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Efficient Synthesis of Aryl Boronates via Zinc-Catalyzed Cross-Coupling of Alkoxy Diboron Reagents with Aryl Halides at Room Temperature

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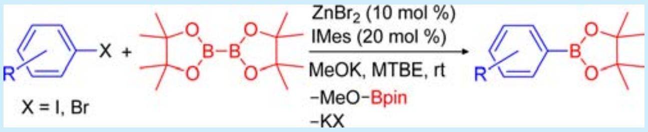
Ⓢ *Supporting Information*

ABSTRACT: A zinc(II)/NHC system catalyzes the borylation of aryl halides with diboron (4) reagents in the presence of KOMe at rt. This transformation can be applied to a broad range of substrates with high functional group compatibility. Radical scavenger experiments do not support a radical-mediated process.



Arylboronic acids and arylboronates have attracted significant attention over the past few decades, due to their extensive applications in organic synthesis, particularly in transition-metal-catalyzed C−C, C−O, and C−N bond-forming reactions, as exemplified by the Suzuki−Miyaura cross-coupling reaction.[1] In comparison with other types of organometallic carbon nucleophiles, arylboronates are most frequently used owing to their ease of handling, functional group compatibility, and low toxicity.[1a] Recent strategies for preparing arylboronates include transition-metal-catalyzed cross-coupling reactions of alkoxy diboron or alkoxy borane reagents with aryl halides[2] or direct C−H borylation of aromatic substrates.[3] Significant examples include Pd-,[4] Ni-,[5] or Cu-catalyzed[6] borylation of aryl halides, and the selective iridium-catalyzed C−H borylation of aromatic and heteroaromatic substrates.[3,7]

In 2009, our group reported that CuI, in the presence of inexpensive phosphine ligands, catalyzes the borylation of aryl halides with diboron reagents to generate arylboronic esters in good to excellent yields.[6b] Recently, Ito et al. reported the transition-metal-free borylation of aryl halides using a more expensive silylborane reagent and metal alkoxide base,[8] and Zhang et al. reported the Cs_2CO_3 mediated borylation of aryl iodides, but not aryl bromides, with diborane reagents in the presence of methanol.[9] The Zn-catalyzed borylation of aryl halides at elevated temperatures (aryl iodides at 75 °C and aryl bromides at 120 °C) purportedly via a borylzincate generated *in situ* from highly pyrophoric diethylzinc, diboron, and metal alkoxide was very recently reported by Uchiyama et al.[10] We recently developed an efficient Zn-catalyzed borylation of unactivated alkyl halides to furnish alkylboronates at rt.[11] In comparison to noble metals, zinc catalysis for such processes is underdeveloped.[12] Zinc is an attractive alternative to the commonly used metals (Pd or Ni), because it is inexpensive (0.07 € per mol), relatively abundant (0.0076% in the earth crust), environmentally benign, and less toxic. Herein we describe a novel Zn-catalyst system for the borylation of aryl halides with alkoxy diboron reagents under mild conditions.

The conditions screened for optimizing the catalytic borylation method using 4-iodotoluene (**1a**) as the substrate are shown in Table 1. With $ZnBr_2$ as the zinc source and B_2pin_2 as the diboron reagent, the corresponding boronate 4-MeC_6H_4Bpin **1b** was formed in good yield (85%, entry 2) at rt in 6 h using IMes (**L1**) as the ligand (IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene) in MTBE (methyl-*tert*-butylether), while $ZnCl_2$ and ZnI_2 (entries 1 and 3) provided the product in slightly lower yields. In the absence of a Zn source, only a trace amount of desired product was obtained; thus, any uncatalyzed reaction is minimal (entry 4). A moderate yield (58%) was obtained upon using a reduced catalyst loading of 5 mol % (entry 5), whereas a higher concentration gave only a slightly higher yield (89%, entry 6). Next, the effects of base were examined (entries 7−12). The use of LiO*t*Bu was ineffective (entry 7). In contrast to the Zn catalyzed borylation of alkyl halides, KO*t*Bu was inferior to KOMe (entry 8).[11] The replacement of KOMe by Cs_2CO_3 or NaO*t*Bu gave only trace product, whereas NaOMe was only somewhat less effective (entries 9−11). When base was omitted from the reaction mixture, no arylboronic ester was formed (entry 12).

