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Introduction

Organoboron derivatives are indispensable multifunctional building blocks that have been widely applied in organic synthesis, drug discovery and materials science,¹⁻³ owing to their broad availability in fine chemistry, high stability in air, and efficient conversion into various functional groups (Fig. 1a).⁴⁻⁶ In particular, the widely employed Suzuki-Miyaura cross-coupling reaction can effectively utilise the $C(sp^3)$ organoboron species and aryl or alkyl halides for the construction of new C-C bonds.⁷ In the past decades, transition-metal-catalysed alkene hydroboration, which involves the addition of a B-H bond across the π -system of an unsaturated double bond,⁸ has been extensively researched in synthetic chemistry. After the emergence of Wilkinson's catalyst, (Ph₃P)₃RhCl,⁹ a variety of transition-metal catalysts containing precious metals¹⁰⁻¹² such as rhodium, iridium and ruthenium and Earth-abundant metals13-18 such as iron, cobalt and nickel have been developed to effectively catalyse the hydroboration of terminal

Selective electrocatalytic hydroboration of aryl alkenes†

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Organoboron compounds are powerful precursors of value-added organic compounds in synthetic chemistry, and transition metal-catalysed borylation has always been dominant. To avoid toxic reagents and costs associated with metal catalysts, simpler, more economical and effective approaches for delivering organoborons are highly desirable. Here, without the use of any metal catalysts, a CH₃CN-involved electrochemical borylation reaction is reported with alkenes and HBpin as substrates. The site-selectivity is realised to achieve mono- or di-functional borylation of an unsaturated bond by regulating the proportion of HBpin. In addition, the success of gram-scale experiments and versatile conversions confirms the potential applications of this strategy in industrial synthesis. The vital auxiliary role of *N*,*N*-diisopropyl-ethylamine (DIEA) in the process of acetonitrile electrolysis is disclosed in the mechanism study. The proposed new strategy provides a generic platform for the discovery of additional challenging electrochemical systems for hydrogenation reactions.

alkenes and pinacolborane (HBpin) to produce the alkylboronate derivatives, which exhibit high chemoselectivity, regioselectivity, and stereoselectivity in some cases.

Despite the significant advances of transition-metal-catalysed hydroboration reactions to access the corresponding alkylboronate esters, the necessity of metal catalysts with ligands severely limits their application in industrial synthesis as the generation of hazardous waste in these transformations is still inevitable.^{19,20} Particularly in large-scale synthesis, the preparation, storage, removal or recovery of metal catalysts imposes significant limitations.²¹ Alternatively, the evolution from transition-metal to metal-free catalysts for directed borylation is highly desirable.²² In recent years, power generation from various renewable energy sources, such as wind and solar, has surged drastically.^{23,24} This shift in green source of energy accounted for almost two-thirds of net new power capacity²⁵ and drives a transition from thermochemical to electrochemical processes.²⁶ Correspondingly, organic electrochemical synthesis research has attracted considerable attention. As a sustainable and eco-friendly synthetic tool,²⁷⁻³⁰ electrochemistry exhibits flexible control in the synthesis of value-added organic compounds by modulating the magnitude of current or voltage. Thereupon, various core skeletons, such as the formation of C-S, C-N, C-C, C-Cl, C-P and other bonds,³¹⁻³⁵ can be constructed successfully through electrochemical synthesis. Although boron chemistry has been acknowledged by two Nobel Prizes, the development of C-B formation by electrochemical synthesis has rarely been reported.^{36,37} Although electrophotocatalytic borylation of aryl

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Fig. 1 Reaction design. (a) Significance of the organoboron derivatives in functional group transformations. (b) Chemical structure of alkylboronate prepared by electrochemical synthesis, fulfilling the requirements of green chemistry. (c) Illustration of the electrochemical synthesis strategy of organoboron esters and its remarkable characteristics.

halides has been realised, research on the selective bonding between carbon and boron atoms through an atom-economical electrosynthesis to produce alkylboronate esters remains lacking (Fig. 1b).

