Article

A Versatile Electrochemical Batch Reactor for Synthetic Organic and Inorganic Transformations and Analytical Electrochemistry

Hamish R. Stephen, Christiane Schotten, Thomas P. Nicholls, Madeleine Woodward, Richard A. Bourne, Nikil Kapur,* and Charlotte E. Willans*

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ABSTRACT: A standardized and versatile electrochemical batch reactor that has wide applicability in both organic and inorganic synthesis and analytical electrochemistry has been developed. A variety of synthetic electrochemical transformations have been performed to showcase the versatility and demonstrate the reactor, including the synthesis of five Cu(I)−NHC complexes, two Au(I)−NHC complexes, and one Fe(II)−NHC complex as well as an Fe(III)−salen complex. The reactor is based on a commercially available vial with an adapted lid, making it inexpensive and highly flexible. It features a fixed interelectrode distance, which is crucial for reproducibility, along with the ability to accommodate a variety of interchangeable electrode materials. The reactor has also been used in conjunction with a parallel plate, allowing rapid screening and optimization of an organic electrochemical transformation. Cyclic voltammetry has been performed within the reactor on a range of imidazolium salt analytes with the use of an external potentiostat. The ability to use this reactor for both analytical and synthetic organic and inorganic chemistry is enabled by a flexible and characterizable design.

KEYWORDS: electrochemistry, electrosynthesis, reactor design, cyclic voltammetry

INTRODUCTION

During the past decade, synthetic electrochemistry has been receiving renewed interest as an enabling technology that typically provides a mild, atom-efficient, and sustainable method for performing chemical transformations.[1−8] This novel and well-understood redox mode of activation,[1] coupled with its broad applicability, has resulted in the development of a raft of new methodologies, including the synthesis of inorganic and organometallic complexes and many other organic transformations.[9−13] While many of the benefits of electrosynthesis have been realized in these new methodologies, there remains a bottleneck to widespread adoption.[14] One reason for this impediment is the lack of simple, characterizable, and reproducible experimental setups.[15−19]

Previously, our group and others have used three-neck flasks to perform electrochemical transformations.[9−13] Electrode leads were passed through the side arms of the flask, allowing electrodes to be lowered into the solution. While this approach has led to the development of efficient methodology, there remain problems with reproducibility across experiments and particularly for the transfer of experimental procedures to other laboratories.[20] One reason for the lack of reproducibility is the inability to keep the interelectrode gap, electrode angles, and depth of the electrode in solution constant, resulting in variable resistance and current density across experiments, both of which have a large effect on the reaction outcome.[21]

More recently, several commercial reactors have been developed that provide a constant interelectrode distance, electrode angle, and depth, with many being used in laboratories throughout the world.[22] A common issue with these reactors is the inability to perform transformations under inert atmospheres, which is necessary for the synthesis of many organometallic and inorganic complexes as well as several organic transformations or analytical techniques.[23]

Currently, the electrosynthesis community has limited access to standardized, flexible, and affordable electrochemical batch reactors. Herein we report the design, development, and characterization of a simple yet versatile electrochemical batch reactor (bottle reactor) that has been used for the synthesis of sensitive organometallic and inorganic complexes as well as an organic electrochemical transformation. Cyclic voltammetry has also been performed in the reactor, showcasing the versatility of the setup.

RESULTS AND DISCUSSION

Reactor Design. An electrochemical batch reactor based upon commercially available vials with an adapted lid was designed (Figure 1); 30 mL vials were used in this study, but the lid is compatible with any vial that has a GL-32 thread. The lid consists of a cap with a hole cut into it and a PTFE insert that fits into this hole. The PTFE insert has an extrusion that overlaps with the lip of the vial such that when the cap is screwed into place a tight seal is created between the vial and the PTFE. The insert is machinable and exhibits four holes for

Figure 1. Images of the bottle reactor. Left: Fully assembled bottle reactor. Top right: PTFE headpiece with O-ring seal as it sits within the bottle cap. Bottom right: PTFE headpiece showing stainless steel electrode contacts.

