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Zinc-Catalyzed Borylation **Hot Paper**

Zinc-Catalyzed Borylation of Primary, Secondary and Tertiary Alkyl Halides with Alkoxy Diboron Reagents at Room Temperature[**]

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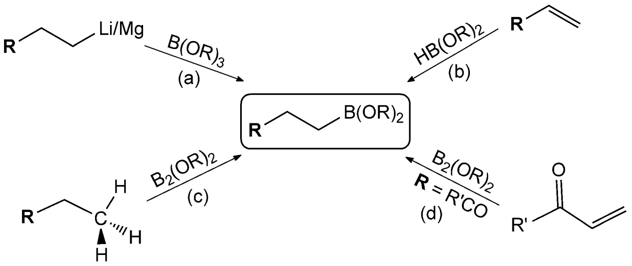
Abstract: *A new catalytic system based on a Zn^{II} NHC precursor has been developed for the cross-coupling reaction of alkyl halides with diboron reagents, which represents a novel use of a Group XII catalyst for C−X borylation. This approach gives borylations of unactivated primary, secondary, and tertiary alkyl halides at room temperature to furnish alkyl boronates, with good functional-group compatibility, under mild conditions. Preliminary mechanistic investigations demonstrated that this borylation reaction seems to involve one-electron processes.*

Alkyl boronic acid derivatives have emerged as versatile intermediates for transition-metal-catalyzed cross-coupling reactions[1,2] and have a wide range of applications in medicinal chemistry.[3] Current approaches for the synthesis of alkyl boronic acid derivatives can be classified into four categories (Scheme 1): a) reaction of alkyl lithium or alkyl magnesium reagents with suitable boron compounds;[4] b) classical or transition-metal-catalyzed hydroboration of olefins;[5] c) transition-metal-catalyzed C−H activation/borylation of alkanes;[6] and d) metal-catalyzed β-borylation of α,β-unsaturated carbonyl compounds.[7] However, these methods have significant limitations, such as functional-group incompatibility in the generation of reactive organolithium/organomagnesium reagents, and regioselectivity in the hydroboration of internal olefins. To address this challenge recent attention has been given to the development of transition-metal-catalyzed borylation of unactivated alkyl electrophiles for the formation of C−B bonds.[8–11] Thus, a versatile and powerful approach for the synthesis of alkyl boronate esters by copper-catalyzed borylation of alkyl halides and pseudohalides was established by our groups,[8] and expanded upon by others using Cu, Ni, and Pd catalysts.[9–11] Being less toxic than Pd or Ni, inexpensive, abundant and environmentally more acceptable, zinc is an attractive alternative to the commonly used expensive noble metals in a number of catalytic reactions.[12] However, the potential for zinc catalysis of borylation or other reactions typically involving oxidation state changes (e.g. oxidative addition/reductive elimination processes) remained to be examined.[13]



Scheme 1. General approaches for the construction of alkyl boronic acid derivatives.

The only example of zinc-mediated C−B bond formation is a stoichiometric reaction reported by Yamashita and Nozaki using a zinc boryl complex.[14] Knochel et al. developed boron zinc transmetalation reactions resulting in the formation of stereochemically pure organozinc species, which can react with several classes of electrophiles with retention of configuration.[15] Recently, zinc-mediated and zinc-catalyzed propargylation of ketones using propargylboronates has also been reported.[16] Given the low cost and low toxicity of zinc, we were interested to explore its use in the borylation of alkyl halides and now report the first efficient zinc-catalyzed borylation of primary, secondary, and tertiary alkyl halides with alkoxy diboron reagents at room temperature.

