We’ve reached the final chapter of our tale. I’m afraid I don’t have a particular message to accompany this project, perhaps it is still too fresh for me to have formed an impression of it. I’ll relate here that, as I’ve alluded to, demonstrating electrocatalytic N$_2$RR was one of the very first targets I latched onto when I started my research with Jonas. The idea seemed optimistic (to say the least) at the time and even until almost the end of my fifth year I didn’t think I would see this result in my time at Caltech. I suppose something can be said here for persistence in pursuing a goal, but probably the better message is that while it is important to work towards big, overarching targets it is also important to be open to things you discover along the way.

5.1 Introduction

There has been substantial recent progress in the development of soluble, well-defined molecular catalysts for N$_2$-to-NH$_3$ conversion, commonly referred to as the nitrogen
reduction reaction (N\textsubscript{2}RR).\textsuperscript{1} Nevertheless, a significant and unmet challenge is to develop molecular catalysts, and conditions, compatible with electrocatalytic N\textsubscript{2}RR. Progress in this area could have both fundamental and practical benefits, including access to informative in situ mechanistic studies via electrochemical techniques, and an electrochemical means to translate solar or otherwise derived chemical currency (H\textsuperscript{+}/e\textsuperscript{−}) into NH\textsubscript{3}. The latter goal, which has been the subject of numerous studies using heterogeneous catalysts, is key to the long-term delivery of new ammonia synthesis technologies for fertilizer and/or fuel.\textsuperscript{2}

Many soluble coordination complexes are now known that electrocatalytically mediate the hydrogen evolution reaction (HER),\textsuperscript{3} the carbon dioxide reduction reaction (CO\textsubscript{2}RR),\textsuperscript{4} and the oxygen reduction reaction (O\textsubscript{2}RR).\textsuperscript{5} The study of such systems has matured at a rapid pace in recent years, coinciding with expanded research efforts towards solar-derived fuel systems. In this context, it is noteworthy how little corresponding progress has been made towards the discovery of soluble molecular catalysts that mediate electrocatalytic N\textsubscript{2}RR. To our knowledge, only two prior systems address this topic directly.\textsuperscript{6,7,8}

More than three decades ago, Pickett and coworkers reported that a Chatt-type tungsten-hydrazido(2−) complex could be electrochemically reduced to release ammonia (and trace hydrazine), along with some amount of a reduced tungsten-dinitrogen product; the latter species serves as the source of the tungsten-hydrazido(2−) complex (via its protonation by acid).\textsuperscript{6a} By cycling through such a process, an electrochemical, but not an electrocatalytic, synthesis of ammonia was demonstrated. Indeed, efforts to demonstrate electrocatalysis with this and related systems instead led to substoichiometric NH\textsubscript{3} yields.\textsuperscript{6c}
An obvious limitation to progress in electrochemical N\textsubscript{2}RR by molecular systems concerns the small number of synthetic N\textsubscript{2}RR catalysts that have been available for study; it is only in the past five years that sufficiently robust catalyst systems have been identified to motivate such studies. In addition, the conditions that have to date been employed to mediate N\textsubscript{2}RR have typically included non-polar solvents, such as heptane, toluene, and diethyl ether (Et\textsubscript{2}O), that are not particularly well-suited to electrochemical studies owing to the lack of compatible electrolytes.\textsuperscript{1}

Nevertheless, several recent developments, including ones from our lab, point to the likelihood that iron (and perhaps other) molecular coordination complexes may be able to mediate electrocatalytic N\textsubscript{2}RR in organic solvent. Specifically, our lab recently reported that a tris(phosphine)borane iron complex, P\textsubscript{3}BFe\textsuperscript{+}, that is competent for catalytic N\textsubscript{2}RR with chemical reductants, can also mediate electrolytic N\textsubscript{2}-to-NH\textsubscript{3} conversion,\textsuperscript{6d} with the available data (including that presented in this study) pointing to bona fide electrocatalysis in Et\textsubscript{2}O.

Focusing on the P\textsubscript{3}BFe\textsuperscript{+} catalytic N\textsubscript{2}RR system, a development germane to the present study was its recently discovered compatibility with reagents milder than those that had been originally employed.\textsuperscript{1c} Thus, decamethylcobaltocene (Cp*\textsubscript{2}Co) and diphenylammonium acid are effective for N\textsubscript{2}RR catalysis; these reagents give rise to fast, and also quite selective (> 70% vs HER), N\textsubscript{2}RR catalysis at low temperature and pressure in ethereal solvent. In addition, based on preliminary spectroscopic evidence and density functional theory (DFT) predictions, it appears that a protonated metallocene species, Cp*(\texteta \textsuperscript{4}-C\textsubscript{5}Me\textsubscript{5}H)Co\textsuperscript{+}, may be an important intermediate of N\textsubscript{2}RR catalysis under such conditions. Indeed, we have suggested that Cp*(\texteta \textsuperscript{4}-C\textsubscript{5}Me\textsubscript{5}H)Co\textsuperscript{+} may serve as a proton-
coupled-electron-transfer (PCET) donor (BDE$_{\text{C-H}}$(calc) = 31 kcal mol$^{-1}$), thereby mediating net H-atom transfers to generate N–H bonds during N$_2$RR. The presence of a metallocene mediator might, we therefore reasoned, enhance N$_2$RR during electrocatalysis.

We present here a study of the effect of p$K_a$ on the selectivity of P$_3$BFe$^+$ for N$_2$RR vs HER. By using substituted anilinium acids, we are able to vary the acid p$K_a$ over 9 orders of magnitude and find that the selectivity is highly correlated with the p$K_a$. In our efforts to investigate the origin of the observed p$K_a$ effect, we found, to our surprise, that in stoichiometric reactions, the catalytically competent anilinium triflate acids are unable to facilitate productive N–H bond formation with early-stage N$_2$-fixation intermediates. We therefore hypothesize that the formation of a protonated metallocene species, Cp*(η$^4$-C$_5$Me$_5$H)Co$^+$, plays a critical role in N–H bond-forming reactions, either via PCET, PT, or a combination of both during N$_2$RR catalysis. DFT studies support this hypothesis and also establish that the observed p$K_a$ correlation with N$_2$RR selectivity can be explained by the varying ability of the acids to protonate Cp*$_2$Co. The suggested role of this protonated metallocene intermediate in N–H bond forming reactions led us to test the effect of Cp*$_2$Co$^+$ as an additive in the electrolytic synthesis of NH$_3$ mediated by P$_3$BFe$^+$. We find that the addition of co-catalytic Cp*$_2$Co$^+$ enhances the yield of NH$_3$ without decreasing the Faradaic efficiency (FE), and furnishes what is to our knowledge the first unambiguous demonstration of electrocatalytic N$_2$RR mediated by a soluble, molecular coordination complex.
5.2 Results and Discussion

5.2.1 $pK_a$ Studies.

