

# Synthesis of 1,1,1-Tris(boronates) from Vinylarenes by Co-Catalyzed Dehydrogenative Borylations–Hydroboration

Lei Zhang and Zheng Huang\*

State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, 345 Lingling Road, Shanghai 200032, China

**S** Supporting Information

**ABSTRACT:** The selective preparation of 1,1,1-tris(boronates) from vinylarenes and bis(pinacolato)diboron is described. The reactions occur at ambient temperature with excellent selectivity, high yields, and good functional group tolerance. Mechanistic studies suggest that Co(I)-catalyzed double dehydrogenative borylations generate a 1,1-diborylalkene intermediate, which undergoes hydroboration with pinacolborane formed *in situ* to yield 1,1,1-tris(boronate).

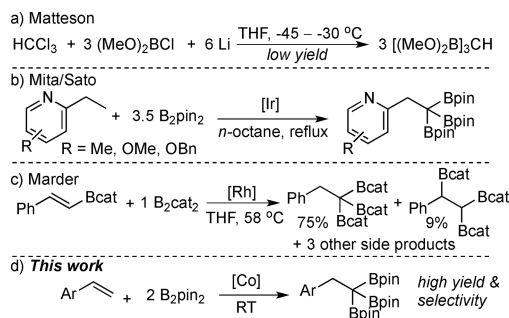
Multiborylated compounds are useful starting materials for the construction of complex molecules.<sup>1</sup> Among them, geminal bis(boronates) have been extensively studied for synthesis of multifunctionalized molecules, and several methods have been established for the preparation of such compounds.<sup>2</sup> 1,1,1-Tris(boronates), which contain three boronate moieties attached to the same carbon atom, are likely versatile building blocks in organic synthesis because of the potential for multiple C–C and C–heteroatom bond formation reactions. However, the chemistry of 1,1,1-tris(boronates) has received much less attention compared to that of 1,1-bis(boronates). One reason for the slow development of 1,1,1-tris(boronates) is that there have been no general, practical methods to construct this type of molecules. Matteson reported that the reaction of  $\text{HCCl}_3$  with  $\text{ClB(OR)}_2$  and lithium metal at low temperatures formed triborylmethane in 25–35% yield (Scheme 1a).<sup>3</sup> Mita and Sato disclosed an Ir-catalyzed, pyridine-directed C(sp<sup>3</sup>)–H triborylation at a single carbon, but only 2-ethylpyridines with electron-donating substituents at the *meta*- or *para*-positions of the pyridine rings afforded 1,1,1-tris(boronates) with good yield and selectivity (Scheme 1b).<sup>4</sup> In addition, two methods involving

reactions of C–C multiple bonds have been reported for synthesis of 1,1,1-tris(boronates). Siebert described the synthesis of 1,1,1-triborylethane via double hydroboration of ethynylboronate with  $\text{HBCl}_2$ , followed by protection with catechol.<sup>5</sup> Marder reported a Rh-catalyzed dehydrogenative borylation–hydroboration of (*E*)-styrylboronates (two examples) with bis-(catecholato)diboron, furnishing 1,1,1-tris(boronates) as the major products (up to 75% NMR yield). However, the reactions also formed multiple side products, rendering the purification of the product difficult (Scheme 1c).<sup>6</sup> Note that the requisite boron-containing starting materials used in these methods are not readily available.<sup>5,6b</sup> Thus, it is highly desirable to develop a synthetically efficient method for preparation of 1,1,1-tris(boronates) from simple alkenes.

Catalysis with base metals has received increasing attention in the past decade due to their low cost, high earth abundance, and environmental advantages.<sup>7</sup> Our group and others have demonstrated that pincer-ligated Fe<sup>8</sup> and Co<sup>9</sup> complexes are highly efficient for anti-Markovnikov hydroboration of  $\alpha$ -olefins with  $\text{HBpin}$ .<sup>10</sup> We found the (PNN)Fe-catalyzed hydroboration of styrenes gave both hydroboration and dehydrogenative borylation products.<sup>8,11</sup> We envisioned that the use of a diboron ( $\text{B}_2\text{pin}_2$ ), instead of  $\text{HBpin}$ , might enhance the selectivity for the dehydrogenative borylation products, which may be involved in further transformations. Herein, we report the first catalytic, general synthesis of 1,1,1-tris(boronates) from vinylarenes using tandem double dehydrogenative borylations–hydroboration. The reactions occur at ambient temperature with excellent selectivity and high yields (Scheme 1d). The triboryl products have been applied to facile synthesis of internal geminal bis(boronates) under mild conditions.

