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Urea-Based Multipoint Hydrogen-Bond Donor Additive Promotes Electrochemical CO_2 Reduction Catalyzed by Nickel Cyclam

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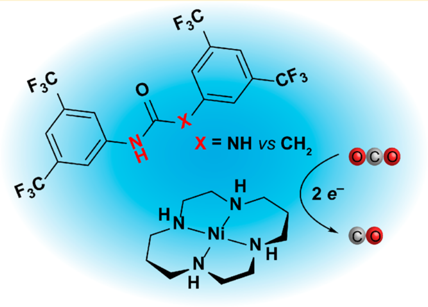
Supporting Information

ABSTRACT: We report that a urea-based multipoint hydrogen-bond donor additive leads to an enhancement in activity for electrochemical CO_2 reduction to CO catalyzed by Ni cyclam without altering this catalyst's high selectivity for CO_2 versus proton reduction. Comparison of peak catalytic currents in the presence of a bis(aryl)urea additive versus an isostructural amide as a one-point hydrogen-bond counterpart, as well as other weakly coordinating acids with comparable pK_a values, reveals that the urea preferentially augments CO_2 electrocatalysis. This observation suggests that the ability of the urea to form cooperative hydrogen-bond interactions is critical for the observed increases in activity rather than its acidity alone. Indeed, the boost in catalytic activity is observed in acetonitrile electrolyte containing up to 1 M water, indicating the organourea's role as a cocatalyst rather than a stoichiometric additive. This work establishes a starting point for applying principles of organocatalysis to electrocatalysis, where rational design and implementation of organic additives to electrocatalytic platforms can be a promising avenue to enhance activity and/or control product selectivity without requiring elaborate ligand synthesis.



INTRODUCTION

Increasing global energy demand and the resulting acceleration in fossil fuel consumption have exacerbated environmental challenges associated with rising atmospheric carbon dioxide levels, motivating the development of technologies that enable the transformation of CO_2 into value-added chemical products.[1,2] Electrochemical approaches to CO_2 reduction are attractive as they may be interfaced with photovoltaic devices or other energy sources with minimized environmental impact. However, key issues of selectivity and energetic efficiency remain challenging due to kinetic and thermodynamic factors.[3−5] Among the molecular catalysts reported for selective CO_2 reduction, aza-macrocycle-based catalysts have featured prominently.[6−13] In particular, Ni cyclam has attracted widespread attention since it was first reported as a CO_2 electrocatalyst platform by Eisenberg, Sauvage, and others in the 1980s.[6−9] Ni cyclam is notable for its excellent selectivity toward CO_2 reduction, even under mildly acidic aqueous conditions, using a mercury electrode; however, because the catalytically active species has been shown to be adsorbed to the mercury surface, this limitation presents a challenge for broader application using more environmentally friendly electrodes.[9,14,15] Along these lines, Ni cyclam was shown to catalyze homogeneous CO_2 reduction on a glassy carbon electrode in both organic and aqueous media, albeit with turnover frequencies (TOFs) lower than those of the heterogeneous mercury adsorbate.[16] As such, significant effort has been geared toward improving activity of the Ni cyclam catalyst platform under homogeneous conditions, including sophisticated ligand modifications to control macrocycle sterics[11] and install additional proton relay groups in the secondary coordination sphere.[12,13,17] Related work from our lab has explored mixed amine−carbene Ni systems inspired by Ni cyclam.[18,19] Pendant groups in the secondary coordination sphere have also been employed in other molecular electrocatalytic systems for CO_2 reduction.[20−24]

