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Electrochemical Radical Borylation of Aryl Iodides[†]

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Summary of main observation and conclusion Herein, we report the first electrochemical strategy for the borylation of aryl iodides *via* a radical pathway using current as a driving force. A mild reaction condition allows an assorted range of readily available aryl iodides to be proficiently converted into synthetically valuable arylboronic esters under transition metal catalyst-free conditions. Moreover, this method also shows good functional group tolerance. Initial control mechanistic experiments reveal the formation of aryl radical as a key intermediate and the current plays important role in the generation of radical intermediate.

Background and Originality Content

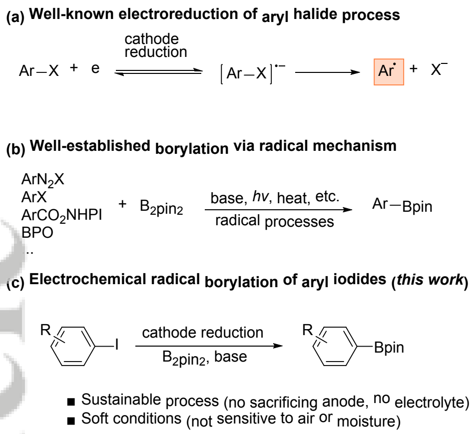
Arylboronic acids and their derivatives have found widespread applications in organic synthesis.[1-3] Consequently, the methods of their preparation have been intensively developed in the past decades. Conventional approaches to the synthesis of arylboronic acids or esters from aryl halides require either prior preparation of highly reactive organometallic reagents,[4-5] or the procedures[6] required transition-metal such as Pd,[7-10] Ni,[11-13] Cu,[14-16] Zn[17] and Fe[18] as a catalyst. These methods are widely used in laboratories and pharmaceutical companies. However, the limited functional group compatibility and the use of expensive metals and/or ligands or strong bases are the obvious drawbacks in these methods. Nevertheless, there is a strong need to the development of efficient, mild, and transition-metal-free synthetic approach for the borylation of aryl halides.

In this context, Organic electrochemistry offers a green and sustainable alternative tool to conventional chemical approaches for organic transformations.[19-35] Various versatile reactive intermediate (e. g., radical cation, radical anion, and radical) can be efficiently generated by anodic oxidation, cathodic reduction, as well as paired electrolysis. Our laboratory has been engaged in the development of organic electrochemistry to overcome unmet synthetic challenges.[36-38] With this background, we thought to the synthesis of aryl boronates from aryl halides through electrochemical transformation (Scheme 1c).

In the context of electro-reduction of aryl halides, it's well known that aryl halide easily transforms to aryl radical via a reversible, dissociative electron transfer (DET) process. Ensuing, this radical is widely used in various organic transformations (Scheme 1a).[39] Except this strategy, transition-metal-free borylation approaches are also well known for the synthesis of a diverse range of organoboron compounds via radical pathway.[40-42] Since the pioneering work of the Wang group in 2010,[43-45] numerous transition-metal-free aromatic borylation protocols have been developed using anilines,[46-49] aryl (pseudo)halides,[50-56] and aryl carboxylates[57] as the coupling substrates (Scheme 1b). Inspired from these strategies, we thought to develop an electrochemical radical borylation of aryl halides via cathodic reduction under transition-metal-free condition (Scheme 1c).

We present herein mild radical borylation of aryl halides with commercially available bis(pinacolato)diboron (B_2pin_2), as the boron source. After the comparison of the present study with the known borylation methods, we found that the electrochemical radical borylation reaction has many advantages over the known protocols. Primarily, the overall process is sustainable in which electron serves as the reductant with solvents being oxidized at the anode, therefore no sacrificing anode is needed. Furthermore, this reaction can be performed under air atmosphere. Moreover, this electrochemical radical borylation of aryl iodides approach got remarkable increase in reaction rate over the reported work on borylation of aryl iodides by Zhang's group under the similar reaction conditions.[54]

Scheme 1 Electrochemical borylation of aryl halides

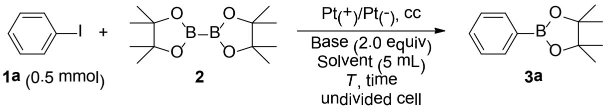


Results and Discussion

Results (sample title, optional)