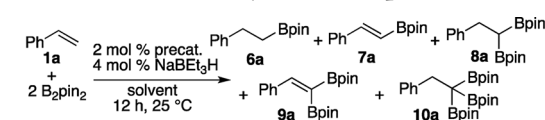
The PNN-ligated Fe and Co complexes were evaluated as precatalysts for reaction of styrene **1a** with  $\text{B}_2\text{pin}_2$ . The results are summarized in Table 1. With (<sup>t</sup>BuPNN)FeCl<sub>2</sub> **2** (2 mol %) as the precatalyst and  $\text{NaBET}_3\text{H}$  (4 mol %) as the activator, the reaction of **1a** with 1.0 equiv of  $\text{B}_2\text{pin}_2$  in THF at 25 °C for 3 h formed 36% of monoborylalkene **7a** and a small amount of monoborylalkane **6a** (2%) (entry 1). The desired product, 1,1,1-tris(boronate) **10a**, was not detected. The precatalyst (<sup>i</sup>Pr<sub>2</sub>PNN)FeCl<sub>2</sub> **3** with isopropyl substituents is inactive for this reaction (entry 2). However, when (<sup>t</sup>BuPNN)CoCl<sub>2</sub> **4** was employed, **10a** was formed in 31% yield, along with **6a** (15%), **7a** (7%), 1,1-diborylalkane **8a** (5%), and 1,1-diborylalkene **9a** (4%) (entry 3). Encouraged by this result, an experiment with 2

**Scheme 1. Methods for Synthesis of 1,1,1-Tris(boronates)**

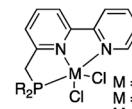


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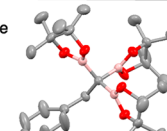
Table 1. Evaluation of Catalysts for Synthesis of 1,1,1-Tris(boronate) **10a** from Styrene and  $B_2pin_2$ <sup>a</sup>


Entry	Precat.	Solvent	Yield [%]				
			6a	7a	8a	9a	10a
1 <sup>b</sup>	2	THF	2	36	0	0	0
2 <sup>b</sup>	3	THF	0	0	0	0	0
3 <sup>b</sup>	4	THF	15	7	5	4	31
4	4	THF	6	0	8	20	54
5	5	THF	46	1	8	18	2
6	4	toluene	6	0	4	0	82
7	4	Et <sub>2</sub> O	4	0	6	5	79
8	4	pentane	2	0	2	0	92
9	4	pentane <sup>c</sup>	0	0	4	0	94



M = Fe, R = *t*Bu, **2**  
 M = Fe, R = *i*Pr, **3**  
 M = Co, R = *t*Bu, **4**  
 M = Co, R = *i*Pr, **5**

Crystal structure of **10a**:



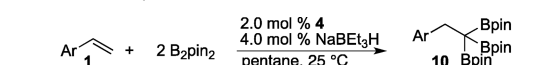
<sup>a</sup>Conditions: **1a** (0.5 mmol),  $B_2pin_2$  (1 mmol), precatalyst (2 mol %), and  $NaBEt_3H$  (4 mol %) in solvent (2 mL) at 25 °C. Yield was determined by GC with mesitylene as an internal standard. <sup>b</sup>1.0 equiv of  $B_2pin_2$  was used. Reaction time: 3 h. <sup>c</sup>5 mL of pentane were used.

equiv of  $B_2pin_2$  was conducted and the reaction time was extended to 12 h. The reaction formed **10a** in 54% yield, although side products **6a** (7%), **8a** (8%), and **9a** (20%) were still detected (entry 4). In contrast, under conditions similar to those used in entry 4, the run with the less sterically demanding Co complex (<sup>*i*</sup>PrPNN)CoCl<sub>2</sub> **5** afforded only 2% of **10a**, but 46% of **6a** and multiple other side products (entry 5).

The solvents have an impact on the product distribution. Reactions using **4** in toluene and diethyl ether formed **10a** in 82% and 79% yield, respectively (entries 6 and 7). The yield of **10a** was increased to 92% when pentane was used as the solvent (entry 8). The reaction in a more diluted solution (5 mL pentane) gave **10a** in 94% yield with **8a** (4%) as the only side product. The triboryl product **10a** is stable and can be purified by flash chromatography. Its structure was confirmed by X-ray diffraction analysis (Table 1).<sup>12</sup>