Electrochemical oxidative cross-coupling reactions have been proved to be a powerful strategy for forming chemical bonds,³¹ and are accompanied by the formation of hydrogen (H_2) on the cathode surface. These distinctive features pose an opportunity and challenge to the feasibility of electrochemical hydroboration. The opportunity is the direct generation of active boron radical intermediates by a single electron transfer between HBpin and the electrode surface, and a boron-free radical coupling reaction catalysed by transition-metal catalysts has been proven to be a powerful way to achieve the alkene hydroboration reaction.^{38,39} The challenge is that hydrogen evolution competes with the hydrogenation conversion reaction. Therefore, effective preparation and utilization of hydrogen ions to synthesise the target product while ensuring a high reaction rate on the cathode under electrochemical conditions is challenging.

Here, we implemented an attractive protocol for the selective electrochemical synthesis of alkene hydroboration products (Fig. 1c): (1) *N*,*N*-diisopropylethylamine (DIEA) was found to play a key role in the electrolysis of the solvent CH₃CN to provide sufficient hydrogen ions to participate in the conversion of hydroboration products effectively; (2) gramscale experiments were successfully performed smoothly; and (3) a detailed mechanism was fully determined. The designed strategy not only conforms to the concept of atom-economic chemistry, but also provides a new idea for the development of electrochemical hydrogenation.

Results

Reaction design

Initially, we began the study with the reaction of styrene (1a) and HBpin (2) as the model substrates. Notably, no hydroboration product was observed without an electric current (Table 1, entry 1), which illustrates the indispensability of the electrochemical reaction. Controlled experiments also revealed that a nitrogen atmosphere was essential to this transformation (Table 1, entry 2). By using tetrabutylammonium hexafluorophosphate (ⁿBu₄NBF₄, 20 mol%) as a supporting electrolyte and CH₃CN as a solvent, the reaction was performed under a constant current (15 mA) in an undivided cell under an inert atmosphere, equipped with two Pt plates as an anode and a cathode. We found that the anode surface was covered with a thick layer of an unknown yellow compound, and the target product 4,4',5,5'-tetramethyl-2-(phenylethyl)-1,3,2-dioxaborolane (3a) was obtained in a yield of 35% (calculated by gas chromatography (GC), Table 1, entry 3), accompanied by the generation of by-products, such as the Markovnikov-selective product 4,4',5,5'-tetramethyl-2-(1-phenylethyl)-1,3,2-dioxaborolane (4a), phenylethane (5) and B_2pin_2 (6) (see GC-MS in Fig. S4 in the ESI[†]). In addition, no product was detected if acetone or DMF was used as the solvent (Table 1, entries 4 and

Table 1 Optimisation of the reaction conditions^a

	A 2	3a + 5	$\begin{array}{c} \text{Bpin} \\ \text{Here} \\$
Entry	Variation from the reaction conditions	Yield of $3a^{b}(\%)$	3a/4a/5/6 ^c
1	No electric current	N.D.	_
2	Air instead of N ₂	N.D.	
3	CH ₃ CN	35	83:1:5:11
4	Acetone	N.D.	_
5	DMF	N.D.	_
6	None	56	62:9:17:12
7	0 °C instead of rt	53	61:10:17:12
8	40 °C instead of rt	42	60:8:22:10
9	C(+) Pt(-) instead of $Pt(+) Pt(-)$	31	63:0:30:7
10	Pt(+) Ni(-) instead of $Pt(+) Pt(-) $	51	57:9:24:10
11	DIEA (0.8 eq.)	72	82:5:11:2

^{*a*} Reaction conditions: **1a** (1.0 mmol), **2** (1.1 mmol), ^{*n*}Bu₄NBF₄ (20 mol%), Pt(+)|Pt(-), constant current (*I*) = 15 mA, CH₃CN: THF = 4:1 (v/v), the total volume of the solvent was 10 mL, N₂, rt, 3 h. ^{*b*} The yields of products were determined using GC analysis using naphthalene as an internal standard. ^{*c*} Selectivity was determined using GC analysis. N.D. = not detected.