a variety of purposes. Two of these form ports that have a standardized $1/4$-28 thread, which allows various standard fittings to be screwed into the lid. This enables the reactor to be attached to a Schlenk line through one of the ports *via* a short piece of tubing with a Luer fitting on the other end, while a blank fitting in the other port may be removed to enable the addition of reagents and solvents or the removal of aliquots for analytical purposes or the insertion of an analytical probe for *in operando* studies. In addition, this may also be fitted with a septum, and solutions can be transferred to and from the reactor using a cannula. Alternatively, one of the ports can be used to insert a silver wire to act as a pseudoreference electrode and also allows the possibility for *in situ* analysis.

Stainless steel electrode contacts were fashioned in a conical shape that is complementary to the shape of the remaining two holes in the PTFE insert. When the insert is screwed into place, the electrode contacts are pulled up and into the PTFE, creating a good seal. The top of the steel contacts are joined to cables that can be connected to a power supply unit. Grooves were made in the bottom of the PTFE insert to allow the electrodes to contact the stainless-steel contacts (Figure 1). A small grub screw in the wall of each groove can be tightened to hold the electrodes in place, thereby allowing any electrode with a thickness of up to 4 mm to be used, while a constant interelectrode distance of 5 mm is maintained.

The ability to maintain a reproducible and constant interelectrode gap while ensuring high flexibility of electrode materials was of great importance during the design process. The distance between the electrodes remains constant to increase the reproducibility of reactions, and a broad range of electrode materials with an assortment of shapes, thicknesses, and lengths can be accommodated. Furthermore, the electrodes can be connected to a range of commercially available power supply units using simple, readily available connectors

to permit use of the reactor with a simple power supply unit or potentiostat.

Synthetic Applications. The electrochemical synthesis of metal−N-heterocyclic carbene (NHC) complexes has previously been reported by our group and others.[9,12] This procedure involves oxidation of a sacrificial anode, which releases metal ions into solution, and the cathodic reduction of imidazolium salts to produce metal−NHC complexes *via* highly reactive carbene intermediates (Scheme 1). These

Scheme 1. Electrochemical Synthesis of Metal−NHC Complexes
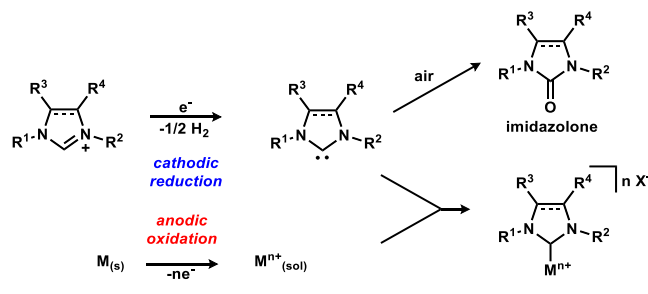
intermediates are sensitive to the presence of both oxygen and moisture, which results in the formation of imidazolone side products.[11] Consequently, initial testing of the bottle reactor was performed by the preparation of a range of metal−NHC complexes whose syntheses rely upon the use of inert atmospheres and anhydrous solvents.

Our investigations began with the preparation of various copper(I)−NHC complexes (Scheme 2) on a 1 mmol scale. These reactions were performed under galvanostatic conditions, as this enabled control over the number of electron