We next explored the substrate scope of our protocol (Table 2). All reactions proceeded smoothly at 25 °C with low catalyst loadings (2–5 mol %) and excellent selectivity. Most reactions gave high isolated yields (>90%). The system is efficient for substrates containing both electron-donating and -withdrawing groups. A range of functional groups, such as ether (**10e**, **10f**), tertiary amine (**10g**), thioether (**10h**), protected phenol (**10m**), and amide (**10s**), can be tolerated. It should be noted that reactions of halogen-substituted styrenes occurred selectively to form the 1,1,1-tris(boronate) products; no aryl boronate esters resulting from C–X bond borylation were detected. Vinylfuran gave the desired product in good yield (**10t**, 81%), but vinylpyridine did not react with  $B_2pin_2$  under the reaction conditions. Substrates bearing naphthyl groups afforded the desired products in high yields (**10v**, 93%; **10w**, 95%). While 1,2- and 1,1-disubstituted vinylarenes were unreactive, vinylalkane gave a mixture of diboryl and monoboryl products (see Supporting Information).

The catalytic process most likely involves Co-catalyzed tandem double dehydrogenative borylations–hydroboration. In fact, the two key intermediates resulting from dehydrogenative

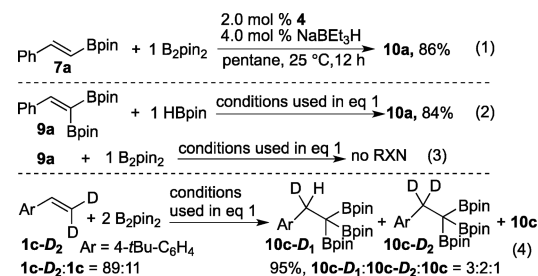
Table 2. Co-Catalyzed Synthesis of 1,1,1-Tris(boronate) **10** from Various Vinylarenes<sup>a</sup>


Product	Yield [%]
<b>10a</b>	93%
<b>10b</b>	94%
<b>10c</b>	94%
<b>10d</b>	94%
<b>10e</b>	89%
<b>10f</b>	97%
<b>10g</b>	83%
<b>10h</b>	97%
<b>10i</b>	94%
<b>10j</b>	87% <sup>b</sup>
<b>10k</b>	96%
<b>10l</b>	74% <sup>c</sup>
<b>10m</b>	98%
<b>10n</b>	91%
<b>10o</b>	72% <sup>c</sup>
<b>10p</b>	46% <sup>c</sup>
<b>10q</b>	94%
<b>10r</b>	93%
<b>10s</b>	61% <sup>d</sup>
<b>10t</b>	81%
<b>10u</b>	0%
<b>10v</b>	93%
<b>10w</b>	95%

<sup>a</sup>Conditions: **1** (0.5 mmol),  $B_2pin_2$  (0.5 mmol), [Co] (2 mol %), in pentane (5 mL) at 25 °C. Isolated yields. <sup>b</sup>Using 3.0 mol % of [Co]. <sup>c</sup>Using 5.0 mol % of [Co]. 1,1-Diborylalkenes **9** were observed in these reactions. <sup>d</sup>With THF (2 mL) as the solvent.

borylations, monoborylalkene **7a** and 1,1-diborylalkene **9a**, have both been reported in Table 1. In addition, in situ monitoring of the reaction using **4** as the precatalyst by GC revealed the formation of **9a** (82%) in substantial yield and a decent amount of **7a** (12%) at the early stage of the reaction (10 min). The two intermediates were converted to **10a** over the course of the reaction (e.g., 60 min, **7a**, <2%; **9a**, 43%; **10a**, 51%).

Studies of individual steps of the process using the intermediates **7a** and **9a** provide additional evidence in support of the proposed pathway. The Co-catalyzed reaction of **7a** with 1 equiv of  $B_2pin_2$  (eq 1) and the reaction of **9a** with 1 equiv of



$HBpin$  (eq 2) afforded **10a** in 86% and 84% yield, respectively. However, **9a** was unreactive with  $B_2pin_2$  in the presence of the catalyst (eq 3). The data suggest that the dehydrogenative borylation of **7a** with  $B_2pin_2$  occurs to generate **9a** and  $HBpin$ , and the subsequent hydroboration of **9a** with  $HBpin$  leads to the triboryl product.

Deuterium labeling studies were conducted by using 4-*tert*-butylstyrene- $\beta,\beta$ -D<sub>2</sub> **1c-D<sub>2</sub>** as the substrate (the level of deuterium content was 89%, eq 4). The reaction gave **10c-D<sub>1</sub>**, **10c-D<sub>2</sub>**, and **10c** in a 3:2:1 ratio (see NMR analysis in Supporting Information). The data are in accord with the dehydrogenative

borylation process. Migratory insertion of vinylarene or monoborylalkene into the Co–B bond occurs in a regioselective manner.  $\beta$ -Deuteride elimination then results in the formation of DBpin, which reacts with 1,1-diborylalkene to give **10c-D<sub>1</sub>** and **10c-D<sub>2</sub>**. The formation of **10c-D<sub>2</sub>** implies that competing 1,2-insertion of vinylarene or monoborylalkene into a Co–D bond occurs during catalysis.

