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A convenient and clean synthetic method for borasiloxanes by Pd-catalysed reaction of silanols with diborons†

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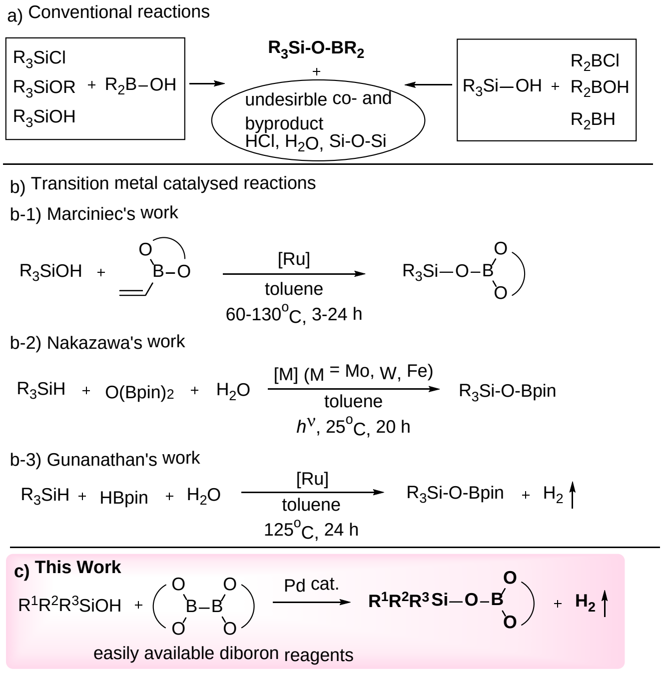
Selective O-borylation of silanols with diborons took place in the presence of Pd catalysts to give the corresponding boryl sily ethers in high yields.

Poly(borosiloxane)s are valuable chemicals in materials chemistry because of their excellent heat resistance and other unique properties applicable to chemical sensors, effective electrolyte additives, ceramic precursors, etc.[1] The backbones of poly(borosiloxane)s consist of Si-O-B linkages. Therefore, efficient and selective synthetic methods of Si-O-B bonds are very important in the synthesis of poly(borosiloxane)s. Conventional methods for the preparation of Si-O-B bonds are based on the condensation of hydroxyboranes with silane derivatives such as chlorosilanes,[2] chlorosiloxanes,[3] alkoxysilanes[1g,4] and silanols,[1a,b,d,5] or condensation of silanols with boron derivatives such as chloroboranes,[1a,6] alkoxyboranes[1a,7] and a hydroborane[6a,8] (Scheme 1a). However, these classical methods have some drawbacks, i.e. the use of toxic and/or moisture-sensitive starting materials, harsh reaction conditions, low selectivity for the desired products and formation of undesired co- and byproducts such as corrosive HCl, azeotropic H_2O, hardly separatable disiloxanes, etc. Therefore, selective and clean Si-O-B bond-forming reaction using low-toxic and easily-handled starting materials has been desired.

Recently, to solve the problems of the conventional methods, some catalytic Si-O-B bond-forming reactions have been reported using silanols or hydrosilanes (Scheme 1b). For the reactions of monosilanols, Marciniec reported that Ru complexes catalysed the O-borylation of silanols with vinylboronates to produce Si-O-B compounds in high yields (Scheme 1b-1).[9] For a poly(borosiloxane) synthesis, Matsumi recently reported effective polycondensation with $ArBH_2$ (Ar = mesityl) in the presence of transition metal complexes.[1h] Regarding the use of hydrosilanes, selective Si-O-B bond formation in the photoreaction with bisboryloxide/boroxine catalysed by Mo, W and Fe complexes was achieved by Nakazawa (Scheme 1b-2).[10] Also, Gunanathan demonstrated selective synthesis of Si-O-B bond by Ru-catalysed reaction of hydroboranes (or boronic acids) with silanes and water (Scheme 1b-3).[11] In addition, Rubinsztajn presented a poly(borosiloxane) synthesis by $B(C_6F_5)_3$-catalysed reaction between Ph_2SiH_2 and $B(OMe)_3$ with liberation of methane.[12]



Scheme 1 The Si-O-B bond-forming processes.