In this investigation, we chose phenyl iodide **1a** as model substrate and pinacol diboron (B_2pin_2) **2** as a borylating agent (Table 1). Interestingly, 54% yield of **3a** was obtained using platinum meshes as the electrodes with 13 mA constant current in the presence of cesium carbonate (entry 1). Notably, either increasing or decreasing the current resulted in lower yields (entries 2 and 3). After that, other bases such as CsF, CsOAc, *t*-BuOK and MeONa were also investigated under similar reaction conditions. However, all these bases were less effective. (entries 4-5 and 7-8). To our delight, the significant change was observed in the yield of the desired product after the elevation of reaction temperature in 2h (entry 6). Moreover, other solvents, such as EtOH, THF and MeCN were also tested to optimize the best reaction solvent. Regrettably, no better yields of **3a** were obtained (entries 9-11). In the cases of THF and MeCN solvents, the reaction media became less conductive (30 V, 1-3 mA). Therefore, electrolyte Bu_4NClO_4 was added in the reaction media to succeed the reaction (entries 10-11). After the screening of additional reaction times, it is revealed that 3 h is the optimum time for the completion of the reaction (entry 12). Moreover, drastically changes were observed in the yield of the desired product after increasing the amount of B_2pin_2 from 3.0 and 4.0 equivalent (entry 1 and entries 12-13). Finally, in the absence of current, deleterious impact was observed in the yield of **3a** (entry 14), which clearly indicates the significant role of current in the generation of aryl radical. Moreover, the "on and off" experiment also indicated the requirement of continuous current (entry 15).

Table 1 Reaction optimization[a]



Entry	Base	**1a** / **2** / Base	Current (mA)	*T* (°C)	Time (h)	Solvent	Conv. of **1a** (%)[b]	Yield (%)[b]
1	Cs_2CO_3	1:3:2	10	50	1	MeOH	69	44
2	Cs_2CO_3	1:3:2	13	50	1	MeOH	61	54
3	Cs_2CO_3	1:3:2	20	50	1	MeOH	79	52
4	CsF	1:3:2	13	50	1	MeOH	71	33
5	CsOAc	1:3:2	13	50	1	MeOH	58	16
6	Cs_2CO_3	1:3:2	13	65	2	MeOH	100	64
7	^{t}BuOK	1:3:2	13	65	2	MeOH	51	40
8	MeONa	1:3:2	13	65	2	MeOH	59	44
9	Cs_2CO_3	1:3:2	13	78	2	EtOH	85	30
10	Cs_2CO_3	1:3:2	13	65	2	THF[c]	40	34
11	Cs_2CO_3	1:3:2	13	65	2	MeCN[c]	64	11
12	$\mathbf{Cs_2CO_3}$	**1:4:2**	**13**	**65**	**3**	**MeOH**	**98**	**76**
13	Cs_2CO_3	1:3.5:2	13	65	3	MeOH	97	67
14	Cs_2CO_3	1:4:2	0	65	3	MeOH	19	14
15[d]	Cs_2CO_3	1:4:2	0 – 13	65	3	MeOH	52	33

[a] Reaction conditions: Platinum mesh electrodes (1 cm × 1 cm), **1a** (0.5 mmol), **2**, base (2.0 equiv.), solvent (5 mL), heating, undivided cell, sealed tube. cc,

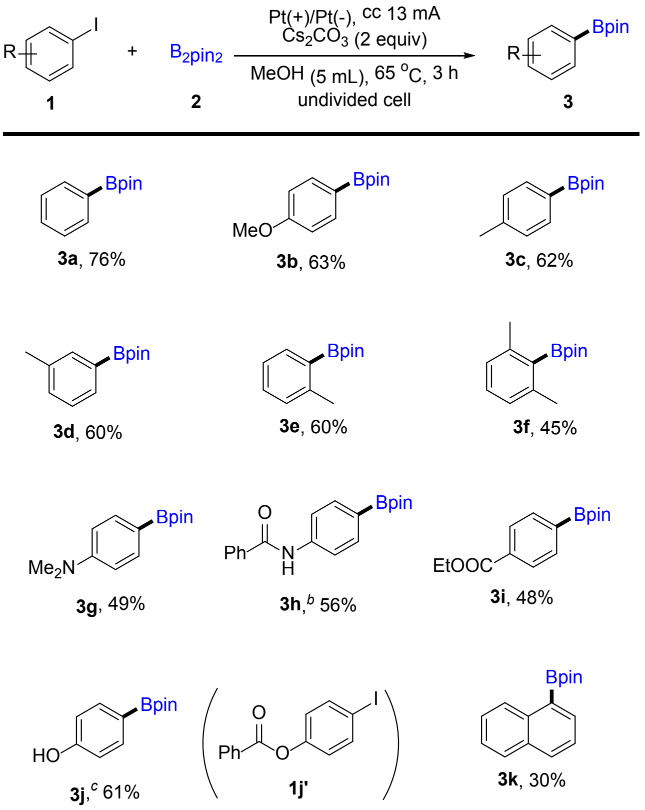
constant current. [b] Determined by GC-FID with *n*-decane as an internal standard. [c] Bu_4NClO_4 as the electrolyte was added. [d] "On and off" control experiment. During a total time of 3 hours, the current continued for 3 min and then interrupted for 27 min, cycled for 6 times.