In our recent study on the ability of $P_3^{8}\text{Fe}^+$ to perform $\text{N}_2\text{RR}$ with $\text{Cp}^*_2\text{Co}$ as the chemical reductant,\(^9\) we found that there was a marked difference in efficiency for $\text{NH}_3$ generation with diphenylammonium triflate ($[\text{Ph}_2\text{NH}_2][\text{OTf}]$) versus anilinium triflate ($[\text{PhNH}_3][\text{OTf}]$). In that study, we posited that this difference could arise from several possibilities, including the differential solubility, steric, or $pK_a$’s of these acids.\(^9\)

To investigate the last possibility, we have studied the efficiency of the catalysis by quantifying the $\text{NH}_3$ and $\text{H}_2$ produced when using substituted anilinium acids with different $pK_a$ values (Table 5.1). The table is organized in increasing acid strength, from $[4-\text{OMePhNH}_3][\text{OTf}]$ as the weakest acid to the perchlorinated derivative ($[\text{per-ClPhNH}_3][\text{OTf}]$) as the strongest. Importantly, good total electron yields ($85.8 \pm 3.3$) were obtained in all cases. As can be seen from the table, the $\text{NH}_3$ efficiencies are found to be strongly correlated with $pK_a$.\(^10\)

In particular, a comparison of the efficiency for $\text{NH}_3$ with the $pK_a$ of the anilinium acid used gives rise to four distinct activity regimes (Table 5.1, Figure 5.1). One regime that is completely inactive for $\text{N}_2\text{RR}$, but active for HER, is defined by the weakest acid, $[4-\text{OMePhNH}_3][\text{OTf}]$ ($pK_a = 8.8$).\(^11\) A gradual increase in observed $\text{NH}_3$ yields, coupled with a decrease in $\text{H}_2$ yield, comprises a second regime, in which the acid is strengthened from $[\text{PhNH}_3][\text{OTf}]$ ($pK_a = 7.8$), to $[2,6-\text{MePhNH}_3][\text{OTf}]$ ($pK_a = 6.8$), to $[2-\text{ClPhNH}_3][\text{OTf}]$ ($pK_a = 5.6$). Yet stronger acids, $[2,5-\text{ClPhNH}_3][\text{OTf}]$ ($pK_a = 4.3$), $[2,6-\text{ClPhNH}_3][\text{OTf}]$ ($pK_a = 3.4$), and $[2,4,6-\text{ClPhNH}_3][\text{OTf}]$ ($pK_a = 2.1$), constitute another, most active $\text{N}_2\text{RR}$ regime, one in which the $\text{H}_2$ yields are nearly invariant.\(^12\) The highest selectivity for $\text{N}_2\text{RR}$ ($\sim 78\%$) was observed
using [2,5-ClPhNH3][OTf] as the acid. A final regime of very low N2RR activity is encountered with [5^or-ClPhNH3][OTf] (pK_a = 1.3) as the acid. We suspect this last acid undergoes unproductive

Figure 5.1. (top) Percentage of electrons being used to form NH3 or H2 at different pH values by the FeMo-nitrogenase in A. vinelandii. Reprinted with permission from Pham, D. N.; Burgess, B. K. Biochemistry 1993, 32, 13725. Copyright 1993 American Chemical Society. (bottom) Percentage of electrons being used to form NH3 or H2 at different pK_a values by P3^Fe+.
Table 5.1. Literature and calculated pKₐ values and efficiencies observed in catalytic N₂-to-NH₃ conversion

<table>
<thead>
<tr>
<th></th>
<th>pKₐ&lt;sub&gt;exp&lt;/sub&gt; (THF)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>pKₐ&lt;sub&gt;calc&lt;/sub&gt; (298 K)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>pKₐ&lt;sub&gt;calc&lt;/sub&gt; (195 K)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Equiv of NH₃/Fe</th>
<th>% yield of NH₃/e⁻</th>
<th>% yield of H₂/e⁻&lt;sup&gt;c&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>[⁴-OMePhNH₃][OTf]</td>
<td>8.8</td>
<td>9.6</td>
<td>15.7</td>
<td>0.04 ± 0.01</td>
<td>0.2 ± 0.1</td>
<td>89.1 ± 0.2</td>
</tr>
<tr>
<td>[PhNH₃][OTf]</td>
<td>7.8</td>
<td>7.7</td>
<td>13.8</td>
<td>7.3 ± 0.1</td>
<td>40.4 ± 0.5</td>
<td>48.6 ± 0.7</td>
</tr>
<tr>
<td>[²,6-MePhNH₃][OTf]</td>
<td>6.8</td>
<td>7.3</td>
<td>13.2</td>
<td>8.6 ± 0.7</td>
<td>47.5 ± 4.0</td>
<td>37.8 ± 0.2</td>
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<tr>
<td>[Cp*(exo-η⁴-C₅Me₅H)Co][OTf]</td>
<td>N/A</td>
<td>9.2</td>
<td>11.8</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>[²-ClPhNH₃][OTf]</td>
<td>5.6</td>
<td>5.6</td>
<td>6.0</td>
<td>10.7 ± 0.1</td>
<td>53.9 ± 0.4</td>
<td>26.1 ± 1.9</td>
</tr>
<tr>
<td>[²,5-ClPhNH₃][OTf]</td>
<td>4.3</td>
<td>4.0</td>
<td>5.0</td>
<td>13.9 ± 0.7</td>
<td>77.5 ± 3.8</td>
<td>10.5 ± 1.1</td>
</tr>
<tr>
<td>[²,6-ClPhNH₃][OTf]</td>
<td>3.4</td>
<td>3.4</td>
<td>3.4</td>
<td>13.8 ± 0.9</td>
<td>76.7 ± 4.9</td>
<td>12.6 ± 2.5</td>
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<tr>
<td>[²,4,6-ClPhNH₃][OTf]</td>
<td>2.1</td>
<td>2.7</td>
<td>1.8</td>
<td>12.8 ± 0.4</td>
<td>70.9 ± 2.2</td>
<td>12.0 ± 0.8</td>
</tr>
</tbody>
</table>
| [⁴-OMePhNH₃][OTf] = 4-methoxyanilinium triflate, [PhNH₃][OTf] = anilinium triflate, [²,6-MePhNH₃][OTf] = 2,6-dimethylanilinium triflate, [²-ClPhNH₃][OTf] = 2-chloroanilinium triflate, [²,5-ClPhNH₃][OTf] = 2,5-dichloroanilinium triflate, [²,6-ClPhNH₃][OTf] = 2,6-dichloroanilinium triflate, [²,4,6-ClPhNH₃][OTf] = 2,4,6-trichloroanilinium triflate, [⁴-ClPhNH₃][OTf] = 2,3,4,5,6-pentachloroanilinium triflate. <sup>a</sup>Acidities calculated at 298 K in THF and referenced to the known literature value for [²,6-ClPhNH₃][OTf]. <sup>b</sup>All species calculated as the ion-paired OTf⁻ species in Et₂O at 195 K and referenced to the known literature value for [²,6-ClPhNH₃][OTf] in THF.
reduction via ET, thereby short-circuiting N₂RR. The only other N₂RR system for which this type of acid-dependent correlation has been systematically studied is the enzyme MoFe-nitrogenase.¹³,¹⁴ As shown in Figure 5.1, the N₂RR vs HER activity of P₃BFe⁺ as a function of acid strength, is, in broad terms, similar to the behavior of the enzyme¹³ across a wide pH range.

