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Pyridine-Catalyzed Radical Borylation of Aryl Halides

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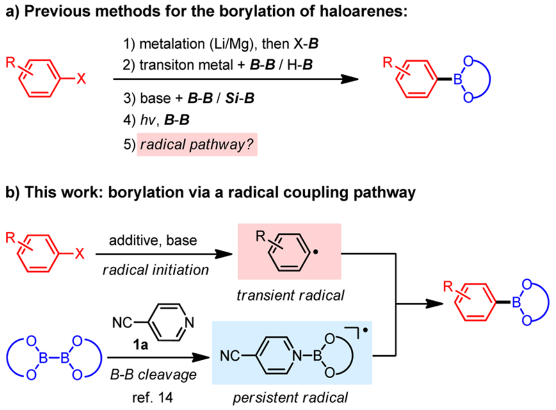
Supporting Information

ABSTRACT: A pyridine-catalyzed transition-metal-free borylation reaction of haloarenes has been developed based on the selective cross-coupling of an aryl radical and a pyridine-stabilized boryl radical. Arylboronates were produced from haloarenes under mild conditions. This borylation reaction features a broad substrate scope, operational simplicity, and gram-scale synthetic ability.

Arylboronates have been widely used in molecular science,[1] in particular as reagents and building blocks in synthetic chemistry.[2] As a result, methods that can efficiently synthesize arylboronates, especially functionalized ones, are highly demanded. Haloarenes are the most commonly employed precursors to arylboronates (Scheme 1a). A classical method for the preparation of arylboronates is stoichiometric metalation of haloarenes (by Li or Mg) and subsequent nucleophilic substitution utilizing trialkyl borates as the boron source.[3] The transition-metal catalyzed methods developed over the past decades enabled an efficient approach to arylboronates employing diboron or hydroborate species as the boron source, which features a broad substrate scope and good functional group compatibility.[4−6] Recently, new pathways have been discovered to prepare arylboronates from haloarenes[7−9] without the need for stoichiometric metalation or a transition metal catalyst.[10,11] Ito reported the borylation of aryl iodides and bromides under basic conditions using a silylborane reagent;[7] Zhang reported a base-promoted borylation of aryl iodides using a diboron reagent;[8] Li, Larionov, and Fu independently reported the photoinduced borylation of haloarenes with a diboron reagent.[9] These achievements represent a new dimension in arylboronate synthesis; however, they often suffer from defects such as high cost for the borylation reagent, low reactivity, or operational inconvenience.

Scheme 1. Previous Borylation Methods and the Proposed Radical Borylation Reaction



Our idea for realizing a new transition-metal-free approach to arylboronates was inspired by two recent advances in radical chemistry. In recent years it has been disclosed that, in the presence of an organic additive and a base, aryl halides can be transformed to aryl radicals via a single electron transfer (SET)/carbon-halogen bond cleavage sequence,[12] representing a novel mode of haloarene activation.[13] Meanwhile, very recently Li and Zhu reported the homolytic cleavage of the B−B bond by a Lewis base, 4-cyanopyridine (**1a**),[14] to produce a pyridine-stabilized boryl radical.[15] We envisioned that, if the transient aryl radical and the stabilized boryl radical were generated in one reaction system, selective cross-coupling of these two species might occur to produce arylboronate (Scheme 1b), subjecting it to the persistent radical effect.[16] This strategy would provide a new radical pathway for the borylation of haloarenes. Although in some previous reports possible radical mechanisms were proposed,[5b,d,9,10a,b,d] the cross-coupling of two radical species for arylboronate formation has not been achieved to date.

