

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

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Supporting Information

ABSTRACT: Selective B–O–Si bond formation was achieved in the reaction of bisboryloxide $O(Bpin)_2$ (pin = $(OCMe_2)_2$)/boroxine (MeBO)_3 system with tertiary silane R₃SiH in the presence of stoichiometric water and a catalytic amount of $[M](CO)_5$ ([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.

B orosilicate 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.¹ Methods for synthesis of boryl silyl ethers can be classified into two major types: (i) reaction of hydroxyborane with chlorosilane,² alkoxysilane,³ and silanol⁴ (Scheme 1, (1)–(3)) and (ii) reaction of chloroborane,^{4d,5}

Scheme 1. Common Synthetic Methods toward Boryl Silyl Ethers

$\[R_2B-OH + R'_3Si-CI \xrightarrow{-HCI} R_2B-O-SR'_3 \]$	(1)
∣ (i) R2B−OH + R'3Si−OR" - R"OH R2B−O−SiR'3	(2)
\downarrow R ₂ B-OH + R' ₃ Si-OH $\xrightarrow{-H_2O}$ R ₂ B-O-SiR' ₃	(3)
_ R₂B−CI + R'₃Si−OH <u>- HCI</u> _ R₂B−O−SiR'₃	(4)
। (ii) R₂B−OR" + R'₃Si−OH <u>- R"OH</u> R₂B−O−SiR'₃	(5)
└ R ₂ B−H + R' ₃ Si−OH <u>- H</u> 2 R 2B−O−SiR'3	(6)

alkoxyborane,⁶ and hydroborane^{Sb,7} 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). 8,9

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 $[M](CO)_5$ ([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), $O(Bpin)_2$ (0.5 mmol), Et_3SiH (1.0 mmol), H_2O (0.5 mmol), and $Mo(CO)_6$ (0.0025 mmol) were charged in a sealed glass tube under a nitrogen atmosphere, and the solution was photoirradiated with a 400 W mediumpressure mercury arc lamp (Pyrex filtered) at 25 $^\circ C$ for 20 h (Table 1, entry 1). The ¹H NMR spectrum in C_6D_6 of the crude reaction mixture revealed the formation of pinB-O-SiEt₃ (1) (92% yield based on NMR) and H₂ (4.47 ppm, vide infra). The results showed that $Mo(CO)_6$ was effective in catalyzing the reaction of $O(Bpin)_2$ with Et₃SiH, 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 $Mo(CO)_6$ 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-SiEt₃ 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, $W(CO)_6$, $Fe(CO)_5$, and $Cp*Fe(CO)_2Me$ $(Cp^* = \eta^5 - C_5 Me_5)$ precursor, were also examined as reaction catalysts; it was found that these catalytic activities were lower than that of $Mo(CO)_6$ (entries 7–9, 11, 13). The activities of

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Table 1. Reaction of $O(Bpin)_2$ with Et_3SiH in the Presence of a Transition-Metal Carbonyl Complex^{*a*}

O(Bpin) ₂ ·	cat. + 2 Et ₃ SiH <u>1 equiv. H₂O</u> h <i>v</i> , 25 °C, 20 h in toluene	► 2 pinB=O=Si	Et ₃ + 2 H ₂
entry	cat. [amount (mol%)] ^b	yield ^{c,d} (%)	TON
1	$Mo(CO)_{6}[0.25]$	92 (89)	368
2	$Mo(CO)_{6}[0.05]$	4	80
3	no catalyst	no reaction	-
4^e	Mo(CO) ₆ [0.25]	94 (92)	376
5^{f}	$Mo(CO)_{6}$ [0.25]	93 (88)	372
6 ^g	Mo(CO) ₆ [0.25]	no reaction	-
7	CpMo(CO) ₃ Me [0.25]	29	116
8	[CpMo(CO) ₃] ₂ [0.25]	56	112
9	$Fe(CO)_{5}[0.5]$	26	52
10	CpFe(CO) ₂ Me [0.5]	trace	_
11	Cp*Fe(CO) ₂ Me [0.5]	55	110
12	$Cr(CO)_{6}$ [0.5]	trace	-
13	$W(CO)_{6}$ [0.5]	57	114
14^h	$Mo(CO)_{6}$ [0.25]	12	48
15^h	$Mo(CO)_{6}$ [2.5]	12	4.8
16 ⁱ	$Mo(CO)_{6}[0.25]$	92 (87)	368
17 ^j	Mo(CO) ₆ [0.25]	93 (89)	372

 ${}^{a}O(Bpin)_{2}/Et_{3}SiH/H_{2}O = 0.5:1.0:0.5 mmol in 0.5 mL of toluene.$ ${}^{b}Based on [Et_{3}SiH]. ^cYield based upon ¹H NMR. ^dIsolated yield in parentheses. ^cReaction was carried out at 25 °C for 10 h. ^fReaction was carried out at 50 °C for 2 h. ^gReaction was carried out at 70 or 110 °C for 20 h without photoirradiation. ^hWithout H₂O. ⁱ2.5 mmol of H₂O. ^j5.0 mmol of H₂O.$

