

# Selective Boryl Silyl Ether Formation in the Photoreaction of Bisboryloxide/Boroxine with Hydrosilane Catalyzed by a Transition-Metal Carbonyl Complex

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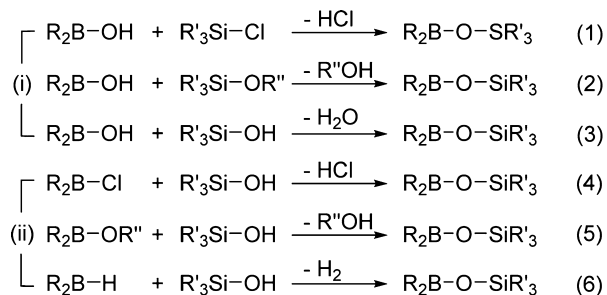
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**S** Supporting Information

**ABSTRACT:** Selective B–O–Si bond formation was achieved in the reaction of bisboryloxide O(Bpin)<sub>2</sub> (pin = (OCMe<sub>2</sub>)<sub>2</sub>)/boroxine (MeBO)<sub>3</sub> system with tertiary silane R<sub>3</sub>SiH in the presence of stoichiometric water and a catalytic amount of [M](CO)<sub>5</sub> ([M] = Mo(CO), W(CO), Fe) to give boryl silyl ethers. Moreover, this reaction can be applied to various hydrosilanes (disilyl compounds and secondary silanes) and hydrogermane. Some of the boryl silyl ethers thus formed were confirmed by X-ray analysis.

Borosilicate materials have been widely used in many areas because of their excellent heat and chemical resistance; boryl silyl ethers have emerged as the most useful precursors in the synthesis of these materials.<sup>1</sup> Methods for synthesis of boryl silyl ethers can be classified into two major types: (i) reaction of hydroxyborane with chlorosilane,<sup>2</sup> alkoxyasilane,<sup>3</sup> and silanol<sup>4</sup> (Scheme 1, (1)–(3)) and (ii) reaction of chloroborane,<sup>4d,5</sup>

## Scheme 1. Common Synthetic Methods toward Boryl Silyl Ethers

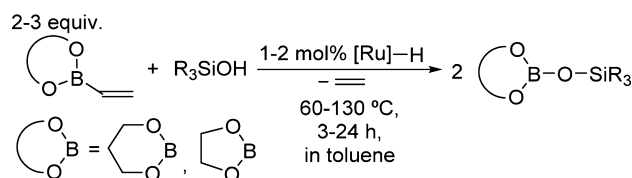


alkoxyborane,<sup>6</sup> and hydroborane<sup>5b,7</sup> with silanol ((4)–(6)). However, these conventional methods have several drawbacks, including the formation of corrosive HCl and use of water- and air-unstable substrates. In addition, these reactions have the potential to generate byproducts such as disiloxanes. Therefore, a selective B–O–Si bond-forming reaction using stable substrates is needed.

Bond-forming reactions via transition-metal catalysts are extremely important transformations since they provide chemoselectivity (e.g., regioselectivity, stereoselectivity). However, to the best of our knowledge, only one example of a catalytic B–O–Si bond-forming reaction using a transition-metal complex has been reported by Marciniec's group, in

which precious metal catalysts and silanol are used (Scheme 2).<sup>8,9</sup>

## Scheme 2. O-Borylation of Silanol with Vinylborane Catalyzed by a Ru–H Complex

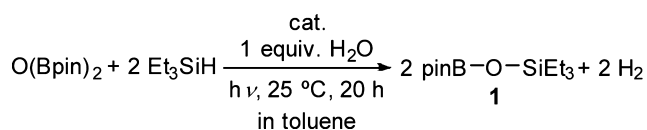


Herein, we present a new catalytic reaction of bisboryloxides with hydrosilanes in the presence of stoichiometric water and a catalytic amount of [M](CO)<sub>5</sub> ([M] = Mo(CO), W(CO), Fe) to form boryl silyl ethers under photoirradiation. In addition, we found that our reaction could be applied to boroxine, disilyl compounds, and secondary silane.