**Scheme 2. Electrochemical Synthesis of Cu(I)−NHC Complexes**[a]
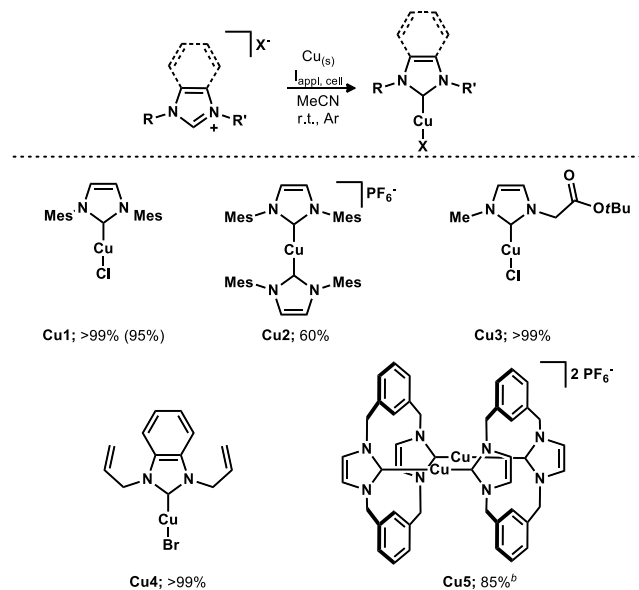
[a]Yields were determined by ^{1}H NMR spectroscopy; an isolated yield is shown in parentheses. Reaction conditions: 1 mmol of ligand precursor, 50 mA, 1.2 F mol^{-1}, 39 min. [b]0.5 mmol of ligand precursor, 30 mA, 1.2 F mol^{-1}, 65 min, with 0.5 equiv of Bu$_4$NBF$_4$ added to the reaction mixture.

equivalents (F mol^{-1}) delivered into solution, allowing a comparison with previously published results.[12] The imidazolium salt plays a dual role in the reaction as both the reactant and the electrolyte. This dispenses with the need to add an additional supporting electrolyte in most cases. Under these conditions, five different copper(I)−NHC complexes were prepared (Scheme 2).

Initially, the imidazolium salt IMes·HCl (**L1**) was chosen as a model substrate, as the electrochemical synthesis of the corresponding mono-NHC Cu(I) complex has been well-documented.[11,12] Galvanostatic conditions utilizing a current of 50 mA were applied for 1.2 electron equivalents, which resulted in complete conversion to the expected neutral mono-NHC complex **Cu1**. This complex could also be isolated in 95% yield after recrystallization. Using the same imidazolium cation but changing the counteranion to non-coordinating hexafluorophosphate gave **L2**, which under identical conditions resulted in 60% conversion to the expected cationic bis-NHC Cu(I) complex **Cu2**. The non-coordinating nature of the anion results in coordination of a second NHC ligand to the Cu(I) center. The lower conversion with hexafluorophosphate relative to that with a halide anion is consistent with previously reported results. The electrochemical synthesis of cationic bis-NHC Cu(I) complexes typically requires a greater number of electron equivalents to reach full conversion.[11,12] When the precursor was replaced with imidazolium salt **L3**, which contains a base-sensitive ester functionality, complete conversion to **Cu3** was observed after 1.2 electron equivalents. The synthesis of this complex highlights the complementary reactivity of the electrochemical approach to traditional chemical methods using strong bases, as the base-sensitive ester functionality remains intact. This is not the case if strong bases are employed. The electrochemical approach provides a different mode of activation that allows access to new complexes. When benzimidazolium salt **L4** was used, full conversion to **Cu4** was observed after 1.2 electron equivalents. The reduction of benzimidazolium salt **L4** is significantly more facile than that of related imidazolium salts, potentially because of the electronic effect exerted by the annulated benzene ring (*vide infra*), and this may explain the good reactivity observed here. When cyclophane-derived bis(imidazolium) salt **L5** was subjected to a current of 30 mA for 1.2 electron equivalents, 85% conversion to the dicationic dinuclear complex [Cu$_2$(NHC)$_2$](PF$_6$)$_2$ (**Cu5**) was observed, as expected from previous literature.[11,12] The addition of a supporting electrolyte was necessary to complete the reaction in a reasonable time frame because of the poor solubility of the ligand precursor **L5** and the low conductivity of the solution.[12]