In a previous study of Cp*₂Co-mediated N₂RR by P₃BFe⁺,⁹ we identified that P₃BFeN₂⁻ forms under the catalytic conditions. Earlier studies on the reactivity of P₃BFeN₂⁻ with an excess of soluble acids, including HOTf and [H(OEt₂)₂][BArF₄] (HBArF₄, BArF₄ = tetrakis(3,5- bis(trifluoromethyl)phenyl)borate)), at −78 °C in Et₂O, established rapid formation of the doubly protonated species, P₃BFeNNH₂⁺.¹⁵ Recent computational work from our group suggests that, under catalytic conditions with a soluble acid, different efficiencies for N₂RR (versus HER) by P₃EFe catalysts (E = B, C, Si) are likely correlated to the rate of formation and consumption of early N₂RR intermediates (i.e., P₃EFeNNH and P₃EFeNNH²⁺).¹⁶ Thus, we were interested in the reactivity of these anilinium triflate acids with P₃BFeN₂⁻, reasoning they may show differential efficiency in the formation of P₃BFeNNH₂⁺.

To our surprise, a freeze-quench EPR spectrum of the reaction of excess [²,₆-CIPhNH₃][OTf] (high N₂RR efficiency regime) at −78 °C in Et₂O with P₃BFeN₂⁻ does not show any P₃BFeNNH₂⁺. Also, freeze-quench Mössbauer analysis shows the formation of the oxidized products P₃BFeN₂ and P₃BFe⁺, but nothing assignable to P₃BFeNNH₂⁺ (see SI for relevant spectra). Analysis of such a reaction for NH₃ or N₂H₄ after warming shows no fixed-N products. The observation of exclusive oxidation, rather than productive N–H bond formation, is analogous to what is observed upon addition of 1 equiv of a soluble acid
(HBArF₄ or HOTf) to P₃BFeN₂⁻. We have previously suggested that if unstable P₃BFeNNH is formed (eq 1) without excess acid to trap it (to form more stable P₃BFeNNH₂⁺, eq 2), then it can decay bimolecularly with the loss of 1/2 H₂ to form P₃BFeN₂ (eq 3).

\[
P₃BFeN₂⁻ + H^+ \rightarrow P₃BFeNNH \quad (1)
\]

\[
P₃BFeNNH + H^+ \rightarrow P₃BFeNNH₂⁺ \quad (2)
\]

\[
P₃BFeNNH \rightarrow P₃BFeN₂ + 1/2 H₂ \quad (3)
\]

The low solubility of the anilinium triflate acids studied herein, in excess (50 equiv) and under the catalytically relevant conditions (1 mL Et₂O, −78 °C), likely leads to a similar scenario; consequently, P₃BFeNNH that is generated is not efficiently captured by excess acid, leading instead to bimolecular H₂ loss. In accord with this idea, a freeze-quench EPR spectrum of the addition of 50 equiv of [2,6-ClPhNH₃][BArF₄], a far more ether soluble derivative of the same anilinium, to P₃BFeN₂⁻ shows P₃BFeNNH₂⁺ formation, and the detection of fixed-N products upon warming (0.20 ± 0.04 eq. NH₃ per Fe).

These observations must next be reconciled with the seemingly contradictory observation that comparatively efficient N₂RR catalysis is observed when [2,6-ClPhNH₃][OTf], and other anilinium triflate acids, are employed under catalytic conditions. For example, [Ph₂NH₂][OTf] leads to better efficiency for NH₃ formation versus [Ph₂NH₂][BArF₄] (72 ± 3% and 42 ± 6%, respectively). A key difference between the stoichiometric reactions described above, and the catalytic reaction, is the presence of Cp*₂Co in the latter.

We have suggested that Cp*₂Co can be protonated under the catalytic reaction conditions, to form Cp*(η⁴-C₅Me₅H)Co⁺,⁹ which may then play a role in N–H bond forming steps.¹⁷ The results presented here (and below) suggest that such a mechanism is
not only plausible, but is likely necessary, to explain the observed catalytic results with anilinium triflate acids. Given the effect of pKₐ on the efficiency for N₂RR, we now hypothesize that this effect can arise from the relative energetics and rates of Cp*₂Co protonation by the different anilinium triflate acids.