Toluene (0.5 mL), O(Bpin)<sub>2</sub> (0.5 mmol), Et<sub>3</sub>SiH (1.0 mmol), H<sub>2</sub>O (0.5 mmol), and Mo(CO)<sub>6</sub> (0.0025 mmol) were charged in a sealed glass tube under a nitrogen atmosphere, and the solution was photoirradiated with a 400 W medium-pressure mercury arc lamp (Pyrex filtered) at 25 °C for 20 h (Table 1, entry 1). The <sup>1</sup>H NMR spectrum in C<sub>6</sub>D<sub>6</sub> of the crude reaction mixture revealed the formation of pinB–O–SiEt<sub>3</sub> (**1**) (92% yield based on NMR) and H<sub>2</sub> (4.47 ppm, vide infra). The results showed that Mo(CO)<sub>6</sub> was effective in catalyzing the reaction of O(Bpin)<sub>2</sub> with Et<sub>3</sub>SiH, with a turnover number (TON) of 368. Notably, after completion of reaction and removal of the volatile materials, pure boryl silyl ether could be readily obtained by extraction with *n*-hexane or diethyl ether and drying in *vacuo*. When the amount of Mo(CO)<sub>6</sub> was reduced from 0.25 to 0.05 mol %, the yield of the product was greatly diminished (entry 2). In addition, the reaction did not proceed in the absence of the transition-metal catalyst (entry 3). Formation of pinB–O–SiEt<sub>3</sub> was completed in 10 h at 25 °C or 2 h at 50 °C (entries 4, 5). The desired product was not obtained by thermal reaction (70 or 110 °C) without photoirradiation (entry 6). Other molybdenum carbonyl complexes, W(CO)<sub>6</sub>, Fe(CO)<sub>5</sub>, and Cp\*Fe(CO)<sub>2</sub>Me (Cp\* = η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>) precursor, were also examined as reaction catalysts; it was found that these catalytic activities were lower than that of Mo(CO)<sub>6</sub> (entries 7–9, 11, 13). The activities of

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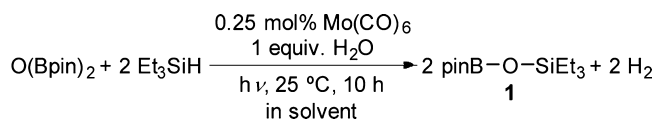
Table 1. Reaction of O(Bpin)<sub>2</sub> with Et<sub>3</sub>SiH in the Presence of a Transition-Metal Carbonyl Complex<sup>a</sup>

| entry           | cat. [amount (mol%)] <sup>b</sup>            | yield <sup>c,d</sup> (%) | TON |
|-----------------|--|--------------------------|-----|
| 1               | Mo(CO) <sub>6</sub> [0.25]                   | 92 (89)                  | 368 |
| 2               | Mo(CO) <sub>6</sub> [0.05]                   | 4                        | 80  |
| 3               | no catalyst                                  | no reaction              | —   |
| 4 <sup>e</sup>  | Mo(CO) <sub>6</sub> [0.25]                   | 94 (92)                  | 376 |
| 5 <sup>f</sup>  | Mo(CO) <sub>6</sub> [0.25]                   | 93 (88)                  | 372 |
| 6 <sup>g</sup>  | Mo(CO) <sub>6</sub> [0.25]                   | no reaction              | —   |
| 7               | CpMo(CO) <sub>3</sub> Me [0.25]              | 29                       | 116 |
| 8               | [CpMo(CO) <sub>3</sub> ] <sub>2</sub> [0.25] | 56                       | 112 |
| 9               | Fe(CO) <sub>5</sub> [0.5]                    | 26                       | 52  |
| 10              | CpFe(CO) <sub>2</sub> Me [0.5]               | trace                    | —   |
| 11              | Cp*Fe(CO) <sub>2</sub> Me [0.5]              | 55                       | 110 |
| 12              | Cr(CO) <sub>6</sub> [0.5]                    | trace                    | —   |
| 13              | W(CO) <sub>6</sub> [0.5]                     | 57                       | 114 |
| 14 <sup>h</sup> | Mo(CO) <sub>6</sub> [0.25]                   | 12                       | 48  |
| 15 <sup>h</sup> | Mo(CO) <sub>6</sub> [2.5]                    | 12                       | 4.8 |
| 16 <sup>i</sup> | Mo(CO) <sub>6</sub> [0.25]                   | 92 (87)                  | 368 |
| 17 <sup>j</sup> | Mo(CO) <sub>6</sub> [0.25]                   | 93 (89)                  | 372 |