5), which demonstrates the necessity of CH_3CN in this electrochemical hydroboration conversion. If a mixed system $CH_3CN/$ THF (v:v = 4:1) was selected as the reaction solvent, we found that a 1.0 equivalent of precursor **1a** led to full conversion in the presence of 1.1 equivalents of 2 at room temperature for 3 h and the yield of product **3a** was increased to 56% (Table 1, entry 6), with a **3a/4a/5/6** ratio of 62:9:17:12. Furthermore, an appropriate ratio of CH_3CN to THF in the mixed solvent was required. Other mixed solvent systems, such as $CH_3CN/$ Et_2O and $CH_3CN/1,4$ -dioxane, were unsuitable for this reaction (Table S1 in the ESI†).

Subsequently, to further optimise the yield and selectivity of the target product, several factors affecting the reaction results were investigated, including temperature, reaction time, amount of current and electrodes. The selected results are listed in Table 1 and Tables S2 and 3 in the ESI.† If the reaction temperature was decreased to 0 °C or increased to 40 °C and 60 °C, 3a was obtained in 53%, 42% and 38% vields, respectively (Table 1, entries 7 and 8, Table S2 in the ESI[†]). Moreover, the reaction efficiency was susceptible to the reaction time and the amount of current, and a detailed condition screening is depicted in Table S3 in the ESI.† In addition, the electrode material had a significant effect on the reaction results; replacing the anode platinum sheet with a graphite rod led to a decreased yield of 3a, and if a nickel sheet was used as the cathode, a slight decrease in the target product was detected (Table 1, entries 9 and 10).

We observed that the surface of the anode had a thin layer of yellow substance after the electrochemical reaction, which may have resulted due to the accumulation of compounds on the electrode surface after the loss of electrons and protons. According to the literature,⁴⁰ DIEA can act as a sacrificial electron donor to promote the turnover of the catalytic cycle. Therefore, DIEA is thought to participate in this system. Further explorations indicated that the addition of DIEA could promote the formation of product 3a (Table 1, entry 11) and a 0.8 equivalent of DIEA was the optimal choice (Table S4 in the ESI[†]), as increasing or decreasing the dosage of DIEA led to a lower yield of 3a. In addition, no unknown yellow compound was observed on the anode surface. Hence, using "Bu₄NBF₄ (20 mol%) as the supporting electrolyte and CH₃CN: THF (v:v = 4:1) as the mixed solvent, with the addition of 0.8 equivalent of DIEA, and 15 mA constant current at room temperature for 3 h under an inert atmosphere, were considered as the optimal reaction conditions, with a 3a/4a/5/6 ratio of 82:5:11:2. Under these conditions, 3a was obtained in 72% isolated yield.

Substrate scope with the methodology

With the optimal reaction conditions established, we set out to explore the substrate scope by varying the peripheral substitutes (\mathbb{R}^1 and \mathbb{R}^2) of skeleton **1**. As depicted in Scheme 1, various alkylboronate derivatives were synthesised in satisfactory yields. Electron-withdrawing fluorinated substitution patterns (*ortho, meta* or *para*) on the reacting aryl rings of the styrene derivatives (**3b**-**3d**) all gave moderate yields without any dehalogenated byproducts. The *para*-substitutes with the



Scheme 1 Electrochemical hydroboration of different aryl alkenes. Reaction conditions: 1 (1.0 mmol), 2 (1.1 mmol), DIEA (80 mol%), ⁿBu₄NBF₄ (20 mol%), Pt(+)|Pt(-), constant current (*I*) = 15 mA, CH₃CN:THF = 4:1 (v/v), the total volume of the solvent was 10 mL, N₂, rt, 3 h. Isolated yields are shown. ^aThe constant current was increased to 20 mA and the reaction time was prolonged to 4 h. N.D. = no detect.