Different NHC ligands that were examined (**L2**−**L5**) provided lower yields than **L1** (entries 13−16). Ligand is essential for this catalytic borylation; no significant yield was obtained when the ligand was omitted (entry 17). Finally, we investigated the effect of the solvents (Table 1, entries 18−22). The use of THF afforded results comparable to those for MTBE (79% yield, entry 18), and both benzene and toluene provided the product in slightly lower yields (entries 19 and 20, respectively). The use of the more polar coordinating solvents *N*,*N*-dimethylformamide (DMF) or acetonitrile (CH_3CN) resulted in a moderate or limited reaction, respectively (entries 21 and 22).

With the optimized reaction conditions identified, we examined the scope of the present borylation reaction with different aryl halides, as summarized in Table 2. Aryl halides with

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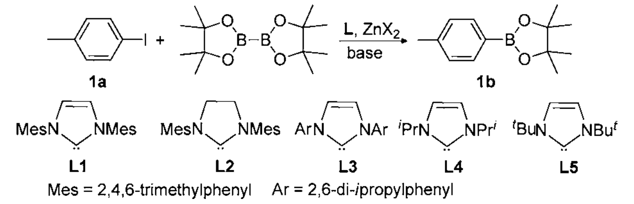
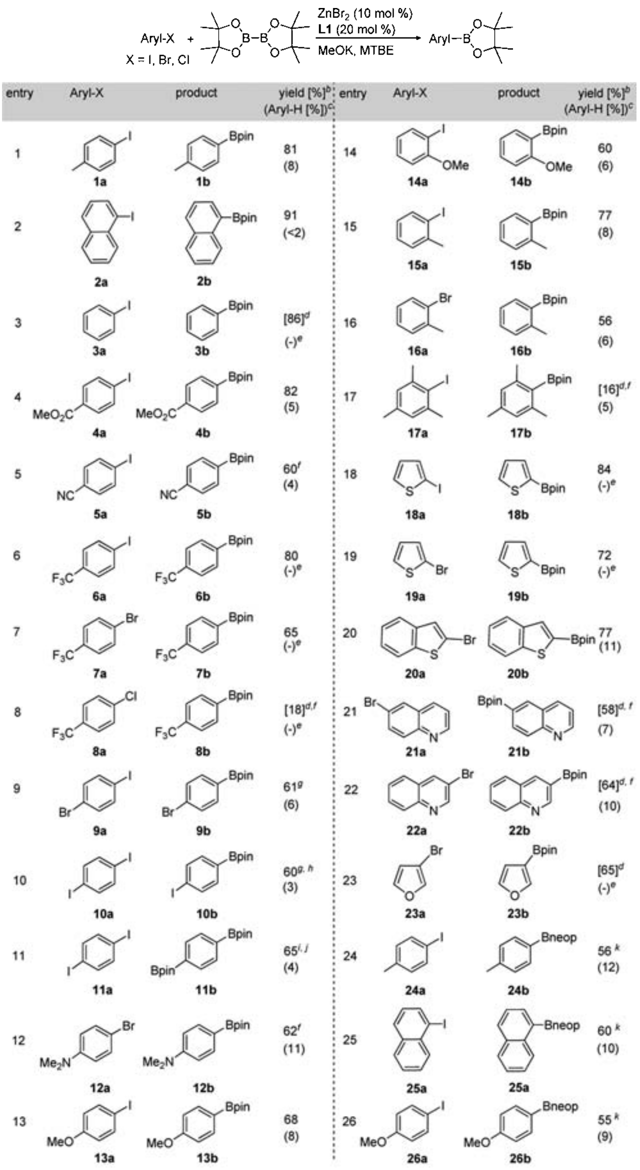
Table 1. Optimization of the Reaction Conditions for the Zinc-Catalyzed Borylation of 4-MeC_6H_4I, 1a[a]