<sup>a</sup>O(Bpin)<sub>2</sub>/Et<sub>3</sub>SiH/H<sub>2</sub>O = 0.5:1.0:0.5 mmol in 0.5 mL of toluene. <sup>b</sup>Based on [Et<sub>3</sub>SiH]. <sup>c</sup>Yield based upon <sup>1</sup>H NMR. <sup>d</sup>Isolated yield in parentheses. <sup>e</sup>Reaction was carried out at 25 °C for 10 h. <sup>f</sup>Reaction was carried out at 50 °C for 2 h. <sup>g</sup>Reaction was carried out at 70 or 110 °C for 20 h without photoirradiation. <sup>h</sup>Without H<sub>2</sub>O. <sup>i</sup>2.5 mmol of H<sub>2</sub>O. <sup>j</sup>5.0 mmol of H<sub>2</sub>O.

CpFe(CO)<sub>2</sub>Me and Cr(CO)<sub>6</sub> were sluggish (entries 10, 12). The different activity among the carbonyl complexes (Mo, W, Cr and Fe) may come from different stability of a catalytic intermediate. In the reaction using the Mo(CO)<sub>6</sub> catalyst but in the absence of H<sub>2</sub>O, the yield decreased to 12% (entry 14) and did not improve even when the catalyst amount was increased to 2.5 mol% (entry 15). When an excess amount of water was used, the reaction proceeded as well as when a stoichiometric amount of water was used (entries 16, 17).

Next, various solvents were screened under the reaction conditions shown in entry 4 in Table 1; it was found that toluene, tetrahydrofuran (THF), diethyl ether, and *n*-hexane were effective in the B–O–Si bond-forming reaction (Table 2, entries 1–4), whereas CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, CH<sub>3</sub>CN, dimethylformamide (DMF), and water were not (entries 5–9). The molybdenum η<sup>2</sup>-silane σ-complex Mo(CO)<sub>5</sub>(η<sup>2</sup>-HSiEt<sub>3</sub>) that is considered to be an intermediate in our system (vide infra) is unstable in CH<sub>2</sub>Cl<sub>2</sub> below rt,<sup>10</sup> so CHCl<sub>3</sub> and CH<sub>2</sub>Cl<sub>2</sub> might lead to a decrease in efficiency. Presumably, CH<sub>3</sub>CN and DMF

Table 2. Solvent Screening for B–O–Si Bond-Forming Reaction<sup>a</sup>

| entry | solvent                         | yield <sup>b,c</sup> (%) | TON |
|-------|---------------------------------|--------------------------|-----|
| 1     | toluene                         | 94 (92)                  | 376 |
| 2     | THF                             | 92 (90)                  | 368 |
| 3     | diethyl ether                   | 89 (82)                  | 356 |
| 4     | <i>n</i> -hexane                | 86                       | 344 |
| 5     | CHCl <sub>3</sub>               | 15                       | 60  |
| 6     | CH <sub>2</sub> Cl <sub>2</sub> | 44                       | 176 |
| 7     | CH <sub>3</sub> CN              | trace                    | —   |
| 8     | DMF                             | 20                       | 80  |
| 9     | water                           | 12                       | 48  |

<sup>a</sup>O(Bpin)<sub>2</sub>/Et<sub>3</sub>SiH/H<sub>2</sub>O/Mo(CO)<sub>6</sub> = 0.5:1.0:0.5:0.0025 mmol in 0.5 mL of solvent. <sup>b</sup>Yield based upon <sup>1</sup>H NMR. <sup>c</sup>Isolated yield in parentheses.

acted as a catalyst poison.<sup>11</sup> The low activity in water may come from the low solubility of Mo(CO)<sub>6</sub> and reagents. In subsequent studies, toluene or THF was used as the solvent.