With the optimal reaction conditions in hand, we explored the substrate scope of aryl iodide (Table 2). Notably, a wide range of aryl iodide derivatives bearing both electron-withdrawing and electron-donating groups could be borylated in moderate to good yields. Aryl iodides with an electron-donating group furnished the corresponding borylation product in good yields (**3a-3e**). A sterically hindered aryl iodide such as **2e** and **2f** smoothly engaged in the reaction and afforded a moderate yield of the respective product. In addition, aryl iodides with an electron-withdrawing group, such as an amide and an ester, produced borylation products in moderate yields (**3g–j**). Notably, for substrate **1j'**, the ester group was converted to phenolic hydroxyl and furnished product **3j** in 60% yield.

To study the mechanism, we designed a series of electron paramagnetic resonance (EPR) experiments. In this context, dimethylpyridine *N*-oxide (DMPO) was introduced as a spin trapping agent to convert the short-living active radical into EPR detectable nitroxide radicals.[58] The EPR spectra were simulated using the least-squares fitting method with EasySpin's function *garlic* (for details, see Supporting Information). The parameters, isotropic *g* values and hyperfine constants *A* were carefully compared with literature data and used as the unique fingerprint of the trapped radicals.

Interestingly, when the current is passed through in a reaction medium for 5 minutes at room temperature, the strong EPR signal is appeared (see **Figure 1a)**. Besides, in the absence of current, the intensity of EPR signal is decreased under similar conditions. This EPR signal is generally assigned to be DMPO•Ph, which is already known in various reported literature.[59-60] However, on the basis of previous reports, we found that the signals of some other species such as DMPO•CH_3,[60-61] DMPO•CH_2OH,[61-62] appear very close or similar to the EPR signal of DMPO•Ph. To verify an electrochemically generating radical species by the reduction of halides on cathode process, we carried out the reaction with n-C_4F_9I in the presence of 45 mA current. As expected, a very special "quasi-quartet" signal of DMPO•C_4F_9[61] appears within 30 minutes shown in **Figure 1b** due to the inductive effect caused by the adjacent fluorine substituents. On the basis of results of control experiments presented in Supporting Information, the mentioned literatures and the cyclic voltammetry studies (*vide infra*), we concluded that the strong EPR signal appears due to the formation of DMPO•Ph species in Figure 1a. Thus, these results indicate toward the generation of aryl radicals and current enhance the rate of formation of aryl radical.

Table 2 Substrate scope[a]



[a] Reaction conditions: **1** (0.5 mmol), **2** (2.0 mmol, 4.0 equiv.), Cs_2CO_3 (1.0 mmol, 2.0 equiv), MeOH (5 mL), platinum mesh electrodes (1 cm × 1 cm), constant current 13 mA, 65 °C, 3 h, undivided cell, sealed tube. [b] Using reticulated vitreous carbon (RVC) electrodes. [c] From **1j'**.

To further clarify the reduction process of iodides, we designed cyclic voltammetry (CV) measurements. Initially, when we mixed phenyl iodide **1a** with $LiClO_4$ solution, a single reduction peak was appeared which is shown in **Figure 2a**. Noteworthy, after the adding of B_2pin_2 and base Cs_2CO_3 in the model reaction, the single reduction peak appeared with a sharp band. While this peak was completely disappeared in the absence of phenyl iodide **1a** as shown in **Figure 2b**. Thus, these results indicate towards the single electron reduction process of aryl iodides on the cathode. In addition, we conducted differential pulsed voltammetry (DPV) experiments to further indicate toward the single electron reduction of aryl iodide shown in Supporting Information.