Using cyclohexyl bromide **9a** as the model substrate in reactions with the diboron compound B_2pin_2 to produce the corresponding cyclohexyl boronate **9b**, we screened a range of conditions, solvents, ligands, zinc sources, and bases to assess the scope and limitations of this reaction (Table 1). The desired alkyl boronic ester **9b** was obtained in 61 % yield at room temperature in 18 h using IMes (**L1**) as the ligand (IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene) and $ZnCl_2$ as zinc source in THF (entry 1). We screened a range of solvents, from benzene to polar solvents (Table 1, entries 2–7), with methyl-*tert*-butylether (MTBE) proving to be optimal giving a yield of 91 % in 1 h (entry 5). The limited solubility of KO*t*Bu or the initially formed B_2pin_2/KO*t*Bu adduct[17,18] may account for the low yield of product in some

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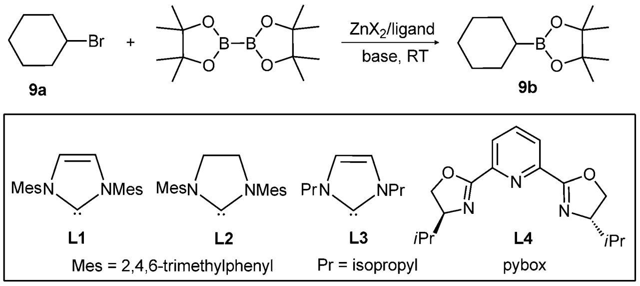
Table 1: Optimization of the zinc-catalyzed borylation of cyclohexyl bromide.



Entry	Catalyst [15 mol%]	Ligand [15 mol%]	Base	Solvent	*t* [h]	Yield [%][a]
1	$ZnCl_2$	**L1**	KO*t*Bu	THF	18	61
2	$ZnCl_2$	**L1**	KO*t*Bu	Benzene	12	49
3	$ZnCl_2$	**L1**	KO*t*Bu	DMSO	12	trace
4	$ZnCl_2$	**L1**	KO*t*Bu	DMF	12	16
5	$ZnCl_2$	**L1**	KO*t*Bu	MTBE	1	91 (82)[b]
6	$ZnCl_2$	**L1**	KO*t*Bu	CH_3CN	18	trace
7	$ZnCl_2$	**L1**	KO*t*Bu	MeOH	24	0
8	$ZnCl_2$	**L2**	KO*t*Bu	MTBE	12	35
9	$ZnCl_2$	**L3**	KO*t*Bu	MTBE	12	11
10	$ZnCl_2$	**L4**	KO*t*Bu	MTBE	12	trace
11	$ZnCl_2$	none	KO*t*Bu	MTBE	24	0
12	$ZnBr_2$	**L1**	KO*t*Bu	MTBE	12	72
13	ZnI_2	**L1**	KO*t*Bu	MTBE	12	78
14	Zn dust	**L1**	KO*t*Bu	MTBE	12	0
15	none	**L1**	KO*t*Bu	MTBE	24	0
16[c]	$ZnCl_2$	**L1**	KO*t*Bu	MTBE	4	81
17	$ZnCl_2$	**L1**	none	MTBE	12	0
18[d]	$ZnCl_2$	**L1**	K_2CO_3	MTBE	12	10
19[d]	$ZnCl_2$	**L1**	KOAc	MTBE	12	trace
20	$ZnCl_2$	**L1**	NaOMe	MTBE	12	45
21	$ZnCl_2$	**L1**	KOMe	MTBE	1	86
22[e]	$Pd(OAc)_2$	**L1**	KO*t*Bu	MTBE	12	0
23[f]	$NiCl_2$	**L1**	KO*t*Bu	MTBE	12	0
24[g]	CuI	**L1**	KO*t*Bu	MTBE	12	7
25[h]	$ZnCl_2$	**L1**	KO*t*Bu	MTBE	12	44

[a] Reactions were carried out using 0.5 mmol of alkyl halide, 1.2 equivalents of B_2pin_2, in 2.0 mL of solvent. The yields were determined by GC-MS analysis versus a calibrated internal standard and are averages of two experiments. [b] Yield of isolated product. [c] 5 mol% of $ZnCl_2$ catalyst and ligand **L1** were used. [d] The reaction was performed at 60 °C under microwave irradiation. [e] 2 mol% of Pd catalyst was used. [f] 2 mol% of anhydrous $NiCl_2$ was used. Similar negative results were obtained with $NiBr_2$. [g] 0.2 mol% of CuI catalyst was used. [h] 18 μL (1 mmol) of water was added.

solvents, but the reason for the lack of catalytic conversion in MeOH (Table 1, entry 7) is currently under investigation.

