Electrocatalytic CO$_2$ Reduction to Formate with Molecular Fe(III) Complexes Containing Pendent Proton Relays

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Abstract

The synthesis, structural characterization, and reactivity of two iron(III) compounds with 6,6'-(2,2'-bipyridine)-6,6'-diyl)bis(4-(methyl)-2-methoxyphenol) ($^{\text{mcrebpy}}[\text{H}]_2$, Fe($^{\text{mcrebpy}}$)Cl, 2) and 6,6'-(2,2'-bipyridine)-6,6'-diyl)bis(4-(tert-butyl)benzene-1,2-diol) ($^{\text{tbcatbpy}}[\text{H}]_4$, Fe($^{\text{tbcatbpy}}$), 3) as ligands under electrochemically reducing conditions is reported. Differences in selectivity and activity for the electrocatalytic reduction of carbon dioxide (CO$_2$) to formate (HCO$_2^-$) were assessed via cyclic voltammetry (CV) and controlled potential electrolysis (CPE) experiments in N,N-dimethylformamide (N,N-DMF). Mechanistic studies suggest that the O atoms in the secondary coordination sphere are important for relaying exogeneous protons to the active site, enhancing the multi-site electron proton transfer (MS-EPT) activation of the catalysts, which leads to a 4-fold TOF$_\text{max}$ increase for 2 and 2-fold for 3 in comparison to our previous studies. Depending on the strength of the interaction between the pendent moiety and the sacrificial proton donor, improvements in catalytic activity and efficiency were observed, suggesting a corresponding electronic effect from the interaction of the pendent functional groups with the Fe-bound O atom when protonated. CPE experiments indicate increased Faradaic efficiencies (FE) for formate (85±2%) with 2, whereas 3 had a lower FE for formate of 70±8%. These results suggest that using secondary sphere moieties to modulate metal-ligand interactions and MS-EPT reactivity in the primary coordination sphere is a powerful strategy for modulating electrocatalytic activity and selectivity.
Introduction
The steadily increasing market share of electricity from renewable sources continues to generate interest in developing electrochemical transformations for storing energy in chemical bonds. One compelling approach is to direct energy from these sources towards electrochemical transformations of CO$_2$, a byproduct of fossil fuel usage and a greenhouse gas, into useful fuel precursors and commodity chemicals. In comparison to molecular electrocatalysts developed for the reduction of CO$_2$ to CO, relatively few catalysts have been developed which selectively produce formate. Formate is currently utilized as an organic hydride source, directly in a fuel cells, and as a H$_2$ storage material.

Previously, we identified a molecular Fe(III) chloride complex based upon 6,6'-di(3,5-di-tert-butyl-2-hydroxybenzene)-2,2'-bipyridine (Fe(tbu$_{\text{Cl}}$dhbpy)Cl, Figure 1, 1) which produced formate with a Faradaic efficiency of 68±4% from CO$_2$ in the presence of 0.5 M phenol (PhOH) with an $E_{\text{cat/2}}$ of $-2.45$ V vs Fc$^+/Fc$. Mechanistic studies suggested that a non-catalytic electrochemical reaction was vital to the observed reactivity: the Fe-bound oxygen atoms underwent protonation upon reduction of the metal center from Fe(III)/(II), a type of multi-site electron and proton transfer (MS-EPT) reaction.

![Figure 1. Molecular Electro catalysts for CO$_2$ reduction to formate studied previously (1; Fe(tbu$_{\text{Cl}}$dhbpy)Cl) and in this work (2; Fe(me$_{\text{Cl}}$crebpy)Cl and 3; Fe(tbu$_{\text{Cl}}$catbpy)]

MS-EPT mechanisms involving ligand protonation upon metal redox changes in the primary coordination sphere are generally invoked for metal oxime and...
dithiolene complexes which catalytically generate H$_2^{13-17}$; similar mechanisms are underdeveloped for other substrates.$^3$

A successful strategy for improving the activity, selectivity, and thermodynamic efficiency of molecular electrocatalysts which facilitate the transformation of CO$_2$ is the incorporation of pendent proton shuttles in the secondary coordination sphere of the respective complexes.$^{18-20}$ The utility of these functional groups holds for many electrocatalytic transformations: examples exist for the hydrogen evolution,$^{21-23}$ oxygen reduction,$^{24-27}$ and CO$_2$ reduction$^{18, 28-31}$ reactions. In studies on molecular electrocatalysts for CO$_2$ reduction, the design emphasis is generally placed on positioning the pendent relay such that it can interact with CO$_2$ bound to the active site of the complex to stabilize intermediates, act as a proton relay, and/or to provide access to new reaction pathways to lower the energy input and increase catalytic rates.$^{18, 19, 31-33}$

MS-EPT has been explored broadly in photochemical and chemical systems, including the photosynthetic oxidation of tyrosine-Z,$^{34}$ ruthenium-based model compounds for phenol oxidation,$^{35}$ and mixed TEMPOH/organic base/chemical oxidant systems.$^{36}$ Under electrochemical conditions, MS-EPT has also been studied as an oxidant for tyrosine by M(bpy)$_3^{3+/2+}$ systems (M = Os, Ru, Fe, bpy = 2,2'-bipyridine).$^{37}$ Intrigued by our initial observations of the MS-EPT reaction and its relationship to the catalytic response,$^9$ we have synthesized two new ligand frameworks containing secondary sphere hydrogen bond donor and acceptor groups which are oriented to interact with the Fe-bound O atoms that are protonated upon reduction of the metal center (Figure 1). By tuning the ability of the secondary sphere moiety to direct the exogenous sacrificial proton donor, an increased TOF$_{\text{max}}$ and selectivity for formate can be achieved. This demonstrates that non-catalytic MS-EPT reactions can be optimized via analogous strategies to those used for enhanced protonation rates of activated substrate at the metal center.

Here, we report the synthesis, structural, and electrochemical behavior of two new Fe(III) complexes containing pendent proton relays oriented to interact with the Fe-bound oxygen atoms of an N$_2$O$_2$ coordination environment. These
complexes are based on the ligands 6,6'-(2,2'-bipyridine)-6,6'-diyl)bis(2-methoxy-4-methylphenol) (\(\text{me}\text{crebpy[H]}_2\), \(\text{Fe}(\text{me}\text{crebpy})\text{Cl}\), \textbf{2}, \textit{Figure 1}) and 6,6'-(2,2'-bipyridine)-6,6'-diyl)bis(4-(tert-butyl)benzene-1,2-diol) (\(\text{tbu}\text{catbpy[H]}_4\), \(\text{Fe}(\text{tbu}\text{catbpy})\), \textbf{3}, \textit{Figure 1}). Initial studies have shown \textbf{2} to be an excellent catalyst for the reduction of CO\(_2\) to formate, with a 4-fold enhancement in rate at 85±2% Faradaic efficiency. In contrast, \textbf{3} behaves very similarly to \textbf{1} with a 2-fold enhancement in rate and no increase in Faradaic efficiency (70±8%). We believe the difference in reactivity for \textbf{2} comes from the advantageous interactions of the second sphere proton shuttle, exogeneous proton donor, and inner sphere Fe-bound oxygen atom, which contribute to a reaction rate enhancement and increase in selectivity.

