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Aminoborate-Catalyzed Reductive Counterreactions for Oxidative Electrosynthetic Transformations

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Abstract

Electrooxidative transformations frequently rely on proton reduction as the terminal electron sink. However, this cathodic counterreaction can be slow in organic solvents and can operate at reducing potentials that are incompatible with catalysts and reagents needed for oxidative reactions. We report aminoborate adducts as redox mediators for proton reduction that operate at mild reducing potentials. This reliable cathodic couple ultimately enables successful oxidative organic transformations, including chlorodeborylation, developed herein, and Cu-catalyzed Chan-Lam coupling, reported previously by our group. Pyridinium borate adducts formed during electrooxidative chlorination of aryl trifluoroborates serve as easily reduced complexes (−1.1 V vs. Fc/Fc^{+}) to catalyze proton reduction. Reactions that promote formation of borate adducts result in high yields, operate at low cell potentials, suppress aryl trifluoroborate decomposition, and mitigate electrode passivation. These studies illustrate the utility of Lewis acid-base complexes in cathodic counterreactions and underscore the importance of developing both anodic and cathodic reactions in electrosynthesis.

Graphical Abstract

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Author Contributions

L.P.D. and C.S.S. designed the study and discovered initial conditions. R.E.S. and L.P.D. performed experimental studies and analyzed the data. R.E.S. and C.S.S. wrote the manuscript.

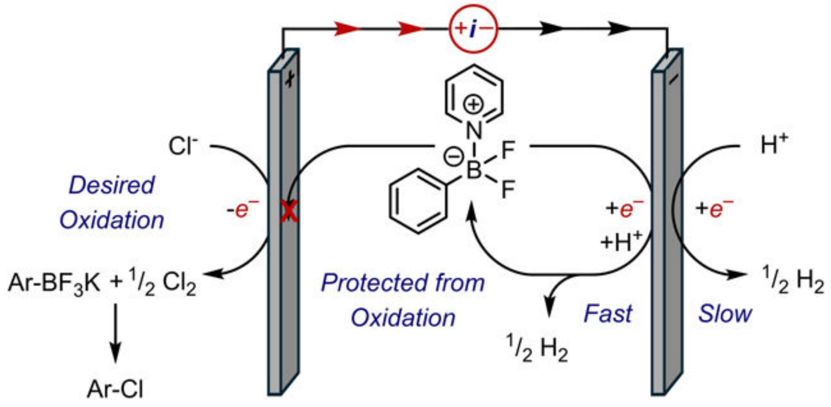
ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Experimental procedures, cell design, characterization of compounds, spectroscopic data, X-ray data, electro-chemical data, and additional experiments are supplied (PDF)

The authors declare no competing financial interest.



Introduction

Electrochemical reactions are most often developed for net-reductive or net-oxidative organic transformations at the respective cathode or anode.[1–4] However, these targeted synthetic reactions represent only one half of a complete electrochemical system. The working electrode at which the reaction of interest occurs is inextricably paired with a counter electrode at which the opposite redox process occurs. As a result, the achievable current for a targeted organic reaction at the working electrode cannot exceed that of current generated from the opposite redox reaction at the counter electrode.

While substantial efforts have been dedicated to designing conditions for reactions at the working electrode, the same level of mechanistic insight and design for reactions at the counter electrode is rare. Reductive electrosynthetic reactions are frequently paired with sacrificial metal anodes or amines that undergo oxidative counter reactions as sacrificial electron donors.[5–7] In contrast, oxidative electrosynthetic reactions are typically coupled to proton reduction as the counter reaction and terminal electron sink.[8] However, direct proton reduction at a heterogeneous electrode can be slow in the absence of high overpotentials, which restricts the overall current. Undesired and irreversible cathodic reactions, like reductive plating of transition metal catalysts designed for oxidative processes, can begin to outcompete proton reduction when electrolysis is performed at synthetic useful currents.[9,10] Consequently, the presence of protons does not guarantee a reliable cathodic reaction for a targeted electrooxidation. This is evidenced by reports from our group[11] and others[12,13] where chemical additives as electron acceptors for reductive half-cell reactions were essential to the success of oxidative synthetic transformations, despite the presence of protic reagents in solution.