entry	ZnX_2 (10 mol %)	L (20 mol %)	base	solvent	*t* (h)	yield (%)[b]
1	$ZnCl_2$	**L1**	KOMe	MTBE	6	66
2	$ZnBr_2$	**L1**	KOMe	MTBE	6	85 (81)[c,d]
3	ZnI_2	**L1**	KOMe	MTBE	6	76
4	-	**L1**	KOMe	MTBE	12	trace
5	$ZnBr_2$(5)	**L1**[e]	KOMe	MTBE	12	58
6	$ZnBr_2$(15)	**L1**[f]	KOMe	MTBE	6	89[d]
7	$ZnBr_2$	**L1**	LiO*t*Bu	MTBE	12	trace
8	$ZnBr_2$	**L1**	KO*t*Bu	MTBE	12	43
9	$ZnBr_2$	**L1**	Cs_2CO_3	MTBE	12	trace
10	$ZnBr_2$	**L1**	NaO*t*Bu	MTBE	12	trace
11	$ZnBr_2$	**L1**	NaOMe	MTBE	12	62
12	$ZnBr_2$	**L1**	-	MTBE	12	0
13	$ZnBr_2$	**L2**	KOMe	MTBE	12	19
14	$ZnBr_2$	**L3**	KOMe	MTBE	12	58
15	$ZnBr_2$	**L4**	KOMe	MTBE	12	62
16	$ZnBr_2$	**L5**	KOMe	MTBE	12	11
17	$ZnBr_2$	-	KOMe	MTBE	12	trace
18	$ZnBr_2$	**L1**	KOMe	THF	12	79
19	$ZnBr_2$	**L1**	KOMe	C_6H_6	12	76
20	$ZnBr_2$	**L1**	KOMe	Toluene	12	72
21	$ZnBr_2$	**L1**	KOMe	DMF	12	52
22	$ZnBr_2$	**L1**	KOMe	CH_3CN	12	5

[a] Reaction conditions: 4-MeC_6H_4I, **1a** (0.5 mmol, 1 equiv), Zn source (10 mol %), ligand (20 mol %), base (1.5 equiv), B_2pin_2 (1.5 equiv), MTBE (2 mL), at rt. [b] The yields were determined by GC-MS analysis vs a calibrated internal standard and are averages of two runs. [c] Isolated yield after chromatographic workup. [d] Complete conversion was observed, determined by GC-MS analysis (see Table S5). [e] 10 mol % of **L1** used. [f] 30 mol % of **L1** used.

Table 2. Screening of Aryl Halides for the Zinc Catalyzed Borylation Reaction[a]



entry	Aryl-X	product	yield [%][b] (Aryl-H [%])[c]	entry	Aryl-X	product	yield [%][b] (Aryl-H [%])[c]
1	**1a**	**1b**	81 (8)	14	**14a**	**14b**	60 (6)
2	**2a**	**2b**	91 (<2)	15	**15a**	**15b**	77 (8)
3	**3a**	**3b**	[86][d] (-)[e]	16	**16a**	**16b**	56 (6)
4	**4a**	**4b**	82 (5)	17	**17a**	**17b**	[16][d,f] (5)
5	**5a**	**5b**	60[f] (4)	18	**18a**	**18b**	84 (-)[e]
6	**6a**	**6b**	80 (-)[e]	19	**19a**	**19b**	72 (-)[e]
7	**7a**	**7b**	65 (-)[e]	20	**20a**	**20b**	77 (11)
8	**8a**	**8b**	[18][d,f] (-)[e]	21	**21a**	**21b**	[58][d, f] (7)
9	**9a**	**9b**	61[g] (6)	22	**22a**	**22b**	[64][d, f] (10)
10	**10a**	**10b**	60[g, h] (3)	23	**23a**	**23b**	[65][d] (-)[e]
11	**11a**	**11b**	65[i, j] (4)	24	**24a**	**24b**	56[k] (12)
12	**12a**	**12b**	62[f] (11)	25	**25a**	**25a**	60[k] (10)
13	**13a**	**13b**	68 (8)	26	**26a**	**26b**	55[k] (9)

[a] Reaction conditions: aryl halide (typically 0.5 mmol, 1 equiv), B_2pin_2 (1.5 equiv), $ZnBr_2$ (10 mol %), **L1** (20 mol %), KOMe (1.5 equiv), MTBE, rt for 6−12 h (see Supporting Information for details). [b] Isolated yield after chromatographic workup unless otherwise stated. [c] Approximate ArH yields were estimated by GC-MS analysis. [d] Yield was determined by ^1H NMR analysis. [e] ArH peak was not separated from the solvent peak. [f] The reaction was performed at 50 °C. [g] The reaction was performed using 1 equiv of B_2pin_2 and 1 equiv of KOMe. [h] 1,4-$(Bpin)_2C_6H_4$ (7%) and C_6H_5Bpin (4%) were also detected by GC-MS. [i] The reaction was performed using 3 equiv of B_2pin_2 and 3 equiv of KOMe. [j] C_6H_5Bpin (25%) and 4-IC_6H_4Bpin (3%) were also detected by GC-MS. [k] The diboron reagent changes from B_2pin_2 to B_2neop_2.