\textbf{Results}

The synthesis of the \([\text{me}\text{crebpy(H)}]_2\) and \([\text{tbu}\text{catbpy(H)}]_4\) ligands was accomplished through Pd-catalyzed cross-coupling procedures which are similar to the synthesis of the \([\text{tbu}\text{dhbpy(H)}]_2\) (see \textbf{Experimental Methods}). The synthesis of the corresponding Fe(III) complexes was achieved by refluxing the ligand in ethanol in the presence of equimolar FeCl\(_3\)•H\(_2\)O with NaOAc as a proton scavenger. Single crystals of sufficient quality for X-ray diffraction studies were obtained for both \textbf{2} and \textbf{3} by slow cooling from supersaturated, boiling acetonitrile solutions. The solid-state structure of complex \textbf{2} is a dimeric species, with a single oxygen atom from each ligand framework coordinated to an axial position of a second Fe complex to create a hexadentate coordination environment (\textit{Figure 2}). Likewise, complex \textbf{3} also exists as a dimeric species in the solid state, however in this case hexadentate coordination is instead facilitated by the partial deprotonation of one of each of the catechol moieties per unit of \textbf{3} in the dimeric structure, replacing the Cl\(^-\) ligand for both Fe centers (\textit{Figure S1}). Microanalysis of the as-synthesized \textbf{3} confirmed that complete chloride loss occurs for the bulk material, with charge for the Fe(III) center balanced by the deprotonation of catechol (\textit{Figure 1}). In both cases the solution-phase behavior suggests that these are monomeric species: diffusion coefficients for \textbf{2} and \textbf{3} determined by CV methods using the Randles-Sevcik equation are consistent with those determined for \textbf{1} and Fe-porphyrins (\textit{Table S1}).\(^{38}\) UV-Vis
spectra of 2 and 3 obtained in N,N-DMF maintain linearity upon dilution—which is consistent with the absence of an equilibrium process (Figure S2-S3). Finally, the magnetic moments determined by Evans’ method of 5.9±0.1 and 6.0±0.1 BM obtained for 2 and 3, respectively, are consistent with a monomeric high spin S = 5/2 Fe(III) species in each case.  

**Figure 2.** (A) Unit cell and (B) overall dimer structure for 2. C = grey, O = red, N= blue, Fe = orange, Cl = green. Thermal ellipsoids set to 50%. Occluded acetonitrile molecules and hydrogen atoms omitted for clarity.

Electrochemical experiments conducted in 0.1 M TBAPF$_6$/N,N-DMF under Ar with each complex demonstrated redox processes at similar potentials to 1. Complex 2 exhibits one irreversible 1e$^-$ reduction with $E_{p,a} = -1.45$ V vs Fc$^+/Fc$ and three reversible 1e$^-$ reductions with $E_{1/2} = -0.84, -1.93$, and $-2.55$ V vs Fc$^+/Fc$, respectively (Figure 3). Complex 3 exhibits two reversible, 1e$^-$ reductions with $E_{1/2} = -1.01$ V and $-1.65$ V vs Fc$^+/Fc$, respectively, followed by two related one-electron
Figure 3. Cyclic Voltammograms of 0.5 mM 2 and 3 under an Ar atmosphere in 0.1 M TBAPF$_6$/N,N-DMF supporting electrolyte. Working electrode is glassy carbon, counter electrode is a glassy carbon rod, AgCl/Ag pseudoreference electrode. Referenced to internal decamethylferrocene (Cp$_2$*Fe) standard. 100 mV/s scan rate.

reductions with $E_{1/2} = -2.24$ V and $E_{\text{p,a}} = -2.58$ V vs Fc$^+/Fc$ (Figure 3). On the return sweep to oxidizing potentials with 3, a feature with $E_{\text{p,c}} = -1.39$ V vs Fc$^+/Fc$ is observed when the CV switching potential is $\sim -2.7$ V vs Fc$^+/Fc$, indicating that this CV feature is associated with the final two reduction waves (Figure 3). Interestingly, a scan rate-dependent relationship is observed between the final two reduction features for 3. The reduction at $-2.24$ V vs Fc$^+/Fc$ produces larger current densities at slow scan rates (<200 mV/s), but the reduction at $-2.58$ V vs Fc$^+/Fc$ becomes more prominent at faster scan rates, at the expense of the more positive redox feature (Figure S4). This is indicative of an ECE mechanism, where at slower scan rates the intermediate chemical process which produces the first of these two features has sufficient time to occur.

Variable scan rate experiments indicate both 2 and 3 behave in a diffusion-limited regime (Figures S5-S6). CVs of the corresponding Zn complexes of 2 and 3 indicate that the final two reductions for 2 and 3 are partially ligand based in nature (Figures S7-S8). As we have shown previously, the initial Fe(III)/(II)
reduction feature is sensitive to the presence of a proton donor: for complex 2 (Figure S9) and complex 3 (Figure S10), distinct shifts and coalescence of more positive reduction features occurs upon addition of PhOH as an added proton donor. These changes are not conducive to simple equilibrium modelling used previously\textsuperscript{40}, which we attribute to multiple competing equilibrium involving the pendent moieties, the Fe-bound O atoms and the proton donor at reducing potentials.

In the presence of CO\textsubscript{2} under aprotic conditions, 2 and 3 exhibit an increase in current, with \(i_p/i_c\) values of 5.5 and 13, respectively, with \(E_D = \text{–}2.50\) V and \(\text{–}2.37\) V vs Fc\textsuperscript{+}/Fc, respectively (Figure 4).\textsuperscript{41} Upon the addition of phenol (PhOH) under CO\textsubscript{2} saturation conditions, each complex shows an increase in current relative to aprotic conditions, consistent with the electrocatalytic response observed for 1 previously (Figure 4, Figure S11-12). Titrations of PhOH show that a plateau current is reached at 0.9 M PhOH for 2 with \(E_{\text{cat/2}} = \text{–}2.33\) V vs Fc\textsuperscript{+}/Fc and 0.5 M PhOH for 3 with \(E_{\text{cat/2}} = \text{–}2.33\) V vs Fc\textsuperscript{+}/Fc at 100 mV/s scan rate (Figures S13-S14).