This work highlights the often-overlooked issue of designing cathodic counterreactions for electrooxidative synthesis. We report the electrocatalytic function of aminoborate adducts as redox mediators for proton reduction at mild potentials (−1.1 V vs Fc/Fc$^+$). The development of this cathodic chemistry ultimately enables oxidative organic transformations that otherwise suffer from high overpotentials and electrode passivation (Figure 1.). Mechanistic studies by cyclic voltammetry (CV), X-ray crystallography, and

NMR spectroscopy reveal these Lewis acid-base complexes to be the predominant cathodic couple in electrooxidative reactions beyond the case study reported herein.

These unexpected findings arose from our studies on electrooxidative halodeborylation reactions. Aryl halides generated from such reactions serve as important intermediates in nearly all of organic synthesis,[14–17] and can be reliably formed with predetermined regioselectivity based on the position of the boryl group.[18,19] Halodeborylation reactions under electrooxidative control can be conducted with simple halide salts[20–24] in place of stoichiometric transition metal-halide salts or electrophilic halogenation reagents.[25–30] However, such electrochemical reactions remain underdeveloped for halides that are challenging to oxidize, such as chloride or fluoride.[31] As an example, the Cai group recently demonstrated electrooxidative iodination and bromination of aryl boronic acids with the corresponding halide salts, but the methodology could not be extended to chlorodeborylation reactions.[32] Strategies that address fundamental limitations to electrooxidative halogenation with the full complement of halides would enable new methodologies to prepare high-value haloarenes.

Results and Discussion

We first evaluated conditions for electrooxidative chlorination on 4-fluorophenyl trifluoroborate (**1a**) because conversion and yield of this model substrate could be easily monitored by ^{19}F NMR spectroscopy (Table 1). Initial reactions were performed under constant current electrolysis (CCE) in MeCN at a Pt cathode and reticulated vitreous carbon (RVC) anode with tetramethylammonium chloride (TMACl) as the chloride source (entry 1). These initial reactions required high cell potentials (>6 V) to drive the applied current and generated only fluorobenzene as a result of protodeborylation. Additionally, we observed deposits on the cathode that likely cause passivation and force higher operating potentials. We tested reactions with protic co-solvents that could provide protons for reduction to establish a more reliable cathodic couple. However, reactions with added 1,1,1,3,3,3-hexafluoroisopropanol (HFIP) generated product **2a** in low yields of 19% yield, and cathodic passivation persisted (entry 2). We observed the first substantial improvement in both product yield (65%) and operating cell potential (E_{cell}, 2.2 V average) over the initial studies when reactions were conducted with the combination of $LiClO_4$ and pyridine (entry 4). Varying the applied current failed to improve the yield beyond 65% (entry 5), and deposits on the cathode were observed in all reactions where a constant current was maintained. We hypothesized that depolarizing the electrodes may improve the outcome of the reaction by promoting dissolution of deposits or by altering the makeup of reagents within the double layer at the cathode during the rest period.[33,34] Electrolysis with pulsed currents in cycles of 60 s on and 30 s off operated at the lowest cell potentials and generated products in near quantitative yields (entry 6). Moreover, the cathode remained pristine following electrolysis. Under these conditions, MeOH can also be utilized as the protic co-solvent with only a minor reduction in yield (entry 7). Finally, control experiments that exclude any component of the standard reaction resulted in low yields and high operating potentials (entries 8–10).

We were surprised that the successful development of this electrooxidative reaction relied almost exclusively on improving the cathodic chemistry. This underscores the importance of establishing both anodic and cathodic reactions in undivided electrosynthetic reactions. As such, we investigated the roles of additives on both half-cell reactions by cyclic voltammetry (CV). Illustrated in Figure 2a, CVs of the standard reaction mixture (black trace) at oxidizing potentials reveal an irreversible oxidation with an onset (E_{onset}) of 0.9 V vs Fc/Fc$^+$. Referenced electrolysis experiments during synthetic reactions reveal that the anode operates at 1.4 V (dashed vertical line). Independent CVs of the individual reactants reveal that both Cl- and organoborate **1a** can undergo oxidation at this potential, with respective E_{onset} values of 0.9 V (blue trace) and 1.3 V (gray trace). These CVs suggest that competitive oxidation of the arylborate would be possible at the operating potentials of the anode during the electrolysis. However, we discovered that addition of pyridine to **1a** completely suppressed any oxidative processes (red trace). This key additive likely serves to protect the substrate from oxidative degradation (*vide infra*).[35]