CpFe(CO)₂Me and Cr(CO)₆ 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 $Mo(CO)_6$ catalyst but in the absence of H₂O, 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 CHCl₃, CH₂Cl₂, CH₃CN, dimethylformamide (DMF), and water were not (entries 5–9). The molybdenum η^2 -silane σ -complex Mo(CO)₅(η^2 -HSiEt₃) that is considered to be an intermediate in our system (vide infra) is unstable in CH₂Cl₂ below rt,¹⁰ so CHCl₃ and CH₂Cl₂ might lead to a decrease in efficiency. Presumably, CH₃CN and DMF

O(Bpin) ₂ + 2 [0.25 mol% M 1 equiv. I h ν, 25 °C, in solve	lo(CO) ₆ H ₂ O 10 h	−SiEt ₃ +2H ₂
entry	solvent	yield ^{b,c} (%)	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 ₃	15	60
6	CH_2Cl_2	44	176
7	CH ₃ CN	trace	_
8	DMF	20	80
9	9 water		48

Table 2. Solvent Screening for B-O-Si Bond-Forming

Reaction^{*a*}

 $^aO(Bpin)_2/Et_3SiH/H_2O/Mo(CO)_6=0.5:1.0:0.5:0.0025$ mmol in 0.5 mL of solvent. bYield based upon 1H NMR. cIsolated yield in parentheses.

acted as a catalyst poison.¹¹ The low activity in water may come from the low solubility of $Mo(CO)_6$ 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 "Pr₃SiH and ^tBuMe₂SiH were slow-reacting substrates (entries 2, 3). Entry 7 should be noted because, although the substrate MePh(CH₂=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)₂ 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)₃ and methylboronic acid MeB(OH)₂ were used as a boron source (entries 16–19). In contrast, $O(BPh_2)_2$ did not undergo the B-O-Si bond-forming reaction (entry 20).

All boryl silyl ethers obtained were characterized by ¹H, ¹¹B, ¹³C, ²⁹Si NMR spectroscopy and elemental analyses (see Supporting Information (SI)). In addition, most of the compounds were analyzed by GC/MS. The molecular structures of pinBOSiPh₃ (6), $Fe{\eta^5-C_5H_4(SiMe_2OBpin)}_2$ (9), and MeB(OSiPh₃)₂ (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_2O and ${H_2}^{18}O$ were used in place of H_2O



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

			Mo(CO) ₆ H ₂ O			
		[6] + [3]	h ν, 25 °C in toluene			
entry	[B]	[Si]	$[B]/[Si]/[Mo(CO)_6]$	[B-O-Si]	time (h)	yield ^{b,c} (%)
1	$O(Bpin)_2$	Et ₃ SiH	1:2:0.03	pinBOSiEt ₃ (1)	10	92
2	$O(Bpin)_2$	"Pr ₃ SiH	1:2:0.03	$pinBOSi^{n}Pr_{3}$ (2)	50	95
3	$O(Bpin)_2$	^t BuMe ₂ SiH	1:2:0.03	pinBOSi ^t BuMe ₂ (3)	100	95
4	$O(Bpin)_2$	Me ₂ PhSiH	1:2:0.03	pinBOSiMe ₂ Ph (4)	0.5	94
5	$O(Bpin)_2$	MePh ₂ SiH	1:2:0.03	pinBOSiMePh ₂ (5)	10	91
6	$O(Bpin)_2$	Ph ₃ SiH	1:2:0.03	pinBOSiPh ₃ (6)	20	93
7	$O(Bpin)_2$	MePh(CH ₂ =CH)SiH	1:2:0.03	pinBOSiMePh(CH=CH ₂) (7)	10	92
8	$O(Bpin)_2$	$O(SiMe_2H)_2$	1:1:0.03	O(SiMe ₂ OBpin) ₂ (8)	20	96
9	$O(Bpin)_2$	$Fe{(\eta^5-C_5H_4(SiMe_2H))}_2$	1:1:0.03	$Fe\{\eta^{5}-C_{5}H_{4}(SiMe_{2}OBpin)\}_{2} (9)$	10	90
10	$O(Bpin)_2$	Et ₂ SiH ₂	1:1:0.03	$(pinBO)_2SiEt_2$ (10)	10	92
11	HBpin	Me ₂ PhSiH	1:1:0.015	pinBOSiMe ₂ Ph (4)	10	95
12	HOBpin	Et ₃ SiH	1:1:0.015	pinBOSiEt ₃ (1)	10	93
13	HOBpin	Me ₂ PhSiH	1:1:0.015	pinBOSiMe ₂ Ph (4)	10	95
14^d	HOBpin	Et ₃ SiH	1:1:0.015	pinBOSiEt ₃ (1)	10	(55)
15^d	HOBpin	Me ₂ PhSiH	1:1:0.015	pinBOSiMe ₂ Ph (4)	10	(60)
16^e	$(MeBO)_3$	Me ₂ PhSiH	1:6:0.09	$MeB(OSiMe_2Ph)_2$ (11)	40	88
17^e	$(MeBO)_3$	Ph ₃ SiH	1:6:0.09	$MeB(OSiPh_3)_2$ (12)	40	82
18^e	$MeB(OH)_2$	Me ₂ PhSiH	1:2:0.015	$MeB(OSiMe_2Ph)_2$ (11)	40	85
19^e	$MeB(OH)_2$	Ph ₃ SiH	1:2:0.015	$MeB(OSiPh_3)_2$ (12)	40	89
20	$O(BPh_2)_2$	Me ₂ PhSiH	1:2:0.03	Ph ₂ BOSiMe ₂ Ph	20	0
^a See SI fo	r details of reacti	on conditions. ^b Isolated vield	d. ^c Yield based upon ¹ H 1	NMR in parentheses. ^d Without H ₂ (D. ^e Solvent is	THF.