Time course experiments were performed to investigate the different rates of formation of the mono- and bis-NHC complexes when either ligand precursor **L1** or **L2** was used. Acetonitrile solutions containing the ligand precursors were subjected to a current of 50 mA for different numbers of electron equivalents. This required sampling of the reaction mixtures at different time points while maintaining an inert atmosphere, which required use of both ports on the PTFE insert. The formation of Cu(IMes)Cl (**Cu1**) is fast, with quantitative conversion being achieved after 1 electron equivalent (Figure 2). The formation of [Cu(IMes)$_2$]PF$_6$ (**Cu2**) is slower, with 85% conversion after 1.6 electron equivalents and only slightly more (92%) after 3.5 electron equivalents. The slower formation of **Cu2** is potentially attributed to either mass transfer limitations or lower
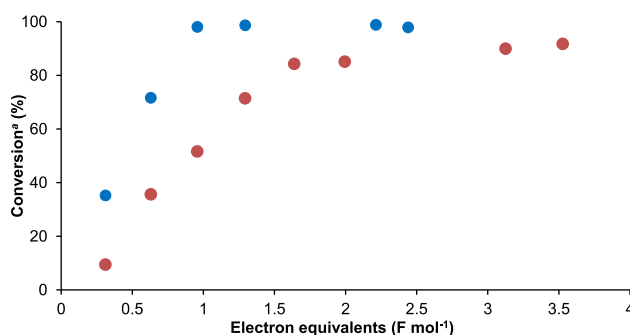

Figure 2. Time course monitoring of the formation of Cu(IMes)Cl (**Cu1**) (blue) and [Cu(IMes)$_2$]PF$_6$ (**Cu2**) (red). ^{a}Determined by ^{1}H NMR analysis.

conductivity of imidazolium salt **L2**, resulting in a higher resistance in solution, which may promote side reactions.[12] The ability to take samples from the reaction mixture through one of the ports machined into the PTFE headpiece while the other is connected to a Schlenk line highlights the ease of manipulation when the bottle reactor is used.

The synthetic methodology can be simply translated to other metals, as the reactor provides the flexibility to change the electrodes to the material of choice. To this end, imidazolium salts **L1**, **L3**, and **L6** and salen ligand **L7** were tested using either gold or iron electrodes (Scheme 3). When IMes·HCl (**L1**) was subjected to a current of 50 mA for 1.2 electron equivalents using PTFE-supported Au electrodes, a conversion of 74% to the mono-NHC product **Au1** was observed. Interestingly, a significant amount (10% yield) of the

Scheme 3. Electrochemical Synthesis of Au−NHC, Fe−NHC, and Fe−Salen Complexes^a
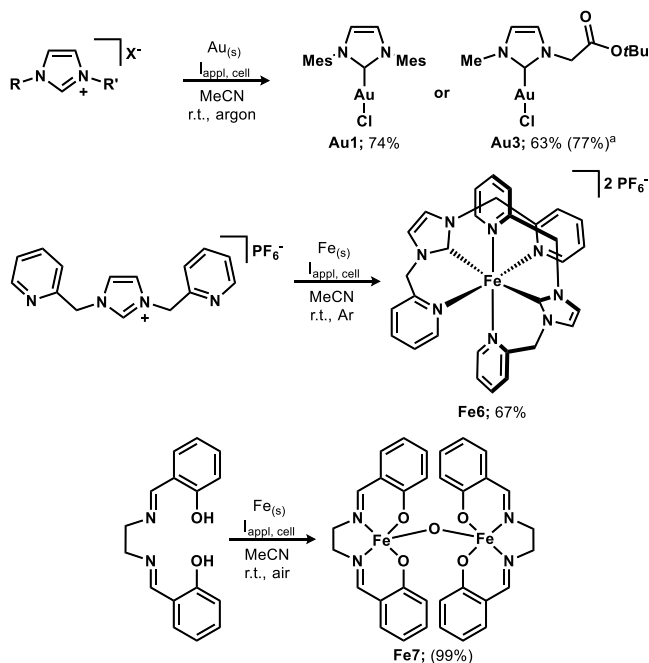