electron-donating groups (-^tBu, -OMe and -Me) on the benzene ring of styrene were tolerated to deliver the corresponding terminal alkene hydroboration products (3e-3g) in satisfactory yields. In addition, the internal trans-/cisβ-methylstyrene was also compatible with our electrochemical method, and the product 3h was successfully afforded in a 71% yield. Obviously, the steric hindrance and multi-substituted modes of the aryl ring had a strong influence on the hydroboration transformation of the terminal alkenes. To obtain the target product (3i-3n) in higher yields, the constant current was increased from 15 mA to 20 mA and the reaction time was extended from 3 h to 4 h. Similarly, the other internal alkenes possessing a larger steric hindrance were proven to be amenable substrates (30-3q). Interestingly, when 2-vinylnaphthalene was chosen as the substrate, the mono-borylation product $(3\mathbf{r})$ and the di-borylation product $(7\mathbf{r})$ were all detected with the yields of 43% and 22%, respectively. This interesting result will be discussed later. Proton, carbon, boron nuclear magnetic resonance (¹H, ¹³C, ¹¹B NMR) spectroscopic data of all the products are smoothly obtained and shown in the ESI;† it is worth noting that the resonances for carbons attached to the borons are not observed in the carbon spectra due to the quadrupolar moment of ¹¹B nuclei.⁴¹ Unfortunately, some alkyl alkenes, such as phenyl vinyl ether,

could not be transformed to the final product and remained in the reaction solution.

Gram-scale experiments

To further test the potential application of the established electrochemical protocol, a series of gram-scale reactions at 10 mmol was conducted. Initially, styrene was selected as the model substrate (Fig. 2a). To shorten the reaction time to some extent, a detailed current screening was performed (shown in Table S5 in the ESI[†]). Ultimately, if the constant current was increased to 45 mA and the reaction time was extended to 12 h, a high conversion of styrene and a high yield of 3a were realised. Meanwhile, in situ ¹H NMR of the scale-up test was successfully performed (Fig. 3a). The detailed sample collection and processing information are described in the note of Fig. 3. The treated data displayed a linear decrease in



Fig. 2 Gram scale experiments and comparisons of our work with the three metal systems in various aspects. (a) Gram scale experiments under electrolysis. Reaction conditions: 1 (10 mmol), 2 (11 mmol), DIEA (80 mol%), $^{n}Bu_{4}NBF_{4}$ (20 mol%), Pt(+)|Pt(-), constant current (/) = 45 mA, CH_3CN : THF = 4:1 (v/v), the total volume of the solvent was 100 mL, N₂, rt, 12 h. Isolated yields are shown. (b-d) Comparison of catalyst loading, reaction time and reaction steps of our work with three metal catalysts. These conclusions are based on 1 mmol styrene, and the synthetic time and steps of ligands are included. (e) Comparison of material costs of our work with the three metal catalyst systems. Cost accounting was based on the gram yield of 3a (6.1 mmol) in our work, and the gram yields of 3a in the metal catalysts were same as the yields when 1 mmol styrene was selected as the substrate. All materials were purchased from Alfa Aesar.



Fig. 3 In situ ¹H NMR data of the electrochemical hydroboration of styrene (10 mmol) with HBpin (11 mmol). (a) ¹H NMR spectra were collected every 0.5 h. The test samples were made up of 0.3 mL of original samples and 0.2 mL of CD₃CN. The total volume of the reaction solvent was 100 mL. (b) Decreased trends of styrene and HBpin under electrolysis, determined by the analysis of the in situ ¹H NMR data. Initial peak areas of the CH group at the benzyl site of styrene and the CH₃ group of HBpin were defined as 100%, respectively. (c) An increased trend of product 3a under electrolysis, determined by the analysis of the in situ ¹H NMR data. Final peak area of CH₂ at the benzyl site of **3a** was defined as 100%.