Table 3. B-O-Si Bond-Forming Reactions of Various Boron Compounds and Hydrosilanes^a

were examined. When D₂O was used, formation of both H₂ and HD was detected in the ¹H NMR spectrum of the reaction mixture (H₂: 4.47 ppm; HD: 4.43 ppm (t, $J_{H-D} = 42.6$ Hz) in C₆D₆) (see SI, Figure S1). The obtained labeled boryl silyl ether (pinB–O–SiPh₃) was also analyzed using high-resolution mass spectroscopy (HRMS). The experiments using H₂¹⁸O gave a peak at m/z = 404.1858, corresponding to pinB–¹⁸O–SiPh₃, in addition to a peak for pinB–¹⁶O–SiPh₃ at m/z = 402.1821. No peak at m/z = 404.1858 for H₂O was observed when H₂O 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)₅, which reacts with R₃SiH to give Mo(CO)₅(η^2 -HSiR₃) (A).^{10,12} Complex A was detected by ¹H NMR spectroscopy after photoirradiation of a $Mo(CO)_{6i}$ O(Bpin)₂, and R₃SiH 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_6D_6). If A reacts with $O(Bpin)_2$ to form B and nucleophilic attack of $[Mo(CO)_{5}H]^{-}$ to one of the boron atoms in $[O(Bpin)_2(SiR_3)]^+$ occurs, then pinBOSiR₃ and C would be formed. Reductive elimination of HBpin from C and coordination of R₃SiH to the molybdenum center regenerates A to complete the catalytic cycle. HBpin thus generated reacts with water to give $O(Bpin)_2$. Silanol was not thought be involved in the catalytic cycle, since the reaction of R₃SiH and H_2O in the presence of $Mo(CO)_6$ under photoirradiation did not give silanol. The reactions similar to entry 14 (also 15) in Table 1 but using $O(Bpin)_2$ and Et_3SiH in a 1:1 molar ratio in the absence of water in toluene and in THF revealed that the yields of pinBOSiEt₃ 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 $O(Bpin)_2$ with R_3SiH Promoted by $Mo(CO)_6$



reaction from A to B and/or that from B to C in addition to participation in the conversion of pinBH to $(pinB)_2O$.

In order to obtain further insight into the catalytic mechanism, we examined a reaction similar to entry 1 in Table 3 using $Mo(CO)_5(THF)^{13}$ or $Mo(CO)_5(NEt_3)^{14}$ 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 pinBOSiEt₃ with vigorous evolution of H₂ gas (entries 3, 6). These results suggest that the light energy is used not only for dissociation of CO from $Mo(CO)_6$

Table 4. Reaction of $O(Bpin)_2$ with Et_3SiH in the Presence of $Mo(CO)_5(THF)$ or $Mo(CO)_5(NEt_3)^a$

O(Bpip) +	2 Et. SiLl	1.5 mol% Mo(CO) ₅ L 1 equiv. H ₂ O	2 ninB−0−SiEt.
	2 13011	in toluene	2 pinb 0 0iLt3 1
entry	L =	conditions	yield ^{b} (%)
1	THF	25 °C, 10 h	12
2	THF	50 °C, 10 h	18
3	THF	hν, 25 °C, 10 h	96
4	NEt ₃	25 °C, 10 h	50
5	NEt ₃	50 °C, 10 h	51
6	NEt ₃	hν, 25 °C, 10 h	93
O(Bpin) ₂ /Et	SiH/H ₂ O/N	$Mo(CO)_5 L = 0.5:1.0:0.5$.5:0.015 mmol in 0.5

mL of toluene. ^bYield based upon ¹H NMR.

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

The reaction of $O(Bpin)_2$ with Et_3GeH in place of Et_3SiH was examined under conditions similar to those in entry 1 in Table 3; the corresponding boryl germyl ether, pinB $-O-GeEt_3$ (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 $O(Bpin)_2$ with Et_3GeH in the Presence of $Mo(CO)_6$

		0.03 equiv. Mo(CO) ₆	
O(Bpin) ₂ + 2 Et₃GeH ·	2 Et₃GeH	1 equiv. H ₂ O	2 pinB-O-GeEt ₃
	h <i>v</i> , 25 ℃, 10 h	13 (93%)	

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; $Mo(CO)_6$ 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

S 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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