The precedent results prompted us to examine Si-O-B bond-forming reactions using easily available diboron reagents such as bis(pinacolato)diboron (B_2pin_2).[13] Carefully searching the literatures, we could find only one such example; Ohmura and Suginome mentioned the formation of $Me_3SiOBpin$ from

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† Electronic Supplementary Information (ESI) available: General information, detailed experimental procedures, characterization data and copies of ^1H, ^{13}C, ^{11}B and ^{29}Si NMR spectra of the products. See DOI: 10.1039/x0xx00000x

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Me_3SiOH and B_2pin_2 catalysed by $[Ir(OMe)(cod)]_2$ (cod = 1,5-cyclooctadiene) in the footnote of their paper on the Ir-catalysed C(sp^3)-H borylation of methylchlorosilanes.[14] Herein, we present a Pd-catalysed selective Si-O-B bond-forming reaction by dehydrogenative O-borylation of a variety of silanols with easily available diborons (Scheme 1c). The reaction can not only efficiently take place under mild conditions, but also proceed with generation of only hydrogen gas, i.e. without generation of any liquid or solid waste.

Firstly, to choose effective catalysts, Et_3SiOH was allowed to react with B_2pin_2 in the presence of various transition metal compounds (Table 1). As the result, we found that Et_3SiOH (1.0 mmol) reacted with B_2pin_2 (0.5 mmol) in the presence of Pd acetate, $Pd_3(OAc)_5(NO_2)$ or $Pd_3(OAc)_6$ (0.5 mol% Pd based on Et_3SiOH), or $Pd(PPh_3)_4$ (1 mol%) at 25 °C for 3 h under nitrogen atmosphere to produce the desired product bearing Si-O-B bond **1a** in 94%, 90% or 93% yield, respectively, without any byproducts (entries 1-3). In this reaction, B_2pin_2 reacted with two equivalents of Et_3SiOH along with coproduction of hydrogen. Indeed, when Et_3SiOH was added to a mixture of B_2pin_2 and $Pd(OAc)_2$ catalyst, vigorous hydrogen gas evolution was observed after an induction period of several minutes. Regarding the Pd acetate, commercially available so-called $Pd(OAc)_2$ consists of trinuclear Pd complexes such as $Pd_3(OAc)_6$ and/or $Pd_3(OAc)_5(NO_2)$ (see ESI). Both forms are active in this reaction, and gave **1a** in high yields. For other Pd complexes, $Pd(acac)_2$ (acac = acetylacetonate) catalysed the reaction at 80 °C for 4 h (entry 4), but decreasing the reaction temperature to 25 °C led to no generation of the product (entry 5). $PdCl_2(PhCN)_2$ mainly catalysed unfavorable formation of a disiloxane **2a**, and **1a** was obtained in only 11% yield (entry 6). $PdCl_2(PPh_3)_2$ and $Pd_2(dba)_3$ (dba = dibenzylideneacetone) did not catalyse the reaction at all (entries 7 and 8), and addition of PPh_3 to $Pd_2(dba)_3$ did not affect the results (entry 9). In the case of $PdCl_2$, the reaction proceeded unselectively to give **1a** and **2a** in 29% and 36% yields, respectively (entry 10). As to other transition metal complexes, $Pt(PPh_3)_4$, $PtCl_2(PhCN)_2$, and $RhCl(PPh_3)_3$ gave **1a** in low to moderate yields (entries 11-13). As previously reported,[14] $[Ir(OMe)(cod)]_2$ also gave **1a** in 64% yield along with a small amount of **2a** in the presence of 3,4,7,8-tetramethyl-1,10-phenanthroline as a ligand (entry 14). $Cu(OAc)_2$, $Ni(cod)_2$ and $Ni(acac)_2$ also catalysed the reaction selectively (entries 15-17). But the yields of **1a** obtained by these Pt, Rh, Ir, Cu and Ni catalysts were lower than those by the Pd catalysts. In the series of group 10 metal complexes, on the basis of the yields of **1a** and the reaction conditions, the order of the catalyst activity is estimated as follows: $Pd_3(OAc)_5(NO_2) \sim Pd_3(OAc)_6 \sim Pd(PPh_3)_4 > Pt(PPh_3)_4 > Pd(acac)_2 > PtCl_2(PhCN)_2 > Ni(acac)_2$.[15] In contrast, when strong Lewis acids such as $Sc(OTf)_3$ (Tf = SO_2CF_3) and $FeCl_3$ were used as the catalysts, the formation of the disiloxane **2a** took place selectively without producing **1a** under similar reaction conditions (entries 18 and 19). In the absence of catalysts, the reaction did not proceed at all (entry 20).