CVs of the standard reaction mixture at reducing potentials (Figure 2b, black trace) reveal a cathodic current with an E_{onset} of just −1.0 V vs Fc/Fc$^+$. This redox event is consistent with the operating potential of the cathode during bulk reactions (−1.2 V vs Fc/Fc$^+$, vertical dashed line). However, none of the individual reaction components undergo redox at this mild potential (gray and blue traces). CVs of protic co-solvent and substrate alone require potentials of −1.8 V before similar cathodic currents are achieved to those of the standard reaction mixture at −1.2 V. The cathodic response measured in standard reactions was only achieved from a combination of **1a** and pyridine in a supporting electrolyte of Li$^+$ (red trace).

We sought to characterize the species generated from the combination of **1a**, pyridine, and $LiClO_4$ because of the dramatic effect it had on the redox reactions at both electrodes and, ultimately, on the success of the oxidative transformation. Analysis of the combination of reagents by ^{19}F NMR spectroscopy revealed two distinct fluorine resonances with a 1:2 integral ratio instead of the expected 1:3 ratio that would result from the Ar-F and Ar-BF_3 of **1a** (see the SI, Figure S10). X-ray diffraction of single crystals grown of a *para*-phenyl analog revealed that trifluoroborate **1b** was converted into the Lewis acid-base adduct **3b** in the presence of pyridine and Li$^+$ salts (Figure 3a). The solid-state structure of **3b** is consistent with the solution state structures of **3a** determined by ^1H, ^{19}F, and ^{11}B NMR spectroscopy. Formation of the aryl difluoro(pyridinium)borate is likely promoted by Li-mediated abstraction of fluoride from the trifluoroborate, followed by trapping of the Lewis acidic $ArBF_2$ by pyridine.

CV scans of pyridinium borate **3c** reveal the same irreversible reductive event observed from CV analyses of the standard reaction mixture (Figure 3b, red trace). While these data implicate **3c** as a key component of the cathodic reaction, the arylborate cannot be irreversibly consumed at the cathode as the terminal electron sink because it is also the substrate for oxidative reactions that were shown to generate products in near-quantitative yields. This quandary suggested that the pyridinium borate is not destroyed upon reduction as the irreversible CV would suggest, but rather that it serves as a redox mediator for reduction of the terminal electron acceptor. Specifically, we detected solvated H_2 by ^1H-

NMR spectroscopy in reaction mixtures following electrolysis (see the SI, Figure S11). These results suggest that reduced **3c** mediates proton reduction to H_2 at mild potentials in place of heterogeneous proton reduction at more negative potentials where electrode passivation can occur.

Although the precise mechanism of the hydrogen evolution reaction (HER) remains unclear, we propose that reduction of **3c** generates an unstable intermediate that fragments to release fluoride and a boryl radical anion **4c**, as indicated by the irreversible CV of **3c**.[36–38] Boryl radical anions are known to mediate H-atom abstraction,[39,40] which can occur from acetonitrile solvent. This hypothesis is supported by H/D exchange studies of MeCN under the reaction conditions (see the SI, Figure S12). Finally, the hydridic borohydride **5c** can react with protic reagents like HFIP to generate H_2 and regenerate **3c** upon recapture by pyridine. This final step is supported by CVs of **3c** that reveal increased cathodic currents with added HFIP (Figure 3b, blue traces) and is indicative of the electrocatalytic process illustrated in Figure 3c. This reductive couple enables the anodic half-cell reaction, which we propose constitutes oxidation of Cl^- followed by electrophilic aromatic substitution at the ipso carbon of the aryl borate complex **3c**.[29,32]

We similarly observed improved yields, lower cell potentials, and mitigated passivation for electrooxidative Chan-Lam coupling reactions under conditions that formed aminoborate adducts. (Figure 4).[41] CVs of solutions containing the boronic acid substrate and an amine base (Figure 4, red trace) result in a positive shift of the peak cathodic current by 450 mV relative to the boronic acid alone (black trace). NMR spectroscopic studies implicate the formation of an ammonium-borate adduct that is analogous to those generated during halodeborylation (see the SI, Figure S13). Additionally, the peak cathodic current of the ammonium-borate complex is nearly double that of any other reducible species present under the reaction conditions, despite the milder reduction potential. These studies suggest that ammonium-borate adducts could potentially serve as general cathodic chemistries for electrooxidative transformations involving boron-based reagents.