The influence of the ligand was studied by using different N-heterocyclic carbenes (NHCs) in MTBE (Table 1, entries 8,9); both **L2** and **L3** provided lower yields than **L1** (see Table S1). In the presence of the chiral nitrogen ligand, pybox,[10] no significant yield was observed (entry 10). There was no reaction in the absence of a ligand (entry 11). Zinc(II) bromide and zinc(II) iodide (entries 12 and 13) were slightly less-effective than zinc(II) chloride; however, zinc dust did not show any catalytic activity (entry 14). In the absence of a Zn source, the reaction does not occur (entry 15). Gratifyingly, with a reduced catalyst loading of 5 mol% (entry 16), we obtained a comparable yield, but with a somewhat longer reaction time (see Figure S1 in the Supporting Information).

When KO*t*Bu was omitted from the reaction mixture, no significant amount of the alkyl boronic ester was formed (Table 1, entry 17). The replacement of KO*t*Bu with less-basic K_2CO_3 or KOAc resulted in limited or no reaction, either under standard conditions or under microwave irradiation at 60 °C (entries 18 and 19). NaOMe was less effective than KO*t*Bu; however, KOMe gave comparable yields (entries 20 and 21). In contrast to the copper-catalyzed process, Li alkoxides were ineffective (Table S2).

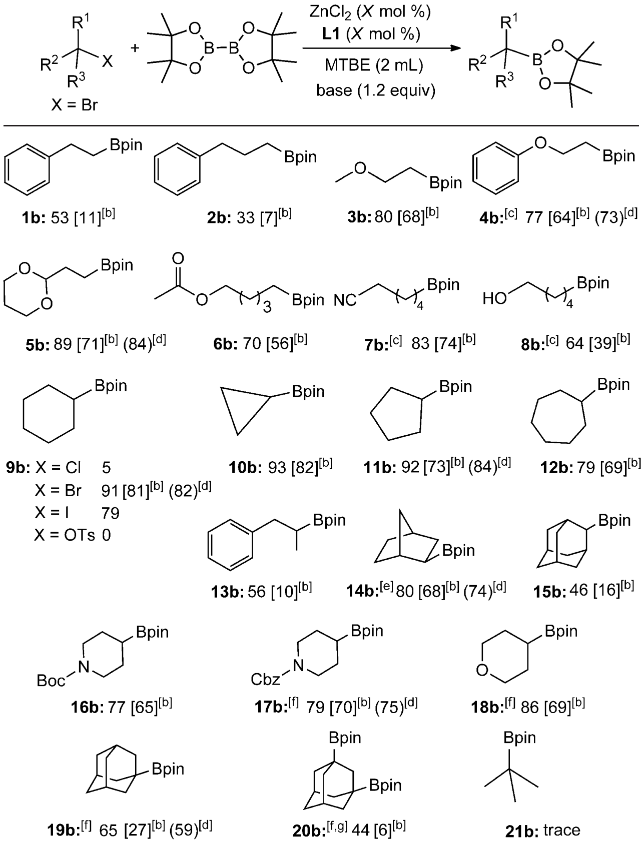
The possible involvement of palladium or nickel contamination in the catalyst was eliminated by the observation that palladium[11] and nickel[10,11] salts did not provide even trace amounts of **9b** under the optimized reaction conditions (entries 22 and 23). It is important to note that the zinc-catalyzed borylation reaction is not caused by Cu contamination,[8,9] as CuI provided a very low yield under the standard reaction conditions (entry 24). Finally, the reaction is not significantly sensitive to air,[19] but is moderately sensitive to moisture, because the addition of 2 equivalents of water reduces the yield to 44% (entry 25). This may be related to the failure of the reaction in neat MeOH.