Table 1 Catalytic O-borylation of Et_3SiOH with B_2pin_2

$$\underset{1.0\ \text{mmol}}{2\ Et_3SiOH} + \underset{0.5\ \text{mmol}}{B_2pin_2} \xrightarrow[\text{neat}]{\text{Catalyst (0.5-26 mol\%)}} \underset{\mathbf{1a}}{2\ Et_3Si\text{-}O\text{-}Bpin} + \underset{\mathbf{2a}}{Et_3Si{-}O{-}SiEt_3}$$

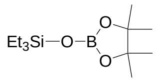
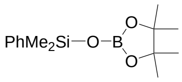
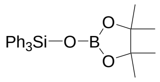
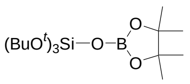
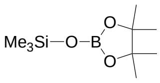
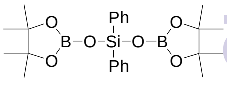
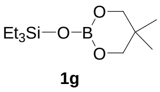
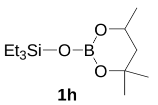
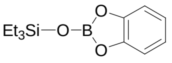
Entry	Catalyst (mol% metal)	Reaction conditions	Yield (%)[a] 1a	2a
1	$Pd_3(OAc)_5(NO_2)$ (0.5)	25°C, 3 h	94	0
2	$Pd_3(OAc)_6$ (0.5)	25°C, 3 h	90	0
3	$Pd(PPh_3)_4$ (1)	25°C, 3 h	93	0
4	$Pd(acac)_2$ (1)	80°C, 4 h	66	0
5	$Pd(acac)_2$ (3)	25°C, 3 h	0	0
6	$PdCl_2(PhCN)_2$ (3)	80°C, 4 h	11	82
7	$PdCl_2(PPh_3)_2$ (3)	80°C, 4 h	0	3
8	$Pd_2(dba)_3$ (5)	80°C, 4 h	0	0
9[b]	$Pd_2(dba)_3$ (5)	80°C, 4 h	0	0
10	$PdCl_2$ (26)	80°C, 4 h	29	36
11	$Pt(PPh_3)_4$ (1)	25°C, 3 h	56	0
12	$PtCl_2(PhCN)_2$ (10)	80°C, 4 h	40	7
13	$RhCl(PPh_3)_3$ (4)	80°C, 4 h	18	0
14[c]	$[Ir(OMe)(cod)]_2$ (5)	80°C, 4 h	64	1
15	$Cu(OAc)_2$ (15)	80°C, 4 h	79	0
16	$Ni(cod)_2$ (8)	80°C, 4 h	15	0
17	$Ni(acac)_2$ (10)	80°C, 4 h	31	0
18	$Sc(OTf)_3$ (7)	80°C, 4 h	0	99
19	$FeCl_3$ (19)	80°C, 4 h	0	99
20	none	80°C, 4 h	0	0

[a] Determined by ^{29}Si NMR using $PhMe_3Si$ as an internal standard.
[b] PPh_3 (5 mol% based on Si-OH bond) was added.
[c] 3,4,7,8-Tetramethyl-1,10-phenanthroline (10 mol%) was added.

This Pd-catalyzed O-borylation was applicable to other silanols and diborons. As shown in Table 2, a variety of silanols were O-borylated by diborons in the presence of a catalytic amount of Pd acetate, producing the corresponding compounds bearing Si-O-B bond **1** in high yields. Various silanols including Et_3SiOH, $PhMe_2SiOH$ and Ph_3SiOH could

Table 2 Pd acetate-catalysed O-borylation of silanols with diborons[a]

$$\underset{1.0\ \text{mmol}}{R^1R^2R^3SiOH} + \underset{0.5\text{-}1.0\ \text{mmol}}{B_2(OR^4)_4} \xrightarrow{\text{Pd acetate 1mol\%}} \underset{\mathbf{1}}{R^1R^2R^3Si\text{-}O\text{-}B(OR^4)_2}$$