5.2.2 Computational Studies.

To investigate the kinetics and thermodynamics of Cp*₂Co protonation by anilinium triflate acids we turned to a computational study. DFT-D₁¹⁸ calculations were undertaken at the TPSS/def2-TZVP(Fe); def2-SVP¹⁹ level of theory, as used previously for studies of this P₃BFe⁺ system.²⁰ The free energy of H⁺ exchange (ΔGₐ) was calculated for all of the anilinium acids used (representative example shown in eq 4), and also for Cp*(exo-η⁴-C₅Me₅H)Co⁺, in Et₂O at 298 K. These free energies were then used to determine the acid pKₐ’s, with inclusion of a term to reference them to the literature pKₐ value for [2,6-ClPhNH₃][OTf] at 298 K in THF (eq 5).

\[
\begin{align*}
\text{PhNH}_2 + 2,6-\text{ClPhNH}_3^+ & \rightarrow \text{PhNH}_3^+ + 2,6-\text{ClPhNH}_2 \\
pK_a(\text{PhNH}_3^+) &= -\Delta G_a/(2.303\times RT) + pK_a(2,6-\text{ClPhNH}_3^+) 
\end{align*}
\]

Because we presume that variable triflate hydrogen bonding effects (0.5-10 kcal mol⁻¹) are likely to be important under the catalytic conditions (low temperature and low polarity solvent), we additionally calculated the free energy for net HOTf exchange reactions (ΔGd) at 195 K in Et₂O (representative example shown in eq 6). The free energies of these reactions can then be used to determine a pKₐ, referenced to the pKₐ value for [2,6-ClPhNH₃][OTf] at 298 K in THF, for ease of comparison (eq 7). Hereafter, we use these pKₐ values for discussion, but note that use of the pKₐ values instead does not substantively alter the conclusions drawn.
PhNH₂ + [2,6-ClPhNH₃][OTf] \rightarrow \\
[PhNH₃][OTf] + 2,6-ClPhNH₂ \quad (6)

pK_d([PhNH₃][OTf]) = -\Delta G_d/(2.303 \times RT) + pK_a(2,6-ClPhNH₃⁺) \quad (7)

Calculations of the pKₐ of all of the relevant species (Table 5.1) shows that the pKₐ of [Cp*(exo-η⁴-C₅Me₅H)Co][OTf] (pKₐ(calc) = 11.8; Table 5.1) falls within the range of the anilinium acids studied (0.4 \leq pKₐ(calc) \leq 15.7), suggesting there should be a significant acid dependence on the kinetics and thermodynamics of Cp*₂Co protonation. To better elucidate the differences in Cp*₂Co protonation between the acids studied, we investigated the kinetics of protonation for three acids, [2,6-ClPhNH₃][OTf] (high selectivity; pKₐ(calc) = 3.4), [2,6-MePhNH₃][OTf] (modest selectivity; pKₐ(calc) = 13.2), and [4-OMePhNH₃][OTf] (poor selectivity; pKₐ(calc) = 15.8).

Transition states for Cp*₂Co protonation were located for all three acids. To confirm that these transition states accurately reflect proton transfer, internal reaction coordinates (IRC) were followed to determine the reactant (IRC-A) and product (IRC-B) minima (Figure 5.2). These minima represent hydrogen bonded arrangements of the reactants and products. Protonation is found to have only a moderate barrier (ΔG ‖ in kcal mol⁻¹) in all three cases: ([4-OMePhNH₃][OTf], +4.5; [2,6-MePhNH₃][OTf], +3.8; [2,6-ClPhNH₃][OTf], +1.3).
Figure 5.2. The kinetics and thermodynamics of protonation of Cp*₂Co for three acids from different catalytic efficiency regimes ([4-OMePhNH₃][OTf] = poor selectivity; [2,6-MePhNH₃][OTf] = modest selectivity; [2,6-ClPhNH₃][OTf] = high selectivity).

This suggests that Cp*₂Co protonation is kinetically accessible in all cases, in agreement with the experimental observation of background HER with each of these acids (see SI).

The small differences in rate, and the large variance in the equilibrium constant $K_{eq}$ defined in eq 8, points to a significant difference in the population of protonated metallocene, $[\text{Cp}^\star(\text{exo}-\eta^4-\text{C}_5\text{Me}_5\text{H})\text{Co}]\text{[OTf]}$, for these anilinium acids during catalysis.

$$K_{eq} = \frac{[\text{RPhNH}_2^-\text{Cp}^\star(\text{exo}-\eta^4-\text{C}_5\text{Me}_5\text{H})\text{Co}^+]}{[\text{RPhNH}_3^+\text{Cp}^\star\text{Co}]} \quad (8)$$

We reason that the low solubility of the anilinium triflate acids, and the low catalyst concentration (2.3 mM P₃BFe), leads to a scenario in which the interaction between the acid and the Cp*₂Co, the latter being present in excess relative to the iron catalyst (measured solubility of Cp*₂Co at −78 °C in Et₂O is ~ 6 mM, see SI), significantly affects the overall kinetics of productive N–H bond formation. As such, the difference in $[\text{Cp}^\star(\text{exo}-\eta^4-\text{C}_5\text{Me}_5\text{H})\text{Co}]\text{[OTf]}$ concentration and formation rate should relate to, and likely dominate,
the origin of the observed pKₐ effect. This explanation, rather than one that involves differences in rates for the direct interaction of a given P₃BFeNxHy species with an anilinium acid, better captures the collected data available.²¹

[Cp⁺⁺(exo-η⁴-CsMesH)Co][OTf], characterized by a very weak C–H bond, should be a strong PCET donor, and we presume it serves such a role under the catalytic conditions being discussed herein.²² Its reactions with P₃BFeNxHy intermediates may occur in a synchronous fashion, akin to HAT, or in an asynchronous fashion more akin to a PT-ET reaction.²³ While many P₃BFeNxHy intermediates may, at least in part, be generated via PCET with [Cp⁺⁺(exo-η⁴-CsMesH)Co][OTf],²⁴ available experimental data point to a critical role for such a reaction via trapping of the highly reactive first fixed intermediate, P₃BFeNNH (Figure 5.3), before it can bimolecularly release H₂ (eq 3). We hence investigated this reaction in more detail.
Figure 5.3. The calculated thermodynamics and kinetics of synchronous PCET and asynchronous PCET (PT-ET), between $P_3^{\text{BFeNNH}}$ and $[\text{Cp}^*\text{(exo-} \eta^4\text{-C}_5\text{Me}_5\text{H})\text{Co}]\text{[OTf]}$ to generate $P_3^{\text{BFeNNH}_2}$. Note: $k_{\text{rel}}$ for ET is defined as $1 \text{ M}^{-1} \text{s}^{-1}$.