^{a}Yields were determined by ^{1}H NMR spectroscopy; isolated yields are shown in parentheses. Reaction conditions: 1 mmol of ligand precursor, 50 mA, 1.2 F mol^{-1}, 39 min. ^{b}1 mmol of ligand precursor, 50 mA, 2.0 F mol^{-1}, 65 min. ^{c}1 mmol of ligand precursor, 50 mA, 2.4 F mol^{-1}, 78 min.

bis-NHC complex was produced in this reaction, in contrast to the analogous reaction with copper electrodes. Au(I)−NHC complexes are often isostructural with Cu(I)−NHC complexes, but in this case the larger size of the Au(I) cation may provide reduced steric hindrance, resulting in the formation of the bis-NHC Au(I) complex.[24,25] When imidazolium salt **L3** was subjected to identical reaction conditions using Au electrodes, a conversion of 63% to the mono-NHC Au(I) complex was observed, and no bis-NHC Au(I) complex was observed. This complex was also isolated in 77% yield with 2.0 electron equivalents (**Au3**). Iron foil was a suitable electrode material for the electrosynthesis of Fe complexes of different oxidation states. When imidazolium salt **L6** was subjected to the standard reaction conditions, 67% conversion to the Fe(II) complex **Fe6** was observed. However, when salen ligand **L7** was used in place of the imidazolium salt and the reaction was carried out in air, full conversion to the Fe(III) complex **Fe7** was obtained with an isolated yield of 99%. This reaction was performed using 2.4 electron equivalents, as the ligand precursor had to be reduced twice.[10,26] This highlights the versatility of the electrochemical procedure to allow access to different metal oxidation states.

To expand the applicability of the bottle reactor, its utility in synthetic organic electrochemistry was examined. Specifically, a sulfonamide synthesis recently reported by Noël and co-workers (Table 1) was investigated.[26] This reaction involves

Table 1. Rapid Screening and Optimization of an Oxidative Coupling of Thiols and Amines Using a Parallel Plate
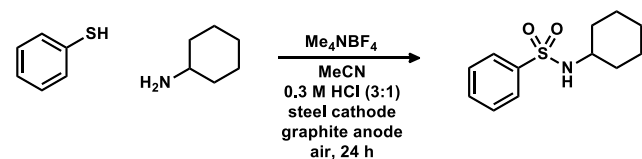
entry	mode	E/ $I_{appl,cell}$	yield 1 (%)	yield 2 (%)	average (%)
1	potentiostatic	3.7 V	<2	—	—
2	potentiostatic	3.4 V	41[a]	37[a]	39[a]
3	potentiostatic	3.2 V	48[a]	54[a] (48[b])	51[a]
4	galvanostatic	20 mA	56[a]	60[a] (58[b])	58[a]
5	galvanostatic	10 mA	40[a,c]	—	—

[a]Determined by ^{1}H NMR spectroscopy with the aid of an internal standard. [b]Isolated yield. [c]48 h reaction time.

the oxidative coupling of amines and thiols through an electrochemical mechanism, with H_2 gas being the only byproduct. To begin the investigation, the reported batch conditions were repeated. Unsurprisingly, the results obtained were different from those obtained by Noël and co-workers because of the different experimental setup, with the most significant difference being the interelectrode gap and lower electrolyte concentration. Utilizing the reaction conditions described by Noël and co-workers involving a potentiostatic mode with the potential set at 3.7 V resulted in no observed product in our setup (Table 1, entry 1). Fortunately, the reaction was quickly optimized by employing a parallel plate and performing a set of three reaction conditions in duplicate (i.e., six reactions were performed simultaneously) (Figure 3). Both galvanostatic and potentiostatic modes with a range of currents and potentials were screened (Table 1). The yield dramatically increased to 39% when the potential was lowered to 3.4 V (Table 1, entry 2). The increase in yield is potentially
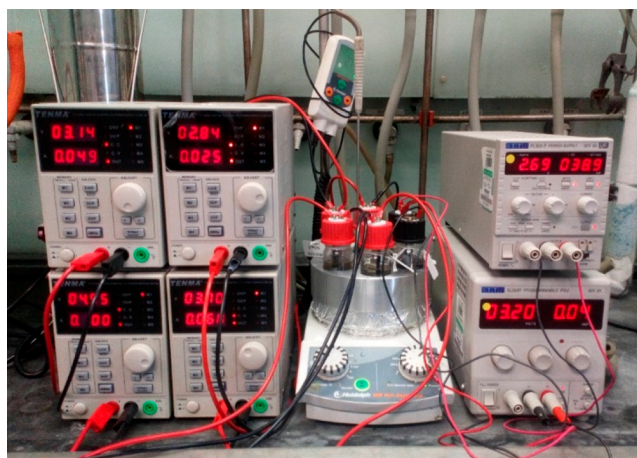
Figure 3. Parallel screening reactions were performed to optimize an oxidative coupling of amines and thiols.