0

10 12

6 Time (h) 8

(%)

Decrease

Styrene

both styrene and HBpin substrates (Fig. 3b) and a linear increase in 3a within 8 h (Fig. 3c), which reveal the high control of the electrochemical borylation reaction. After 8 h, the entire reaction tended to be stable, which guides largescale experiments in the future. Styrene derivatives (terminal alkenes with the electron-withdrawing and electron-donating groups, and internal alkenes, 10 mmol) were added to react with HBpin (11 mmol); satisfactory yields of various organoboron esters were obtained (Fig. 2a). The simple and easy-tooperate characteristics of the electrochemical synthesis are desirable for industrial application.⁴² In this electrochemical hydroboration reaction, the excellent site-selectivity and yields obtained in the gram scale highlight the high potential for scale-up.

In addition, to further evaluate the gram-scale application of this electrochemical hydroboration reaction, three transition-metal catalysts^{12,14,18} (including precious and Earthabundant metals) for the hydroboration of alkenes were selected and compared with the electrochemical method in various aspects. Styrene was selected as the model substrate. We concluded that our electrochemical method dominated in catalyst loading, reaction time and reaction steps (Fig. 2b-d). The reaction time included the synthesis time of various ligands and the catalytic reaction time of styrene with HBpin, but excluded the post-treatment time to obtain the pure product 3a. In addition, the summary standards of the reaction steps were the same as those of the reaction time. Gramscale experiments catalysed by metal catalysts were not conducted in previous literature and the results shown in Fig. 2e are only magnifications of the original experimental amounts. In addition, material costs only covered the costs of various substrates, and did not include the costs of solvent, reprocessing, human resources and other experimental conditions. The gram-scale material cost of our electrochemical method was slightly higher than that in the Cat. 1 system, but lower than those of the other two catalytic systems. All in all, the electrochemical hydroboration method explored in this paper was simpler, more convenient, and economical in large-scale experiments, which provides a new platform for the application of electrochemical hydroboration in industry.

Mechanism research

(a)

Deuterium-labelling tests. To further elucidate the transformation process of the whole electrochemical system, a series of deuterium-labelling experiments was conducted to confirm the transfer of various groups. As shown in Scheme 2a, if styrene reacted with HBpin in the mixed solvent of $CH_3CN/THF-d_8$, no deuterium product was detected, which

Pt(+) | Pt(-), I = 15 mA



Scheme 2 Deuterium-labelling experiments.

indicated that THF did not participate in the hydroboration reaction directly. ²D NMR data further confirmed that no deuterium atom was added to the target product. However, if CD₃CN/THF was chosen as the solvent (Scheme 2b), a mixture of the mono-deuterated linear alkylborate ester d_1 -3a with the deuterium incorporation at the benzyl position and the protioboronic ester 3a was obtained with a molar ratio of 84:16, which was obtained from the analysis of the ¹H NMR data. The analysis of the ²D NMR data further confirmed the position of the deuterium atom in the product, which indicates that the solvent CD₃CN was involved in the hydroboration conversion reaction. d_1 -Pinacolborane (DBpin)^{43,44} was reacted with styrene under the standard conditions (Scheme 2c), and only a small amount of the mono-deuterium boronic ester d_1 -3a was observed and the molar ratio was 16:84 with 3a determined from the analysis of the ¹H NMR data. In addition, a moderate yield of the mono-protio-boronic ester d_8 -3a was synthesised by employing d_8 -styrene and HBpin as the substrates (Scheme 2d). Accordingly, we speculated that the Bpin group of 3a originated from HBpin, whereas the H species at the benzyl site of 3a originated from both HBpin and the CH₃CN solvent, and the latter was the primary hydrogen donor.