Both a synchronous PCET ($\Delta G_{\text{PCET}} = -17.3 \text{ kcal mol}^{-1}$; eq 9) and an asynchronous PCET path ($\Delta G_{\text{PT}} = -5.7 \text{ kcal mol}^{-1}$, $\Delta G_{\text{ET}} = -11.6 \text{ kcal mol}^{-1}$; eq 10 and 11), are predicted to be thermodynamically favorable.

$$P_3^{\text{BFeNNH}} + [\text{Cp}^*\text{(exo-} \eta^4\text{-C}_5\text{Me}_5\text{H})\text{Co}]\text{[OTf]} \rightarrow$$

$$P_3^{\text{BFeNNH}_2} + [\text{Cp}^*_2\text{Co}]\text{[OTf]}$$  \hspace{1cm} (9)

$$P_3^{\text{BFeNNH}} + [\text{Cp}^*\text{(exo-} \eta^4\text{-C}_5\text{Me}_5\text{H})\text{Co}]\text{[OTf]} \rightarrow$$

$$[P_3^{\text{BFeNNH}_2}]\text{[OTf]} + \text{Cp}^*_2\text{Co}$$  \hspace{1cm} (10)

$$[P_3^{\text{BFeNNH}_2}]\text{[OTf]} + \text{Cp}^*_2\text{Co} \rightarrow$$

$$P_3^{\text{BFeNNH}_2} + [\text{Cp}^*_2\text{Co}]\text{[OTf]}$$  \hspace{1cm} (11)
To evaluate the kinetics of these reactions the Marcus theory expressions\textsuperscript{25} and the Hammes-Schiffer method\textsuperscript{26} were used to approximate relative rates of bimolecular ET and PCET. We find that there is a slight kinetic preference for the fully synchronous PCET reaction ($k_{rel}^{PCET} \sim 3 \times 10^3 \text{M}^{-1}\text{s}^{-1}$) compared to the fully asynchronous PT-ET reaction ($k_{rel}^{PT-ET} \simeq k_{rel}^{ET} \equiv 1 \text{M}^{-1}\text{s}^{-1}$; Figure 5.3).\textsuperscript{27}

The above discussion leads to the conclusion that the efficiency for NH\textsubscript{3} formation in this system is coupled to the kinetics and/or thermodynamics of the reaction between the anilinium triflate acid and the Cp*\textsubscript{2}Co reductant. This conclusion is counterintuitive, as the protonation of Cp*\textsubscript{2}Co is also the requisite first step for background HER.\textsuperscript{28} The fact that a key HER intermediate can be intercepted and used for productive N\textsubscript{2}RR steps is an important design principle for such catalysis. Similar design strategies are currently being used to repurpose molecular cobalt HER catalysts for the reduction of unsaturated substrates.\textsuperscript{29}

Efforts are often undertaken to suppress background reactivity between acid and reductant in catalytic N\textsubscript{2}RR systems.\textsuperscript{1a-b} We were hence particularly interested to explore whether the inclusion of a metallocene co-catalyst, in this case Cp*\textsubscript{2}Co, might improve the yield, and/or the Faradaic efficiency (FE), for N\textsubscript{2}RR versus HER, in controlled potential electrolysis (CPE) experiments with P\textsubscript{3}BFe\textsuperscript{+} under N\textsubscript{2}.

5.2.3 Electrolysis Studies.

To set the context for this section of the present study, we had shown previously that $\sim$ 2.2 equiv NH\textsubscript{3} (per Fe) could be generated via controlled potential electrolysis (CPE; $\sim$2.3 V vs Fc$^{+/0}$) at a reticulated vitreous carbon working electrode, using P\textsubscript{3}BFe\textsuperscript{+} as the (pre)catalyst in the presence of HBArF\textsubscript{4} (50 equiv) at $\sim$45 °C under an atmosphere of N\textsubscript{2}.
This yield of NH₃ corresponded to a ~ 25% FE which, while modest in terms of overall chemoselectivity, compares very favorably to FE’s most typically reported for heterogeneous electrocatalysts for N₂RR that operate below 100 °C (< 2%).²,³⁰

To further explore the possibility of using P₃BFe⁺ as an electrocatalyst for N₂RR, various conditions were surveyed to determine whether enhanced yields of NH₃ could be obtained from CPE experiments. For example, various applied potentials were studied (ranging from −2.1 to −3.0 V vs Fe⁺/⁰), the concentrations of P₃BFe⁺ and HBArF₄ were varied, the ratio of acid to catalyst was varied, and the rate at which acid was delivered to the system was varied (e.g., initial full loadings, batch-wise additions, reloadings, or continuous slow additions). None of these studies led to substantial improvement in N₂RR; in all cases, < 2.5 equiv of NH₃ was obtained per P₃BFe⁺. Attempts to vary the ratio of the electrode surface area to the working compartment solution volume, either by employing smaller cell geometries or by using different morphologies of glassy carbon as the working electrode (e.g., reticulated porous materials of different pore density or plates of different dimensions), also failed to provide substantial improvement in NH₃ yield. The replacement of HBArF₄, the original acid used in our electrolysis studies,⁶d by 50 equiv of [Ph₂NH₂][OTf] led to similar yields of NH₃ (Table 5.2, entry 1).

We next investigated the effect of Cp*₂Co⁺ as an additive on the electrolysis/electrocatalysis. Traces of relevant cyclic voltammograms (Figure 5.4A and 5.4B) collected with glassy carbon as the working electrode in Et₂O under glovebox atmosphere N₂ at −35 °C are provided. Background traces including only [Ph₂NH₂][OTf] are present in both panels (gray traces). Cp*₂Co⁺ (panel A, yellow trace), Cp*₂Co⁺ with the addition of ten equiv of [Ph₂NH₂][OTf] (panel A, green trace), P₃BFe⁺ (panel B, dark blue
trace), \( \text{P}_3^{\text{B}}\text{Fe}^+ \) with the addition of ten equiv of \([\text{Ph}_2\text{NH}_2][\text{OTf}]\) (panel B, light blue trace), and \( \text{P}_3^{\text{B}}\text{Fe}^+ \) with the addition of one equiv of \( \text{Cp}^{\ast}\text{Co}^+ \) and ten equiv of \([\text{Ph}_2\text{NH}_2][\text{OTf}]\) (both panels, red trace).