According to our mechanistic investigations and recent relevant literatures,[63-64] a plausible mechanism for this electrochemical borylation of aryl iodides is proposed (Scheme 2). Initially, at the cathode, aryl iodide **1** undergoes reduction to afford the corresponding radical anion **C**, which is further transformed into the aryl radical **D** via carbon−halogen bond cleavage. Further, aryl radical **D** interacts with B_2pin_2 in the presence of a base (RO^-) to generate the desired product **3** along with the formation of **G** through intermediate **E** and **F**. Meanwhile, the reaction becomes redox neutral due to the anodic oxidation of the solvent to give oxides which balance the overall transformation. Consequently, intermediate **G** quenched by solvent, oxides or other aryl iodides via SET to afford **E**. However, the possibility of the formation of desired product **3** via the generation of boron-centered radical **I** cannot be ruled out at this stage.

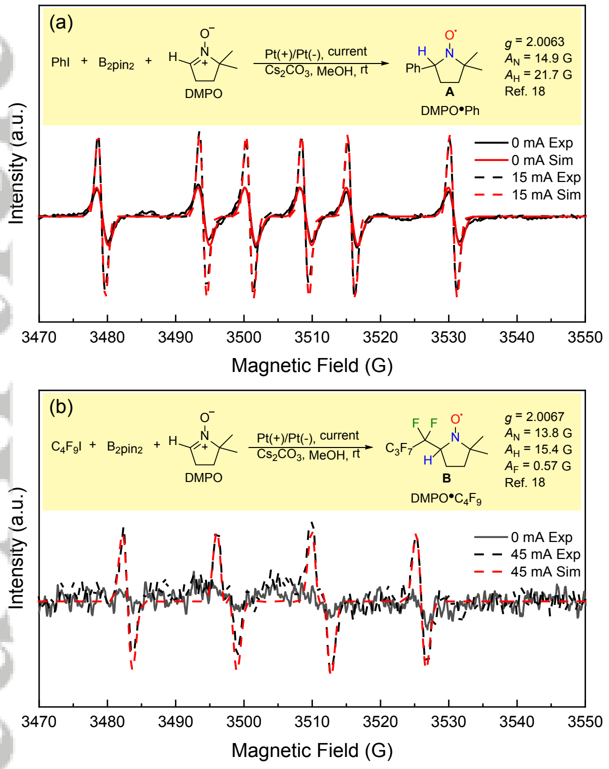
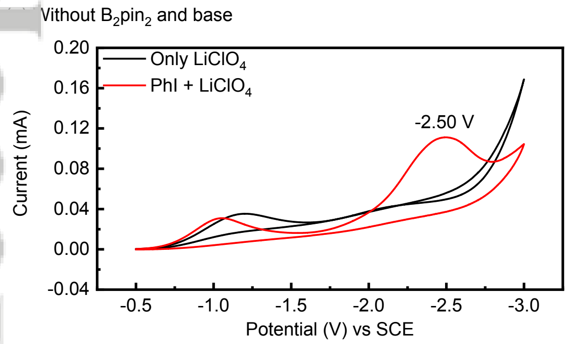


Figure 1 EPR experiments. Reaction conditions: iodides (0.3 mmol), B_2Pin_2 (1.2 mmol, 4.0 equiv.), Cs_2CO_3 (0.6 mmol, 2.0 equiv), DMPO (0.3 mmol, 30 μL), MeOH (3 mL), platinum mesh electrodes (1 cm × 1 cm), stirred at room temperature with given current and time.