In our previous study, we noted that 1 showed decreased current densities under larger CO\textsubscript{2} concentrations due to the suppression of competitive HER activity, no dependence on PhOH concentration, and a first order dependence on catalyst concentration.\textsuperscript{40} For 2, current saturation was observed above concentrations of 0.04 M CO\textsubscript{2} in the presence of 1.0 M PhOH, and a first-order concentration dependence on PhOH was observed under CO\textsubscript{2} saturation conditions (Figures S15-S16). We again observed electrocatalytic current saturation above 0.04 M CO\textsubscript{2} for complex 3; however, varied PhOH concentrations under saturated CO\textsubscript{2} give a slope of 0.15, suggesting a kinetically limiting effect in the overall mechanism (Figures S17-S18). These results are consistent with a CO\textsubscript{2} activation step that is kinetically limited by proton transfer. Plots comparing the current response to the [catalyst] were linear for both 2 and 3, suggesting the reaction is first order with respect to each, consistent with our prior study (Figure S19-S20).\textsuperscript{40}
Figure 4. CVs of (A) 2 and (B) 3 under Ar (black) and CO$_2$ (red, blue, and green) saturation conditions. Blue and green traces are in the presence of PhOH added as a proton source. Working electrode is glassy carbon, counter electrode is a glassy carbon rod, AgCl/Ag pseudoreference electrode. Referenced to internal Cp$_2^*$Fe standard. 100 mV/s scan rate.

Catalytic rate constants were determined for each complex utilizing variable scan rate experiments at 0.5 M PhOH for 3 and both 0.5 and 0.9 M PhOH for 2 by previously described methods.$^{42}$ At 0.5 M PhOH, 3 exhibits a TOF$_{\text{max}} = 436\pm1$ s$^{-1}$, while 2 exhibits TOF$_{\text{max}} = 303\pm1$ s$^{-1}$. At 0.9 M PhOH, 2 exhibits an increased TOF$_{\text{max}} = 587\pm1$ s$^{-1}$ (Figures S21-S23).

The catalytic efficiencies and selectivities of 2 and 3 for the reduction of CO$_2$ were determined by controlled potential electrolysis (CPE) experiments at the peak catalytic potentials for their respective PhOH saturation concentrations (Table 1). CPE at $-2.50$ V vs Fc$^+/Fc$ with 2 and 0.9 M PhOH under CO$_2$ saturation conditions produced 85$\pm$2% formate with the remainder of current going to H$_2$ (12$\pm$4%) and CO (5$\pm$1%) through 11.0 TON (22 electron equivalents passed per catalyst molecule (Figure S24)). CPE at $-2.60$ V vs Fc$^+/Fc$ with 3 and 0.5 M PhOH under CO$_2$ saturation conditions yielded 71$\pm$3% formate, with the remainder of current going to H$_2$ (23$\pm$9%) and CO (0.8$\pm$0.1%) (Figure S25). Following these electrolysis experiments, the working electrode was rinsed with ethanol and allowed to air dry before a second electrolysis experiment was conducted where the putative molecular precatalyst was omitted under otherwise identical conditions of proton
donor concentration and CO₂ saturation (Figure S24-S25). The rinse test with both 2 and 3 indicated no formate production (Table 1). Additional control experiments with no added catalyst material and a freshly polished electrode generated no formate under either set of conditions (Table 1).

Table 1. Summary of Controlled Potential Electrolysis Data.^[a]

<table>
<thead>
<tr>
<th>Trial</th>
<th>Complex</th>
<th>TON</th>
<th>Formate[^b]</th>
<th>CO[^b]</th>
<th>H₂[^b]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1^c</td>
<td>2</td>
<td>9.0</td>
<td>85±3</td>
<td>9±2</td>
<td>10±2</td>
</tr>
<tr>
<td>2^c</td>
<td>2</td>
<td>11.0</td>
<td>84±1</td>
<td>5±1</td>
<td>12±4</td>
</tr>
<tr>
<td>3^c</td>
<td>Rinse 2</td>
<td>-</td>
<td>ND</td>
<td>6±2</td>
<td>32±4</td>
</tr>
<tr>
<td>4^c</td>
<td>-</td>
<td>-</td>
<td>ND</td>
<td>ND</td>
<td>60±10</td>
</tr>
<tr>
<td>5^d</td>
<td>3</td>
<td>9.4</td>
<td>70±8</td>
<td>2±1</td>
<td>28±4</td>
</tr>
<tr>
<td>6^d</td>
<td>3</td>
<td>9.8</td>
<td>71±3</td>
<td>0.8±0.1</td>
<td>23±9</td>
</tr>
<tr>
<td>7^d</td>
<td>Rinse 3</td>
<td>-</td>
<td>ND</td>
<td>4±1</td>
<td>ND</td>
</tr>
<tr>
<td>8^d</td>
<td>-</td>
<td>-</td>
<td>ND</td>
<td>1.0±0.5</td>
<td>17±7</td>
</tr>
</tbody>
</table>

Conditions were 0.1 M TBAPF₆/N,N-DMF supporting electrolyte with 0.5 M Fc as sacrificial oxidant. Working and counter electrodes were graphite rods, pseudoreference was AgCl/Ag. ^b Faradaic Efficiency. ^c 0.9 M PhOH, –2.5 V vs Fc⁺/Fc. ^d 0.5 M PhOH, –2.6 V vs Fc⁺/Fc.

To assess the proposed pendent proton relay mechanisms for 2 and 3, CV experiments were repeated using 2,4,6-tri-tert-butyl-phenol as a sterically hindered proton source (Figure S26).^[43] At concentrations of 2,4,6-tri-tert-butyl-phenol comparable to that of PhOH at saturation of the catalytic response, only 2 showed an increase in current relative to the background electrode current. This suggests that the pendent methoxy group in 2 is more efficient at relaying the proton donor to the active site than the hydroxy/phenolate moieties present in 3.[^28]

Discussion

In the case of both 2 and 3, an enhanced TOF_{max} in comparison to our original report with 1 is observed under saturation conditions. Only complex 2 shows increased selectivity for formate, which suggests that under catalytic conditions, the production of H₂ is suppressed. We ascribe this in part to differences in the efficiency of the proton relay
mechanism and to differences in the effective $pK_a$ of the catalytically relevant hydride intermediate.\textsuperscript{44} To boost a molecular electrocatalytic response, the forward reaction rate constant of proton transfer from exogenous proton source through the pendent relay to the active site must compare favorably to protonation directly at the active site by the exogenous proton source Figure 5. We propose that the zwitterionic state of 3 in the

![Figure 5](image)

**Figure 5.** Summary of the basic relay mechanism of exogenous proton donor. For boosting effects to be observable in an electrocatalytic response, the forward reaction rate constants of the relay need to be competitive with the rate of direct protonation.\textsuperscript{28} $K$ are equilibria, and $k$ are rate constants. In this case, the pendent relay would be either the methoxy ether (2) or the hydroxyl (3), and AH and A$^-$ are PhOH and its conjugate base.

secondary sphere is suggestive of possible deleterious effects on catalyst turnover due to the partial or complete deprotonation of the pendent –OH groups during the reaction. If deprotonation occurs during the catalytic turnover of 3, non-covalent interactions with the sacrificial proton donor will be much stronger than for the neutral methoxy groups in complex 2, for purely electrostatic reasons, which would be expected to inhibit the catalytic response.\textsuperscript{45, 46} Consistent with this interpretation, the experimental results with a sterically hindered proton source demonstrated catalytic increases in current only with 2. This suggests that for complex 2, the
outer-sphere pendent Lewis basic site is operating as a more accessible site for protonation, and more efficiently shuttling the proton to the metal center. It cannot be discounted, however, that the hydricity or $pK_a$ values of the putative hydride intermediates for 2 and 3 are different based on changes in the electronic structure in their respective protonated and reduced forms. If the strength of the Fe–O moiety with the pendent relay and proton donor interaction is different for charged and neutral forms, comparable differences in electronic structure at Fe could also occur.