**Table 5.2. Yields and Faradaic Efficiencies of NH\(_3\) from CPE Experiments with \( \text{P}_3^{\text{B}}\text{Fe}^+ \)**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Equiv Cp(^{\ast})Co(^+)</th>
<th>Equiv NH(_3) (per Fe)</th>
<th>Equiv NH(_3) (per Co)</th>
<th>NH(_3) FE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>2.6 ± 0.3(^d)</td>
<td>—</td>
<td>24 ± 5</td>
</tr>
<tr>
<td>2(^a)</td>
<td>0</td>
<td>2.6 ± 0.6</td>
<td>—</td>
<td>18 ± 1</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>4.0 ± 0.6</td>
<td>4.0 ± 0.6</td>
<td>28 ± 5</td>
</tr>
<tr>
<td>4</td>
<td>5</td>
<td>4.0 ± 0.6(^d)</td>
<td>0.8 ± 0.1</td>
<td>25 ± 3</td>
</tr>
<tr>
<td>5(^a)</td>
<td>5</td>
<td>5.5 ± 0.9(^e)</td>
<td>1.1 ± 0.2</td>
<td>19 ± 1</td>
</tr>
<tr>
<td>6</td>
<td>10</td>
<td>4 ± 1</td>
<td>0.4 ± 0.1</td>
<td>24 ± 7</td>
</tr>
<tr>
<td>7(^b)</td>
<td>5</td>
<td>1.9 ± 0.2</td>
<td>0.4 ± 0.1</td>
<td>10 ± 1</td>
</tr>
<tr>
<td>8(^c)</td>
<td>5</td>
<td>0.9 ± 0.4</td>
<td>0.2 ± 0.1</td>
<td>6 ± 3</td>
</tr>
</tbody>
</table>

All CPE experiments conducted at \(-2.1 \text{ V vs Fc}^{+/0}\) with 0.1 M NaBAr\(^F_4\) in Et\(_2\)O as solvent at \(-35 \text{ °C}\) under an N\(_2\) atmosphere, featuring a glassy carbon plate working electrode, Ag\(^{+/0}\) reference couple isolated by a CoralPor\(^\text{TM}\) frit referenced externally to Fc\(^{+/0}\), and a solid sodium auxiliary electrode. Working and auxiliary chambers separated by a sintered glass frit. See SI for further experimental details, controls, and additional data. Averages represent two runs unless noted. \(^a\) After initial electrolysis with 50 equiv \([\text{Ph}_2\text{NH}_2][\text{OTf}]\), an additional 50 equiv \([\text{Ph}_2\text{NH}_2][\text{OTf}]\) in 0.1 M NaBAr\(^F_4\) Et\(_2\)O solution
was added to the working chamber, via syringe through a rubber septum, followed by additional CPE at $-2.1$ V vs Fc$^{+/0}$. The listed Equiv NH$_3$ (per Fe) for these runs is the total yield after both electrolysis experiments are completed. $^b$[2,6-ClPhNH$_3$][OTf] employed as the acid. $^c$[PhNH$_3$][OTf] employed as the acid. $^d$Average of three runs. $^e$Average of five runs.

The cyclic voltammogram of Cp*$_2$Co$^+$ is shown in panel A (yellow trace), displaying the reversible Cp*$_2$Co$^{+/0}$ couple at $-2.0$ V. The addition of [Ph$_2$NH$_2$][OTf] to Cp*$_2$Co$^+$ causes an increase in current at this potential, consistent with HER
catalyzed by Cp*₂Co⁺ (panel A, green trace).

Panel B provides the cyclic voltammogram of P₃BFe⁺ in the absence (dark blue trace, showing previously assigned and quasi-reversible P₃BFeN₂⁰⁻⁻ couple at ~ −2.1 V) and in the presence (light blue trace) of [Ph₂NH₂][OTf]. The latter is indicative of modest HER and N₂RR. Also evident upon the addition of acid is the disappearance of a wave corresponding to the P₃BFe⁺⁰⁻ couple at ~ −1.6 V. This wave, in the absence of acid, is broad and shows a large peak-to-peak separation, likely due to the presence of both P₃BFe⁺ and P₃BFeN₂⁺ in solution at −35 °C. The addition of a large excess of [Ph₂NH₂][OTf] presumably results in triflate binding (to generate P₃BFeOTf, thereby attenuating the waves associated with the reduction of P₃BFe⁺ and P₃BFeN₂⁺). The red trace of Panel A is reproduced in Panel B to illustrate the marked increase in current observed when Cp*₂Co⁺ is added.

CPE studies were undertaken to characterize the reduction products associated with the red trace at ~ −2.1 V vs Fc⁺⁰. These studies employed a glassy carbon plate electrode, a Ag⁺⁰ reference electrode that was isolated by a CoralPor™ frit and referenced externally Fc⁺⁰ redox couple, and a solid sodium auxiliary electrode. The latter was used to avoid excessive, non-productive redox cycling between the working and auxiliary chambers. Unless otherwise noted, CPE experiments were performed at −2.1 V versus Fc⁺⁰, with 0.1 M NaBAR₄ as the ether-soluble electrolyte, under a glovebox N₂ atmosphere at −35 °C. The electrolysis was continued until the current had dropped to 1% of the initial current measured, or until 21.5 hours had passed. The Supporting Information provides additional details.
CPE experiments were conducted with the inclusion of 0, 1, 5, and 10 equiv of Cp*2Co+ with respect to P3BFe+, using excess [Ph2NH2][OTf] as the acid. In the absence of added Cp*2Co+, a significant amount of NH3 was generated (2.6 ± 0.3 equiv per Fe, entry 1), consistent with the previous finding that, in the presence of a strong acid, P3BFe+ can electrolytically mediate N2-to-NH3 conversion.6d Notably, when a CPE experiment that did not include Cp*2Co+ was reloaded with additional acid after electrolysis and electrolyzed again, the total yield of NH3 (2.6 ± 0.6 equiv NH3 per Fe, entry 2) did not improve.

We found that inclusion of 1.0 equiv of Cp*2Co+ enhanced the NH3 yield, by a factor of ~ 1.5 (Table 5.2, entry 3) without decreasing the FE. The data provide a total yield, with respect to both Fe and Co, that confirm modest, but still unequivocal, N2RR electrocatalysis. In single run experiments, the highest NH3 yield in the absence of Cp*2Co+ was 2.8 equiv, compared with 4.4 equiv in the presence of 1 equiv of Cp*2Co+. Conversely, the lowest single run NH3 yield in the absence of Cp*2Co+ was 2.3 equiv, compared with 3.5 equiv in the presence of 1 equiv of Cp*2Co+.