 **1a** 94% (81%)	 **1b** 99% (92%)	 **1c** 95% (84%)
 **1d** 99% (83%)	 **1e** 98% (64%)	 **1f** 97% (86%)
 **1g** 94% (77%)	 **1h** 98% (85%)	 **1i** 99% (94%)

[a] Reaction Conditions: **1a** cat 0.5 mol%, B_2pin_2 0.55 mmol, 25°C, 3 h; **1b** B_2pin_2 0.54 mmol, 25°C, 3 h; **1c** B_2pin_2 0.58 mmol, THF 0.25 mL, 80°C, 4 h; **1d** B_2pin_2 1.0 mmol, THF 0.25 mL, 80°C, 4 h; **1e** B_2pin_2 1.0 mmol, 25°C, 4 h; **1f** B_2pin_2 2.0 mmol (2equiv.), THF 0.25 mL, 80°C, 4 h; **1g** B_2neop_2 1.0 mmol, 80°C, 4 h; **1h** B_2hexl_2 1.0 mmol, 80°C, 4 h; **1i** B_2cat_2 1.0 mmol, 25°C, 3 h. The yields were determined by ^{29}Si NMR. Isolated yields are shown in parentheses.

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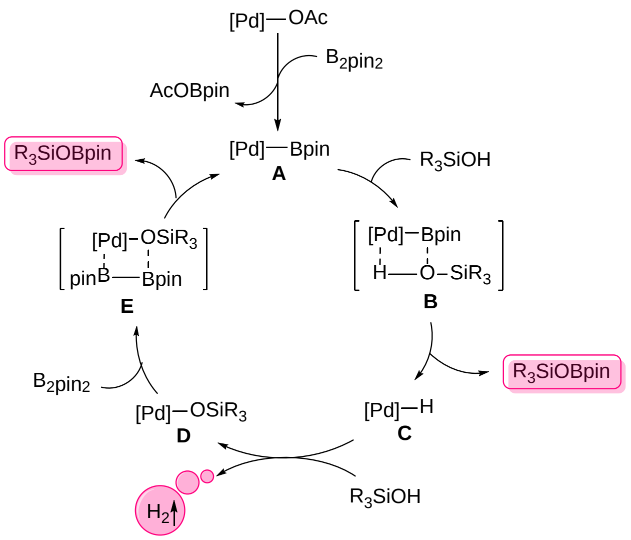
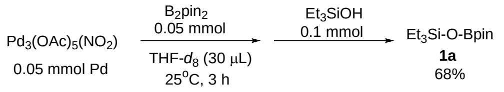
react with B_2pin_2 to give the corresponding Si-O-B compounds. The reaction of a trialkoxysilanol, $(^tBuO)_3SiOH$, with B_2pin_2 also smoothly proceeded to provide **1d** quantitatively. Me_3SiOH also reacted with B_2pin_2 to give the expected product **1e** in 64% yields. $Ph_2Si(OH)_2$ bearing two Si-OH group was smoothly O-borylated with B_2pin_2, giving the corresponding product **1f** in good yield. Furthermore, the present Pd-catalysed O-borylation was applicable to other diboron compounds. In addition to B_2pin_2, bis(neopentyl glycolato)diboron (B_2neop_2), bis(hexylene glycolato)diboron (B_2hexyl_2) and bis(catecholato)diboron (B_2cat_2) also reacted with Et_3SiOH to produce the corresponding compounds (**1g**-**i**). When the starting silanols are liquid compounds (Et_3SiOH, $PhMe_2SiOH$), the reactions could be conducted without any solvent, providing an environmentally benign process. These reaction were very efficient, and the products **1a-h** were formed in excellent NMR yields (≥94%). In addition, **1a-h** could be easily isolated in high yields by simple purification processes such as short-path distillation under reduced pressures.