We started to test this concept on a model borylation reaction of iodoarene **2a** employing bis(pinacolato)diboron (B_2pin_2) (Table 1). First, when 4-cyanopyridine (**1a**) was used to activate B_2pin_2, potassium *tert*-butoxide (*t*-BuOK) was employed as the base, and the reaction was carried out in tetrahydrofuran (THF); no borylation product was observed, and most of the iodoarene remained intact (entry 1). When sodium methoxide was used in place of *t*-BuOK, the desired borylation product **5a** was observed in a low yield, together with a significant amount of dehalogenation product, anisole (entry 2). Given that hydrogen atom transfer (HAT) between the aryl radical and THF might be the reason for dehalogenation, methyl *tert*-butyl ether (MTBE) was employed as the solvent to suppress the formation of anisole. Indeed, the yield improved remarkably (entry 3), and a more concentrated reaction afforded an even better yield (entry 4). Replacing **1a** by another electron-deficient pyridine, 4-trifluoromethylpyridine (**1b**), diminished the reactivity remarkably (entry 5), while simple pyridine (**1c**) was as efficient as **1a** (entry 6). Control experiments showed that the reaction could not proceed without either the pyridine catalyst or the base, supporting the proposed reaction pathway.

Bromoarenes are more easily available than iodoarenes and are widely utilized in industry and the laboratory, and we hoped to apply the present borylation method to bromoarenes. However, the optimized conditions were found to be inefficient (entry 7).

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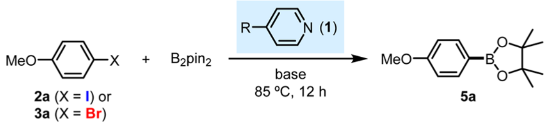
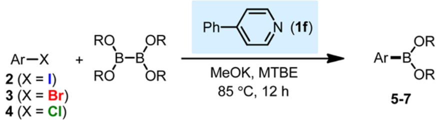
Table 1. Optimization of the Borylation Reaction[a]