With the successful development of the cathodic reaction, electrooxidative chlorodeborylation reactions can be performed for a variety of aryl, heteroaryl, and vinyl trifluoroborate salts (Chart 1). Reactions of electron rich aryl substrates generated chloroarenes in excellent yields (**2c-2f, 2h**). Reactions with electron-poor arenes that are traditionally unreactive in electrophilic aromatic substitution reactions were isolated in good to moderate yields (**2b, 2i-2o**). Substrates that are exceedingly electron rich (**2g**) or exceedingly electron deficient (**2p**) undergo competitive oxidation and reduction, respectively, and are incompatible under the developed conditions. Finally, ortho-substituted trifluoroborates (**2d, 2h, 2k, 2t, 2u**) as well as vinyl (**2q**) and heteroaryl substrates (**2r-2u**) undergo chlorination in good yields. Milder conditions that employ lithium chloride instead of TMACl and that operate at room temperature instead of 80 °C could also be performed with a slight reduction in yield (see SI Chart S1).

In summary, we report an electrochemical chlorodeborylation methodology that circumvents common oxidative electrosynthetic limitations. Counterintuitively, the success of this electrooxidative transformation relied on the study and development of the reductive counterreaction. The formation of a pyridinium-borate adduct of the substrate serves to catalyze proton reduction at the cathode, allowing for higher currents at lower overpotentials. The adduct also suppresses aryl trifluoroborate oxidation at the anode leading to higher yields. Finally, these mechanistic studies illustrate the utility of Lewis acid-base complexes as cathodic mediators and underscore the importance of developing both anodic and cathodic reactions in electrosynthesis.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Data Availability Statement

The data underlying this study are available in the published article and its Supporting Information.

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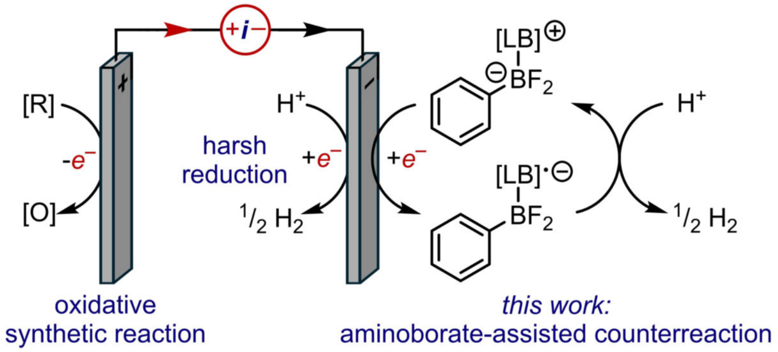


Figure 1.

The cathodic counter reaction to synthetically useful oxidative transformations can be improved upon the addition of amino-borate complexes.