Stoichiometric experiments were conducted to probe the Co intermediacy (Figure 1). Addition of 1 equiv of NaBEt<sub>3</sub>H to

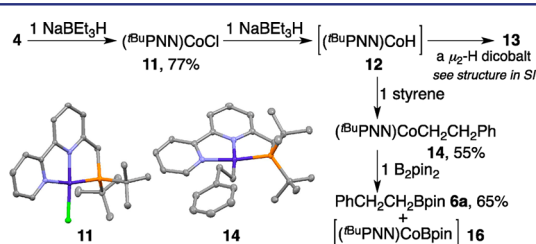
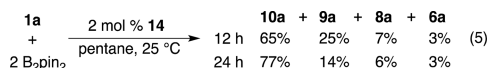


Figure 1. Stoichiometric experiments.

(<sup>t</sup>BuPNN)CoCl<sub>2</sub> **4** formed a monochloride complex (<sup>t</sup>BuPNN)-CoCl **11** in 77% yield.<sup>13</sup> Treatment of **11** with another equivalent of NaBEt<sub>3</sub>H presumably generated a Co(I) hydride complex **12**, which was unstable and decomposed under the reaction conditions to yield a C<sub>1</sub> symmetric  $\mu$ -hydride dicobalt complex **13** (see NMR data and the proposed structure in the Supporting Information).<sup>14</sup> However, in the presence of 1 equiv of styrene, the reaction of **11** with NaBEt<sub>3</sub>H formed (<sup>t</sup>BuPNN)-CoCH<sub>2</sub>CH<sub>2</sub>Ph **14** in 55% isolated yield, consistent with the formation of the hydride species **12**, followed by 1,2-insertion of styrene into the Co–H bond.<sup>13b</sup> Both **11** and **14** were fully characterized, and their structures were determined by X-ray diffraction analysis (Figure 1).

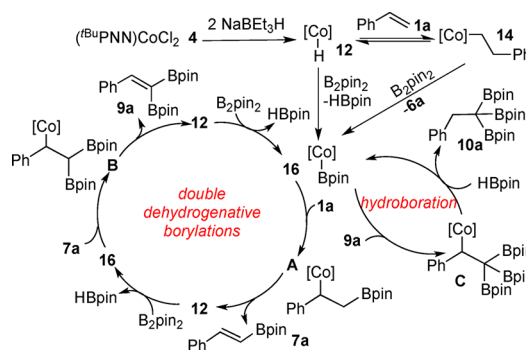
Treatment of the isolated Co(I) alkyl complex **14** with 1 equiv of B<sub>2</sub>pin<sub>2</sub> gave 65% of the monoborylalkane **6a**, 54% of the  $\mu$ -hydride dicobalt complex **13**, and other unidentified species. Based on the stoichiometry of this reaction, the initial Co product was likely a Co(I) boryl species **16** formed via transmetalation (Figure 1 and Scheme S1).<sup>15,18</sup> Notably, isolated **13** proved inactive for the catalytic reaction of **1a** with B<sub>2</sub>pin<sub>2</sub>; however, the reaction catalyzed by 2 mol % of **14** formed the triboryl product **10a** in 65% and 77% yields after 12 and 24 h, respectively (eq 5).



Although the catalytic efficiency of **14** is somewhat lower than the catalyst generated in situ (Table 1, entry 9),<sup>16</sup> the results suggest that **14** reacts with B<sub>2</sub>pin<sub>2</sub> to generate a catalytic active species.

On the basis of our experimental observations and precedents regarding related catalytic dehydrogenative borylation processes,<sup>6,17</sup> we proposed the mechanism shown in Scheme 2. The reaction of the precatalyst **4** with 2 equiv NaBEt<sub>3</sub>H forms the Co(I) hydride species **12**.<sup>13b</sup> Upon transmetalation with B<sub>2</sub>pin<sub>2</sub>, **12** is converted to HBpin and the Co(I) boryl complex **16**.<sup>15,18</sup> 2,1-Insertion of styrene into the Co–B bond in **16** generates a  $\beta$ -boryl-substituted Co(I) species **A**,<sup>19</sup> which undergoes  $\beta$ -hydride elimination to give monoborylalkene **7a** and **12**. The latter reacts with B<sub>2</sub>pin<sub>2</sub> again to yield **16** and HBpin. The intermediate **7a** undergoes another step of dehydrogenative borylation to form diborylalkene **9a**. Insertion of **9a** into the Co–B bond in **16**