derived from the smaller interelectrode gap in this setup (5 mm) compared with that used by Noël and co-workers (7 mm).[26] Decreasing the potential further to 3.2 V resulted in an increase in the yield to 51% (Table 1, entry 3). The galvanostatic mode was found to be more efficient, as a yield of 58% was obtained when a constant current of 20 mA was applied (Table 1, entry 4). This yield is comparable to that reported by Noël and co-workers. Finally, because of the success of the galvanostatic mode, a further experiment was performed. A constant current of 10 mA was applied for double the time (48 h) to deliver the same number of electron equivalents at a lower potential, but this delivered a decreased yield of 40% (Table 1, entry 5). The successful and fast optimization of this synthetic organic electrochemical reaction by performing six reactions in parallel showcases the bottle reactor's versatility and highlights the requirement for well-characterized experimental setups to enable interlaboratory reproducibility.

Cyclic Voltammetry. In addition to a synthetic setup, the bottle reactor can be used to perform cyclic voltammetry and other analytical experiments. When the reactor was connected to an external potentiostat and a reference electrode was used, high-quality voltammograms were obtained. This was achieved by connecting a glassy carbon disk working electrode and platinum wire counter electrode as they would be for synthetic electrochemistry in the bottle reactor. A silver wire, acting as a pseudoreference electrode, was connected using a standard ${}^1/_4$-28 fitting through one of the ports.[23] Cyclic voltammograms of ligand precursors **L1**−**L5** using ferrocene as an internal standard were obtained in this manner (Figure 4). All of the voltammograms showed an irreversible reduction between −1.9 and −2.5 V vs SCE, corresponding to reduction of the imidazolium salt (Figure 4). Also, **L1**, **L3**, and **L4** displayed peaks corresponding to the oxidation of Cl− and Br−,[27] and additional peaks were observed for **L4** that were potentially due to oxidation of the allyl groups.[28]

◼ CONCLUSIONS

A new flexible and standardized electrochemical batch reactor enabling both organic and inorganic transformations and analytical electrochemistry has been designed, developed, and tested. This has enabled the synthesis of Cu(I)−, Au(I)−, and Fe(II)−NHC complexes as well as an Fe(III)−salen complex.
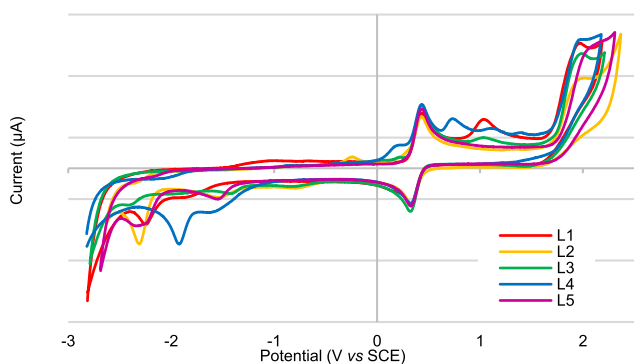
Figure 4. Cyclic voltammograms of imidazolium salts **L1**−**L5** (1 mM). Experiments were performed in MeCN with TBAPF$_6$ as a supporting electrolyte (0.1 M). Ferrocene (1 mM) was added as an internal standard. **L1**, red; **L2**, yellow; **L3**, green; **L4**, blue; **L5**, purple.