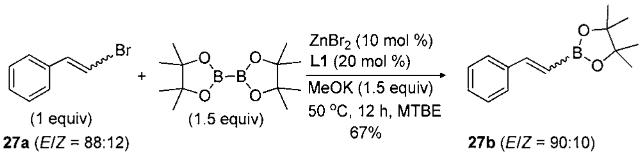
different electronic properties as well as different halogen substituents were investigated. Neutral (**2a**, **3a**) or electron-withdrawing substituents, such as ester (**4a**), cyano (**5a**), and trifluoromethyl (**6a**) groups, are well tolerated, affording the desired arylboronates in moderate to good yields. Aryl bromides can also be utilized (**7a**, **12a**, **16a**, **19a**−**23a**). Furthermore, the effects of the halides were investigated with *para*-CF_3-containing substrates (**6a**−**8a**); 4-bromobenzotrifluoride is readily converted into **7b** (yield = 65%), but 4-chlorobenzotrifluoride was only borylated in 18% yield (NMR), even at higher temperature (50 °C), and the addition of $(Bu_4N)I$ did not facilitate the transformation.

4-Bromophenyl boronate (**9b**) was the sole borylated product from the reaction of 4-bromophenyl iodide (**9a**) with 1 equiv of B_2pin_2/KOMe. 1,4-Diiodobenzene (**10a**) also underwent predominantly monoborylation when only 1 equiv of the borylating reagent was used (Table 2, entry 10), but with 3 equiv of B_2pin_2/KOMe, the 1,4-diborylated product **11b** was formed in good yield (entry 11). Reactions with electron-rich substrates containing *o*- or *p*-Me or -OMe groups (**1a**, **13a**−**16a**) also gave the desired boronates (**1b**, **13b**−**16b**, respectively) in moderate to good yields, and 4-bromo-*N*,*N*-dimethylaniline (**12a**), containing a strong *π*-donor substituent, gave a 62% yield of the corresponding arylboronic ester, along with a small amount of dimethylaniline via hydrodehalogenation.[6b]

Sterically congested, *ortho*-substituted phenyl derivatives were borylated in moderate to good yields (entries 2, 14−16). However, 2-iodo-1,3,5-trimethylbenzene (**17a**; disubstituted at both *ortho* positions) reacted to give the borylation product in only 16% yield (**17b**), along with unreacted starting material, as indicated by GC-MS analysis. This zinc-catalyzed method is also applicable to the borylation of a variety of heteroaryl halides, such as thiophene, benzothiophene, quinoline, and furan systems (entries 18–23). Furthermore, this protocol shows not only a wide scope with respect to the aryl halide substrate but also that bis(neopentylglycolato)diboron[13] can be substituted for bis(pinacolato)diboron, giving the corresponding aryl boronates (**24b**–**26b**) in moderate yields.

This zinc-catalyzed borylation reaction can also be successfully applied to the alkenyl bromide **27a** (*β*-bromostyrene; *E*/*Z* = 88:12) to give a 67% yield of the corresponding alkenyl boronate ester **27b** (mixture containing *E*/*Z* = 90:10), but at 50 °C (Scheme 1). The borylation reaction does have some substrate restrictions. For example, when hydroxy- or aldehyde-substituted arenes were used, the aryl boronate was detected in only trace amounts by GC-MS and was not readily isolated.

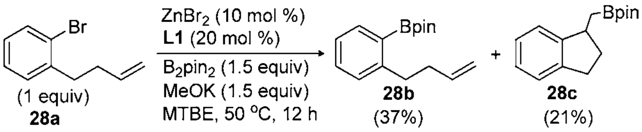
Scheme 1. Borylation of *β*-Bromostyrene, 27a