 H_2 detection experiments. Meanwhile, bubbles were observed during the electrochemical hydroboration with styrene and HBpin (ESI Video†). They were determined as H_2 using GC (Fig. S5 in the ESI†). To determine the source of H_2 and mechanism of production, the time dependence of the H_2 production rates (mL min⁻¹) was monitored in real time under different conditions. The H_2 production rates under the standard conditions (Fig. 4a) gradually decreased with time and the amount of H_2 released was approximately zero at 180 min, which matched perfectly with the screened reaction time of 3 h. The H_2 release values after 30 min under substrate-free conditions (absence of styrene and HBpin, Fig. 4b) were substantially higher than those under the standard conditions, which not only illustrates that the hydroboration reaction con-



Fig. 4 Time-dependent H_2 production rates recorded under different control conditions. The conditions shown in the legend are displayed with reference to the standard electrochemical conditions.

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sumes a massive amount of hydrogen ions, but also confirmed that the mixed solvent system can produce large amounts of H_2 during the electrochemical process. Considering the limited hydrogen evolution of 0.8 equivalent of DIEA⁴⁵ and the outcome of the deuterium-labelling experiment, if CD₃CN/THF was chosen as the solvent, we deduced that CH₃CN is essential for hydrogen evolution.

In addition, the overall stable curve depicted in Fig. 4c indicates that CH₃CN could be electrolysed on the surface of the two platinum electrodes to generate H₂, which corresponds to CH₃CN as one of the main sources of hydrogen ions in the deuterium-labelling experiment and the redox behaviour of CH₃CN reported in the previous literature.^{46,47} In particular, the amount of H₂ released shown in Fig. 4b was higher than that shown in Fig. 4e, demonstrating the vital role of DIEA in assisting the electrolysis of CH₃CN. Referring to the literature,⁴⁰ we speculated that DIEA could be a sacrificial electron donor to pull the continuous electrolysis of CH₃CN and complete the entire electrochemical cycle. In addition, the release rates of H₂ shown in Fig. 4e were slightly lower than those shown in Fig. 4c without THF. On the one hand, this result indicated that THF was not the source of hydrogen ions in the electrochemical reaction, corresponding to the outcome of the THF- d_8 experiment. On the other hand, the reduction of H_2 production rate in the presence of THF might be explained by the protonation of THF,48-51 which facilitated the transfer of the hydrogen ions to the target compounds.

Radical capture experiments. Details relating to the origin and transfer of H and Bpin groups were determined through deuterium-labelling and H_2 detection experiments. But in what form did HBpin react and what was the explicit mechanism of this electrochemical borylation reaction? To further explore the reaction mechanism and capture the possible intermediates, the electrochemical hydroboration of styrene and HBpin was performed in the presence of the radical scavenger 2,2',6,6'-tetramethyl-1-piperidinyloxy (TEMPO) or the galvinoxyl free radical, respectively.^{52,53} As shown in Scheme 3, with the increase of TEMPO loading added to the system, the yield of electrochemical product **3a** decreased sharply from 72% (the



Scheme 3 Radical inhibition experiments.

standard conditions) to 8% (1.0 equivalent of TEMPO). Whereas no product was detected when one equivalent of the galvinoxyl radical was added. The above results demonstrated the radical nature of this electrochemical reaction. In addition, two possible intermediates existing in the electrochemical cycle were successfully captured by the radical scavengers and characterised by mass spectrometry. One was the addition compound of the boryl radical and the galvinoxyl free radical, namely alkyl-galvinoxyl **8**, with an m/z of 548.4141. The other was alkyl-TEMPO **9**, formed by the addition of a carbon radical at the benzyl site with TEMPO, with an m/z of 387.3053.

