: (i) dilution with hexane (1 mL), (ii) vigorous stirring at room temperature for 5 min, and (iii) evaporation under reduced pressure. The obtained solid was washed with hexane (2 mL) with vigorous stirring and filtered. The solid on the filter paper was washed with hexane (total volume 8 mL) to give **6** (530 mg, 91% yield) as a white solid. Recrystallization of **6** from THF−hexane gave colorless crystals of **6**·0.5THF.

1,8-Diazabicyclo[5.4.0]-7-undecenium 5,5-dimesityl-2,2-dimethyl-3,4-benzo-1,2,5-oxasilaboratacyclopentene (6·0.5THF). Mp: 178−180 °C (decomposed in a sealed tube). ^{1}H NMR ($CDCl_3$, δ): 0.18 (s, 6H), 1.63−1.73 (br, 8H, DBU·H^+), 1.86 (m, 2H, THF), 1.94 (s, 12H), 2.14 (s, 6H), 2.20 (m, 2H, DBU·H^+), 2.71 (m, 2H, DBU·H^+), 3.20 (m, 2H, DBU·H^+), 3.32 (m, 2H, DBU·H^+), 3.75 (m, 2H, THF), 6.54 (s, 4H), 7.00−7.08 (m, 2H), 7.38 (d, ^3J = 7 Hz, 1H), 7.42 (d, ^3J = 6 Hz, 1H), 11.6 (br, 1H, DBU·H^+). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 2.42, 19.78, 20.74, 24.44 (DBU·H^+), 25.58 (DBU·H^+), 25.86, 26.80 (THF), 29.05 (DBU·H^+), 31.90 (DBU·H^+), 37.55 (DBU·H^+), 48.48 (DBU·H^+), 53.91 (DBU·H^+), 67.94 (THF), 122.89, 127.56, 128.50, 128.57, 131.26, 131.53, 139.91, 142.43, 155.24, 165.09, 171.98. ^{11}B NMR (C_6D_6, δ): 6 (br). ^{29}Si{^{1}H} NMR (C_6D_6, δ): 10.5. Anal. Calcd for $C_{38}H_{57}BN_2O_{1.5}Si$: C, 75.55; H, 9.00; N, 4.76. Found: C, 75.29; H, 9.03; N, 4.44.

Formation of 4·DBU from 6. A suspension of **6** (173 mg 0.29 mmol) in THF-d_8 (0.6 mL) in a J. Young valve NMR tube was heated at 80 °C for 120 h to afford teh DBU adduct of **4** (**4**·DBU) and mesitylene. The yields of **4**·DBU and mesitylene were estimated to be 87% and 87%, respectively, by ^{1}H NMR analysis of the solution using anisole, which was added prior to the analysis, as an internal standard.

4·DBU. ^{1}H NMR (C_6D_6, δ): 0.39 (s, 6H), 1.10−1.15 (m, 2H, DBU), 1.24−1.30 (m, 2H, DBU), 1.39−1.54 (m, 4H, DBU), 2.43−2.45 (m, 2H, DBU), 2.59−2.67 (m, 4H, DBU), 2.28 (s, 6H), 2.36 (s, 12H), 3.58−3.63 (m, 2H, DBU), 6.89 (s, 2H), 7.23 (dd, ^3J = 7 Hz, ^3J = 7 Hz, 1H), 7.31 (dd, ^3J = 7 Hz, ^3J = 7 Hz, 1H), 7.54 (d, ^3J = 7 Hz, 1H), 7.70 (d, ^3J = 7 Hz, 1H). ^{11}B NMR (C_6D_6, δ): 42 (br).

Hydrolysis of 1 with D_2O: Formation of 5-*d*. The title compound was prepared in a manner similar to that for **5** using D_2O. The deuterated ratio of **5-*d*** was determined to be 83 atom % D by ^{2}H NMR (THF) using CD_3CN as an internal standard.

***o*-(Deuterioxydimethylsilyl)(dimesitylboryl)benzene (5-*d*).** ^{1}H NMR (C_6D_6, δ): 0.14−0.38 (br, 6H), 1.79−2.38 (br, 18H), 6.72−6.81 (br, 4H), 7.15−7.26 (m, 2H), 7.53 (ddd, ^3J = 8 Hz, ^4J = 1 Hz, ^5J = 1 Hz, 1H), 7.57 (ddd, ^3J = 8 Hz, ^4J = 1 Hz, ^5J = 1 Hz, 1H). ^{2}H NMR (THF δ) 6.79.

Cyclization of 5-*d*: Formation of 4 and Mesitylene-*d*. A solution of **5-*d*** (83 atom % D, 120 mg, 0.30 mmol) in THF (0.60 mL) in a J. Young valve NMR tube was degassed by the freeze−pump−thaw process. Then, the solution was heated at 80 °C for 96 h in the dark to afford **4** and mesitylene-*d*. The yield of mesitylene-*d* was estimated to be 100% (based on 83 atom % D of **5-*d***) by ^{2}H NMR analysis of the solution using CD_3CN, which was added after the reaction, as an internal standard. Then, the solvent was removed in vacuo. In order to remove volatile materials, the residue was treated twice with the following procedures: (i) dilution with hexane (1 mL), (ii) vigorous stirring at room temperature for 5 min, and (iii) evaporation under reduced pressure, giving a highly viscous oil of **4**. The oil was diluted with C_6D_6 (1 mL), and the yield of **4** was estimated to be 92% by ^{1}H NMR analysis of the solution using anisole, which was added prior to the analysis, as an internal standard.

Reaction between 1 and 5: Formation of 3. A solution of **1** (191 mg, 0.50 mmol) and **5** (200 mg, 0.50 mmol) in THF (1.0

mL) was stirred at room temperature for 120 h. Then, the solvent was removed in vacuo. In order to remove volatile materials completely, the resulting highly viscous oil was treated twice with the following procedures: (i) dilution with hexane (1 mL), (ii) vigorous stirring at room temperature for 5 min, and (iii) evaporation under reduced pressure, giving a white solid containing **3** and **4**. The solid was dissolved in C_6D_6 (1.0 mL). The yields of **3** and **4** were estimated to be 91% and 6%, respectively, by ^1H NMR analysis of the solution using anisole, which was added prior to the analysis, as an internal standard. Then, the solvent was removed in vacuo. The residue was washed with CH_3CN (2 mL) with vigorous stirring, and the resultant white solid was filtered. The solid on the filter paper was washed with CH_3CN (total volume 8 mL) to give **3** (320 mg, 82% yield) as a white solid.

X-ray Crystallographic Analysis. Crystals of **6** suitable for X-ray crystallographic analysis were obtained by recrystallization from THF−hexane. A crystal was mounted using silicon oil to a cryoloop (Hampton Research). The data were collected at 173 K on a Mac Science DIP2030 imaging plate equipped with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å). The data were solved using SHELX by direct methods. The non-hydrogen atoms were refined anisotropically. All of the hydrogen atoms were located at the expected positions by geometrical calculations and refined isotropically.

Computational Methods. Calculations were performed with the Gaussian 98[8] program package on the HIT HPC-PA264U-6CPU model. The initial geometry of **6** was obtained from the crystal structure of **6**, and a hydrogen atom was added to the amidinium nitrogen. Then the geometry was fully optimized at the HF/6-31+G(d) level.

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Supporting Information Available: A CIF file, tables, and figures giving crystallographic data for **6** and computational work on **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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