**Conclusions**

We have reported the synthesis, characterization, and reactivity for the electrocatalytic reduction of CO$_2$ to formate of two new Fe(III) complexes with pendent proton relays. Enhancement of the catalytic rate constant is observed for both methyl-ether and hydroxy pendent functional groups. However, enhanced selectivity was only observed for the methyl-ether pendent functional group, suggesting that the strength of interaction between the external proton donor and the pendent relay site causes corresponding changes in the hydricity or $pK_a$ of the putative intermediate hydride species. These results demonstrate that the pre-catalytic MS-EPT mechanism we observed in our original report is vital to the intrinsic catalytic properties and that the overall effect can be modulated through non-covalent secondary sphere interactions to optimize the catalytic response. This suggests that secondary sphere moieties which do not interact directly with substrate bound at the active site are a complementary way to modulate activity and selectivity in this class of catalyst.

**Conflicts of interest**

There are no conflicts to declare.

**Acknowledgements**

We acknowledge the generous support of the University of Virginia.

**Notes and references**

Cif files for 2, 3, and for 3-bromo-5-(tert-butyl)benzene-1,2-diol can be found in the CCSD under the deposition numbers 1938478, 1938479, and 1940614.
References

R = –OMe
TOF$_{\text{max}}$ = 587 s$^{-1}$
FE$_{\text{HCOO}^-}$ = 85%

R = –OH
TOF$_{\text{max}}$ = 436 s$^{-1}$
FE$_{\text{HCOO}^-}$ = 70%

Relay effect enhances proton transfer
Supporting Information for

Electrocatalytic CO₂ Reduction to Formate with Molecular Fe(III) Complexes Containing Pendent Proton Relays

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Materials and Methods

General. All chemicals and solvents (ACS or HPLC grade) were commercially available and used as received unless otherwise indicated. For all air-sensitive reactions and electrochemical experiments, solvents were obtained as anhydrous and air-free from a PPT Glass Contour Solvent Purification System. Gas cylinders were obtained from Praxair (Ar as 5.0; CO₂ as 4.0) and passed through molecular sieves prior to use. NMR spectra were obtained on a Varian 600 MHz instrument and referenced to the residual solvent signal. Microwave reactions were carried out using an Anton-Parr Multiwave Pro SOLV, NXF-8 microwave reactor. Flash chromatography columns were run utilizing Teledyne ISCO CombiFlashRf+. UV-vis absorbance spectra were obtained on a Cary 60 from Agilent. GC experiments were performed using an Agilent 7890B Gas Chromatograph with an Agilent J&W Select Permanent Gases/CO₂ column and thermal conductivity detector; eluent retention times and product characterization were determined by standard injections. Formate was quantified by a previously reported NMR method.¹ HRMS data were obtained by the Mass Spectrometry Lab at the University of Illinois at Urbana-Champaign or on an Agilent 6545 Q-TOF LC/MS at UVA and elemental analyses were performed by Midwest Microlab.

Electrochemistry. All electroanalytical experiments were performed using a Metrohm Autolab PGSTAT302N or Biologic SP-50 potentiostats. Glassy carbon working (3 mm) and non-aqueous silver/silver chloride pseudoreference electrodes behind PTFE tips were obtained from CH Instruments. The pseudoreference electrodes were obtained by depositing chloride on bare silver wire in 10% HCl at oxidizing potentials and stored in a solution of 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) in N,N-dimethylformamide (DMF) prior to use. The counter electrode was a glassy carbon rod (Alfa Aesar, 99.95%, 3 mm diameter). All CV experiments were performed in a modified scintillation vial (20 mL volume) as a single-chamber cell with a cap modified with ports for all electrodes and a sparging needle. Controlled potential electrolysis (CPE) experiments were performed in a H-cell with a porous glass frit separating the working and counter chambers. Prior to electrolysis, a CV of ferrocene was obtained to reference the cell. CPE experiments were run with graphite working and counter electrodes (Electron Microscopy Sciences, type A, 3 mm diameter) a custom silver/silver chloride pseudoreference electrode (BASI, non-aqueous reference electrode kit), and ports for head-space sampling and gas sparging via needles through septa. The working chamber was separated from the counter and pseudoreference electrodes utilizing a porous glass frit, and 0.05 M ferrocene was added to the counter chamber as a sacrificial reductant. TBAPF₆ was purified by recrystallization from ethanol and dried in a vacuum oven before being stored in a desiccator. All data were referenced to an internal decamethylferrocene (Cp₂Fe) standard (decamethylferricenium/decamethylferrocene reduction potential under stated conditions) which was subsequently corrected relative to the relative E₁/₂ of ferrocene² unless otherwise specified.
**Determination of TOF\textsubscript{max}**

Calculation of TOF\textsubscript{max}

\[
TOF\textsubscript{max} = 0.1992 \frac{n_p^3 F v}{n_{\text{cat}}^2 RT (i_p)^2} \]

Where \(n_p\) is the number of electrons transferred under faradaic conditions, \(n_{\text{cat}}\) is the number of electrons transferred under catalytic conditions, \(R\) is the ideal gas constant, \(F\) is Faraday’s constant, \(v\) is the scan rate, \(T\) is temperature, \(i_{\text{cat}}\) is the catalytic current, and \(i_p\) is the faradaic current. By plotting \(i_{\text{cat}}/i_p\) vs \(v^{-1/2}\), the slope of the linear region can be used to determine TOF\textsubscript{max}:

\[
\text{Slope} = \frac{n_{\text{cat}}}{n_p^3/2} \cdot \frac{1}{0.4663} \cdot \sqrt{\frac{RT}{F} \cdot \text{TOF}_{\text{max}}} \]

\[
\text{TOF}_{\text{max}} = 0.1992 (\text{slope})^2 \frac{n_p^3}{n_{\text{cat}}^2} \frac{F}{RT} \]

For the production of formate, \(n_{\text{cat}} = 2\). We chose the first reduction feature \(i_p; n_p = 1\).