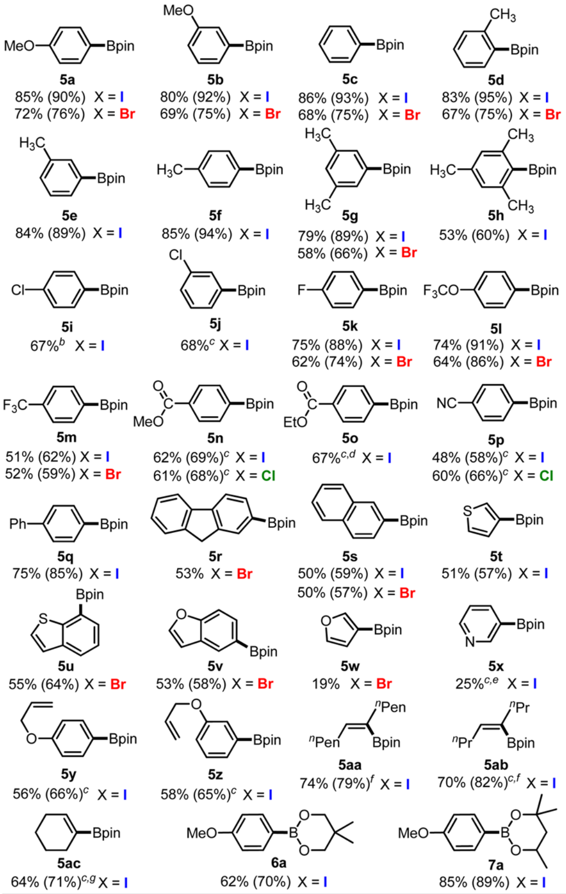


entry	Ar-X	base	additive	solvent	conv. (%)	yield (%)
1	Ar–I	*t*-BuOK	*p*-NCC_5H_4N (**1a**)	THF	–	trace
2	Ar–I	MeONa	*p*-NCC_5H_4N (**1a**)	THF	89	19[b]
3	Ar–I	MeONa	*p*-NCC_5H_4N (**1a**)	MTBE	>99	60
4	Ar–I	MeONa	*p*-NCC_5H_4N (**1a**)	MTBE[c]	>99	87[d]
5	Ar–I	MeONa	*p*-$CF_3C_5H_4N$ (**1b**)	MTBE	38	24
6	Ar–I	MeONa	C_5H_5N (**1c**)	MTBE[c]	>99	85
7	Ar–Br	MeONa	*p*-NCC_5H_4N (**1a**)	MTBE[c]	33	25
8	Ar–Br	MeONa	C_5H_5N (**1c**)	MTBE[c]	37	25
9	Ar–Br	MeONa	*p*-$MeOC_5H_4N$ (**1d**)	MTBE[c]	10	7
10	Ar–Br	MeONa	*p*-$Me_2NC_5H_4N$ (**1e**)	MTBE[c]	6	5
11	Ar–Br	MeONa	*p*-PhC_5H_4N (**1f**)	MTBE[c]	79	58
12	Ar–Br	MeOK	*p*-PhC_5H_4N (**1f**)	MTBE[c]	98	76
13	Ar–I	MeONa	*p*-PhC_5H_4N (**1f**)	MTBE[c]	>99	90[d]
14	Ar–I	MeOK	*p*-PhC_5H_4N (**1f**)	MTBE[c]	>99	90
15	Ar–I	MeOK	*p*-PhC_5H_4N (**1f**)	DMSO[e]	>99	83

[a] Reaction conditions: **2a** or **3a** (0.5 mmol, 1 equiv), base (2 equiv), B_2pin_2 (2 equiv), additive (20 mol %), solvent (2 mL), sealed tube, 85 °C for 12 h. The conversions and yields were determined by GC using *n*-dodecane as an internal standard. [b] Anisole was obtained in 57% yield as the byproduct. [c] 0.4 mL of solvent was used. [d] Reaction time was 3 h. [e] 1 mL of solvent was used.

Table 2. Scope of Haloarenes[a]





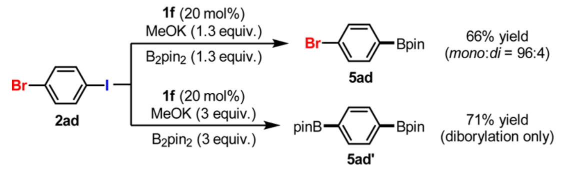
[a] Reaction conditions: **2**, **3**, or **4** (0.5 mmol, 1 equiv), **1f** (20 mol %), MeOK (2 equiv), diboron reagent (2 equiv) in 0.4 mL of MTBE, 85 °C for 12 h. Yields of isolated products are reported, and GC yields are shown in parentheses. [b] Together with 4.3% diborylation product **5ad′**. [c] 1.3 equiv of MeOK and 1.3 equiv of B_2pin_2 were used. [d] Contained 9.7% transesterification product **5n**. [e] NMR yield. [f] *E*/*Z* = 89:11. [g] 40 mol % of **1f** was used.

To solve this problem, pyridine catalysts **1c–e** with different electronic natures were attempted, but none of them produced improved results (entries 8–10). Considering that a pyridine molecule that can further stabilize the boryl radical might be helpful, we employed 4-phenylpyridine (**1f**) as the catalyst and indeed observed a significant increase in the yield of **5a** (entry 11). When MeOK was used instead of MeONa, the yield was further improved (entry 12). Application of these conditions to iodoarene **2a** afforded similarly good results (entries 13 and 14). Therefore, the optimal conditions for pyridine-catalyzed borylation of iodo- and bromoarenes (entry 12) were utilized in the following studies.