Increasing the amount of added Cp*2Co+ did not affect the NH3 yield (entry 4). However, the addition of a second loading of [Ph2NH2][OTf] following the first electrolysis (entry 5), followed by additional electrolysis, led to an improved yield of NH3, suggesting that some active catalyst is still present after the first run.6d,9 Even higher Cp*2Co+ loading did not lead to higher NH3 yields (entry 6).

CPE of P3BFe+ in the presence of Cp*2Co+ was also explored with other acids. Replacing [Ph2NH2][OTf] in these experiments with [2,6-ClPhNH3][OTf] led to lower yields of NH3, and with [PhNH3][OTf] even lower yields of NH3 were observed (entries 7 and 8 respectively). The lower, but nonzero, yield of NH3 provided by [PhNH3][OTf] in these
CPE experiments is consistent with chemical trials employing various acids (vide supra) and can be rationalized by the relative $pK_a$ of the acids (Table 5.1). The intermediate yield of NH$_3$ provided by [2,6-ClPhNH$_3$][OTf] in these CPE experiments is less consistent with simple $pK_a$ considerations, suggesting that additional factors are at play, perhaps including the relative stability of the acid or conjugate base to electrolysis.

To probe whether electrode-immobilized iron might contribute to the N$_2$RR electrocatalysis, X-ray photoelectron spectroscopy (XPS) was used to study the electrode. After a standard CPE experiment with P$_3$BFe$^+$, 5 equiv of Cp*$_2$Co$^+$, and 50 equiv [Ph$_2$NH$_2$][OTf], the electrode was removed, washed with fresh 0.1 M NaBAR$_4^-$ Et$_2$O solution, then fresh Et$_2$O, and probed by XPS. A very low coverage of Fe (< 0.3 atom % Fe) was detected in the post-electrolysis material; no Fe was detected on a segment of the electrode which was not exposed to the electrolytic solution. This observation implies a detectable but likely small degree of degradation of P$_3$BFe$^+$ over the course of a 15 hour CPE experiment. Worth noting is that no Co was detected on the post-electrolysis electrode. This may be consistent with the known stability of metallocenes and the recently discovered stability of protonated-Cp$^*$ ligands on Rh.33

To test whether the small amount of deposited Fe material might be catalytically active for N$_2$RR, following a standard CPE experiment the electrode was removed from the cold electrolysis solution, washed with fresh 0.1 M NaBAR$_4^-$ Et$_2$O at $-35$ °C (the electrode itself was maintained at $-35$ °C at all times), and then used for an additional CPE experiment, under identical conditions except that P$_3$BFe$^+$ was excluded. This CPE experiment yielded no detectable NH$_3$. The charge passed, and H$_2$ yield, were very similar to a “no P$_3$BFe$^+$” control experiment conducted with a freshly cleaned electrode (See SI for
Accordingly, a CPE experiment in the absence of P$_3^{3\text{B}}$Fe$^+$ demonstrated that Cp*$_2$Co$^+$ serves as an effective electrocatalyst for HER with [Ph$_2$NH$_2$][OTf] as the acid source, but does not catalyze the N$_2$RR reaction (0% FE for NH$_3$, 75% FE for H$_2$; see SI). This background HER, and the observed catalytic response to the addition of [Ph$_2$NH$_2$][OTf] at the Cp*$_2$Co$^{+/-0}$ couple, provides circumstantial evidence for the formation of a protonated decamethylcobaltocene intermediate, Cp*($\eta^4$-C$_5$Me$_5$H)Co$^+$, on a timescale similar to that of the N$_2$RR mediated by P$_3^{3\text{B}}$Fe$^+$.

To probe whether the sodium auxiliary electrode used in the CPE experiments might play a non-innocent role as a chemical reductant, a standard CPE experiment with P$_3^{3\text{B}}$Fe$^+$, 5 equiv Cp*$_2$Co$^+$, and 50 equiv [Ph$_2$NH$_2$][OTf] was assembled, but was left to stir at $-35$ °C for 43 hours without an applied potential bias. This experiment yielded 0.3 equiv NH$_3$ (relative to Fe), suggesting that background N$_2$RR due to the sodium auxiliary electrode is very minor.

To ensure the NH$_3$ produced was derived from the N$_2$ atmosphere during these electrolysis experiments, as opposed to degradation of the anilinium acid used, a standard CPE experiment using P$_3^{3\text{B}}$Fe$^+$, 5 equiv Cp*$_2$Co$^+$, and 50 equiv of [Ph$_2$^{15}$\text{NH}_2$][OTf] was performed. Only $^{14}$NH$_3$ product was detected.

We also sought to compare the chemical N$_2$RR catalysis efficiency of the P$_3^{3\text{B}}$Fe$^+$ catalyst under conditions similar to those used for electrocatalysis. Hence, chemical catalysis with P$_3^{3\text{B}}$Fe$^+$, employing Cp*$_2$Co as a reductant and [Ph$_2$NH$_2$][OTf] as the acid at $-35$ °C instead of the more typical temperature of $-78$ °C, in a 0.1 M NaBAr$_4$ Et$_2$O solution, afforded lower yields of NH$_3$ (1.8 ± 0.7 equiv of NH$_3$ per Fe) than the yields observed via electrolysis with Cp*$_2$Co$^+$ as an additive. The lower yields of NH$_3$ in these
chemical trials, compared with our previously reported conditions (12.8 ± 0.5 equiv of NH₃ per Fe at −78 °C),⁹ may be attributable to increased competitive HER resulting from a more solubilizing medium (0.1 M NaBAR₄ Et₂O vs pure Et₂O) and a higher temperature (−35 °C vs −78 °C).⁹ These results suggest that an electrochemical approach to NH₃ formation can improve performance, based on selectivity for N₂RR, of a molecular catalyst under comparable conditions.