A complementary approach to molecular design involves the use of additives/cocatalysts to promote electrocatalytic activity in order to circumvent the need for elaborate ligand synthesis. Indeed, the effects of cationic additives have been explored in the context of nonaqueous electrochemical CO_2 reduction, both as stoichiometric Lewis acids leading to formation of CO and metal carbonates,[25] as well as chelated Lewis acid cocatalysts (i.e., Zn(cyclam)).[26] Cation effects have also been reported under aqueous conditions as a result of differential hydrolysis and buffering of the boundary layer of a metal electrode.[27,28] In addition, ionic liquid additives have been applied to modulate electrochemical CO_2 reduction over numerous heterogeneous metal and material electrodes, resulting in lowered overpotentials and, in some cases, changes

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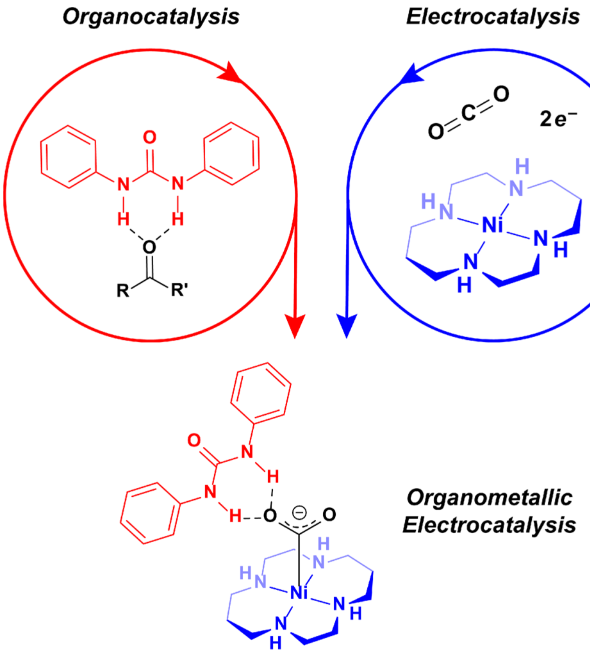
in product selectivity.[29−33] Finally, hydride donor additives have been explored in the context of CO_2 reduction, promoting the synthesis of more highly reduced carbon products such as methanol, albeit with issues in reusability.[34,35]

The foregoing examples illustrate the promise of additives to promote activity or alter selectivity of electrocatalytic transformations, but their design scope is limited compared to the broad use of additives in development of organic reaction methods.[36] In particular, we were drawn to bis(aryl)urea and thiourea additives, which have been widely applied to a number of organocatalytic transformations owing to their ability to hydrogen bond with both electrophilic species and anions.[37−45] Specifically, (thio)ureas have been shown to activate carbonyls toward nucleophilic attack and selectively stabilize oxyanions such as acetate and oxalate. These properties led us to consider their application to CO_2 reduction catalysis, where the ability of these ureas to engage with metal-bound CO_2 intermediates through multiple interactions could be envisioned to stabilize transition states and/or activate reaction intermediates.

Here, we report that an electron-deficient bis(aryl)urea additive leads to an enhancement in electrochemical CO_2 reduction activity catalyzed by Ni cyclam without altering this catalyst's high selectivity for CO_2 reduction over proton reduction. The observed improvement in electrocatalytic activity is dependent on the urea's ability to engage in cooperative, two-point hydrogen-bonding interactions by comparison with control additives bearing only one hydrogen bond or proton donor per molecule. These findings offer a starting point for designing a broader range of additives to act as cocatalysts in electrochemical transformations, merging the fields of organocatalysis and electrocatalysis (Scheme 1).

