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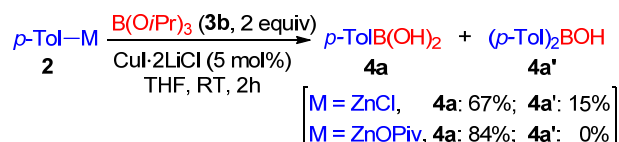
# Copper-Catalyzed Monoorganylation of Trialkyl Borates with Functionalized Organozinc Pivalates

Ying Fu,<sup>\*,[a]</sup> Bei-Lei Gou,<sup>[b]</sup> Chun-Zhao Shi,<sup>[a]</sup> Zhengyin Du<sup>[a]</sup> and Tong Shen<sup>[b]</sup>

**Abstract:** Organozinc pivalates, a recently developed air- and moisture-stable organozinc species, were found for the first time as excellent organometallic species in the monoorganylation of trialkyl borates whereby boronic acids were prepared in high yields. The significant advantage of organozinc pivalates over any other previously employed organometallic reagents, e.g., organolithium reagents, Grignard reagents and organozinc halides, is that the generation of multiorganylation byproducts such as boronic acids and trialkylboranes were completely suppressed. Additionally, the *in situ* generated boronates could be directly arranged into Suzuki-Miyaura type cross-coupling reactions to produce biaryls in high yields.

The great success of organylboronic acids and their derivatives in organic synthesis,<sup>[1]</sup> pharmaceuticals<sup>[2]</sup> and material chemistry<sup>[3]</sup> has inspired dramatic synthetic interests<sup>[4]</sup> on these privileged molecules. Thus, a range of protocols have been developed to convert aryl<sup>[5]</sup> and alkyl<sup>[6]</sup> halides, carboxylic acid derivatives,<sup>[7]</sup> anilines,<sup>[8]</sup> diaryliodonium salts,<sup>[9]</sup> arenes,<sup>[10]</sup> alkenes<sup>[11]</sup> and quaternary ammonium salts<sup>[12]</sup> etc. into boronic acids or their esters. However, due to the employment of unaffordable expensive borylating agents or expensive transitional metal catalysts, most of these protocols are rarely employed in the practical boronic acids synthesis. Thus, the conventional approach, the electrophilic trapping of organometallics (generally the lithium reagents,<sup>[13]</sup> Grignard reagents<sup>[14]</sup> and organozinc reagents<sup>[15]</sup>) with trialkyl borates, still occupies a large portion in modern factory manufacture. The common defects involved in this approach are, cryogenic conditions demanding, poor functional groups tolerance (largely due to high reactivity of organometallics), unavoidable boronic acid and borane byproducts (arise from second and third additions of the organometallic reagents into the borate esters), low isolated yields. To avoid multiple addition of organometallics to borate esters, Wang et al.<sup>[14d]</sup> reported that bis[2-(*N,N*-dimethylamino)ethyl]ether could be employed as a ligand to suppress these side reactions. Alternatively, Leermann et al.<sup>[14b]</sup> reported that excellent yields of boronic acids were obtained *via* reactions of Grignards with B(OMe)<sub>3</sub> in the presence of LiCl.

Organozinc pivalates<sup>[16]</sup> are a privileged class of organometallics particularly known to their air- and moisture-stability and broad spectrum of functional groups tolerance. These reagents exhibit excellent reactivity in reactions, e.g., Negishi cross coupling reactions<sup>[17]</sup> and were successfully used in the synthesis of complex molecules.<sup>[18]</sup> Based on our interests



**Scheme 1.** Borylation of organozinc reagents.

on expanding the applicability of organozinc reagents in organic synthesis,<sup>[19]</sup> we here first describe a CuI-catalyzed chemospecific borylation of organozinc pivalates with trialkyl borates to afford boronic acids in high yields.