To explore the scope and limitation for this bond-forming reaction, several combinations of boron compounds and hydrosilanes were examined (Table 3). The reaction proceeded effectively for various tertiary and secondary silanes (entries 1–10), although <sup>n</sup>Pr<sub>3</sub>SiH and <sup>t</sup>BuMe<sub>2</sub>SiH were slow-reacting substrates (entries 2, 3). Entry 7 should be noted because, although the substrate MePh(CH<sub>2</sub>=CH)SiH has a vinyl group and a Si–H bond, the vinyl group can tolerate hydrosilylation conditions. Our reaction system is applicable not only for O(Bpin)<sub>2</sub> but also for pinacol borane HBpin (entry 11) and pinacol borinic acid HOBpin (entries 12 and 13). When reactions were carried out without water, the yields of products decreased (entries 12 vs 14, 13 vs 15). The corresponding B–O–Si compounds were obtained when trimethylboroxine (MeBO)<sub>3</sub> and methylboronic acid MeB(OH)<sub>2</sub> were used as a boron source (entries 16–19). In contrast, O(BPh<sub>2</sub>)<sub>2</sub> did not undergo the B–O–Si bond-forming reaction (entry 20).

All boryl silyl ethers obtained were characterized by <sup>1</sup>H, <sup>11</sup>B, <sup>13</sup>C, <sup>29</sup>Si NMR spectroscopy and elemental analyses (see Supporting Information (SI)). In addition, most of the compounds were analyzed by GC/MS. The molecular structures of pinBOSiPh<sub>3</sub> (**6**), Fe{η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>(SiMe<sub>2</sub>OBpin)}<sub>2</sub> (**9**), and MeB(OSiPh<sub>3</sub>)<sub>2</sub> (**12**) were confirmed by single crystal X-ray structure analysis (Figure 1). These X-ray structures furnished definitive proof of B–O–Si bond formation.

In order to obtain insight into the reaction mechanism, reactions in which D<sub>2</sub>O and H<sub>2</sub><sup>18</sup>O were used in place of H<sub>2</sub>O

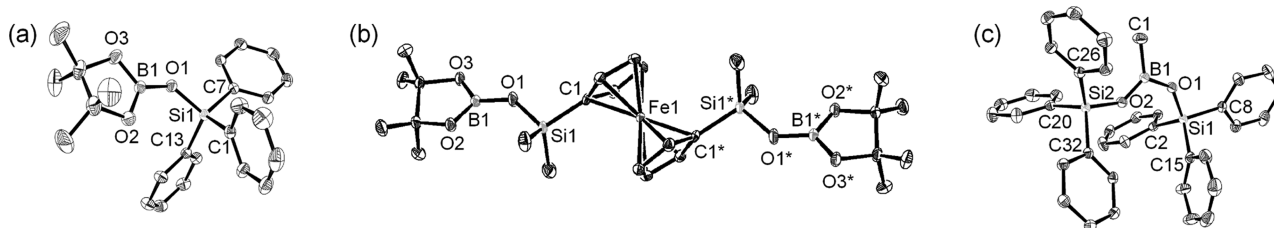
Figure 1. ORTEP drawing of **6** (a), **9** (b), and **12** (c) with 30% thermal ellipsoidal. Hydrogen atoms have been omitted for clarity.

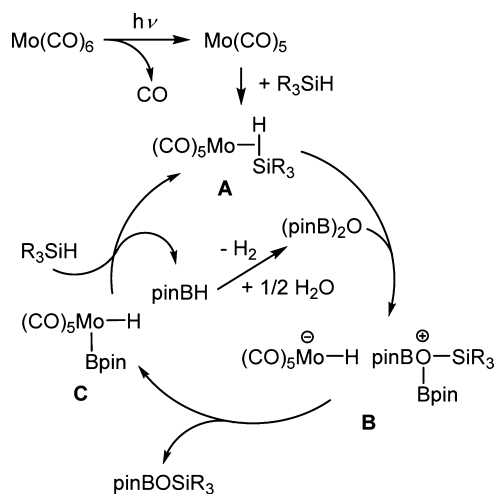
Table 3. B–O–Si Bond-Forming Reactions of Various Boron Compounds and Hydrosilanes<sup>a</sup>