5.3 Conclusion

Herein we described the first systematic pKa studies on a synthetic nitrogen fixation catalyst and find a strong correlation between pKa and N₂RR vs HER efficiency. Chemical studies reveal that, on their own, the anilinium triflate acids employed in the catalysis are unable to generate the N–H bonds of early-stage N₂RR intermediates such as P₃BFeNNH₂⁺. We propose that the insolubility of these triflate acids prevents the sufficiently rapid proton transfer necessary to capture the critical but unstable first fixed intermediate, P₃BFe NNH. Under catalytic conditions, we believe that the presence of the metallocene reductant (Cp*₂Co) is essential, as this species can be protonated in situ to form Cp*(η⁴-C₅Me₅H)Co⁺, which in turn is effective in N–H bond formation with early intermediates. This leads to the intriguing conclusion that an intermediate of the background HER pathway is redirected for productive N₂RR chemistry during catalysis.

DFT studies illustrate that the pKa effect on the N₂RR efficiency may be explained by the variation in the kinetics and thermodynamics of Cp*₂Co protonation by the different acids. Investigation of the reactivity of Cp*(exo-η⁴-C₅Me₅H)Co⁺ with the P₃BFeNNH intermediate revealed that PCET reactivity, either synchronous or asynchronous, is favorable and may proceed with only a small barrier, suggesting that P₃BFeNNH can be
rapidly trapped by Cp*(*exo-η⁴-C₅Me₅H)Co+. We suspect Cp*(*η⁴-C₅Me₅H)Co⁺ is likely involved in a variety of N–H bond forming reactions during the overall catalysis, including reactions with late-stage nitrogen fixation intermediates.

Despite the fact that Cp*₂Co⁺ itself catalyzes HER under the conditions employed for electrocatalytic N₂RR, we found that its inclusion in CPE experiments containing P₃Fe⁺ and acid under an N₂ atmosphere led to modest improvements in the overall catalytic yield of NH₃. This system represents what is to our knowledge the first unambiguous example of electrocatalytic N₂RR mediated by a soluble, molecular coordination complex.

5.4 REFERENCES


8 Very recently there was a report of electrolytic NH₃ synthesis by Cp₂TiCl₂. Although rates and Faradaic efficiencies are discussed, no yields of NH₃ are reported: Jeong, E.-Y.; Yoo, C.-Y.; Jung, C. H.; Park, J. H.; Park, Y. C.; Kim, J.-N.; Oh, S.-G.; Woo, Y.; Yoon, H. C. *ACS Sustainable Chem. Eng.* **2017**, *5*, 9662.


10 In some cases, the pKₐ of a particular anilinium acid was already known in THF in which case this value was used. In cases where the pKₐ has not been reported in THF a literature procedure was used to appropriately convert the pKₐ from the solvent in which it was measured into a value for THF. See SI for details.

11 Consistent with this observation is that efforts to use other weak, non-anilinium acids such as benzylammonium triflate (pKₐ in THF of 13.2) and collidinium triflate (pKₐ in THF of 11.2) also led to no observed NH₃ formation.
These results are also consistent with our previous observation of [Ph₂NH₂][OTf] (pKₐ in THF of 3.2) yielding 72 ± 3 % NH₃. See reference 9.

Pham, D. N.; Burgess, B. K. *Biochemistry* 1993, 32, 13275.

In some other reports on N₂RR by molecular catalysts, efficiencies for NH₃ have been reported for several acids, but typically these acids span only a small pKₐ range, electron yields are inconsistent, and variations are not explained. For a representative example, see Reference 1b.


Recent results on a Cr–N₂ species also support the role of PCET in the formation of early-stage N₂ fixation intermediates in the presence of collidinium triflate and a cobaltocene: Kendall, A. J.; Johnson, S. I.; Bullock, R. M.; Mock, M. T. *J. Am. Chem. Soc.* 2018, 140, 2528.


For the P₃FeNₓHy and related systems, this combination of functional and basis sets is able to reproduce not only crystallographic details, but also experimentally measured singlet-triplet gaps, reduction potentials, and N–H BDFE’s, as described in reference 16.

In all cases where the basicity of P₃FeNₓHy intermediates has been evaluated, they are predicted to be readily protonated by the anilinium triflate acids employed (see SI for details).

DFT calculations suggest that almost all of the P₃FeNₓHy intermediates on the N₂RR pathway have N–H bonds stronger than the C–H bond in Cp*(exo-η⁴-C₅Me₅H)Co⁺, suggesting that, at least thermodynamically, the formation of these N–H bonds by PCET is favorable. See reference 16.
23. The reactivity of ring-functionalized Cp* rings has been discussed previously in the context of
electrocatalytic HER by 4d and 5d metals, but via a mechanism involving hydride transfer, rather than
via PCET. See: (a) Pitman, C. L.; Finster, O. N. L.; Miller, A. J. M. *Chem. Commun.* 2016, 52, 9105. (b)

24. Productive N–H bond formation via PCET with models of late-stage N₂ fixation intermediates (i.e.,
M≡N or M–NH₂) has been observed previously: (a) Scepaniak, J. J.; Young, J. A.; Bontchev, R. P.;
137, 3498. (c) MacLeod, K. C.; McWilliams, S. F.; Mercado, B. Q.; Holland, P. L. *Chem. Sci.* 2016, 7,
139, 5305.


27. We have assumed a PT-ET mechanism in which ET is rate limiting based on significantly lower
reorganization energies and barriers for PT compared to ET. See SI for full description.


30. Very recently there has been a study of electrocatalytic N₂RR under ambient conditions in ionic
liquids with Fe nanoparticles that reports FE’s for NH₃ as high as 60%: Zhou, F.; Azofra, L. M.; Ali, M.; Kar, M.; Simonov, A. N.; McDonnell-Worth, C.; Sun, C.; Zhang, X.; MacFarlane, D. R. *Energy
Environ. Sci.* 2017, 10, 2516.
31 We believe that the quasi-reversible nature of the electrochemical couple results from a high reorganization energy, but the couple is fully chemically reversible: Moret, M.-E.; Peters, J. C. Angew. Chem. Int. Ed. 2011, 50, 2063.

32 Due to the extensive diffusion between the working and auxiliary chambers, production of an oxidation product which can diffuse to the working electrode and be re-reduced at −2.1 V vs Fc+/0 leads to excessive, nonproductive redox cycling between chambers over the course of the lengthy CPE experiments. Sodium metal as an electrode material provides a suitable solution to this technical challenge, as the product of its oxidation (Na+) is stable to the CPE conditions.