Furthermore, the batch reactor has been used to perform a synthetic organic reaction in conjunction with a parallel plate that enabled six reactions to be screened simultaneously. This allows rapid screening and optimization of reaction conditions. Cyclic voltammetry can be performed in the reactor with the use of an external potentiostat. This allows low concentrations of analyte and high sensitivity to be achieved. The design of this batch reactor is freely available, inexpensive, and versatile, enabling a range of synthetic and analytical electrochemistry.

■ EXPERIMENTAL SECTION

Synthesis of Metal Complexes: General Procedure. A bottle reactor vial was charged with the ligand precursor (1 mmol), and then the reactor was assembled with the appropriate electrodes (Cu, Au, or Fe) and placed under an atmosphere of argon. MeCN (anhydrous, 15 mL) was added, and a constant current of 50 mA was applied for 39 min (1.2 F mol^{-1}) from a benchtop power supply (Tenma 72-10480 from Farnell). A 0.5 mL sample was taken at the end of the reaction and filtered through Celite (under an inert atmosphere for complexes that were not air-stable: **Cu3**, **Cu4**, **Cu5** and **Fe6**), after which the solvent was removed under reduced pressure. The resultant solid was redissolved in a suitable deuterated solvent and analyzed using ^{1}H NMR spectroscopy. Integrals for the complex and ligand were used to calculate the conversion.

Oxidative Coupling of Thiols and Amines: General Procedure. A bottle reactor vial was charged with tetramethylammonium tetrafluoroborate (32 mg, 0.2 mmol), MeCN (15 mL), and aqueous HCl (0.3 M, 5 mL). Then cyclohexylamine (0.345 mL, 3 mmol) and thiophenol (0.205 mL, 2 mmol) were added. The bottle reactor lid was fitted with an IKA graphite anode and an IKA stainless steel cathode, and a potential difference was applied for the specific time (potentiostatic or galvanostatic). After completion the reaction mixture was diluted with water (10 mL) and extracted with EtOAc (3 × 20 mL). The combined organic layers were washed with brine (20 mL), dried over MgSO$_4$, and filtered. The solvent was removed under reduced pressure to deliver the crude product as a light-brown oil, to which 2,4,6-trimethoxybenzene (internal standard, 112 mg, 0.66 mmol) and CDCl$_3$ (3 mL) were added to form a homogeneous solution that was analyzed by ^{1}H NMR spectroscopy. The sample was further purified via flash column chromatography (silica gel, 0−20% EtOAc in hexane) to deliver the product as an off-white solid.

Cyclic Voltammetry. Cyclic voltammetry of **L1**−**L5** was performed at room temperature in the bottle reactor using a Metrohm DropSens μSTAT 400 potentiostat, and data were acquired with DropView 8400 software. Experiments were performed in anhydrous degassed MeCN (1 mM) containing Bu$_4$NPF$_6$ (0.1 M) as a supporting electrolyte at a scan rate of 300 mV s^{-1} with a Metrohm glassy carbon disk (3 mm) working electrode, platinum wire counter electrode, and silver wire pseudoreference electrode. Ferrocene (Fc) was added as an internal standard (1 mM, Fc$^+$/Fc at +0.380 V vs SCE) to reference experiments.

■ ASSOCIATED CONTENT

ⓈI Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.oprd.0c00091.

     Bottle reactor design, experimental methods, and characterization data (PDF)

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Author Contributions

The manuscript was written through contributions of all authors. All of the authors approved the final version of the manuscript.

Notes

The authors declare no competing financial interest.
The crystallographic data for this paper have been deposited in the Cambridge Structural Database (CSD) as entry 1987952.

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