Scheme 1. Merger of Organocatalysis and Electrocatalysis Offers Promising Opportunities for Enhancing Activity or Tuning Selectivity



RESULTS AND DISCUSSION

We initiated a study to test the effects of hydrogen-bond donor additives on electrochemical CO_2 reduction using [Ni(cyclam)][PF_6]$_2$ as the catalyst and bis(3,5-trifluoromethyl)phenylurea (**1**, Schreiner's urea) as an additive. Under an Ar atmosphere, the cyclic voltammogram (CV) of [Ni(cyclam)][PF_6]$_2$ in acetonitrile containing 0.1 NBu_4PF_6 supporting electrolyte exhibits a reversible reduction at −1.82 V vs Fc/Fc$^+$, corresponding to the Ni$^{II/I}$ couple (Figure 1, black dashed line). Under CO_2 with only adventitious water, the peak becomes chemically irreversible and slightly positively shifted, reflecting slow catalytic turnover under these proton-limiting conditions (Figure 1, red line). Titration of **1** into a solution of [Ni(cyclam)][PF_6]$_2$ under CO_2 results in a dose-dependent increase in current (Figures 1 and S2). The urea additive **1** is electrochemically inert in this potential range, displaying an irreversible reductive event only at −2.4 V (Figure S1). Furthermore, control CVs in the presence of 1−20 equiv of **1** under Ar show no change in the position or shape of the Ni$^{III/II}$ or Ni$^{II/I}$ couples, indicating that **1** does not participate in background reductive transformations and does not coordinate to the nickel center of the catalyst (Figure S3).

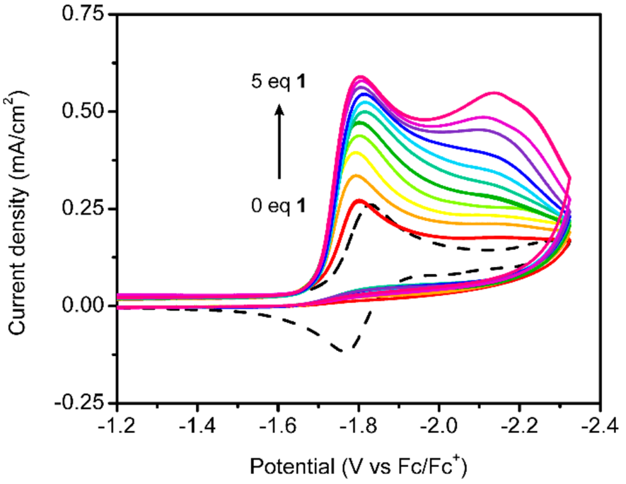
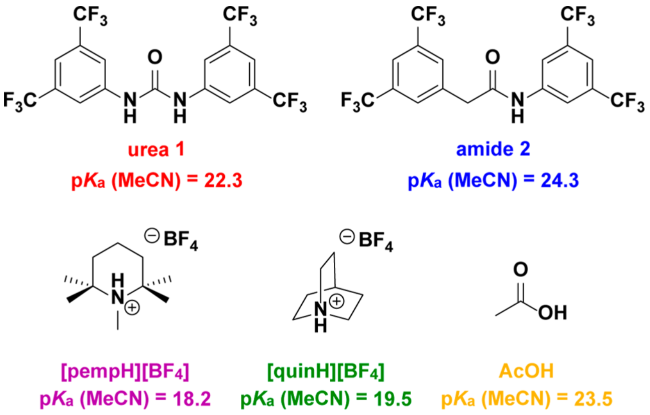


Figure 1. Cyclic voltammograms showing [Ni(cyclam)][PF_6]$_2$ (1 mM) under Ar (black dashed line) and under CO_2 (colored lines) with 0−5 equiv of urea **1**.

Given the critical role of protons in promoting C−O bond cleavage during CO_2 reduction, we sought to compare the effects of two-point hydrogen-bond donor **1** with single-point hydrogen-bond donors or acids (Scheme 2). An analogous additive bearing only one NH donor moiety, 3,5-bis(trifluoromethyl)phenylamide (**2**), was prepared as a control lacking the ability to form two-point, cooperative hydrogen bonds.[24] Amide **2** does not bind to the Ni cyclam complex (Figure S4), and addition of up to 20 equiv of **2** to a solution of [Ni(cyclam)][PF_6]$_2$ under CO_2 results in virtually no enhancement in catalytic activity (Figure S5). The significant differences in electrocatalytic activity observed upon addition of two-point donor **1** versus one-point donor **2** are not due to large differences in acidity, as the pK_a values of **1** and **2** measured via spectrophotometric titration in MeCN were found to be 22.3 ± 0.2 and 24.3 ± 0.6, respectively (Figures S22 and S24). Owing to the slight difference in pK_a between urea **1** and amide **2**, we sought to further explore the effects of other single-point donor additives that are more acidic than