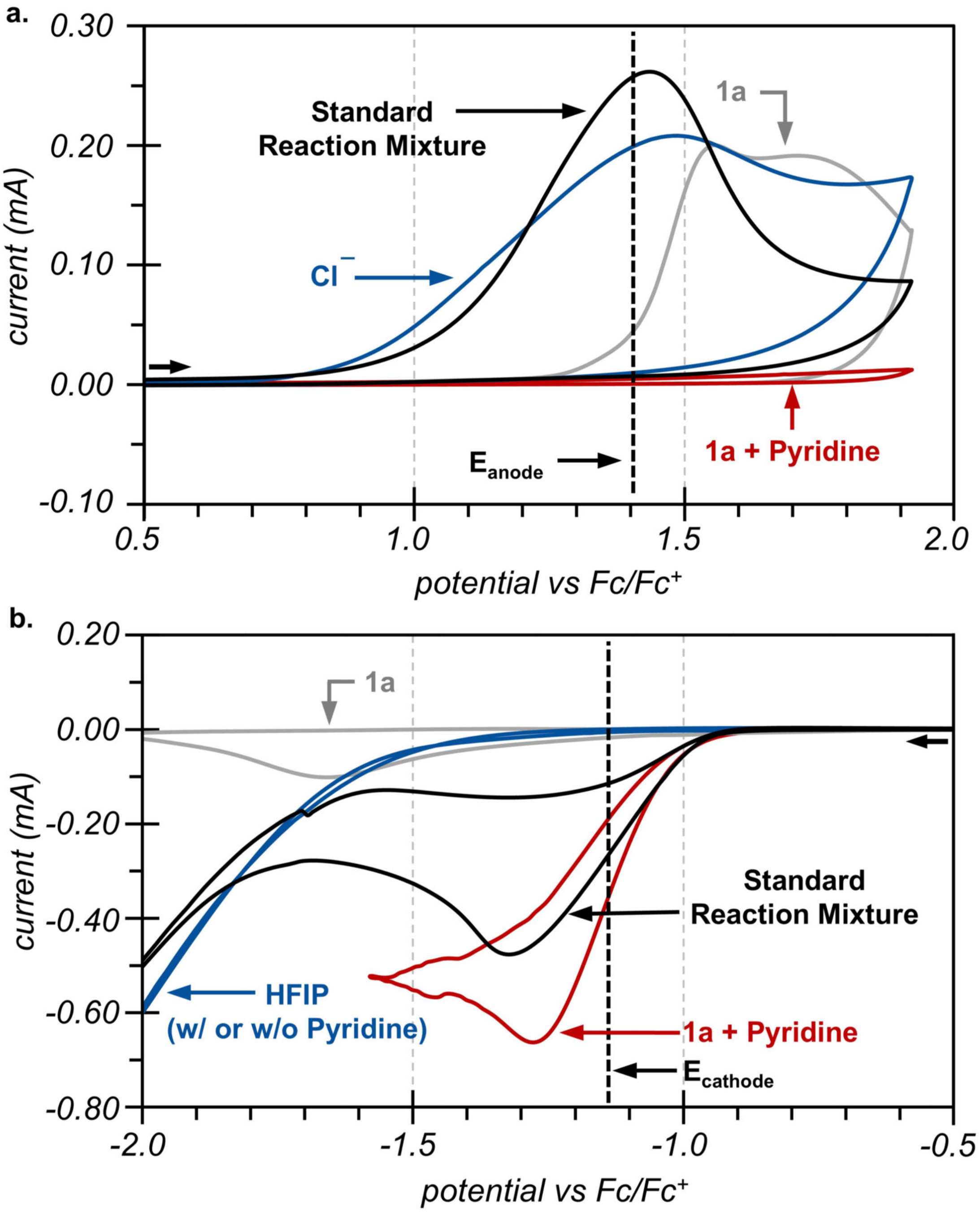


Figure 2.

(a) CVs of standard reaction conditions (black trace), TMACl (blue trace), **1a** (grey trace), **1a** and pyridine but without TMACl (red trace). (b) CVs of standard reaction conditions (black trace), HFIP and pyridine (blue trace), **1a** (grey trace), **1a** and pyridine (red trace). CVs are run in acetonitrile with $LiClO_4$ as supporting electrolyte and are reported in IUPAC convention. Standard reaction conditions comprise analytes **1a**, pyridine, TMACl, and HFIP.