|                 |                                   | $\text{Mo}(\text{CO})_6$<br>$\text{H}_2\text{O}$  |                                 |   |          |  |  |
|-----------------|-----------------------------------|---|---------------------------------|---|----------|--|--|
|                 |                                   | $[\text{B}] + [\text{Si}]$  |                                 | $\xrightarrow[\text{in toluene}]{h\nu, 25^\circ\text{C}}$                                       |          | $[\text{B}-\text{O}-\text{Si}] + \text{H}_2$ |  |
| entry           | [B]                               | [Si]  | [B]/[Si]/[Mo(CO) <sub>6</sub> ] | [B–O–Si]  | time (h) | yield <sup>b,c</sup> (%)                     |  |
| 1               | O(Bpin) <sub>2</sub>              | Et <sub>3</sub> SiH   | 1:2:0.03                        | pinBOSiEt <sub>3</sub> (1)  | 10       | 92   |  |
| 2               | O(Bpin) <sub>2</sub>              | <sup>n</sup> Pr <sub>3</sub> SiH  | 1:2:0.03                        | pinBOSi <sup>n</sup> Pr <sub>3</sub> (2)  | 50       | 95   |  |
| 3               | O(Bpin) <sub>2</sub>              | <sup>t</sup> BuMe <sub>2</sub> SiH  | 1:2:0.03                        | pinBOSi <sup>t</sup> BuMe <sub>2</sub> (3)  | 100      | 95   |  |
| 4               | O(Bpin) <sub>2</sub>              | Me <sub>2</sub> PhSiH   | 1:2:0.03                        | pinBOSiMe <sub>2</sub> Ph (4)   | 0.5      | 94   |  |
| 5               | O(Bpin) <sub>2</sub>              | MePh <sub>2</sub> SiH   | 1:2:0.03                        | pinBOSiMePh <sub>2</sub> (5)  | 10       | 91   |  |
| 6               | O(Bpin) <sub>2</sub>              | Ph <sub>3</sub> SiH   | 1:2:0.03                        | pinBOSiPh <sub>3</sub> (6)  | 20       | 93   |  |
| 7               | O(Bpin) <sub>2</sub>              | MePh(CH <sub>2</sub> =CH)SiH  | 1:2:0.03                        | pinBOSiMePh(CH=CH <sub>2</sub> ) (7)  | 10       | 92   |  |
| 8               | O(Bpin) <sub>2</sub>              | O(SiMe <sub>2</sub> H) <sub>2</sub>   | 1:1:0.03                        | O(SiMe <sub>2</sub> OBpin) <sub>2</sub> (8)   | 20       | 96   |  |
| 9               | O(Bpin) <sub>2</sub>              | Fe{(η <sup>5</sup> -C <sub>5</sub> H <sub>4</sub> (SiMe <sub>2</sub> H)) <sub>2</sub> } | 1:1:0.03                        | Fe{(η <sup>5</sup> -C <sub>5</sub> H <sub>4</sub> (SiMe <sub>2</sub> OBpin)) <sub>2</sub> } (9) | 10       | 90   |  |
| 10              | O(Bpin) <sub>2</sub>              | Et <sub>3</sub> SiH <sub>2</sub>  | 1:1:0.03                        | (pinBO) <sub>2</sub> SiEt <sub>2</sub> (10)   | 10       | 92   |  |
| 11              | HBpin                             | Me <sub>2</sub> PhSiH   | 1:1:0.015                       | pinBOSiMe <sub>2</sub> Ph (4)   | 10       | 95   |  |
| 12              | HOBpin                            | Et <sub>3</sub> SiH   | 1:1:0.015                       | pinBOSiEt <sub>3</sub> (1)  | 10       | 93   |  |
| 13              | HOBpin                            | Me <sub>2</sub> PhSiH   | 1:1:0.015                       | pinBOSiMe <sub>2</sub> Ph (4)   | 10       | 95   |  |
| 14 <sup>d</sup> | HOBpin                            | Et <sub>3</sub> SiH   | 1:1:0.015                       | pinBOSiEt <sub>3</sub> (1)  | 10       | (55)   |  |
| 15 <sup>d</sup> | HOBpin                            | Me <sub>2</sub> PhSiH   | 1:1:0.015                       | pinBOSiMe <sub>2</sub> Ph (4)   | 10       | (60)   |  |
| 16 <sup>e</sup> | (MeBO) <sub>3</sub>               | Me <sub>2</sub> PhSiH   | 1:6:0.09                        | MeB(OSiMe <sub>2</sub> Ph) <sub>2</sub> (11)  | 40       | 88   |  |
| 17 <sup>e</sup> | (MeBO) <sub>3</sub>               | Ph <sub>3</sub> SiH   | 1:6:0.09                        | MeB(OSiPh <sub>3</sub> ) <sub>2</sub> (12)  | 40       | 82   |  |
| 18 <sup>e</sup> | MeB(OH) <sub>2</sub>              | Me <sub>2</sub> PhSiH   | 1:2:0.015                       | MeB(OSiMe <sub>2</sub> Ph) <sub>2</sub> (11)  | 40       | 85   |  |
| 19 <sup>e</sup> | MeB(OH) <sub>2</sub>              | Ph <sub>3</sub> SiH   | 1:2:0.015                       | MeB(OSiPh <sub>3</sub> ) <sub>2</sub> (12)  | 40       | 89   |  |
| 20              | O(BPh <sub>2</sub> ) <sub>2</sub> | Me <sub>2</sub> PhSiH   | 1:2:0.03                        | Ph <sub>2</sub> BOSiMe <sub>2</sub> Ph  | 20       | 0  |  |