Proposed electrochemical cycle

Based on the above results and literature reports,^{46,47,54} a plausible mechanism for the electrochemical hydroboration of styrene is presented in Scheme 4. In the first step, DIEA is preferentially oxidised to an N-centred radical cation A through a single electron transfer on the anode surface. The lower oxidation peak of DIEA compared to CH₃CN and HBpin validated the presumption (Fig. S111 in the ESI[†]). Then intermediate A extracts electrons from CH₃CN and HBpin and regenerates to DIEA, accompanied by the generation of intermediates B and C. Next, B and C released hydrogen ions to produce the carboncentred radical D and boron-centred radical E. Simultaneously, the partial produced hydrogen ions are protonated by THF and DIEA. Afterwards, radical E is added to styrene, which results in the formation of the carbon-centred radical intermediate F. Then F is further reduced to the boronate alkyl intermediate G on the cathode surface. Finally, G reacts with a hydrogen ion, to produce the target compound 3a. Meanwhile, the remaining hydrogen ions are reduced at the cathode surface and formed H_2 . As for the radical 'CH₂CN (D), the electron paramagnetic



Scheme 4 A possible mechanism of electrochemical hydroboration.

resonance (EPR) signal of the carbon-centred radical (g = 2.0052, $A_{\rm N} = 14.47$ G, $A_{\rm H} = 20.82$ G) trapped by 5,5-dimethyl-1pyrroline *N*-oxide (DMPO) was recorded (Fig. S113 in the ESI†), and the corresponding adduct DMPO–CH₂CN **10** was also successfully detected by mass spectrometry.^{55,56} This confirms the presumption that CH₃CN is involved in the formation of H₂. In the whole electrochemical cycle, the ability of CH₃CN and HBpin to produce hydrogen ions assisted by DIEA and the ability of THF and DIEA to combine hydrogen ions are crucial for the transformation as it provides sufficient hydrogen protons to participate in this conversion.

Although the possible reaction mechanism has been proposed, there are still several points worthy of further discussion, such as the dynamic tracking and detection of free radicals generated in the hydroboration reaction. So far, it is difficult to explore suitable testing means to monitor and analyse the real-time state of free radical production and transformation, because of their own instability, sensitivity to air and humidity, the nature of coupling, and binding to itself or other compounds.^{57–60} The first issue is the stability of the free Bpin radical. In many related literature studies, the free boryl radicals can be stabilized by DMA,^{61,62} DMF or Et₃N.⁶³ In 2019, the Mo group performed density functional theory (DFT) calculations on the C-B bond formation steps using the free Bpin radical.⁶⁴ In our system, we can only detect the free Bpin radical qualitatively but not quantitatively, maybe they are stabilized by DIEA or THF with certain alkenes, but it was difficult to find direct experimental evidence. The second issue is the lifetime of the benzyl radical F. Although the migration of persistent radicals between two electrodes is common in the traditional paired electrolysis, few works presented a detailed elaboration on the study of lifetimes of radicals during the migration. Compared to the proposed reaction mechanism of the hydrosilylation reaction in the reported reference,⁶⁵ the hydroboration reaction mechanism shown in our system seems feasible. More detailed work should be conducted to disclose the reaction details, which will help to improve the reaction efficiency and lay the foundation for industrialization.

Reaction expansion

Compared to monoboronate esters, diboronate esters are more attractive, because the chemical transformations of diborongroups to target-oriented synthesis are more diverse.⁶⁶ Surprisingly, if 2-vinylnaphthalene was chosen as the substrate, even in the presence of 1.1 equivalents of HBpin, a partial diboronate ester 7r was detected. Therefore, we speculated whether it was possible to selectively produce a diboronate ester by increasing the proportion of HBpin. 2-vinylnaphthalene was selected as the model substrate to explore the optimal proportions of alkene and HBpin to form the diboronate compound. Further exploration (Table S6 in the ESI[†]) indicated that if 4.4 equivalents of HBpin were added into the system, 2-vinylnaphthalene was completely transformed and the diboronate ester 7r was obtained in 71% isolated yield. A plausible mechanism for the electrochemical hydroboration with 2-vinylnaphthalene as a substrate is presented in