This borylation reaction exhibits a broad substrate scope with respect to haloarenes (Table 2). In general, aryl halides with various substituents, as well as heteroaryl and alkenyl halides, were compatible substrates. Haloarenes with electron-donating substituents were transformed to the corresponding arylboronates in good yields, regardless of the substitution pattern (**5a–g**). A sterically hindered substrate **2h** participated in the reaction well to afford the borylation product **5h** in 53% yield. The reactions of electron-deficient haloarenes, such as chloro-, fluoro-, and trifluoromethyl-substituted ones, produced borylation products in good to moderate yields (**5i–p**). Notably, activated aryl chlorides **4n** and **4p** could also undergo the borylation reaction. Biphenyl, fluorenyl, and naphthyl halides, together with some heteroaromatic halides, took part in the borylation reaction smoothly to produce arylboronates **5q–v**. However, 3-bromofuran (**3w**) and 3-iodopyridine (**2x**) proved to be poor substrates. In many cases aryl bromides were also good substrates compared with the corresponding aryl iodides, albeit lower yields were obtained. Interestingly, olefin-containing haloarenes **2y** and **2z** were also compatible, despite the fact that diboronation of a C═C bond could occur in the presence of B_2pin_2 and a base.[17] In addition to aryl halides, alkenyl iodides **2aa–ac** afforded the corresponding alkenylboronates **5aa–ac** in good yields, further broadening the scope of this borylation method. Finally, this reaction also worked well with bis(neopentyl glycolato)diboron and bis(1,1,3-trimethylethylene glycolato)diboron to produce arylboronates **6a** and **7a** in good yields.

Interestingly, dihaloarene **2ad** could undergo selective mono- or diborylation reaction (Scheme 2). Monoborylation product **5ad** was obtained as the major product by applying a lower loading of base and B_2pin_2, while diborylation product **5ad′** was tuned to the sole product by increasing the loading of base and B_2pin_2. This feature is different from that observed in the base-promoted homolytic aromatic substitution reaction, in which selective monosubstitution of a dihaloarene was difficult.[13a,g]

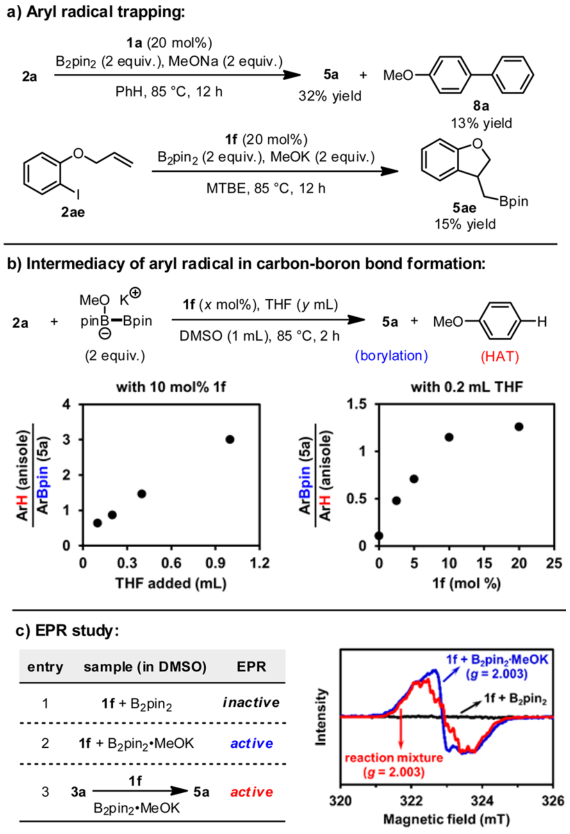
Scheme 2. Selective Borylation Reaction of Dihaloarene 2ad



The borylation reactions of several aryl iodides were conducted on gram scale employing inexpensive pyridine (**1c**) as the catalyst (Scheme S1). In these reactions the yields were comparable to those in small scale reactions, affording grams of arylboronates in one batch. Since the diboron reagent is much less expensive than the silylborane reagent,[7] this method provides a simple and cost-effective approach to arylboronates in a transition-metal-free manner.