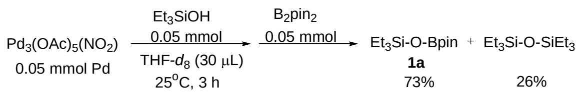
A possible reaction mechanism for the present O-borylation of silanols (R_3SiOH) with a diboron (B_2pin_2) is shown in Scheme 2. An active Pd species would be generated by transmetalation between the Pd acetate ([Pd]-OAc) and B_2pin_2, leading to a borylpalladium species [Pd]-Bpin **A**. Formation of similar [Pd]-Bpin species has been suggested in the Pd acetate-catalysed reaction of N-heteroaromatics with water in the presence of B_2pin_2[16,17] and also in the Pd-catalysed reactions of aryl halides with B_2pin_2 in the presence of potassium acetate.[18] Therefore, we suppose that some borylpalladium species would be involved in the catalytic cycle, although we have not been able to observe the Pd specie, presumably because of its high reactivity. Coordination of a silanol (R_3SiOH) to the Pd species **A** would give a four-centered intermediate species **B**. Hydrogen atom transfer from R_3SiOH to the Pd center forms an [Pd]-H species **C** along with production of $R_3SiOBpin$. Then, another R_3SiOH would interact with the Pd species **C** to give a [Pd]-$OSiR_3$ species **D** with release of hydrogen. Attack of B_2pin_2 to the Pd species **D**, possibly via a four-centered intermediate species **E**, would afford another molecule of $R_3SiOBpin$ with regeneration of the Pd species **A**.[19]



Scheme 2 A possible mechanism.



(1)



(2)

To get information on the reaction mechanism, we examined a stoichiometric reaction of Pd acetate ($Pd_3(OAc)_5(NO_2)$) with B_2pin_2 and Et_3SiOH at 25 °C (eqn (1)). The Pd acetate was mixed with B_2pin_2 in THF-d_8 and kept at 25 °C for 3 h. Addition of Et_3SiOH to the resulting mixture gave the desired product $Et_3SiOBpin$ **1a** in 68% yield along with unreacted Et_3SiOH. In contrast, when B_2pin_2 was added to a mixture of stoichiometric amount of the Pd acetate and Et_3SiOH, the formation of **1a** was accompanied by a considerable amount of a disiloxane ($Et_3SiOSiEt_3$); the yields of **1a** and $Et_3SiOSiEt_3$ were 73% and 26%, respectively (eqn (2)). In the present Pd catalysis, such disiloxane formation was not observed at all. This indicates that the interaction of the Pd acetate with B_2pin_2 in the initial stage is an important process leading to the generation of active Pd species, although the structure has not been confirmed yet.

In conclusion, we have disclosed a new simple method for the preparation of Si-O-B compounds by using easily available silanols and diboron reagents. The successful use of diborons coupled with Pd catalysts for borasiloxane synthesis is most unique point in the comparison with the previously reported methods using hydroxyboranes, hydroboranes or boroxanes as boron sources. The high activity of the commonly-used air-stable Pd acetate catalyst is also noteworthy in the practical viewpoint. Since the Pd catalysis is facile and clean, the present method would have a potential applicability to modification of silanol group-containing materials, such as silicone polymers, to improve their physical properties and/or to add new chemical properties based on the boron moieties. Further studies on the application of the present Pd catalysis and other reactions for the formation of Si-O-B compounds are under way.

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15 At the moment, the reason of the high activity and selectivity observed for Pd acetate and $Pd(PPh_3)_4$ is not clear, and further mechanistic study will be required to understand the results.

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17 (a) In our case, when a Pd acetate, $Pd_3(OAc)_5(NO_2)$ (0.05 mmol Pd), was treated with B_2pin_2 (0.05 mmol) in C_6D_6 (30 μL) at 25 °C for 3 h, new singlet ^1H NMR signals, probably due to AcO-Bpin, appeared at 1.01 (CH_3 of Bpin) and 1.56 (CH_3 of AcO) ppm, which were well consistent with the reported values.[17b] (b) C. J. Pell and O. V. Ozerov, *Inorg. Chem. Front*., 2015, **2**, 720.

18 (a) T. Ishiyama, M. Murata and N. Miyaura, *J. Org. Chem.*, 1995, **60**, 7508; (b) M. Sumimoto, N. Iwane, T. Takahama and S. Sakaki, *J. Am. Chem. Soc.*, 2004, **126**, 10457.

19 Although the mechanism of the catalysis has not been elucidated yet, transmetalation process between the [Pd]-$OSiR_3$ and the B-B bond seems to be a kinetically relevant step. The hypothesis is consistent with the observation that the reaction of sterically less-hindered B_2cat_2 has been much faster than that of B_2pin_2.