**Synthesis of 2-methoxy-4-methyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenol\textsuperscript{3}**

In a glovebox, 2-methoxy-4-methyl-phenol (2.5 mL, 19.7 mmol) and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2.5 mL, 21.7 mmol) were combined and stirred for 10 m in a 250 mL pressure flask. Vigorous effervescence was observed. After this time, 4,4,5,5-tetramethyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolane (3.51 g, 13.8 mmol), 4-tert-butyl-2-(4-tert-butyl-2-pyridyl)pyridine (0.318 g, 6 mol %), Irf[(cod)(OMe)]\textsubscript{2} (0.392 g, 3 mol %), and 100 mL of dry cyclohexane were added. The flask was capped, and heated to 90 °C for 21 h. After this time, the flask was allowed to cool to room temperature, 10 g of silica gel was added, and solvent was removed to dryness under reduced pressure. A silica gel column was run using a Combiflash purification system (ramp 0 to 10 % EtOAc/Hexanes) and the fraction which eluted after the starting material was isolated (very little UV-Vis absorbance is observed for the product). Solvent was removed to yield 2.52 g of a pale-yellow solid. Yield: 48.4%. Characterization was consistent with prior reports.\textsuperscript{3}

**Synthesis of "crebpy"**

A 500 mL pressure flask with stir bar was charged with 6,6'-dibromobipyridine (0.7 g, 2.23 mmol), K\textsubscript{3}PO\textsubscript{4} (2.56 g, 12 mmol), 2-methoxy-4-methyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenol (1.77 g, 6.69 mmol), Pd(PPPh\textsubscript{3})\textsubscript{4} (0.260 g, 0.22 mmol), and dioxane (250 mL). After this time, the mixture was cooled to RT, diluted with brine (250 mL), and extracted with toluene (6x50 ml) and CH\textsubscript{2}Cl\textsubscript{2} (6x50 mL). The organic layers were combined and dried with MgSO\textsubscript{4}, filtered, and dried under reduced vacuum. The yellow product elutes from a CH\textsubscript{2}Cl\textsubscript{2}/MeOH ramp of 0-5 % MeOH using a Combiflash purification system. Recrystallization of the product fraction from CH\textsubscript{2}Cl\textsubscript{2}/hexanes yields pure product. Yield: 0.430 g, 45%. ESI-MS (m/z) [M+H]\textsuperscript{+}: Calc’d 429.181 Found: 429.181. CHN analysis: Theory (CHN): C: 72.88, H: 5.65, N: 6.54. Found: C: 72.59, H: 5.53, N: 6.32. ¹H
NMR (DMSO-d$_7$, 600 MHz): δ (ppm) 2.34 (s, 6H), 3.82 (s, 6H), 6.92 (s, 2H), 7.50 (s, 2H), 8.13 (d, 2H), 8.21 (t, 2H), 8.29 (d, 2H), 13.18 (s, 2H). $^{13}$CNMR (DMSO-d$_7$, 600 MHz): δ (ppm) 20.82, 55.79, 114.71, 119.11, 119.18, 119.25, 121.60, 127.17, 139.59, 146.37, 148.50, 151.86, 157.10.

**Synthesis of Fe($^{mcrebpy}$)Cl, 2**

Ferric chloride hexahydrate (Fe(Cl)$_3$·6H$_2$O, 0.088 g, 0.33 mmol), sodium acetate (NaOAc, 0.052 g, 0.64 mmol), and 6,6’-{[2,2’-bipyridine]-6,6’-diyl}bis(2-methoxy-4-methylphenol) (0.133 g, 0.310 mmol) were combined in a 100 mL round-bottom flask (RBF) equipped with stir bar. EtOH (20 mL) was added to the solids and the solution was brought to reflux overnight for 16 h. The resulting suspension was removed from heat, and the remaining dark red-black solid was collected by vacuum filtration, washed with water (3x10 mL) and diethyl ether (3x5 mL). Crystals suitable for X-ray diffraction were grown by slow cooling a boiling saturated acetonitrile solution. Yield: 0.120 g, 74.1%. UV-vis in N,N-DMF: $\lambda_{max}$: 354 nm (ε: 28000 M$^{-1}$ cm$^{-1}$) and 473 nm (ε: 5300 M$^{-1}$ cm$^{-1}$). CHN Analysis: Theory (FeC$_{26}$H$_{22}$O$_4$N$_2$): C: 59.13, H: 4.21, N: 5.09. ESI-MS (m/z) [M+Na]$^+$: Calc’d 540.052 Found: 540.045. Magnetic Moment: 5.9±0.1 BM.

**Synthesis of Zn($^{mcrebpy}$)**

6,6’-{[2,2’-bipyridine]-6,6’-diyl}bis(2-methoxy-4-methylphenol) (0.61 g, 0.142 mmol), sodium acetate (23.9 mg, 0.29 mmol), zinc dichloride (0.020 g, 0.149 mmol), and absolute ethanol (20 mL) were combined in a 100 mL RBF equipped with stir bar and condenser. The mixture was brought to reflux (78 °C) overnight (16 h). After this time, a yellow-orange precipitate formed and was collected via vacuum filtration, washed with DI water (1x5 mL) and diethyl ether (1x5 mL). Yield: 21 mg, 30%. CHN analysis Theory (ZnC$_{26}$H$_{22}$N$_2$O$_4$·3H$_2$O): C: 57.21, H: 5.17, N: 5.13. Found: C: 56.90, H: 4.26, N: 5.05. $^1$H NMR (DMSO-d$_7$, 600 MHz): δ (ppm) 2.25 (s, 6H), 3.76 (s, 6H), 6.65 (s, 2H), 7.10 (s, 2H), 8.01 (d, 2H), 8.13 (t, 2H), 8.31 (d, 2H).

**Synthesis of 3-bromo-5-tert-butyl-benzene-1,2-diol$^b$:**

4-tert-butyl catechol (A) (10.0 g, 0.0602 mol) was dissolved in N,N-DMF (25 mL) in a 200 mL Schlenk RBF with a stir bar under nitrogen. A 2.0 M solution of N-bromosuccinimide in N,N-DMF (30.0 mL, 0.0662 mol) was added to the solution dropwise via syringe with vigorous stirring. After 2 h the solution was diluted with 100 mL ethyl acetate, washed with water (3x50 mL), and washed with brine (3x50 mL). The organic fraction was collected, dried over MgSO$_4$, filtered, and the solvent was removed under reduced pressure to yield a dark red oil. Note: the oil can be used without further purification, however, sublimation of the oil produces white X-ray quality crystals of analytical purity. (Yield: 13.2 g, 89.5%). ES-MS (m/z) [M]$^+$: Calc’d 244.0099 Found: 244.0098. $^1$H NMR (CDCl$_3$, 600 MHz): δ (ppm) 1.26 (s, 9H), 6.92 (d, 1H), 6.99 (d, 1H). $^{13}$C NMR (CDCl$_3$, 600 MHz): (L$^1$) δ (ppm) 31.43, 34.55, 109.23, 112.69, 120.16, 137.98, 144.08, 145.78.