Initially, *p*-TolZnBr·MgCl<sub>2</sub>·LiCl (**2a'**), *in situ* prepared from *p*-tolylbromide (**1a**) *via* magnesium insertion-ZnCl<sub>2</sub> transmetalation sequence, was treated with an equimolar ratio of B(OMe)<sub>3</sub> (**3a**) without or in the presence of various catalysts at room temperature (Table 1). As was demonstrated by Komeyama et al.,<sup>[15b]</sup> organozinc reagent **2a'** was inactive to B(OMe)<sub>3</sub> and the desired borylation product **4a** was not formed (entry 1). When using iron(II) or copper(II) catalysts, the main product is the corresponding homodimer (e.g. 4,4'-dimethylbiphenyl, entries 2 & 3). Better results were obtained with Ni(II) catalysts (entries 4 & 5). Interestingly, THF-soluble CuI·2LiCl was proven to be the most effective catalyst and afforded *p*-TolB(OH)<sub>2</sub> (**4a**) in 52% yield (entry 6). Notably, a considerable amount of bis-*p*-tolylboronic acid **4a'** (18%) was also formed as the main byproduct. To suppress the second addition of organozinc reagent to B(OMe)<sub>3</sub>, 2 equivalents of B(OMe)<sub>3</sub> was introduced and that improved the yield of **4a** to 63% isolated yield (entry 7). Replacement of B(OMe)<sub>3</sub> (**3a**) with B(O*i*Pr)<sub>3</sub> (**3b**) slightly improved the yield of **4a** to 67%. However, 15% bis-*p*-tolylboronic acid **4a'** was still generated (table 1, entry 8 and Scheme 1). Enlightened by recent advances from Prof. Knochel' group that organozinc pivalates are air- and moisture-stable organometallics possessing higher reactivity than their organozinc halides siblings,<sup>[16]</sup> *p*-TolMgBr·Zn(OPiv)<sub>2</sub>·LiCl (**2a**), *in situ* prepared from *p*-tolylbromide (**1a**) *via* magnesium insertion/Zn(OPiv)<sub>2</sub> transmetalation sequence, was introduced. (For the sake of clarity, ArZnCl·Mg(OPiv)<sub>2</sub>·LiCl is abbreviated henceforth as ArZnOPiv).<sup>[20]</sup> Remarkably, *p*-TolB(OH)<sub>2</sub> **4a** was obtained as the only boronated organic compound (84% isolated yield, table 1, entry 9). In this case, (*p*-Tol)<sub>2</sub>BOH **4a'** was not detected according to our <sup>1</sup>H NMR analysis. Replacement of CuI·2LiCl with CuBr·2LiCl, CuCl·2LiCl and CuCN·2LiCl all provided **4a** as a sole product albeit the yields of which did not improved further<sup>[21]</sup> (entries 10-12). Attempts to introduce TMEDA, PPh<sub>3</sub> and bipyridine as ligands<sup>[22]</sup> also failed to improve the yield of **4a** further, possibly because these ligands combined preferentially with B(O*i*Pr)<sub>3</sub> rather than organozinc pivalates. It is worth to mention here that commonly at least one equivalent of cuprous salts are required to improve the reactivity of organozinc reagents.<sup>[23]</sup> Thus this protocol, with only a catalytic amount of CuI (5 mol%) deployed, is quite rare in copper catalyzed organozinc chemistry.

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**Table 1.** Optimization of reaction conditions.<sup>[a]</sup>

Entry	Catalyst	B(OR) <sub>3</sub>	2	4a/%
1	-	B(OMe) <sub>3</sub> <b>3a</b>	<b>2a'</b>	0
2	Fe(acac) <sub>2</sub>	B(OMe) <sub>3</sub> <b>3a</b>	<b>2a'</b>	23
3	Cu(OAc) <sub>2</sub>	B(OMe) <sub>3</sub> <b>3a</b>	<b>2a'</b>	32
4	NiCl <sub>2</sub>	B(OMe) <sub>3</sub> <b>3a</b>	<b>2a'</b>	36
5	Ni(PPh <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub>	B(OMe) <sub>3</sub> <b>3a</b>	<b>2a'</b>	44
6	CuI·2LiCl	B(OMe) <sub>3</sub> <b>3a</b>	<b>2a'</b>	52
7	CuI·2LiCl	B(OMe) <sub>3</sub> <b>3a</b>	<b>2a'</b>	63 <sup>[b,c]</sup>
8	CuI·2LiCl	B(O <i>i</i> Pr) <sub>3</sub> <b>3b</b>	<b>2a'</b>	67 <sup>[b,c]</sup>
9	CuI·2LiCl	B(O <i>i</i> Pr) <sub>3</sub> <b>3b</b>	<b>2a</b>	84 <sup>[b,c]</sup>
10	CuBr·2LiCl	B(O <i>i</i> Pr) <sub>3</sub> <b>3b</b>	<b>2a</b>	82 <sup>[b,c]</sup>
11	CuCl·2LiCl	B(O <i>i</i> Pr) <sub>3</sub> <b>3b</b>	<b>2a</b>	78 <sup>[b,c]</sup>
12	CuCN·2LiCl	B(O <i>i</i> Pr) <sub>3</sub> <b>3b</b>	<b>2a</b>	75 <sup>[b,c]</sup>

[a] Yields were determined by crude <sup>1</sup>H NMR analysis. [b] 2 equivalents of B(OR)<sub>3</sub> **3** was employed. [c] Isolated yield.