Preliminary mechanistic studies were conducted to disclose some mechanistic information in this radical borylation process. First, the generation of aryl radical from the haloarene under the borylation conditions was confirmed by inter- and intramolecular trapping reactions (Scheme 3a). When conducted in benzene, the reaction of **2a** afforded the borylation product **5a** together with a phenylation product **8a**, which was attributed to trapping of the aryl radical by benzene. On the other hand, when aryl iodide **2ae** with an *ortho*-allyloxy side chain was subjected to the standard conditions, cyclic alkylboronate **5ae** was obtained, indicating an intramolecular trapping of the aryl radical by the olefin moiety, followed by coupling with the boryl species.[10e]

Scheme 3. Preliminary Mechanistic Studies

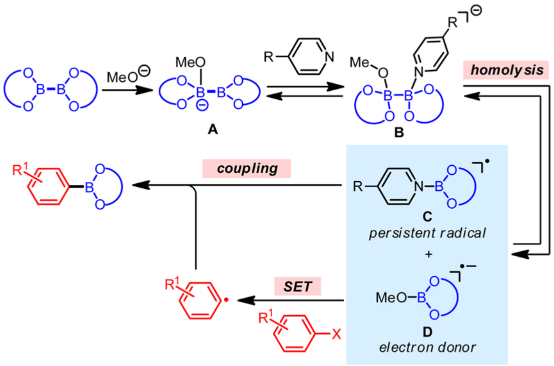


Second, the involvement of both aryl radical and pyridine-related boryl species in carbon−boron bond formation was confirmed by a series of competition experiments (Scheme 3b). In the reaction of **2a** and a preformed diboron ate complex (B$_2$pin$_2$·MeOK)[18] in the presence of 10 mol % pyridine **1f**, addition of THF (0.1−1.0 mL) resulted in the formation of a significant amount of HAT product, anisole, and the product distribution ArH/ArBpin correlated well with the amount of THF added (left plot). This observation was in agreement with a competition scenario, in which the hydrogen atom donor THF competed with the boryl species to react with the aryl radical. Meanwhile, it was observed that, with a fixed amount of added THF (0.2 mL), the loading of pyridine catalyst **1f** (0−20 mol %) had a remarkable impact on the product ratio, ArBpin/ArH: the preference for borylation significantly increased with increasing amount of **1f** (right plot). In the competition kinetics, the promoting effect of pyridine clearly indicated the involvement of pyridine-related boryl species in the formation of the C−B bond and excluded the simple S$_{RN}$1-type reaction between the aryl radical and boryl species unrelated to pyridine (e.g., the ate complex).

Third, EPR experiments confirmed the formation of radical species under the reaction conditions (Scheme 3c). Radical species could be produced by the reaction of pyridine **1f** with the preformed diboron ate complex, but not with diboron itself (entries 1 and 2). A similar EPR signal was observed for the borylation reaction mixture (entry 3). This result confirmed the radical nature of the reaction and suggested that the homolysis of diboron to form the pyridine-stabilized boryl radical occurred at the stage of the ate complex.

Given the experimental evidence and the reported stabilization effect of pyridine derivatives on boryl radicals,[14,19] a plausible reaction mechanism was proposed (Scheme 4). A methoxide anion reacts with B$_2$pin$_2$ to produce the ate complex **A**, which can further react with pyridine to afford intermediate **B**. Homolytic cleavage of the adduct **B** generates a pair of radicals, pyridine-stabilized boryl radical **C** and methoxyboronate radical anion **D**. The latter acts as a strong electron donor[20] to undergo SET to an aryl halide, producing an aryl radical after carbon-halogen bond cleavage. Finally, capture of the aryl radical by boryl radical **C** produces the borylation product.

Scheme 4. Plausible Reaction Mechanism



In conclusion, a pyridine-catalyzed radical borylation reaction of aryl and alkenyl halides has been realized, which is efficient, easy-to-use, and scalable. This reaction utilizes the cross-coupling of a transient radical and a persistent radical, representing a new application of aryl radical produced in a transition-metal-free reaction system.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b11813.

Experimental procedures, additional information, and characterization data (PDF)

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Notes

The authors declare no competing financial interest.

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