	21 Pt(+) Pt(-) "Bu₄NBF₄ 1 DIEA (80 m + HBpin 2 N ₂ , rt	, I = 20 mA (20 mol%) ol%) IF = 4:1, 4 h	+ C
Entry	Substrate	Yield of 3^{b} (%)	Yield of 7^{b} (%)
1		6	71
2	1r	3	84
3	1s	2	88
4^c	1t	26	41
5 ^{<i>c</i>}		48	43
6 ^{<i>c</i>}	16	59	20
	1a		

^{*a*} Reaction conditions: **1** (1.0 mmol), **2** (4.4 mmol), DIEA (80 mol%), ^{*n*}Bu₄NBF₄ (20 mol%), Pt(+)|Pt(-), constant current (l) = 20 mA, CH₃CN:THF = 4:1 (v/v), the total volume of the solvent is 10 mL, N₂, rt, 4 h. ^{*b*} Isolated yields are shown. ^{*c*} The amount of **2** is increased to 8.8 mmol.

Fig. S131 in the ESI.[†] As depicted in Table 2, if 1-vinylnaphthalene and 2-isopropenylnaphthalene were chosen as the substrates, the corresponding diboronate esters (7s and 7t) were also smoothly isolated in 88% and 84% yields, respectively. To obtain more structural information, compound 7t was determined by X-ray diffraction analysis. The solid-state structure was confirmed by X-ray crystallography (Fig. S6 in the ESI[†]), which indicated that 7t contained a linear and a branched benzylic boron substituent. In addition, we considered whether diborylation could be expanded to substrates containing one single benzene ring when reacting with excess HBpin. As a result, compared to the systems containing naphthalene rings, the yields of diboronate esters with different substituents (3a, 3b and 3g) were slightly inferior. In addition, to use styrene as the model substrate, a detailed proportion screening of styrene and HBpin and *in situ* ¹H NMR monitoring data are provided in Table S7 and Fig. S107 in the ESI,† respectively.

Derivatisation of diboronate esters

Diboronate esters are versatile synthetic intermediates, which could be converted into various functional groups. Here, to further demonstrate the potential synthetic utility of this electrochemical borylation reaction, several transformations of the diboronate ester 7t were examined. As illustrated in Scheme 5, firstly, a gram-scale reaction using 10 mmol 1t was successfully conducted under a constant current (45 mA) for 12 h to produce compound 7t in 85% isolated yield. For the



Scheme 5 Multi-functional transformations of diboronate esters.

two borane groups in **7t**, the one at the benzyl site was easily removed by NaO'Bu, followed by protonation and alkylation to afford compounds **3t** and **11** in 61% and 45% yields, respectively.⁶⁷ In addition, oxidation of the diboronate ester to the diol compound **12** could also be achieved in the presence of the oxidant NaBO₃·4H₂O.⁶⁸ The smooth transformations of the above products provided a basis for more valuable molecules.

Conclusions

In summary, an environmentally friendly electrochemical mono- and di-borylation reaction of alkenes with HBpin was successfully developed. Notably, gram-scale reactions and versatile transformations confirm the synthetic applications of this electrochemical protocol. In consideration of the flexible controllability and eco-friendliness of the electrochemical method exhibited in this paper, further efforts toward the exploration of simpler, milder, more economic, and larger-scale experiments are underway in our laboratory, cooperating with the Sinopec Dalian (Fushun) Research Institute of Petroleum and Petrochemicals. The perfect combination of microfluidic technology and electrochemistry to synthesise high-value fine chemicals has progressed from a concept in the laboratory to practical applications in industry.⁶⁹ Meanwhile, the exploration of milder conditions (such as in air or a non-toxic solvent) or the transformations involved in chirality in an undivided or divided cell is considered in our research efforts.70-73 In addition, the strategy of CH₃CN producing hydrogen ions with the assistance of DIEA under electrolysis has provided a new idea for current electrochemical methods, which will also inspire the development of an alternative mild route for the existing hydrogenation reactions in industry.

Conflicts of interest

There are no conflicts to declare.

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