Scheme 2. Hydrogen-Bond Donor and Acidic Additives Explored in This Work, with Associated pK_a Values in MeCN[a]



[a] Only urea **1** can uniquely form cooperative, two-point hydrogen-bond interactions.

urea **1**. Notably, to make reasonable comparisons, such additives must be noncoordinating and electrochemically inert in the relevant potential window. Pempidinium tetrafluoroborate ([pempH][BF_4], pK_a(MeCN) = 18.2[46]), quinuclidinium tetrafluoroborate ([quinH][BF_4], pK_a(MeCN) = 19.5[47]), and acetic acid (AcOH, pK_a(MeCN) = 23.5[48]) satisfy these criteria (Figures S6−S11).

Under an atmosphere of CO_2, CVs of [Ni(cyclam)][PF_6]$_2$ in the presence of 1−10 equiv of [pempH][BF_4] or [quinH][BF_4] show modest increases in catalytic current (Figures S12 and S13), whereas addition of 1−10 equiv of AcOH shows a very slight increase (Figure S14). Figure 2 shows a comparison of the catalytic wave for [Ni(cyclam)]-[PF_6]$_2$ under CO_2 in the presence of 10 equiv of each additive, where current density has been normalized to the height of the $Ni^{II/I}$ couple under Ar. The urea additive **1** increases the rate of CO_2 reduction more than the pempidinium or quinuclidinium additives, despite being 3−4 pK_a units less acidic. Furthermore, addition of as little as 5 equiv of urea **1** results in larger normalized peak catalytic current densities than with 10 equiv of any other additive (Figure S15), indicating that **1** is superior at promoting catalysis even when the effective concentration of hydrogen-bond donors is controlled. A plot of estimated TOF versus additive pK_a shows that all four single-point additives examined here exhibit a linear correlation, whereas **1** results in a much larger TOF than would be predicted by its pK_a alone (Figure S16). Although it is challenging to determine the precise contributions of electrostatic effects with neutral versus cationic additives, the linear relationship observed between TOF and additive pK_a implies that electrostatics do not play a primary role here. These results suggest that the unique ability of **1** to engage in cooperative, two-point hydrogen-bonding interactions with catalytically relevant species is the reason for the observed catalytic enhancement. It is also interesting to note that the amide additive **2** results in virtually no change in current at the catalytic wave over Ni(cyclam) alone, which we speculate is due to an inability of **2** to protonate the CO_2 adduct and thus could set a lower limit for estimating the pK_a value of such an intermediate. The collective data are summarized in Table 1, where turnover frequencies are estimated from the normalized peak catalytic current densities, i/i_p^0 (see Supporting Information for details).

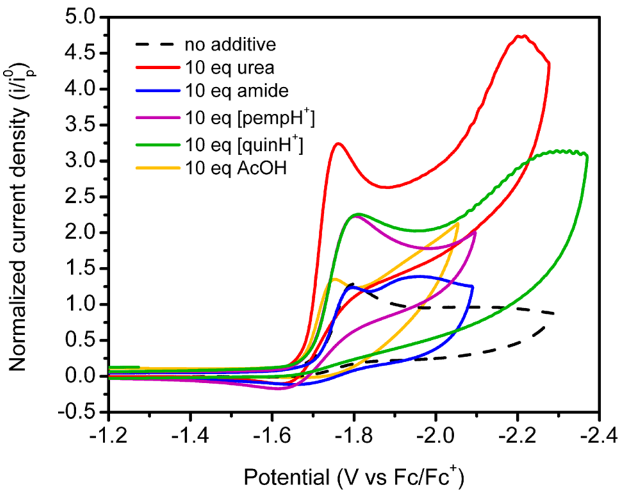


Figure 2. CVs showing catalytic responses of [Ni(cyclam)][PF_6]$_2$ (1 mM) under CO_2 in the presence of 10 equiv of various additives. Current has been normalized to i_p^0, the peak current under Ar. Urea **1** results in the largest normalized catalytic current despite being less acidic than two of the additives.