<sup>a</sup>See SI for details of reaction conditions. <sup>b</sup>Isolated yield. <sup>c</sup>Yield based upon <sup>1</sup>H NMR in parentheses. <sup>d</sup>Without H<sub>2</sub>O. <sup>e</sup>Solvent is THF.

were examined. When D<sub>2</sub>O was used, formation of both H<sub>2</sub> and HD was detected in the <sup>1</sup>H NMR spectrum of the reaction mixture (H<sub>2</sub>: 4.47 ppm; HD: 4.43 ppm (t, *J*<sub>H-D</sub> = 42.6 Hz) in C<sub>6</sub>D<sub>6</sub>) (see SI, Figure S1). The obtained labeled boryl silyl ether (pinB–O–SiPh<sub>3</sub>) was also analyzed using high-resolution mass spectroscopy (HRMS). The experiments using H<sub>2</sub><sup>18</sup>O gave a peak at *m/z* = 404.1858, corresponding to pinB–<sup>18</sup>O–SiPh<sub>3</sub>, in addition to a peak for pinB–<sup>16</sup>O–SiPh<sub>3</sub> at *m/z* = 402.1821. No peak at *m/z* = 404.1858 for H<sub>2</sub>O was observed when H<sub>2</sub>O was used (see SI, Figure S2). These results indicate that water acts as a reactant in our reaction system.

Scheme 3 shows a proposed catalytic cycle for the B–O–Si bond-forming reaction. One CO ligand in the precursor is released to yield Mo(CO)<sub>5</sub>, which reacts with R<sub>3</sub>SiH to give Mo(CO)<sub>5</sub>(η<sup>2</sup>-HSiR<sub>3</sub>) (A).<sup>10,12</sup> Complex A was detected by <sup>1</sup>H NMR spectroscopy after photoirradiation of a Mo(CO)<sub>6</sub>, O(Bpin)<sub>2</sub>, and R<sub>3</sub>SiH mixture in a 0.05:1:2 ratio, respectively, over 20 h (R = Et; the hydride signal was observed at δ = –9.90 ppm in C<sub>6</sub>D<sub>6</sub>). If A reacts with O(Bpin)<sub>2</sub> to form B and nucleophilic attack of [Mo(CO)<sub>5</sub>H]<sup>–</sup> to one of the boron atoms in [O(Bpin)<sub>2</sub>(SiR<sub>3</sub>)]<sup>+</sup> occurs, then pinBOSiR<sub>3</sub> and C would be formed. Reductive elimination of HBpin from C and coordination of R<sub>3</sub>SiH to the molybdenum center regenerates A to complete the catalytic cycle. HBpin thus generated reacts with water to give O(Bpin)<sub>2</sub>. Silanol was not thought to be involved in the catalytic cycle, since the reaction of R<sub>3</sub>SiH and H<sub>2</sub>O in the presence of Mo(CO)<sub>6</sub> under photoirradiation did not give silanol. The reactions similar to entry 14 (also 15) in Table 1 but using O(Bpin)<sub>2</sub> and Et<sub>3</sub>SiH in a 1:1 molar ratio in the absence of water in toluene and in THF revealed that the yields of pinBOSiEt<sub>3</sub> were 8–10%. Therefore, the role of water in this catalytic cycle seems not simple: water may promote the