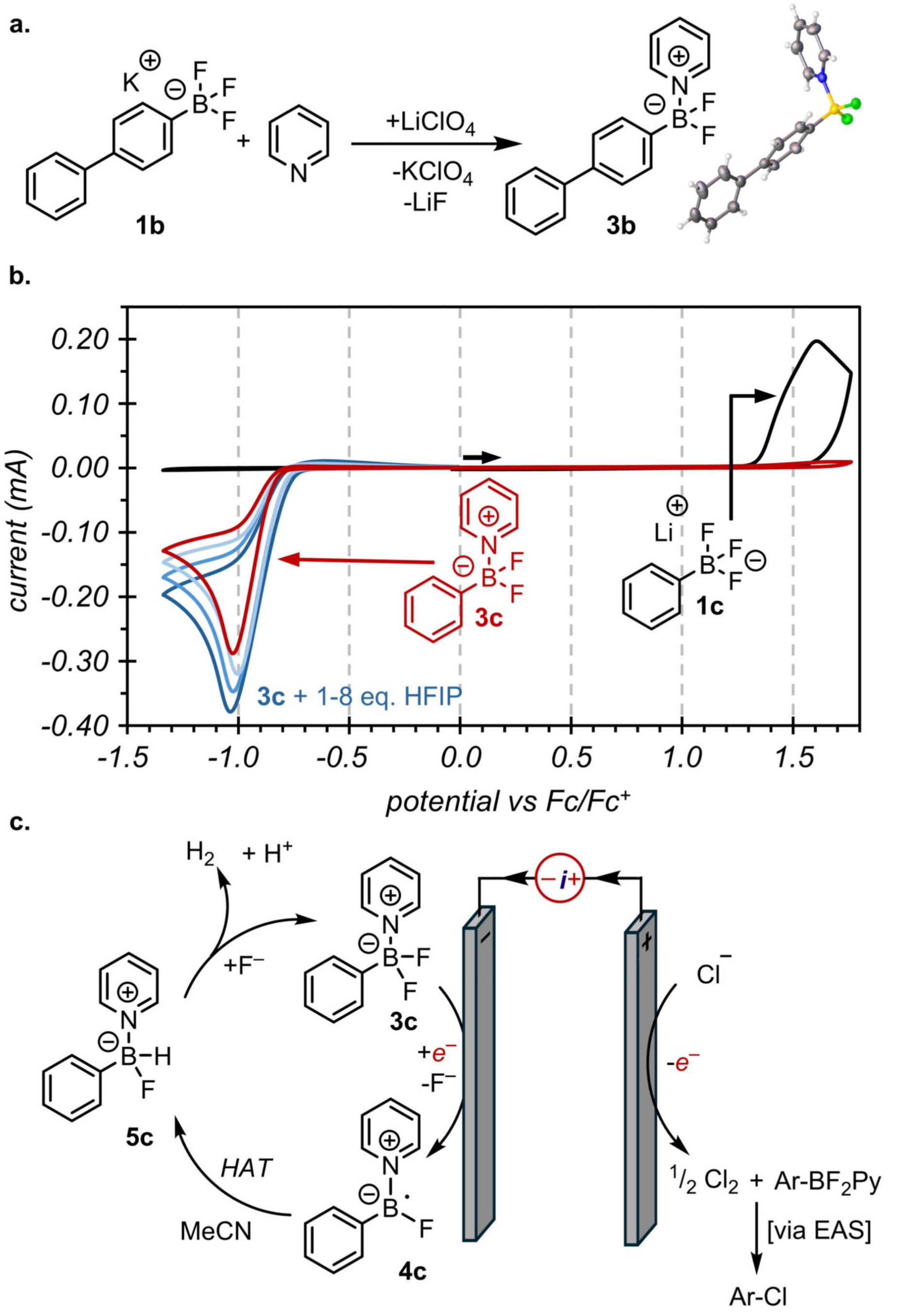


Figure 3.

(a) Reaction scheme for the formation of the aryl-BF$_2$-pyridine Lewis acid-base adduct with X-ray crystal structure of isolated complex. (b) CVs of **1c** (black trace), **1c** and pyridine (red trace), **1c** and pyridine and HFIP (increasing concentrations)(blue traces). CVs are run in acetonitrile with LiClO$_4$ and TBAClO$_4$ as supporting electrolyte and are reported in IUPAC convention. (c) Proposed mechanism of complex reduction and HER.

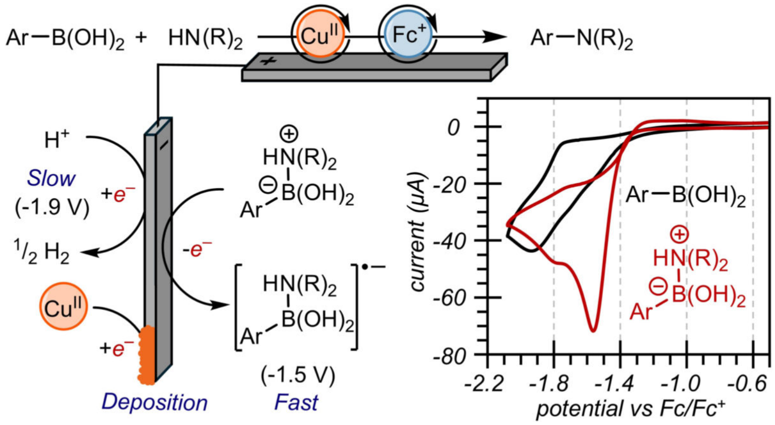


Figure 4.