Table 1. Summary of Additive pK_a and TOF

additive (10 equiv)	pK_a (MeCN)	i/i_p^0	estimated TOF (min^{-1})
none		1.20	67
urea **1**	22.3	3.14	460
amide **2**	24.3	1.16	63
[pempH][BF_4]	18.2	2.12	209
[quinH][BF_4]	19.5	2.13	211
AcOH	23.5	1.23	70

Additional information regarding the role of the urea additive was obtained from concentration dependence studies and examination of its influence on CO_2 and CO binding. A plot of normalized peak catalytic current density as a function of urea concentration shows that catalytic behavior rapidly saturates above 5 equiv of **1** (Figure S17). This observation is attributed to product inhibition via formation of [Ni(cyclam)-CO]$^+$, as previously described by Kubiak and co-workers.[49] Indeed, this saturation behavior disappears upon addition of 5 equiv of a stoichiometric CO scavenger, nickel tetramethylcyclam [Ni(TMC)][PF_6]$_2$, resulting in a linear dependence of normalized peak current density on urea concentration (Figures S18 and S19). The urea additive was not found to have any effect on CO binding to Ni(cyclam), as evidenced by the similarity of CVs recorded under a CO atmosphere in the presence and absence of **1** (Figure S20). Attempts to probe whether urea **1** alters the equilibrium constant for CO_2 binding were unsuccessful due to loss of reversibility of the $Ni^{II/I}$ couple under these conditions, even at fast scan rates (Figure S21). This observation is likely due to an acceleration in the chemical steps following CO_2 binding.

The effect of the urea additive in acetonitrile/water solvent mixtures was subsequently explored. Addition of up to 1 M water to a CO_2-saturated acetonitrile solution of [Ni(cyclam)]-[PF_6]$_2$ alone results in a modest current increase at the $Ni^{II/I}$ wave (Figure 3, left panel), consistent with water's role as a weak acid. The same titration in the presence of 1 mM urea **1** results in a significantly larger current increase per amount of

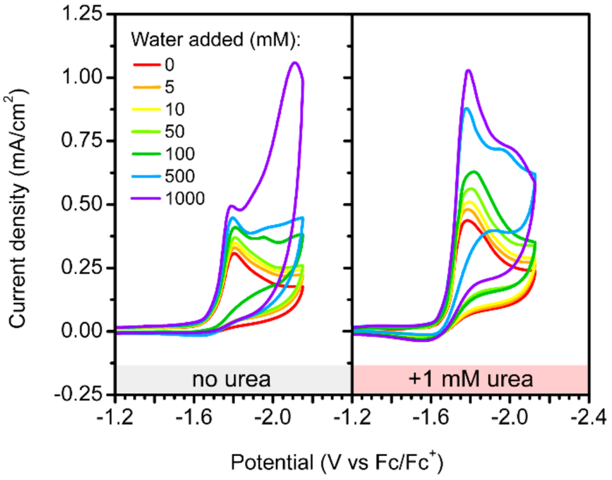


Figure 3. Titration of water to CO_2-saturated solutions of $[Ni(cyclam)][PF_6]_2$ (1 mM) in MeCN electrolyte alone (left) and in the presence of 1 mM urea **1** (right).

water added, culminating in over twice the peak catalytic current observed in the absence of urea (Figure 3, right panel). These data suggest that urea **1** facilitates CO_2 reduction as a cocatalyst rather than as a stoichiometric reagent, with water serving as the ultimate source of protons.