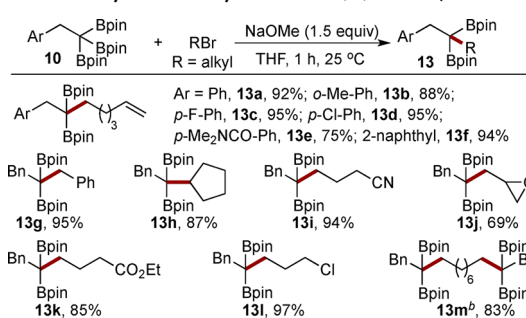
## Scheme 2. Proposed Mechanism



would give a  $\beta,\beta,\beta$ -triboryl-substituted complex **C**, which then reacts with HBpin via H–B bond oxidative addition and C–H bond reductive elimination to furnish the 1,1,1-tris(boronate) product **10a** and regenerates **16**.<sup>18,20</sup>

The 1,1,1-tris(boronate) products were applied to the synthesis of internal geminal bis(boronates) using a deborylative alkylation strategy initially developed by Morken.<sup>1f</sup> In the presence of 1.5 equiv of NaOMe, deborylative alkylations of 1,1,1-tris(boronates) with alkyl bromides occurred efficiently at 25 °C (Table 3). Noteworthy, 1,1,1-tris(boronates) are more

Table 3. Deborylative Alkylation of 1,1,1-Tris(boronates)<sup>a</sup>



<sup>a</sup>Conditions: **10** (0.55 mmol), RBr (0.5 mmol), NaOMe (0.75 mmol), in THF (1 mL) at 25 °C. Isolated yields. <sup>b</sup>With 1.1 mmol of **10a**.

reactive than 1,1-bis(boronates) for deborylative alkylations, as the reactions with the latter require the use of an excess of a stronger base NaOtBu (3 equiv) and longer reaction times (3–14 h).<sup>1f</sup> Various functionalities in the electrophiles, including terminal olefin (**13a–f**), cyanide (**13i**), propylene epoxide (**13j**), ester (**13k**), and halide (**13l**), can be tolerated under our reaction conditions, furnishing internal geminal bis(boronates) in good to high isolated yields. Alkylations of 1,1,1-tris(boronates) bearing halide (**13c**, **13d**) and amide (**13e**) functionalities occurred smoothly.<sup>21</sup> The reaction of 2 equiv of **10a** with 1 equiv of 1,8-dibromooctane formed a tetraboryl compound **13m** in 83% yield.

In summary, we have described an efficient and selective Co-catalyzed method for synthesis of 1,1,1-tris(boronates), for the first time, from readily available alkenes. This novel 1,1,1-tris(boronate) class proved highly active in deborylative reactions. Further applications of these compounds for multiple C–C bond formation are being explored in our laboratory and will be reported in due course.

## ■ ASSOCIATED CONTENT

## S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b11366.

Experimental procedures, characterization and spectral data (PDF)

Crystallographic data for 10a (CIF)

Crystallographic data for 11 (CIF)

Crystallographic data for 14 (CIF)

## ■ AUTHOR INFORMATION

## Corresponding Author

\*E-mail: [huangzh@sioc.ac.cn](mailto:huangzh@sioc.ac.cn).

## Notes

The authors declare no competing financial interest.

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- (19) Insertion of 1,2- and 1,1-disubstituted vinylarenes is unlikely due to steric hindrance, which is consistent with our experimental data.
- (20) An alternative, but less likely, pathway involves the insertion of 9a into the Co–H bond in 12 to form a,  $\alpha,\alpha$ -diboryl-substituted complex D, which reacts with HBpin to form 10a and 12 (see Scheme S2). Due to the steric effect, the formation of D is presumably difficult because it has two sterically congested Bpin groups  $\alpha$  to the metal.
- (21) Morken reported that internal geminal bis(boronates) can also be prepared from 1,1-bis(boronates) using a conventional deprotonation–alkylation approach (see ref 1f). The method uses a superbase LiTMP for deprotonation of 1,1-bis(boronates). Thus, some reactive functionalities in 1,1-bis(boronates) may not be tolerated. Indeed, we showed that 13e with an amide group cannot be prepared by alkylation of 1,1-bis(boronate) using LiTMP as the base (see Supporting Information for details).