Similar reduction improvement observed upon the complexation of aryl boronic acid and alkyl amines. CV’s of phenylboronic acid (black trace), phenylboronic acid, aniline, and triethylamine (red trace).

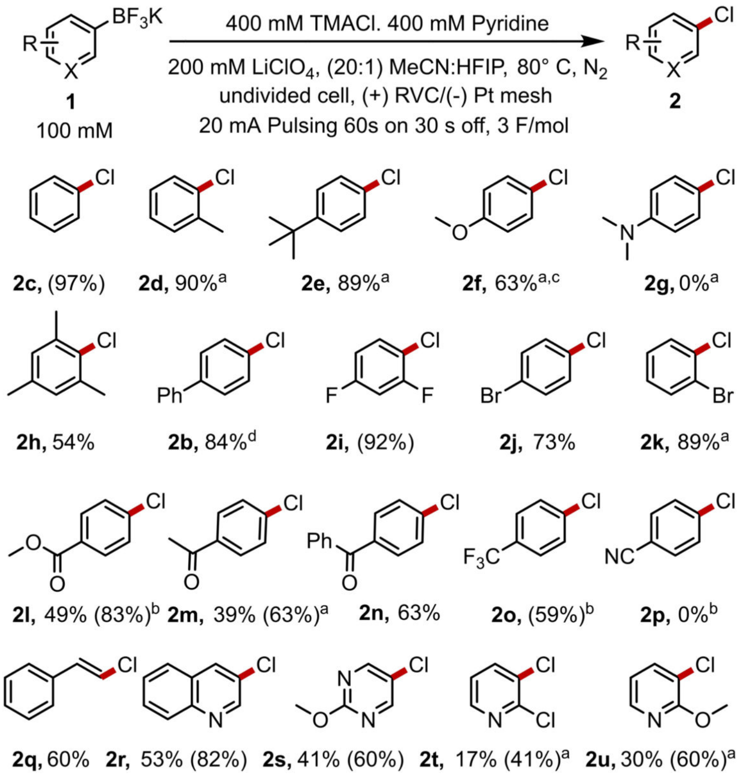
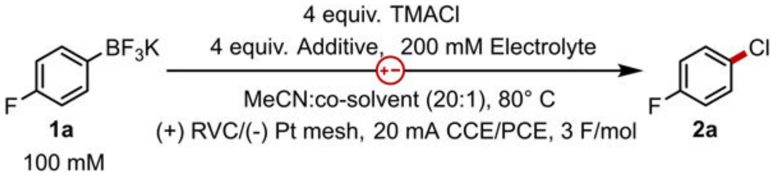


Chart 1.

Isolated yields of products generated via electrochemical chloro-deborylation on a 0.30 mmol scale (GC yields are in parentheses for low-boiling products that cannot be readily isolated). (a) (20:1) MeCN:TFE, 2.5 V PPE. (b) (20:1:1) MeCN:TFE:AcOH, 100 mM pyridine. (c) 1.5 F/mol instead of 3.0 F/mol. (d) 1.0 mmol scale.

Table 1.

Reactions conducted on a 0.30 mmol scale. Yields were determined by ^{19}F-NMR analysis using 1,3,5-trifluoro-benzene as the internal standard.



Entry	Electrolyte	Co-Solv.	Additive	Electrolysis Conditions	Yield 2a(%)	Measured E_{cell}
1	KPF_6	–	–	CCE	0	6.4 V
2	KPF_6	HFIP	–	CCE	19	4.0 V
3	KPF_6	HFIP	Pyridine	CCE	37	3.4 V
4	$LiClO_4$	HFIP	Pyridine	CCE	65	2.2 V
5	$LiClO_4$	HFIP	Pyridine	CCE (10 mA)	6	2.2 V
6	**$LiClO_4$**	**HFIP**	**Pyridine**	**60s on 30s off**	**95**	**1.8 V**
7	$LiClO_4$	MeOH	Pyridine	60s on 30s off	80	2.0 V
8	$LiClO_4$	HFIP	Pyridine	–	0	–
9	$LiClO_4$	HFIP	–	60s on 30s off	11	4.0 V
10	$LiClO_4$	–	Pyridine	60s on 30s off	5	3.7 V