Product selectivity was determined by controlled potential electrolysis using a home-built electrochemical cell designed for nonaqueous experiments. The cell headspace could be directly linked to a gas chromatograph for gaseous product analysis. Electrolysis of a solution of $[Ni(cyclam)][PF_6]_2$ (2 mM catalyst, 0.1 M $TBAPF_6$ in MeCN with 1 M water) at a potential of −1.77 V vs Fc/Fc$^+$ results in a Faradaic efficiency of 85% for CO, with no H_2 detected. Electrolysis at the same potential in the presence of 5 equiv of urea **1** results in a sustained increase in current density over the course of the run (120 min) and a Faradaic efficiency of 91% for CO, again with no H_2 detected (Figure 4). We estimate an error of ±10% in these Faradaic efficiency values; thus, differences in selectivity in the absence or presence of urea **1** are the same within experimental error. These experiments establish that urea **1** promotes the reaction of interest, CO_2 reduction, over competing proton reduction without altering the selectivity of this process to generate CO as the major product.

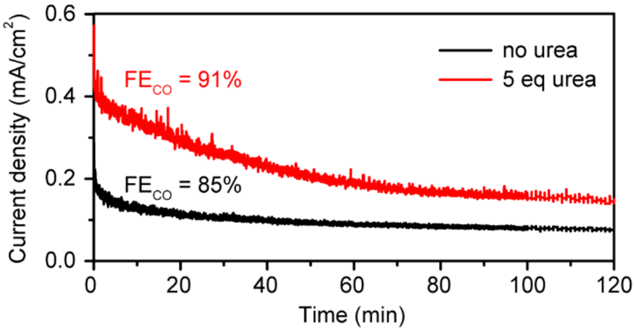


Figure 4. Controlled potential electrolysis of 2 mM $[Ni(cyclam)][PF_6]_2$ in the presence and absence of **1** (MeCN electrolyte with 1 M H_2O, $E_{applied}$ = −1.77 V vs Fc/Fc$^+$). Faradaic efficiencies for CO are noted; no H_2 was detected.

■ CONCLUSION

In summary, we have shown that homogeneous electrochemical CO_2 reduction catalyzed by the classic Ni cyclam system is promoted by an organourea cocatalyst additive. Comparison of peak catalytic currents in the presence of neutral and cationic additives with varying pK_a values suggests that the urea additive is uniquely positioned to promote catalytic turnover owing to its ability to form cooperative, multipoint hydrogen-bond interactions rather than as a consequence of acidity alone. The enhancement in CO_2 reduction activity is observed in acetonitrile electrolyte containing up to 1 M water, and controlled potential electrolysis under these conditions reveals that the additive does not alter the catalyst's high selectivity for CO_2 reduction versus proton reduction. By merging concepts of organocatalysis and electrocatalysis, this work provides a framework for the broader exploration of organic cocatalyst additives applied to a variety of electrochemical transformations, to enhance activity and/or alter product selectivity.

■ EXPERIMENTAL SECTION

General Synthetic and Physical Methods. Unless noted otherwise, all manipulations were carried out at room temperature under a dinitrogen atmosphere in a VAC glovebox or using high-vacuum Schlenk techniques. Anhydrous DCM and proteo-MeCN were obtained from a JC Meyer solvent purification system. $[Ni(cyclam)][PF_6]_2$ and $[Ni(TMC)][PF_6]_2$ were synthesized as previously reported.[49] Urea **1** was prepared according to literature methods.[50] All other reagents and solvents were purchased from commercial sources and used without further purification. NMR spectra were recorded on Bruker spectrometers operating at 300, 400, or 500 MHz as noted. Chemical shifts for ^1H and $^{13}C\{^1H\}$ spectra are reported in parts per million relative to residual protiated solvent; those for ^{19}F spectra are reported in parts per million relative to an external $CFCl_3$ standard. Coupling constants are reported in hertz.