With the optimized reaction conditions identified, we examined the scope of the new borylation reaction with different alkyl halides. Unactivated primary alkyl halides were converted into the corresponding alkyl boronates in good yields (Table 2). Many synthetically important functional groups including ether (**3b, 4b**), ketal (**5b**), ester (**6b**), and cyano (**7b**) groups are well tolerated, with yields of the desired alkyl boronates ranging from 50% to 90%. Alkyl boronates having a β-alkoxy group are not readily accessible by classical alkyl lithium/alkyl magnesium methods,[4] because of facile β-alkoxy elimination. Our method enables direct conversion of β-alkoxy alkyl halides **3a** and **4a** into the corresponding alkyl boronate **3b** and **4b**. Significantly, the presence of a free alcohol group (**8b**) does not interfere with the reaction. This feature compares favorably with alkyl boronate syntheses involving highly reactive alkyl lithium or alkyl magnesium reagents.[4]

As illustrated in Table 2, unactivated secondary alkyl halides furnished the desired secondary alkyl boronates in good yields. Cyclic, bicyclic, and acyclic secondary bromides can be smoothly borylated (**9b**–**15b**). The effects of the halide or pseudo halide were investigated with cyclohexyl substrates (**9b**); cyclohexyl iodide is readily converted into **9b** (yield 79%), whilst cyclohexyl chloride and tosylate are not effectively borylated, the conversions being very low, even at higher temperature, and the addition of $(Bu_4N)I$ did not induce the transformation. Furthermore, protected amines (**16b**, **17b**) are good substrates, and a cyclic ether (**18b**) was readily borylated by our method. Moreover, this route could be carried out on a gram scale (5 mmol) with the same efficiency, as demonstrated for cyclohexyl bromide **9a** (**9b**: 0.9 g, 82%).

In addition to primary and secondary alkyl electrophiles, tertiary alkyl halides can also be borylated. Reactions of 1-bromo and 1,3-dibromoadamantane proceeded smoothly to produce the corresponding mono- and bis(boryl) products,

Table 2: Substrate scope of zinc-catalyzed borylation of primary, secondary, and tertiary alkyl halides.[a]



1b: 53 [11][b]
2b: 33 [7][b]
3b: 80 [68][b]
4b:[c] 77 [64][b] (73)[d]
5b: 89 [71][b] (84)[d]
6b: 70 [56][b]
7b:[c] 83 [74][b]
8b:[c] 64 [39][b]
9b: X = Cl 5
X = Br 91 [81][b] (82)[d]
X = I 79
X = OTs 0
10b: 93 [82][b]
11b: 92 [73][b] (84)[d]
12b: 79 [69][b]
13b: 56 [10][b]
14b:[e] 80 [68][b] (74)[d]
15b: 46 [16][b]
16b: 77 [65][b]
17b:[f] 79 [70][b] (75)[d]
18b:[f] 86 [69][b]
19b:[f] 65 [27][b] (59)[d]
20b:[f,g] 44 [6][b]
21b: trace

[a] Reaction conditions: alkyl halide (typically 0.5 mmol, 1 equiv), diboron reagent (1.2 equiv), $ZnCl_2$ (15 mol%), Ligand: **L1** (15 mol%), KO*t*Bu (1.2 equiv), MTBE (2 mL), at room temperature unless otherwise stated. The yields were determined by GC-MS analysis versus a calibrated internal standard and are averages of two experiments.
[b] 5 mol% of $ZnCl_2$ catalyst and ligand **L1** were used (see Tables S3 and S4). [c] The optimal base changes from KO*t*Bu to KOMe. [d] Yield of isolated product. [e] *Exo*-2-bromonorbornane was used. [f] The structure was confirmed by single-crystal X-ray diffraction. [g] The reaction was performed using 2.2 equiv of B_2pin_2 and 2.2 equiv of KO*t*Bu.