Scheme 3. Proposed Catalytic Cycle for the Formation of Boryl Silyl Ethers in the Reaction of O(Bpin)<sub>2</sub> with R<sub>3</sub>SiH Promoted by Mo(CO)<sub>6</sub>

reaction from A to B and/or that from B to C in addition to participation in the conversion of pinBH to (pinB)<sub>2</sub>O.

In order to obtain further insight into the catalytic mechanism, we examined a reaction similar to entry 1 in Table 3 using Mo(CO)<sub>5</sub>(THF)<sup>13</sup> or Mo(CO)<sub>5</sub>(NEt<sub>3</sub>)<sup>14</sup> as a catalyst. The reaction proceeded even at 25 or 50 °C, but the yield of the product dropped (Table 4, entries 1, 2, 4, and 5). In contrast, photoirradiation of the solution at 25 °C resulted in the efficient formation of pinBOSiEt<sub>3</sub> with vigorous evolution of H<sub>2</sub> gas (entries 3, 6). These results suggest that the light energy is used not only for dissociation of CO from Mo(CO)<sub>6</sub>

**Table 4. Reaction of O(Bpin)<sub>2</sub> with Et<sub>3</sub>SiH in the Presence of Mo(CO)<sub>5</sub>(THF) or Mo(CO)<sub>5</sub>(NEt<sub>3</sub>)<sup>a</sup>**

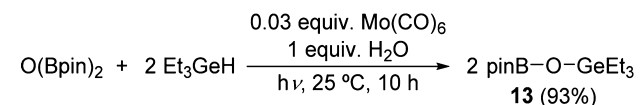
| entry | L =              | conditions      | yield <sup>b</sup> (%) |
|-------|------------------|-----------------|------------------------|
| 1     | THF              | 25 °C, 10 h     | 12                     |
| 2     | THF              | 50 °C, 10 h     | 18                     |
| 3     | THF              | hν, 25 °C, 10 h | 96                     |
| 4     | NEt <sub>3</sub> | 25 °C, 10 h     | 50                     |
| 5     | NEt <sub>3</sub> | 50 °C, 10 h     | 51                     |
| 6     | NEt <sub>3</sub> | hν, 25 °C, 10 h | 93                     |

<sup>a</sup>O(Bpin)<sub>2</sub>/Et<sub>3</sub>SiH/H<sub>2</sub>O/Mo(CO)<sub>5</sub>L = 0.5:1.0:0.5:0.015 mmol in 0.5 mL of toluene. <sup>b</sup>Yield based upon <sup>1</sup>H NMR.

but also for promotion of the catalytic cycle shown in Scheme 3, although the details are currently unclear.

The reaction of O(Bpin)<sub>2</sub> with Et<sub>3</sub>GeH in place of Et<sub>3</sub>SiH was examined under conditions similar to those in entry 1 in Table 3; the corresponding boryl germyl ether, pinB–O–GeEt<sub>3</sub> (**13**), was found to form in 93% yield (Scheme 4). This shows that our catalytic reaction system is also available to perform selective B–O–Ge bond-forming reactions.

**Scheme 4. Reaction of O(Bpin)<sub>2</sub> with Et<sub>3</sub>GeH in the Presence of Mo(CO)<sub>6</sub>**



In conclusion, we have established an unprecedented selective B–O–Si bond-forming reaction of bisboryloxide or boroxine with hydrosilane catalyzed by a transition-metal carbonyl complex; Mo(CO)<sub>6</sub> has especially high catalytic activity. This work provides a new direction in the expansion of materials chemistry, particularly for B–O–Si-containing products, which is a great step toward the development of functional inorganic materials.

## ■ ASSOCIATED CONTENT

### Supporting Information

Detailed experimental procedures and characterization of products. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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