General Electrochemical Methods. Nonaqueous electrochemical experiments were conducted under Ar, CO_2, or CO atmosphere in 0.1 M NBu_4PF_6 electrolyte in ambiently wet MeCN. A bubbler filled with MeCN was used to presaturate the gas stream to limit concentration changes due to evaporation. Cyclic voltammetry experiments were performed using either an Epsilon potentiostat from Bioanalytical Systems, Inc. (West Lafayette, IN) or a 600E electrochemical analyzer from CH Instruments, Inc. (Austin, TX). The working electrode for cyclic voltammetry was a 3.0 mm diameter glassy carbon disk (Bioanalytical Systems, Inc.) and was polished between every scan with 0.05 μm alumina powder on a felt pad. The auxiliary electrode was a platinum wire. A silver wire in porous Vycor tip glass tube filled with 0.1 M NBu_4PF_6 in MeCN was used as a pseudoreference electrode. All potentials were referenced against ferrocene/ferrocenium as an external standard. The scan rate for all cyclic voltammograms was 100 mV/s unless otherwise noted. All scans were compensated for internal resistance.

Details for Controlled Potential Electrolysis Experiments. Controlled potential electrolysis (CPE) was conducted in a homemade gastight PEEK electrolysis cell with a working compartment (30 mL liquid volume) and counter compartment (12 mL liquid volume) separated by an ultrafine glass frit, as described elsewhere.[24] A 1 cm^2 glassy carbon plate (Tokai Carbon; Kanagawa, Japan) was used as the working electrode, and a 2.5 cm diameter graphite planchet (Ted Pella; Redding, CA) was used as the auxiliary electrode. The working compartment was filled with 30 mL of a 2 mM solution of Ni cyclam dissolved in 0.1 M $TBAPF_6$/MeCN containing 1 M H_2O. The counter electrode chamber was filled with 12 mL of a 20 mM solution of tetrabutylammonium acetate dissolved in 0.1 M $TBAPF_6$/MeCN containing 1 M H_2O. This soluble source of acetate was sacrificially oxidized via the Kolbe reaction to generate CO_2 and ethane, thereby preventing GC detection of solvent oxidation byproducts. Both compartments were sealed to be gastight. The working compartment was sparged with CO_2 for 15 min, then closed and injected with 0.5 mL of ethylene as a gaseous internal standard. A CV scan was collected to benchmark CPE potential versus the known Ni(II/I) reduction potential. The CPE experiment was performed while the mixture was stirred at 300 rpm with a 1 cm stirbar. Upon completion, the headspace was injected directly into a SRI-GC equipped with 6′ Hayesep D and 13X molecular sieve chromatographic columns, as well as a second Hayesep D guard column to trap solvent volatiles. Two in-line detectors were used: a TCD for H_2 detection and a FID with methanizer for $CO/CO_2/C_2H_4$ detection. Analytes of interest were quantified by comparing a ratio of analyte/internal standard peak integrals to a calibration curve with known amounts of analyte.