respectively (**19b**, **20b**). However, the reaction of *tert*-butyl bromide was quite sluggish (**21b**). It is important to note that in copper-catalyzed cross-couplings of organometallic reagents with aliphatic electrophiles, tertiary alkyl halides have seldom been used successfully (only two examples: 2-bromo-2-methylbutane 0% yield and 1-bromoadamantane 17% yield).[9a] Recently, nickel-catalyzed borylation of unactivated tertiary alkyl electrophiles yielded the desired tertiary alkyl boronates.[10] Our zinc-catalyzed borylation reaction provides an additional option for cross-coupling of tertiary alkyl electrophiles.

This zinc-catalyzed method not only shows wide scope with respect to the alkyl halide substrate, but B_2neop_2 (neop = $OCH_2CMe_2CH_2O$)[20] can be substituted for B_2pin_2 to give the corresponding alkyl Bneop compounds (see Scheme S1). The borylation reaction does have some substrate restrictions. For example, for 4-bromobenzyl bromide, the alkyl boronate was detected in only small amounts by GC-MS, and was not readily isolated. Although 3-bromocyclohexene (an allylic bromide) reacted under the conditions employed no borylated product could be identified by GC-MS (a trace amount of 3,3′-bicyclohexene was observed).

The mechanism of this transformation is not immediately obvious. In analogy to previous studies on Cu-catalyzed borylation,[17,21] an NHC zinc complex might activate the diboron reagent, thus forming a zinc boryl complex, which promotes boryl addition to the electrophilic alkyl halides. While [(NHC)$ZnCl_2$] (NHC = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene)[22] did not appear to react with 1 equivalent of B_2pin_2 at room temperature, addition of KO*t*Bu does lead to reaction, and we have isolated **I**, a zinc-containing product of this reaction (Figure 1). This novel three-coordinate Zn complex results from the insertion of Zn into the N–C bond of one NHC ligand, with migration of a Bpin moiety to the carbene carbon atom, and insertion of another Bpin group into the N–C bond of a second NHC ligand. As evidenced by ^{11}B NMR spectroscopy, and confirmed by single-crystal X-ray diffraction, the product contains two expanded "carbene-based" ligands, one still C- bound to Zn, but containing a four-coordinate boron center in the ring, adjacent to the carbon atom, the second one being C,N-bound to Zn, but containing a three-coordinate boron moiety attached to the carbenoid carbon atom. Clearly, it is too early to speculate in any detail on the mechanism of formation of this complex product. However, isolated **I** failed to catalyze the borylation of **9a**, suggesting that it represents a channel for catalyst deactivation. The isolation of

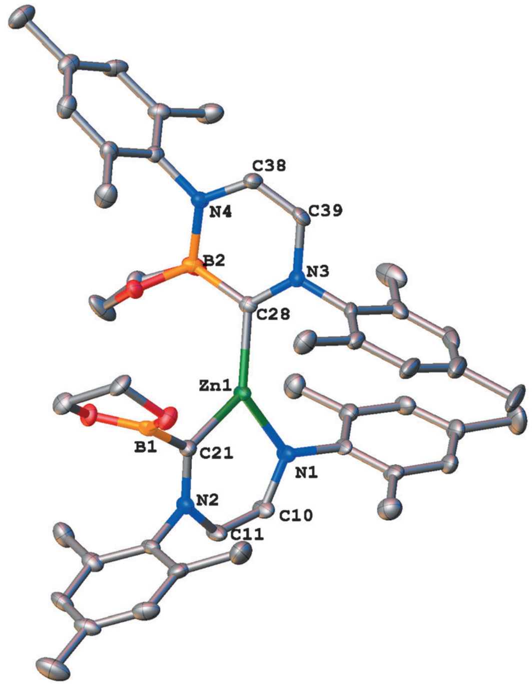
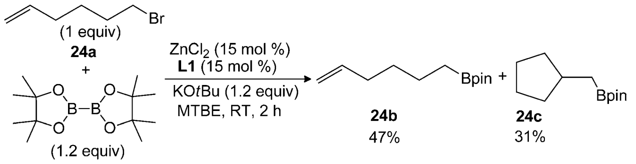