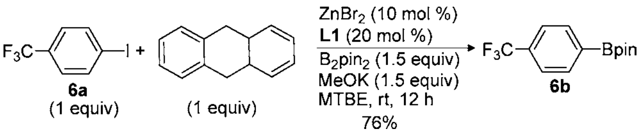
As illustrated in Table 2, in some cases, the formation of the hydrodehalogenation byproduct, ArH, was observed. The hydrodehalogenating byproduct was previously detected during Pd- and Ni-catalyzed coupling reactions of aryl halides with dialkoxyhydroboranes,[4c−e,h,5a−c] and recently in Cu-catalyzed borylation reactions involving alkoxy diboron reagents.[6b] We attempted to determine the hydrogen source in our borylation reaction by conducting the reaction with 4-iodoanisole **13a** using 10 mol % $ZnBr_2$, 20 mol % **L1**, 1.5 equiv of B_2pin_2, and KOMe in $[D_8]$THF for 12 h at rt; however, no deuterium incorporation into the hydrodehalogenation product was observed by GC-MS. Thus, solvent is not a hydrogen atom source in this reaction. Moreover, the addition of D_2O (1 equiv) to the reaction mixture shut down the reaction almost completely (trace of **13b**, determined by GC-MS analysis). However, the borylation of **13a** in the presence of 20 mol % D_2O led to selective deuteration at the *para* position of the resulting anisole (determined by GC-MS analysis and ^2H NMR spectroscopy),[14] along with the borylation product in only 8% yield (**13b**). Hydrodehalogenation was also observed when the borylation of **13a** was conducted using rigorously dried solvent in an argon-filled glovebox, but in small amounts (observed by GC-MS). Surface OH groups on the glass vessels were ruled out as the cause of this undesired side reaction by a test using plasticware.

The mechanism of this Zn-catalyzed borylation of aryl halides remains under investigation. We first explored the possibility of a radical-mediated mechanism by performing the reaction on *o*-(3-butenyl)bromobenzene (**28a**) (Scheme 2). The corresponding aryl radical has been reported to undergo 5-*exo*-trig cyclization to form 1-methylindane after H-atom abstraction.[15] The reaction of **28a** at 50 °C afforded arylboronic ester product **28b** in 37% yield, along with the cyclized (borylmethyl)indane product **28c** in 21% yield. The formation of cyclized product **28c** suggested the possibility of a radical mechanism, although insertion of alkene into a Zn-aryl bond cannot be excluded.[16] Therefore, we examined the reaction of **6a** in the presence of a radical scavenger (Scheme 3). Addition of 9,10-dihydroanthracene or TEMPO had no effect, indicating that the borylation does not appear to be a radical process (similar results were obtained with **1a**, **12a**, and **13a**; increasing the radical inhibitor to 3 equiv did not inhibit the borylation reaction).

Scheme 2. Borylation of *o*-(3-Butenyl)bromobenzene, 28a



Scheme 3. Mechanistic Investigations with 9,10-Dihydroanthracene as a Radical Scavenger



To shed further light on this reaction mechanism, we endeavored to prepare a Zn–boryl complex. First, we prepared the Zn–*bis*(aryloxide) complex (NHC)Zn(O-2,6-$iPr_2C_6H_3)_2$ via alcoholysis of (NHC)$ZnEt_2$ (NHC = **L1**) with 2,6-diisopropylphenol.[17] Reaction of this Zn–*bis*(aryloxide) with 2 equiv of B_2pin_2 in $[D_8]$THF at rt was examined by *in situ* ^{11}B NMR spectroscopy. The original ^{11}B signal of B_2pin_2 at $\delta = 30.5$ ppm was partially transformed into two new signals at $\delta = 38.7$ and 21.7 ppm. The former resonance could be assigned to a Zn–boryl complex,[6b,12a,18] and the latter to the aryloxy-Bpin species (low intensity signals between 5 and 2 ppm were also observed).[19] Interestingly, when 4-iodotoluene (**1a**) was added to the above mixture, the signal at $\delta = 38.7$ ppm assigned to the Zn–boryl complex partially disappeared and a signal corresponding to the 4-tolylBpin appeared at $\delta = 30.9$ ppm (overlapped with the B_2pin_2 signal) in the ^{11}B NMR spectrum (the presence of the arylboronic ester product was confirmed by GC-MS). Therefore, it is possible that the mechanism of the present borylation reactions is related in some ways to that of the previously reported Cu-catalyzed borylation reactions.[6b] Further detailed mechanistic investigations are underway to establish unambiguously the reaction pathway.

In summary, we have demonstrated a novel and efficient Zn-catalyzed cross-coupling reaction of aryl halides with diboron reagents, under mild conditions. The low associated cost and low toxicity of Zn support it as an attractive alternative to the widely employed Pd- and Ni-based systems. This method tolerates a variety of functional groups with both iodo- and bromo-substituted aryls (although alcohol and aldehyde are not compatible) and can be extended to heteroaryl halides, providing easy access to the corresponding aryl- and heteroarylboronates in good yields. Our Zn(II)–NHC catalyst is much more active than that recently reported by Uchiyama et al., and it avoids the use of pyrophoric Et_2Zn.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Details of experimental procedures and ^1H, ^{13}C, ^{11}B spectra and GC-MS of the 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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