Synthesis of [3,5-Bis(trifluoromethyl)phenyl]amide (2). A 50 mL Schlenk flask was charged with 20 mL of anhydrous DCM, 3,5-bis(trifluoromethyl)phenylacetic acid (1.00 g, 3.67 mmol), and a catalytic amount of anhydrous dimethylformamide (29 μL, 0.37 mmol). Freshly distilled $SOCl_2$ (0.32 mL, 4.41 mmol) was added under a N_2 atmosphere, and the solution was stirred at room temperature for 1.5 h. Solvent was removed under reduced pressure to afford a yellow oil. Anhydrous toluene (5 mL) was added and then removed under reduced pressure to assist in removal of excess $SOCl_2$. The resulting acid chloride was dissolved in anhydrous DCM (20 mL), and 3,5-bis(trifluoromethyl)aniline (0.86 mL, 5.51 mmol) was added, followed by triethylamine (0.61 mL, 4.41 mmol). After the mixture was reacted overnight at room temperature, the solvent was removed under reduced pressure. The product was dissolved in EtOAc and washed with water; combined organic fractions were dried over $MgSO_4$, and solvent was removed under reduced pressure. The crude product was purified by column chromatography (starting at 2:1 hexane/DCM and progressing to 1:3 hexane/DCM) on silica (0.65 g, 37% yield): ^{1}H NMR (500 MHz, CD_3CN) δ 9.02 (br s, 1H), 8.15 (s, 2H), 7.94 (s, 3H), 7.70 (s, 1H), 3.92 (s, 2H); $^{13}C\{^1H\}$ NMR (126 MHz, CD_3CN) δ 169.80, 141.30, 138.77, 132.46 (q, J = 33.3 Hz), 131.76 (q, J = 32.8 Hz), 131.37 (m), 124.49 (q, J = 271.8 Hz), 124.29 (q, J = 271.9 Hz), 121.87 (m), 120.12, 117.84 (m), 43.06; ^{19}F NMR (376 MHz, $CDCl_3$) δ −62.57, −62.89; IR (ATR, solid, ν (cm^{-1})) 3264 (w), 3222 (w), 3186 (w), 3096 (w), 1670 (m), 1569 (m), 1469 (m), 1374 (s), 1272 (s), 1171 (s), 1127 (s); ESI-MS calcd for $C_{18}H_8F_{12}NO$ $(M - H)^-$ 482.0, found 482.4; $C_{18}H_9ClF_{12}NO$ $(M + Cl)^-$ 518.0, found 518.4.

Synthesis of [Pempidinium][BF_4]. A solution of pempidine (0.35 mL, 1.93 mmol) in 10 mL of diethyl ether was cooled to 0 °C. To this was added $HBF_4 \cdot Et_2O$ (0.26 mL, 1.91 mmol). A white precipitate formed instantaneously and was collected by filtration and subsequently washed with excess cold diethyl ether. The salt was dried in a vacuum oven overnight at 80 °C to afford the product, which was stored in a nitrogen-filled glovebox (0.46 g, 99% yield): ^{1}H NMR (400 MHz, CD_3CN) δ 6.31 (t, J_{N-H} = 47.9 Hz, 1H), 2.71 (d, J = 3.3 Hz, 3H), 1.87−1.54 (m, 6H), 1.37 (s, 6H), 1.33 (s, 6H); ^{19}F NMR (376 MHz, CD_3CN) δ −150.46; ESI-MS calcd for $C_7H_{14}N$ $(M)^+$ 112.1, found 112.2.

Synthesis of [Quinuclidinium][BF_4]. A solution of quinuclidine (0.5 g, 4.5 mmol) in 20 mL of diethyl ether was cooled to 0 °C. To this was added $HBF_4 \cdot Et_2O$ (0.58 mL, 4.27 mmol). A white precipitate formed instantaneously and was collected by filtration and subsequently washed with excess cold diethyl ether. The salt was dried in a vacuum oven overnight at 80 °C to afford the product, which was stored in a nitrogen-filled glovebox (0.745 g, 88% yield): ^{1}H NMR (400 MHz, CD_3CN) δ 6.44 (s, 1H), 3.23−2.91 (m, 6H), 1.78 (dq, J = 4.5, 2.3 Hz, 1H), 1.72 (dq, J = 8.3, 3.6 Hz, 6H); ^{19}F NMR (376 MHz, CD_3CN) δ −151.08; ESI-MS calcd for $C_{10}H_{22}N$ $(M)^+$ 156.2, found 156.2.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.8b00308.

Additional electrochemical and spectroscopic data (PDF)

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Notes

The authors declare no competing financial interest.

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