**Synthesis of 1-bromo-5-tert-butyl-2,3-bis(methoxymethoxy)benzene:**

Dry dichloromethane (50 mL) was dispensed in an oven-dried RBF (250 mL). To this flask, an oven-dried stir bar, 3-bromo-5-tert-butyl-benzene-1,2-diol (8.67 g, 35.4 mmol) were added. The headspace was flushed with nitrogen and diisopropylethylamine (21.6
mL, 124.0 mmol) was added. A color change from brown to maroon was observed. The RBF was cooled to 0 °C using an ice bath. Methoxymethylchloride (8.1 mL, 110 mmol) was added dropwise with vigorous stirring. After the addition, the ice bath was removed and the solution was allowed to stir for 5 h. The reaction was quenched with aqueous NH₄OH (2 N, 120 mL), the organic layer was separated, and the aqueous layer was extracted using diethyl ether (3x50 mL). The organic fractions were combined, washed with brine (3x50 mL), dried over MgSO₄, and condensed in vacuo to yield a red oil. Yield 11.2 g, 94.9%.

EI-MS (m/z) [M]+: Calc’d 332. Found: 332.

1H NMR (CDCl₃, 600 MHz): δ (ppm) 1.28 (s, 9H), 3.51 (s, 3H), 3.67 (s, 3H), 5.16 (s, 2H), 5.18 ppm (s, 2H) 7.10 (d, 1H), 7.21 (d, 1H).

13CNMR (CD₂Cl₂, 600 MHz): δ (ppm) 31.39, 34.91, 56.52, 58.08, 95.83, 98.97, 114.07, 117.42, 123.81, 142.04, 148.99, 150.64.

Synthesis of the bis(MOM)catbpy
A 500 mL Schlenk flask with stir bar was charged with 1-bromo-5-tert-butyl-2,3-bis(methoxymethoxy)benzene (11.2 g, 33.6 mmol) and dry diethyl ether (100 mL). The resulting solution was cooled to -78°C under N₂. n-Butyllithium (1.6 M in hexanes) was added dropwise via syringe (23.1 mL, 36.9 mmol) still under N₂, after which the solution was allowed to warm to room temperature with vigorous stirring. At this point the reaction mixture was a brown suspension. After two hours the solution was returned to -78°C. Trimethylborate was added rapidly by syringe (3.95 mL, 35.3 mmol) with vigorous stirring and left for 10 minutes before the cold bath was removed and the mixture left overnight under N₂ (16 h). After this time the reaction was quenched with deionized water (50 mL) and opened to air. The suspension was extracted and the aqueous and organic layers separated. The aqueous layer was carefully neutralized to pH = 7 with ~0.1 M HCl, washed with diethyl ether (3x50 mL), and all organic fractions were combined. The combined layers were then washed with brine (3x50 mL). The resulting solution was dried with MgSO₄ for 10 minutes, before the mixture was filtered to remove solid and the solvent was removed under reduced pressure. The resulting dark orange oil was used as isolated without further purification.

A microwave-assisted Suzuki-Miyaura coupling reaction was performed with 6,6′-dibromo-2,2′-bipyridine and the crude boronic acid generated above using an Anton Paar Multiwave Pro equipped with Rotor 8NXF100. Two PTFE reaction tubes were equipped with a magnetic stir bar and charged with 6,6′-dibromo-2,2′-bipyridine (1.0 g, 3.2 mmol) and Na₂CO₃ (2.0 g, 38 mmol), each. Deionized water and methanol were degassed with Ar. The loaded PTFE tubes, solvents, and crude boronic acid were pumped into a N₂ glovebox. Pd(PPh₃)₄ (0.18 g, 0.16 mmol) was added to each tube. The boronic acid was added to this suspension by diluting in toluene (20 mL total volume) and splitting this stock solution equally between the two PTFE vessels. Methanol (10 mL), deionized water (10 mL), and toluene (30 mL) were added to the vessels. The vessels were sealed, and loaded into the microwave. The power was ramped to 280 W for 10 m, and then held at this value for 5 h. After cooling to room temperature, the tubes were combined, and the organic and aqueous layers were separated. The aqueous layer was extracted with CH₂Cl₂ (3 x 50 mL) and all organic fractions were combined, dried with MgSO₄, filtered to remove solids, and condensed under vacuum to yield a crude red oil. This oil was left overnight at room temperature, and an off-white crystalline solid formed overnight. This solid was collected, and washed with hexanes. Upon combination of the hexanes wash
and the initial fraction, more crystalline material was produced. Characterization of each fraction was consistent with the desired product. Yield 2.85 g, 67.7%. El-MS (m/z) [M-H]^+': Calc'd 661.3489. Found: 661.3486. Theory (CHN): C: 69.07, H: 68.83, N: 7.32.

Synthesis of Zn(\textbf{tbu}catbpy)
6,6'-bis(5-(tert-butyl)-2,3-bis(methoxymethoxy)phenyl)-2,2'-bipyridine (2.50 g, 3.78 mmol) was dissolved in minimal EtOAc (~100 mL) in a 250 mL RBF equipped with stir bar. Excess anhydrous HCl was generated by adding concentrated H\textsubscript{2}SO\textsubscript{4} dropwise to solid NaCl in an airtight vessel that vented through the EtOAc solution via PTFE cannula. Excess HCl was quenched by venting through an outlet flask containing saturated aq. NaHCO\textsubscript{3}. The flask containing EtOAc was sealed, and left to stir overnight. During the ~9 h of stirring, the EtOAc solution changed from colorless to yellow, and a solid precipitated from solution. After purging the EtOAc solution with N\textsubscript{2}, saturated aq. NaHCO\textsubscript{3} was added to ensure neutralization. The resultant solid was collected by vacuum filtration, washed with water, and triturated with CHCl\textsubscript{3} to yield the desired product as an orange powder. Yield: 1.71 g, 93.3%. El-MS (m/z) [M-H]^+': Calc'd 485.2440. Found: 485.2435. CHN analysis: Theory (C\textsubscript{36}H\textsubscript{42}N\textsubscript{2}O\textsubscript{4}•0.8CHCl\textsubscript{3}): C: 63.77, H: 5.70, N: 4.83. Found: C: 63.84, H: 5.69, N: 4.69. \textsuperscript{1}H NMR (DMSO-d\textsubscript{6}, 600 MHz): δ (ppm) 1.31 (s, 18 H), 6.89 (s, 2H), 7.49 (s, 2H), 8.04-8.20 (m, 4H), 8.45 (s, 2H). \textsuperscript{13}CNMR (DMSO-d\textsubscript{6}, 600 MHz): δ (ppm) 31.33, 33.94, 113.88, 114.71, 118.78, 118.92, 121.44, 139.64, 141.06, 145.01, 145.86, 151.91, 157.70.