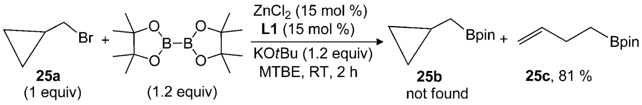
Figure 1. Molecular structure of **I**. C gray, N blue, Zn dark green, B orange, O red. Hydrogen atoms, pinacolato methyl groups, and a second symmetry-independent molecule are omitted for clarity; atomic displacement ellipsoids are set at 50% probability.

I should serve as a warning to those using NHC ligands in catalysis, or even their protonated imidazolium salts as ionic liquid solvents, that ring-expansion reactions involving main-group or post-transition-metal elements are possible. In this regard, we note three recent examples involving Be,[23] B,[24] or Si,[25] for which ring expansion took place at elevated temperatures (80–120 °C), and very recent theoretical studies[26] on the mechanism of the ring expansion of NHCs.[27] Another catalyst deactivation pathway is the formation of metallic Zn, as demonstrated by X-ray powder diffraction (see Figure S4).

Although additional experimental and theoretical studies are underway to obtain a full understanding of the mechanism, a few preliminary experiments provided interesting results. For example, borylation of 6-bromohex-1-ene afforded **24b** as anticipated, along with the cyclized product cyclopentylmethyl boronate **24c** (Scheme 2). Furthermore, the zinc-catalyzed borylation of cyclopropylmethyl bromide (**25a**, Scheme 3), gave 3-butenylboronate **25c** (81 %) exclusively; the simple boryl substitution product **25b** was not detected. The formation of the ring-opened product **25c**, as well as **24c**, suggests a radical mechanism. In addition, borylation of either *exo*- or *endo*-2-bromonorbornane produced predominantly the *exo* product (**14b**) (*exo*:*endo* ratio of 18:1), consistent with the involvement of a radical pathway. Therefore, we examined the reaction of **9a** in the presence of the radical scavenger, 9,10-dihydroanthracene (see Scheme S2). When the reaction was performed in the presence of 1 equiv of the radical inhibitor, the desired product **9b** was obtained in a lower yield (**9b**: 54 %); increasing the radical inhibitor to 8 equivalents shuts down the reaction almost completely (trace of **9b**, determined by GC-MS analysis). Consequently, the borylation reaction seems to involve one-electron processes. As a result, it is possible that the mechanism of the present borylation reactions is related in some ways to that of the reported nickel-catalyzed (Ni^I/Ni^{III}) cross-coupling of aliphatic electrophiles with organoboronic acids.[10,11] Further mechanistic studies are underway to examine this hypothesis.



Scheme 2. Borylation of 6-bromohex-1-ene (**24a**).



Scheme 3. Borylation of cyclopropylmethyl bromide (**25a**).

Having established an efficient and highly versatile entry to alkyl boronic esters it was of interest to explore their utility. Treatment with KHF_2 converts the alkyl boronic esters into the corresponding organotrifluoroborates (see Scheme S3),[28] which have been shown to be efficient reagents in Suzuki–Miyaura cross-coupling reactions.

In conclusion, we have developed the first Group XII transition-metal-catalyzed borylation reaction of unactivated alkyl halides with diboron reagents. This reaction proceeds under mild conditions (room temperature), in the presence of non-precious metal (Zn), and in a solvent which has a reduced tendency to form explosive organic peroxides (MTBE). The reaction is not drastically sensitive to air and tolerates a variety of functional groups, allowing rapid access to products which would be difficult to access by other means. Preliminary mechanistic investigations suggest that this borylation reaction involves one-electron processes. Detailed mechanistic studies are in progress and further applications of zinc catalysts for other processes are under investigation.

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