Having established the optimum conditions (Table 1, entry 8), we then tested the generality and limitation of organozinc pivalates, *in situ* prepared *via* LiCl mediated magnesium insertion and subsequent transmetalation with Zn(OPiv)<sub>2</sub>. As showed in Table 2, the reaction scope with respect to a variety of organozinc pivalates is quite broad, allowing facile preparation of boronic acids from aryl and heteroaryl boronic acids in high yields (Table 2, compounds **4b-4i**). Arylzinc pivalates bearing electron-neutral (**4b** & **4c**) and -rich (**4d-f**) substituents are borylated smoothly with B(O*i*Pr)<sub>3</sub> to the corresponding arylboronic acids in 63-84% isolated yields. In the cases of cyclopentyl and 4-*tert*-butylbenzylzinc pivalates, good reactivity was observed and the boronic acid products **4j** and **4k** were isolated in good quantities.

The metal-halogen exchange reaction provides the direct transformation of aryl, heteroaryl and also alkyl halides into the corresponding organometallic reagents. Sensitive functional groups are well tolerated in these privileged organometallic reagents. Pioneered by the excellent studies from Knochel's group,<sup>[24]</sup> the turbo Grignard reagent *i*-PrMgCl·LiCl<sup>[25]</sup> has been praised not only in accelerating halogen (or sulfoxide) magnesium exchange reactions, but also in a wide range of elegant applications in laboratory syntheses and up-scaled industrial processes. By this protocol, a wide range of highly functionalized organozinc reagents were prepared and transformed into desired products. To evaluate the efficacies of

**Table 2.** The scope of organozinc pivalates prepared *via* Mg-insertion/Zn(OPiv)<sub>2</sub> transmetalation<sup>[a]</sup>

1	2	4

[a] Isolated yield based on **1**.

**Table 3.** Borylation of arylzinc pivalates derived from metal-halide exchange reactions.<sup>[a]</sup>

5	6

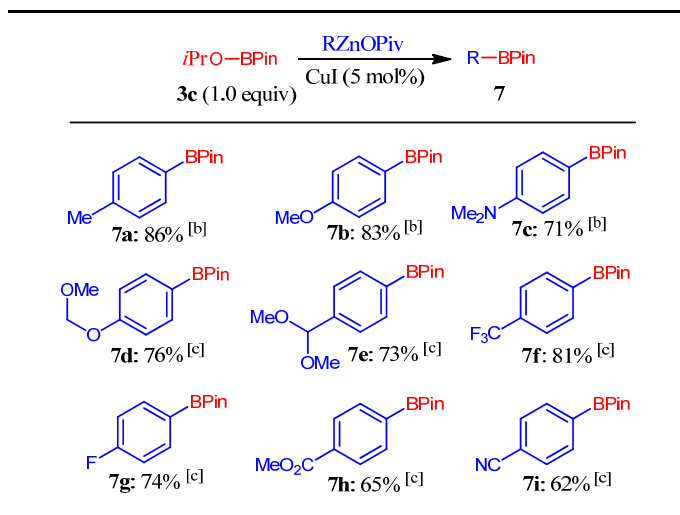
[a] Isolated yields based on aryl halides. [b] BuLi was used instead of *i*-PrMgCl·LiCl.

organozinc pivalates thus prepared, especially these aromatic organozinc reagents bearing an electron-withdrawing group, a two-step, one-pot CuI:2LiCl catalyzed borylation were carried out (Table 3). Thus, 4-fluoriodobenzene (**5a**) was treated with turbo Grignard reagent at -20 °C and then with Zn(OPiv)<sub>2</sub>. Under CuI catalysis, this *in situ* formed organozinc pivalate performed a smooth borylation to give boronic acid **6a** in 78% isolated yield. Similarly, arylzinc pivalates bearing F, Cl as well as CF<sub>3</sub> substituents at the meta and para positions performed this type of transformations smoothly, giving the corresponding boronic acids in 67-78% yields (**6b-6f**). Also, 2-OCF<sub>3</sub> and 2-SCH<sub>3</sub> substituted arylzinc pivalates were successfully prepared and reacted with **3b** to furnish the ortho-substituted arylboronic acids in good yields, implying that steric hindrance does not play a key role here (**6g** & **6h**). Heterocyclic boronic acids (**6i-6n**) featuring a furan, thiophene, pyridine or quinoline as the key structural core were all successfully prepared in acceptable yields.