Synthesis of Fe(\textbf{tbu}catbpy), 3
6,6'-(2,2'-bipyridine)-6,6'-diyl)bis(4-(tert-butyl)benzene-1,2-diol) (0.150 g, 0.310 mmol), NaOAc (52.1 mg, 0.63 mmol), Fe(Cl\textsubscript{3}•6H\textsubscript{2}O (0.088 g, 0.33 mmol), and absolute ethanol (20 mL) were combined in a 100 mL RBF equipped with stir bar and condenser. The mixture was brought to reflux (78 °C) overnight (16 h). The resulting black suspension was removed from heat and the volume reduced to ~10 mL \textit{in vacuo} before DI H\textsubscript{2}O (5 mL) was added, inducing the formation of a black precipitate. The solid was collected by vacuum filtration and washed with H\textsubscript{2}O (3 x 5 mL) and Et\textsubscript{2}O (3x5 mL). Yield: 0.119 g, 71%. UV-vis in N,N-DMF: λ\textsubscript{max}: 290, 345, and 560 nm. ε: 31000, 20000, and 3700 M\textsuperscript{-1}cm\textsuperscript{-1}, respectively El-MS (m/z) [M-H]^+': Calc'd 535.1555. Found: 535.1553. CHNCl analysis: None. Theory (FeC\textsubscript{36}H\textsubscript{42}N\textsubscript{2}O\textsubscript{4}•2H\textsubscript{2}O): C: 62.82, H: 5.80, N: 4.89, Cl: None. Found: C: 63.08, H: 5.26, N: 4.92, Cl: None. Magnetic Moment: 6.1±0.1 BM.

Synthesis of Zn(\textbf{tbu}catbpy)
6,6'-(2,2'-bipyridine)-6,6'-diyl)bis(4-(tert-butyl)benzene-1,2-diol) (0.052 g, 0.108 mmol), sodium acetate (18.1 mg, 0.22 mmol), zinc dichloride (0.015 g, 0.11 mmol), and absolute ethanol (20 mL) were combined in a 100 mL RBF equipped with stir bar and condenser. The mixture was brought to reflux (78 °C) overnight (16 h). After this time, a yellow-orange
precipitate formed and was collected via vacuum filtration, washed with DI water (1x5 ml) and diethyl ether (1x5mL). Yield: 39 mg, 68%. CHN analysis Theory: C: 65.76, H: 5.52, N: 5.11. Found: C: 65.20, H: 5.29, N: 4.90. $^1$H NMR (DMSO-d$_7$, 600 MHz): $\delta$ (ppm) 1.26 (s, 18H), 6.80 (s, 2H), 7.02 (s, 2H), 8.05 (d, 2H), 8.15 (t, 2H), 8.34 (d, 2H). $^{13}$C($^1$H) NMR (DMSO-d$_7$, 600 MHz): $\delta$ (ppm) 31.47, 33.75, 110.26, 114.18, 116.55, 118.00, 135.09, 140.47, 147.74, 149.71, 154.32, 159.82.
Figure S1. (A) Representative monomer structure (one of two structurally inequivalent units crystallographically) from (B) overall dimer structure of 3. C = grey, O = Red, N= Blue, Fe = Orange. Thermal ellipsoids set to 30%. Non-catecholate H-atoms, occluded MeCN and second set of coordinates for disordered tert-butyl groups and bpy ring omitted for clarity.

Figure S2. UV-Vis absorbance spectra of serial dilutions of 2 in N,N-DMF showing absence of equilibrium processes. Pathlength 1 cm.
**Figure S3.** UV-Vis absorbance spectra of serial dilutions of 3 in N,N-DMF showing absence of equilibrium processes. Pathlength 1 cm.

**Figure S4.** (A) Plots of 3rd and 4th reduction potentials of 3 showing scan rate dependence of the relative current response of these two features. (B) Plot of the ratio of the peak current of the 3rd and 4th reductions of 3 vs. scan rate. Glassy carbon working and counter electrodes, Ag/AgCl pseudoreference electrode, referenced to internal Cp₂*Fe standard.
Figure S5. Plots of current density vs $u^{1/2}$ for the reductions with $E_{1/2} = -0.84$ V (A) and -1.93 V (B) vs Fc+/Fc for 2. Linearity indicates 2 is operating in a diffusion limited regime. Glassy carbon working and counter electrodes, Ag/AgCl pseudoreference electrode, referenced to internal Cp₂*Fe standard.
Figure S6. Plots of current density vs $v^{1/2}$ for the reductions with $E_{1/2} = -1.01$ V (A) and -1.65 V (B) vs Fc+/Fc for 3. Linearity indicates 3 is operating in a diffusion limited regime. Glassy carbon working and counter electrodes, Ag/AgCl pseudoreference electrode, referenced to internal Cp$_2$*Fe standard.
Figure S7. Cyclic voltammogram of 0.5 mM 2 or Zn\(^{\text{crebpy}}\) in 0.1 M TBAPF\(_6\)/N,N-DMF supporting electrolyte under Ar saturation conditions. Glassy carbon working and counter electrodes, Ag/AgCl pseudoreference electrode, referenced to internal Cp\(_2\)\(^+\)Fe standard, 100 mV/s scan rate.

Figure S8. Cyclic voltammogram of 0.5 mM 3 or Zn\(^{\text{catbpy}}\) in 0.1 M TBAPF\(_6\)/N,N-DMF supporting electrolyte under Ar saturation conditions. Glassy carbon working and counter electrodes, Ag/AgCl pseudoreference electrode, referenced to internal Cp\(_2\)\(^+\)Fe or Cp\(_2\)Co standard, 100 mV/s scan rate.
Figure S9. Cyclic voltammograms of 0.5 mM 2 in 0.1 M TBAPF$_6$/N,N-DMF supporting electrolyte under Ar saturation conditions with varied amounts of PhOH showing a shift in the first two reduction features. Glassy carbon working and counter electrodes, Ag/AgCl pseudoreference electrode, referenced to internal Cp$_2^+$Fe or Cp$_2$Co standard, 100 mV/s scan rate.

Figure S10. Cyclic voltammograms of 0.5 mM 3 in 0.1 M TBAPF$_6$/N,N-DMF supporting electrolyte under Ar saturation conditions with varied amounts of PhOH showing a shift in the first two reduction features. Glassy carbon working and counter electrodes, Ag/AgCl pseudoreference electrode, referenced to internal Cp$_2^+$Fe or Cp$_2$Co standard, 100 mV/s scan rate.
Figure S11. Cyclic voltammograms of 0.5 mM 2 in 0.1 M TBAPF$_6$/N,N-DMF supporting electrolyte under labeled conditions. Glassy carbon working and counter electrodes, Ag/AgCl pseudoreference electrode, referenced to internal Cp$_2^*$Fe or Cp$_2$Co standard, 100 mV/s scan rate.

Figure S12. Cyclic voltammograms of 0.5 mM 3 in 0.1 M TBAPF$_6$/N,N-DMF supporting electrolyte under labeled conditions. Glassy carbon working and counter electrodes, Ag/AgCl pseudoreference electrode, referenced to internal Cp$_2^*$Fe or Cp$_2$Co standard, 100 mV/s scan rate.
Figure S13. Cyclic Voltammograms of 0.5 mM Fe(me
tcrebpy)Cl2 in 0.1 M TBAPF6/N,N-DMF supporting electrolyte with scans to the catalytic wave showing current saturation occurs at ~0.9 M PhOH. Glassy carbon working and counter electrodes, Ag/AgCl pseudoreference electrode, referenced to internal Cp2*Fe standard, 100 mV/s scan rate.