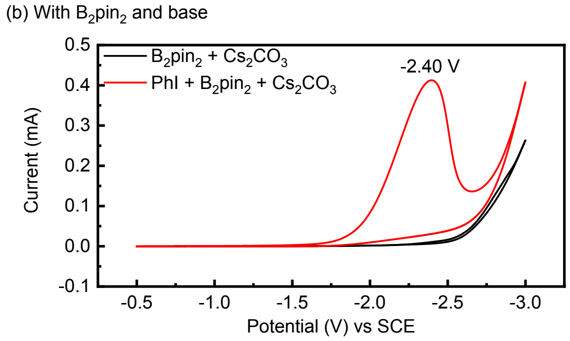
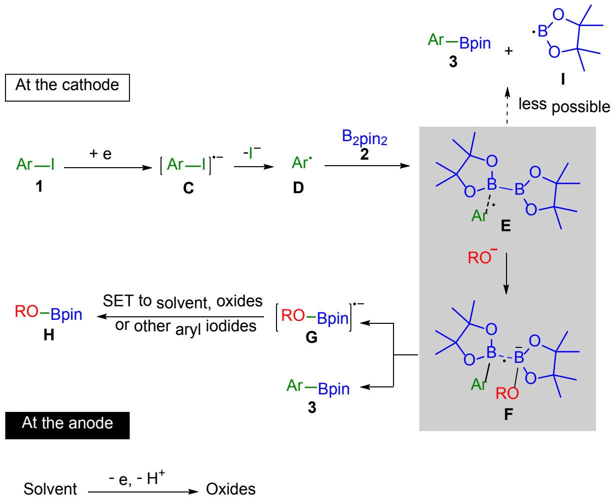


Figure 2 Cyclic voltammetry (CV) experiments. Reaction conditions: **1a** (3 mmol), $LiClO_4$ (3 mmol), B_2pin_2 (6 mmol), Cs_2CO_3 (3 mmol), MeOH (30 mL), 20 °C. L-type glassy carbon as working electrode, Pt wire as counter electrode and saturated calomel electrode (SCE) as reference. Scan rate: 0.02 V/s.

Scheme 2 Proposed mechanism



Conclusions

In summary, we have developed a sustainable and practical electrochemical borylation of aryl iodides, providing a very useful approach to arylboronic esters. EPR, CV and PVD experiments verified the formation of aryl radicals in this electrochemical borylation reaction, which supports a radical borylation mechanism. This electrochemical borylation reaction is complementary to other borylation methods and might inspire further investigations in the radical borylation strategy.

Experimental

An undivided cell was equipped with two platinum mesh electrodes and connected to a DC regulated power supply. Aryl iodide **1** (0.5 mmol), B_2pin_2 (2 mmol, 508 mg, 4 equiv), Cs_2CO_3 (1.0 mmol, 326 mg, 2 equiv) and 5 mL of anhydrous MeOH was added to the cell. The mixture was electrolyzed using constant current conditions (13 mA) at 65 °C under magnetic stirring. After almost 3 hours, the TLC analysis indicated that the electrolysis was complete (witnessed by the disappearance of the aryl iodide). Upon cooling to room temperature, the reaction mixture was transferred to a 100 mL flask by methanol, and then a little silica gel was added into it. After removal of the solvent *in vacuo*, the residue was poured onto a silica gel column and purified by column chromatography to give the desired product **3**.

Supporting Information

The supporting information for this article is available on the WWW under https://doi.org/10.1002/cjoc.2018xxxxx.

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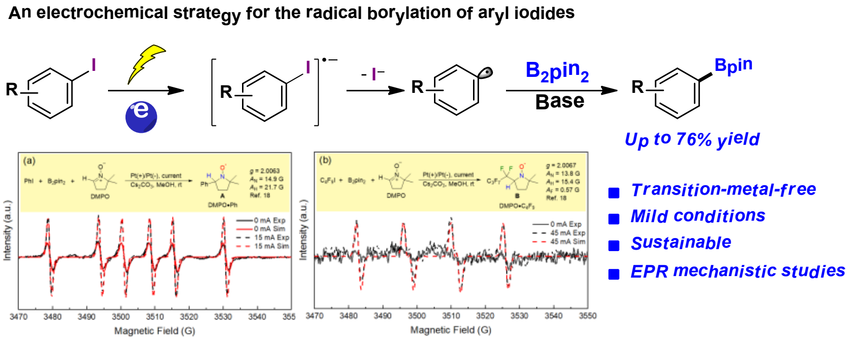
Electrochemical Radical Borylation of Aryl Iodides

Junting Hong, Qianyi Liu, Feng Li, Guangcan Bai, Guoquan Liu, Man Li, Onkar S. Nayal and Fanyang Mo*



The first electrochemical strategy for the radical borylation of aryl iodides is reported in this paper. The significant promoting effect of current in the aryl radical generation revealed by EPR studies.