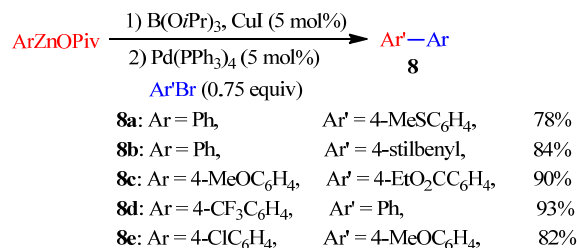
Finally, this CuI-catalyzed borylation of organozinc pivalates was extended to boronic acid pinacol ester synthesis (Table 4). In this respect, arylzinc pivalates prepared either *via* magnesium insertion/Zn(OPiv)<sub>2</sub> transmetalation (**7a-7e**) or by metal-halogen exchange reaction/Zn(OPiv)<sub>2</sub> transmetalation (**7f-7i**) react with isopropoxyboronic acid pinacol ester (*i*PrOBPin **3c**) to afford the boronic acid pinacol esters (R-BPin, **7**) in good yields. Notably, only one equivalent of **3c** was used. Sensitive functional groups, e.g., acetal, CF<sub>3</sub>, F and ester are compatible to the optimized reaction conditions, highlighting the superiority of this approach over previously reported borylation of arylzinc reagents<sup>[15b]</sup> whereby only low yields of boronic acid pinacol ester were obtained (e.g., **7g**: 74% v.s. 23%; **7i**: 62% v.s. 38%).

Since the borylation reaction of the organozinc pivalates with boric acid ester **3** generates organyl boronates, subjecting the crude reaction mixture to Suzuki-Miyaura cross-coupling should result in an overall diaryl synthesis. Such a process would make

**Table 4.** Borylation of arylzinc pivalates with *i*PrOBPin<sub>2</sub>.<sup>[a]</sup>



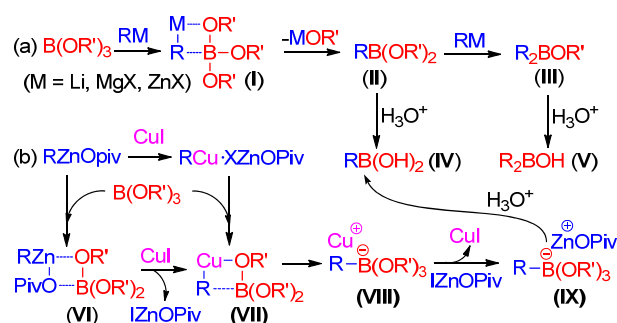
[a] Isolated yields based on **3c**. [b] RZnOPiv were prepared *via* Mg insertion/Zn(OPiv)<sub>2</sub> transmetalation. [c] RZnOPiv were prepared *via* Mg-X exchange reaction/Zn(OPiv)<sub>2</sub> transmetalation sequence.



**Scheme 2.** Pd catalyzed cross-couplings of aryl bromides with *in situ* formed aryl boronic acid esters.

economic use of the aryl groups of the organozinc pivalates. Indeed, the anticipated reaction sequence comprising the C-B bond formation as a transient path to C-C coupling could be realized. After the borylation reaction, the palladium catalyst Pd(PPh<sub>3</sub>)<sub>4</sub> and carbonate base was introduced (Scheme 2). By this approach, the mentioned product mixtures from C-B bond formation with aryl bromides engage in the desired direct Suzuki-Miyaura coupling to provide the corresponding diaryl compounds **8a-e** as the only C-C coupling products.