Figure S14. Cyclic Voltammograms of 0.5 mM Fe(tbu
catbpy)3 in 0.1 M TBAPF6/N,N-DMF supporting electrolyte with scans to the catalytic wave showing current saturation occurs at 0.5 M PhOH. Glassy carbon working and counter electrodes, Ag/AgCl pseudoreference electrode, referenced to internal Cp2*Fe standard, 100 mV/s scan rate.
Figure S15. Log-log plot of current density and [CO₂] for 0.5 mM 2, Fe(mecrebpy)Cl with 1.0 M PhOH. Kinetic current saturation is observed above 0.04 M CO₂. Glassy carbon working and counter electrodes, Ag/AgCl pseudoreference electrode, referenced to internal Cp₂⁺Fe standard, 100 mV/s scan rate.

Figure S16. Log-log plot of current density and [PhOH] for 0.5 mM 2, Fe(tbu)catbpy) under CO₂ saturation conditions. Slope of 0.5 is indicative of 1ˢᵗ order kinetics with respect to [PhOH]. Glassy carbon working and counter electrodes, Ag/AgCl pseudoreference electrode, referenced to internal Cp₂⁺Fe standard, 100 mV/s scan rate.
Figure S17. Log-log plot of current density and $[\text{CO}_2]$ for 0.5 mM 3, $\text{Fe}^{(\text{tbu} \text{catbpy})}$ with 0.5 M PhOH. Kinetic current saturation is observed above 0.04 M CO$_2$. Glassy carbon working and counter electrodes, Ag/AgCl pseudoreference electrode, referenced to internal Cp$_2^*$Fe standard, 100 mV/s scan rate.

Figure S18. Log-log plot of current density and $[\text{PhOH}]$ for 0.5 mM 3, $\text{Fe}^{(\text{mecrebp})}$Cl under CO$_2$ saturation conditions. Slope of 0.5 is indicative of 1$^{\text{st}}$ order kinetics with respect to [PhOH]. Glassy carbon working and counter electrodes, Ag/AgCl pseudoreference electrode, referenced to internal Cp$_2^*$Fe standard, 100 mV/s scan rate.
Figure S19. Plot of current density and [2], Fe\textsuperscript{mcorebpy}Cl under CO\textsubscript{2} saturation conditions with 1.0 M PhOH. Linearity is consistent with 1\textsuperscript{st} order kinetics with respect to [2]. Glassy carbon working and counter electrodes, Ag/AgCl pseudoreference electrode, referenced to internal Cp\textsubscript{2}^*Fe standard, 100 mV/s scan rate.

Figure S20. Plot of current density and [3], Fe\textsuperscript{tbutcatbpy} under CO\textsubscript{2} saturation conditions with 0.5 M PhOH. Linearity is consistent with 1\textsuperscript{st} order kinetics with respect to [3]. Glassy carbon working and counter electrodes, Ag/AgCl pseudoreference electrode, referenced to internal Cp\textsubscript{2}^*Fe standard, 100 mV/s scan rate.
Figure S21. (A) Cyclic voltammograms and (B) plot of \( \frac{i}{\nu^{1/2}} \) vs. \( \nu^{-1/2} \) for 0.5 mM Fe(mcrebpy)Cl \(_2\) under saturated CO\(_2\) conditions with 0.54 M PhOH in 0.1 M TBAPF\(_6\)/N,N-DMF supporting electrolyte. Glassy carbon working and counter electrodes, Ag/AgCl pseudoreference electrode, referenced to internal Cp\(_2\)*Fe standard. Linear region of plot used to determine TOF\(_{\text{max}}\) by a previously reported procedure.\(^5\) Scan rates alternate black and red: 0.02, 0.1, 0.2, 0.5, 1.0, 2.0, 5.0, 10, 20, 40 V/s.

Figure S22. (A) Cyclic voltammograms and (B) plot of \( \frac{i}{\nu^{1/2}} \) vs. \( \nu^{-1/2} \) for 0.5 mM Fe(tbucatbpy) \(_3\) under saturated CO\(_2\) conditions with 0.51 M PhOH in 0.1 M TBAPF\(_6\)/N,N-DMF supporting electrolyte. Glassy carbon working and counter electrodes, Ag/AgCl pseudoreference electrode, referenced to internal Cp\(_2\)*Fe standard, 100 mV/s scan rate. Linear region of plot used to determine TOF\(_{\text{max}}\) by a previously reported procedure.\(^5\) Scan rates alternate black and red: 0.02, 0.1, 0.2, 0.5, 1.0, 2.0, 5.0, 10, 20, 40 V/s.
Figure S23. (A) Cyclic voltammograms and (B) plot of $i/i_p$ vs $v^{-1/2}$ for 0.5 mM Fe(me$\text{crebpy}$)Cl$_2$ under saturated CO$_2$ conditions with 1.0 M PhOH in 0.1 M TBAPF$_6$/N,N-DMF supporting electrolyte Glassy carbon working and counter electrodes, Ag/AgCl pseudoreference electrode, referenced to internal Cp$_2^*$Fe standard. Linear region of plot used to determine $\text{TOF}_{\text{max}}$ by a previously reported procedure.$^5$ Scan rates alternate black and red: 0.02, 0.1, 0.2, 0.5, 1.0, 2.0, 5.0, 10, 20, 40 V/s.
Figure S24. Current vs. Time and Charge Passed vs. Time Plots for CPE experiments at –2.50 V vs Fc+/Fc with 0.5 mM Fe(IIcrebpy)Cl₂, 0.9 M PhOH, and CO₂ atmosphere. Graphite working and counter electrodes were used. Rinse test and catalytic runs come from separate experiments.
Figure S25. Current vs. Time (A) and Charge Passed vs. Time plots (B) for CPE experiments at −2.60 V vs Fc+/Fc with 0.5 mM Fe(tbu3catbpy) 3, 0.5 M PhOH, and CO2 atmosphere. Graphite working and counter electrodes were used. Rinse test and catalytic runs come from separate experiments.
Figure S26. Cyclic Voltammograms of 0.5 mM Fe(tBu)dhbpy)Cl (red), Fe(me)crebpy)Cl (green), and Fe(tBu)catbpy)Cl (blue) in 0.1 M TBAPF$_6$/N,N-DMF supporting electrolyte with 0.5 M 2,4,6-tri-tert-butyl-phenol (tBu$_3$PhOH) under CO$_2$ saturation conditions. Control experiment is under identical conditions with no catalyst material added. Glassy carbon working and counter electrodes, Ag/AgCl pseudoreference electrode, referenced to internal Cp$_2^*$Fe standard, 100 mV/s scan rate.

Figure S27. Crystal structure for 3-bromo-5-(tert-butyl)benzene-1,2-diol. C = grey, O = red, Br = brown. Thermal ellipsoids set to 50%.
Table S1. Diffusion coefficients determined using the Randles-Sevcik equation and variable scan rate studies.⁶ a - as determined at first reduction potential. b - as determined at second reduction potential.

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