Mechanistically, the reaction of an organometallic reagent (RM: M = Li, MgX, ZnX; X = halide) with trialkyl borate B(OR')<sub>3</sub> proceeded *via*: First, a complex **I** was formed which, after R migration and MOR' extrusion, yielded the boronate **II**. **II** is still a reactive borylating agent to RM and a second reaction took place to produce borinate **III** as the byproduct. Similarly, borinate **III** further reacted with RM to produce borane R<sub>3</sub>B as another byproduct. Acid hydrolysis of **II** and **III** produced the desired boronic acid **IV** and boronic acid **V** as a mixture (Scheme 3a). On the contrary, organozinc pivalate RZnOPiv first combined with trialkyl borate B(OR')<sub>3</sub> to form an inactive complex **VI** which, after a Zn/Cu metathesis, yielded the reactive complex **VII**. Rearrangement of **VII** produced the copper(I) trialkoxy(organyl)borate **VIII**. Zn/Cu metathesis of **VIII** with IZnOPiv delivered **IX**<sup>[26]</sup>. Acid hydrolysis of **IX** gave boronic acid **IV** as a sole product. CuI was regenerated in this step to complete the catalytic cycle of Cu<sup>I</sup>. Alternatively, Zn/Cu metathesis of R'ZnOPiv and CuI provided R'Cu-XZnOPiv, which then combined with B(OR')<sub>3</sub> to form complex **VII**. (Scheme 3b).



**Scheme 3.** Proposed reaction mechanism.

In summary, we have developed an efficient and practical CuI catalyzed method to achieve C-B bond formation through

the reaction of air- and moisture-stable organozinc pivalates with trialkylborates. By employment of the air- and moisture-stable organozinc pivalates, the formation of borinic acid and borane byproducts were completely suppressed thus providing a more practical method for boronic ester synthesis. Furthermore, these *in situ* formed boronic acid esters could be directly introduced into Suzuki-Miyaura cross-couplings to afford biaryls in high yields.

## Experimental Section

### General

All reactions were performed in Schlenk tubes under argon. THF was distilled from benzophenone and sodium wire prior to use.  $^1\text{H}$  (400 or 600 MHz),  $^{13}\text{C}$  (101 or 151 MHz) spectra were recorded in  $\text{CDCl}_3$  solutions. Flash chromatography was performed on silica gel (300-400 mesh). organic pivalates were prepared according to literature<sup>[16c]</sup>

### Synthesis of boronic acids and pinacol esters 4, 6 and 7.

A dry and argon-flushed 10 mL Schlenk tube, equipped with a stirring bar and a septum, was charged with  $\text{CuI}\cdot 2\text{LiCl}$  solution in THF (1.00 M, 0.1 mL, 0.1 mmol). The  $\text{B}(\text{O}^i\text{Pr})_3$  (4.0 mmol, 2.0 equiv) was added at room temperature. Then, a solution of the appropriate organozinc pivalate (2.0 mmol) was added dropwise over 5 min *via* syringe. The reaction was stirred at room temperature overnight. Hydrochloric acid (1N, 10 mL) and ethyl acetate (5 mL) were added and the phases were separated. The aqueous phase was extracted with ethyl acetate (3 × 10 mL). The combined organic layers were washed with saturated brine solution (10 mL) and dried over  $\text{Na}_2\text{SO}_4$ . The solvents were evaporated and the residue was subjected to column chromatography purification on silica yielding the respective title compound.

### General procedure of Suzuki-Miyaura cross coupling reaction

To a solution of organozinc pivalate was charged with  $\text{CuI}\cdot 2\text{LiCl}$  solution in THF (1.00 M, 0.2 mL, 0.2 mmol).  $\text{B}(\text{O}^i\text{Pr})_3$  (4.0 mmol, 2.0 equiv) was added at room temperature. The reaction mixture was stirred at room temperature for 2h.  $\text{ArBr}$  (1.5 mmol) and  $\text{Pd}(\text{PPh}_3)_4$  (87 mg, 0.075 mmol) in THF (5 mL) was then added. After which, a solution of  $\text{K}_2\text{CO}_3$  in water (10%, 2.0 mL) was added and the reaction mixtures were heated to reflux for 6 hours. Saturated aqueous  $\text{NH}_4\text{Cl}$  solution (5 mL) and ethyl acetate (5 mL) were added. The phases were separated and the aqueous phase was extracted with ethyl acetate (3 × 10 mL). The combined organic layers were washed with saturated brine solution (10 mL) and dried over  $\text{Na}_2\text{SO}_4$ . The solvents were evaporated and the residue was subjected to column chromatography purification on silica yielding the biaryls.

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**Keywords:** boronic acid • copper catalysis • organozinc pivalate • trialkylborate • Suzuki-Miyaura coupling

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